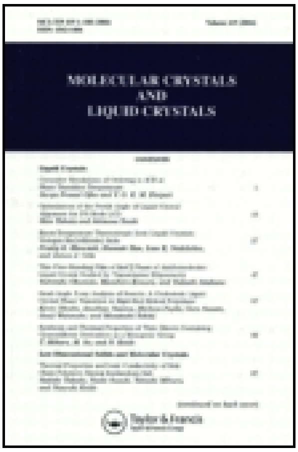

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Orienting Layers Preparation Technology for Photoaligment in Liquid Crystal Displays

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To cite this article: M. M. Chrzanowski, J. Zieliński, E. Nowinowski-Kruszelnicki, W. Piecek, M. Olifierczuk, H. Lendzion & J. Brzeziński (2011): Orienting Layers Preparation Technology for Photoaligment in Liquid Crystal Displays, Molecular Crystals and Liquid Crystals, 544:1, 170/[1158]-177/[1165]

To link to this article: http://dx.doi.org/10.1080/15421406.2011.569399

Mol. Cryst. Liq. Cryst., Vol. 544: pp. 170/[1158]–177/[1165], 2011
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ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2011.569399

Orienting Layers Preparation Technology for Photoaligment in Liquid Crystal Displays

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The present paper gives an account of selected alignment methods alternative to rubbing with particular stress being put on photoalignment methods. Technological process aiming at obtaining proper and useful, anisotropic and homogeneous orienting layers prepared using polarised and unpolarised ultraviolet light has been discussed in detail.

Keywords Photoalignment; photocrosslinking; photodegradation; polyimide

1. Introduction

Because of their unmistakable advantages, flat panel displays practically superseded traditionally used cathode ray tube (CRT) displays. Nowadays liquid crystal displays (LCDs) have won dominant position and efficiently rival with plasma display panels (PDPs) for the large-scale display market. This state may imply that all problems associated with liquid crystal technology have been solved, which turns out not to be entirely true.

Liquid crystals can be used in many optoelectronics applications, such as simple television displays, television screens and computer projector systems and with telecommunication components. In all of these applications the key feature is homogeneity of the liquid crystal layer. This homogeneity results from interaction with an anisotropic orienting layer.

As a consequence the main target to achieve in LCD technology is to receive orienting layers which are aligned anisotropically and enable liquid crystals to orient properly. Such a homogeneous layer is referred to as *texture*. Thin coats made of polymer materials (usually polyimide or polyamide) are routinely used for obtaining aligned liquid crystals and they are prepared by means of rubbing technique. Rubbing consists in unidirectional buffing of the aforementioned layer with a specially

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selected cloth. Despite its vide usage the method has considerable shortcomings that are especially salient in high-resolution displays. Polishing may prove highly nocuous to the active matrix and, which is particularly harmful to thin liquid crystal layers, dust may appear. Moreover, more and more frequently the process can charge the orienting surface electrostatically [1]. Therefore, homogeneous as the alignment might seem, it is not such at microscopic level.

In addition, time and again need for electrooptical effects occurs. These, such as IPS and ferroelectrics, require special alignment, which means that different areas within the same liquid crystal cell are characterized by different types of alignment, appropriate molecular tilt and controlled anchoring energy. By no means is rubbing is sufficient in such cases.

Because of that there is a number of diverse methods that can fulfil specific requirements connected with particular purposes. Apart from traditional rubbing micro-rubbing is used [1]. One of these is oblique evaporation silicon oxide onto a substrate [2]. Another one consists in attaching a stretched polymer film to a substrate [3]. In the dip-coat method a substrate is dipped into a polymer solution and pulled up slowly [4]. In another approach a polymer film can be stripped from a substrate. There is also a method where Langmuir-Blodgett layer is stacked on a substrate [5]. Finally there is a possibility of iron-beam irradiation of a substrate covered with polymer [6–8]; a similar procedure may also involve using laser beam writing [9].

All of the above-mentioned methods have some features that are useful for some liquid crystals modes, so it should be borne in mind that there is no universal method that would suit all applications; for instance, a distinct method will be suitable for nematics or various kind of smectics, such as ferroelectrics. Unfortunately, all of them present some disadvantages that sometimes make them difficult to use or ineffective for some applications.

Yet, there is, another group of alignment techniques that use ultraviolet irradiation to reach anisotropy in the organic layer. It is then worth being discussed and as such will be the object of the present paper.

