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## Uniform Planar Alignment of Nematics on Photo-Oriented Linear Polysilane

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We present herein a study on the alignment of nematic liquid crystals by a thin spincoated film of linear polysilane. The in-plane alignment of the polysilane chains was achieved by pre-illumination of the azobenzene containing monolayer, lying underneath, with a linear polarized light. Such a polysilane layer was found to align nematic liquid crystals in a uniform planar texture with preferred direction of orientation of the liquid crystal molecules lying along the polysilane main chains. In addition, the observed strong thermal fluctuations far below from the transition to isotropic phase indicated that the anchoring of the nematic on the polysilane film seems to be rather weak. The present study illustrates an approach for aligning liquid crystals through two-step transfer of orientational order from a photocromic monolayer to the liquid crystal via a buffer layer.

**Keywords:** azobenzene monolayer; polysilane film; LC alignment; orientational transfer

## **INTRODUCTION**

The alignment of liquid crystals is of great importance for the performance of liquid crystal displays and devices. Therefore, the activities of many research groups are focused on this particular subject. To control the physical properties of the solid substrates, and thus to control the alignment and the anchoring strength of liquid crystals in contact with these substrates, is both of scientific and of application importance.

The liquid crystal-solid surface interactions play an important role in the alignment and switching behavior of liquid crystals (LCs). In general, two are the important parameters characterizing the liquid crystal alignment, namely, the easy axis of alignment and the anchoring strength. These two parameters are very important for the appearance and for the performance of liquid crystal displays and devices. Usually the planar alignment is achieved by means of unidirectionally rubbed polymer layers. The usage of rubbed polymer layers for alignment of liquid crystals, however, has certain disadvantages such as generation of surface charges and mechanical defects. At present, only by the photoalignment, which is a non-contact method, is possible to achieve a highly uniform alignment of nematic LCs and, moreover, to pattern it. The big advantage of this method is that the alignment characteristics of the liquid crystal, like preferred direction of orientation and anchoring strength, can effectively be controlled by the illuminating light. Photoalignment of nematic LC can be realized by photopolymer thin films<sup>1,2</sup> or photochromic monolayers<sup>3,4</sup> which are irradiated with a linearly polarized light. On a photochromic monolayer such as an LB layer containing azobenzene (Az) side chain groups (6Az10-PVA),<sup>4</sup> for instance, the planar alignment of the LC is altered to homeotropic after several hours due to the proceeding of the cis-to-trans thermal back reaction. On the other hand, our recent work revealed that the azimuthal orientation of the backbone of poly(dihexylsilane) (PDHS) can be achieved in a highly ordered manner through the transfer from the photochromic Az monolayer.<sup>5</sup> Once the polymer chain is photochemically aligned it is very stable and not influenced by a