1.1. *Photoalignment Techniques*

First announcements concerning photoalignment date back to 1988 when Ichimura reported isomerisation of azobenzene with photoaligment properties [10]. In this

Table 1. Measurements results for polyimide HD-8820. C (V/V) – PI volume to volume concentration, SD – standard deviation [nm]

	HD-4100				HD-4110				HD-8820			
C	LPUV		UPL		LPUV		UPL		LPUV		UPL	
(V/V)	[nm]	SD	[nm]	SD	[nm]	SD	[nm]	SD	[nm]	SD	[nm]	SD
30%	9820	630	6540	120	13300	2100	14910	890	7980	120	7944	61
20%	2970	140	2820	180	4240	320	4000	340	2230	260	2174	85
15%	1399	57	1308	69	2150	480	1730	420	1234	19	1193	48
6%	125	11	103	23	70	18	106	40	118	26	127	27

project reversible photophysical *cis*-*trans* isomerisation of azobenzene units attached to a glass substrate (the so-called *command surface*) was used. In 1991 Gibbons and co-workers reported having reached photoalignment with the use of azobenzene-doped polyimide.

In 1994, Hasegawa and Thaira discovered that irradiation of undoped polyimide with polarized deep UV light yielded anisotropy sufficient to achieve good liquid crystal alignment.

Among four routes of performing photoalignment two work for azo-compounds (above-mentioned *cis*-*trans* isomerisation and pure reorientation of stable azo-dye chromophore in UV-light-induced potential field [11,12]) while two others (photocrosslinking and photodecomposition) can be applied in photosensitive polyimide precursor materials. An account has recently been given of using *cis*-*trans* isomerisation techniques for photoalignment in polyimides as well [13]. The scope of the present work is to show photoalignment phenomena in polyimide materials; thus azo-compounds will not be discussed further on.

1.2. *Photoalignment in Polyimide (PI) Materials*

Photosensitive polyimides are polymers composed of imide monomers. In photosensitive polyimides irradiation with ultraviolet or visible light provokes changes in their physical properties through certain photochemical reactions under linearly polarised UV (LPUV) or unpolarised light (UPL) exposition [14,15]. One can distinguish two tones of photosensitive materials, the so-called positive-tone and negative-tone materials. In positive-tone materials the agent undergoes decomposition in previously irradiated areas, whereas in negative-tone materials trigger linear photopolimerisation.

1.2.1. *Photodecomposition in Positive-Tone Agents.* The polyimide layer gets irradiated with a beam of high intensity ultraviolet light (usually linearly polarised), which leads to the excitation of some of the weakest bonds and subsequently to their rupture. This process takes place through homolytic dissociation in presence of free radicals. Hence for the process to be effectual, presence of oxygen is indispensable. Hasegawa and Horie report that when photolysis is performed without presence of oxygen even extended irradiation hardly brings about any chain breaking and there is no photooxidative splitting [16]. Anisotropy is obtained due to decomposition of polyimide chains the direction of which was more or less parallel to the polarisation axis; chains perpendicular to the light polarisation axis remain unaffected. These chains interact with LC molecules causing their alignment thanks to Van der Waals and dispersive forces.

1.2.2. *Photocrosslinking in Negative-Tone Materials.* Upon UV light irradiation polymers containing specific moieties in side chains can undergo cycloaddition [$2+2$]; some authors [17] use the term *dimerisation* in such cases, reserving the term *crosslinking* for a situation when two radical components combine as is Figure 1.

The term photocrosslinking is used by other authors when double bonds parallel to the polarization axis of the UV light give a cyclic product, e.g., cyclobutane. Distribution of cyclobutane moieties on polyimide layer is anisotropic.

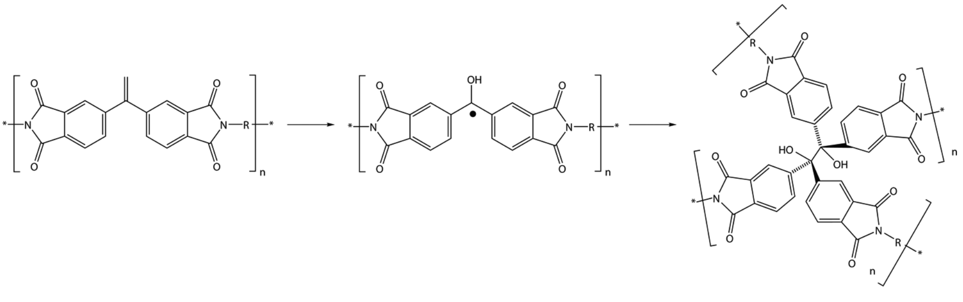

Figure 1. Crosslinking in a polyimide containing benzofenone moiety.

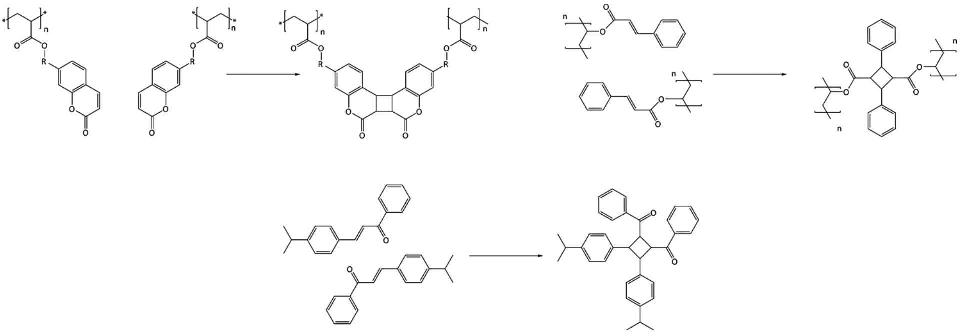

Figure 2. Photocrosslinking reaction: on the left: coumarin, on the right: poly (vinyl cinnamate), at the bottom: chalcone.

The long axis of cyclobutane molecules is perpendicular or parallel to the activating ultraviolet light polarisation axis, which depends on the type of side chain moiety–whether it is, for instance, a coumarin [18] a chalcone [19], or a cinnamate moiety [20], Figure 2.

2. Experimental Methods

In the present work three different agents (manufactured by HD Microsystems) representing two types of photosensitive polyimides were investigated. These were: HD-8820 (positive-tone PI), HD-4100 and HD-4110 (negative-tone PIs), customarily used in semiconductor technology as photorestits. Aligning layer preparation technology is multistep. It involves the following procedures: (1) cleaning and drying the substrates, (2) preparation of the polyimide solutions, (3) adhesion promoter deposition (optional), (4) aligning agent (PI) deposition – usually spin-coating, (5) evaporation of the diluent–soft bake, (6) UV exposure (with polarised or unpolarised light), (7) temperature exposure (cure), (8) development, (9) post development bake (optional), (10) temperature cure in gaseous nitrogen atmosphere. The stages no: 2, 4, 6, 7, 8 and 10 were paid particular attention to in the present paper, since they have (apart from step 6) remarkable influence on the thickness and homogeneity of prepared layers.

2.1. *Preparation of the Layers*

Polyimide precursors solutions were deposited onto substrates (glass plate covered with indium-tin oxide, ITO) previously cleansed in ultrasound cleaners. There were various concentrations of the PI used, including: 30%, 20%, 15% and 6%. For the negative-tone polyimides the diluent was N,N-dimethylformamide, while the positive-tone polyimide was diluted in N-methyl-2-pyrrolidinone. The centrifuge was set as follows, subsequently: 500 cpm for 2 s, then 1500 cpm for 5 s and eventually 3000 cpm for 5 s. Afterwards the samples were soft-baked for 10 min; the negative-tone samples at 80°C, the positive-tone samples at 120°C.

2.2. *Irradiation with Polarised UV*

The next step consisted in irradiating the samples (30% PI solution as discussed above) with polarised UV. The UV source was a broadband 350 W high-pressure UV lamp (manufactured by Oriel). The polariser used was HNPB/plastic (manufactured by 3 M). To optimize the irradiation time '*checkerboard-like*' LC cells were prepared. Two substrates covered with the same polyimide were divided in five zones and then irradiated with polarised UV light so that (in case of the polyimide HD-4100) the first zone received the dose about 50 mJ/cm^2, the second received 100 mJ/cm^2, and the following 150 mJ/cm^2, 200 mJ/cm^2 and 250 mJ/cm^2. Then the two substrates were assembled by twisting them perpendicularly to each other in the way that the diagonal of the 'checkerboard' represented the same radiation doses. Thus a cell was obtained and filled with nematic liquid crystal W602lc (manufactured at the Institute of Chemistry, MUT). Cells obtained in that way were investigated using polarized and unpolarized light. After this assessment of the areas located on the diagonal and indentifying the area of the best uniformity, the procedure was repeated for the chosen dose together with one slightly higher and one slightly lower dose. These steps were applied for the three agents analysed with different doses for each polyimide material. In the Figure 3 the brighter area with better alignment of the liquid crystal is shown. It was the prerequisite to choose the dose as the optimal dose for irradiating polyimide HD-4100 layer. The optimal doses of polarised UV light turned out to be about: 168 mJ/cm^2 for HD-4100, and for HD-4110 and about 17 mJ/cm^2 for HD-8820.

2.3. *Layer Thickness Measurements*

In order to avoid greater increase in electric capacitance of the cells prepared, the thickness of the PI layer should be as small as possible. For that reason a series of PI layer thickness measurements was performed for all of the three polyimides in the four concentrations mentioned above. Half of the samples were irradiated with polarised UV light, and the rest with unpolarised UV light (as a reference) using the optimized doses described in section 2.2. The thickness was measured using an SPM 9001 spectrophotometer (Prema) and an MII-4 microinterferometer (Linnik). The results are shown in Table 1.

The main aim of this investigation was to obtain homogenous layers with the smallest possible thickness. Because the aligning agents were prepared through the diluting of the original HD solution, the adhesion to the ITO was decreasing with the rising degree of dilution. The smallest concentration of the material which

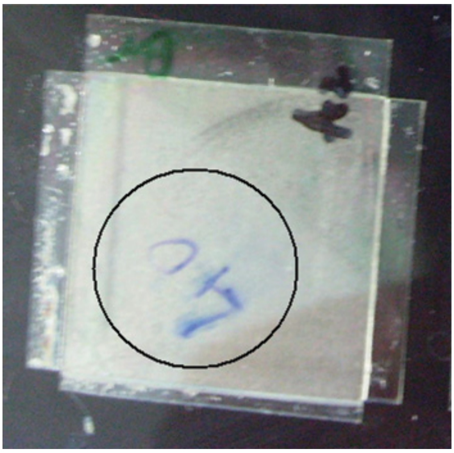

Figure 3. Photograph of the LC cell (made of two substrates with polyimide HD-4100) between crossed polarizers. In the encircled area one can see the homogeneous LC alignment. (Figure appears in color online.)

enabled preparation of the homogenous layers was about 6%. To prepare layers with thickness smaller than 70 nm an adhesion promoter has to be used.

2.4. *Homogeneity of the Prepared Polyimide Layers*

Photographs of HD-4110 polyimide layer obtained with Scanning Electron Microscope (Phenom, FEI Company) are shown in Figure 4. On the left, a rim of a substrate covered with polyimide can be seen (white diagonal line). There are conspicuous heterogeneities within the vision field. The picture on the right presents a homogeneous layer in the middle of the plate (not at the rim).

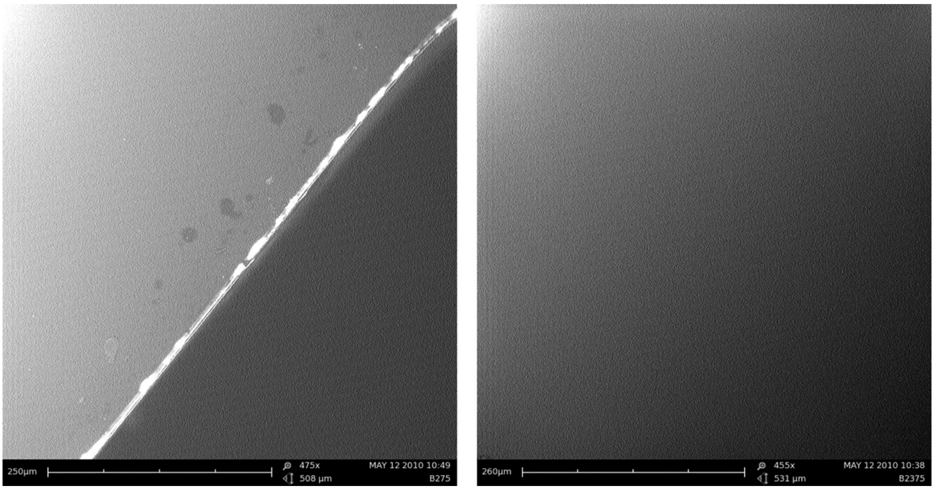

Figure 4. Photographs of non-homogeneous (left) and homogeneous (right) PI layer.

3. Conclusions and Perspectives

In the present paper a technological process for three photosensitive polyimides was presented. A series of layers was obtained and optimized through changing relevant parameters. First of all, a choice of polyimide concentrations was used so as to obtain lower layer thickness. Doses of linearly polarised ultraviolet light necessary for generating anisotropy in the layer were determined. Then thickness of a series of layers characterized by different concentrations and submitted to different irradiation doses and types (LPUV/UPL) was measured. This showed that there is no important influence of the light being polarised or unpolarised on the thickness of the layer obtained. Nonetheless, a mere sixfold decrease in concentration resulted in a considerable fall in the thickness – from 63 times in HD-8820 UPL to 190 times in HD-4110 LPUV – was achived.

The homogeneity and thickness of the PI layers are vital for the preparation of liquid crystals cells. As it has been stated above, the factors of utmost importance in this process are: PI precursor concentrations, centrifuge speed and spinning time, solution viscosity as well as the choice of correct soft bake parameters.

Acknowledgment

This paper was prepared in year 2010 with financial support of the Polish Ministry of Science and Higher Education, Key Project POIG.01.03.01-14-016/08 "New Photonic Materials and their Advanced Applications".

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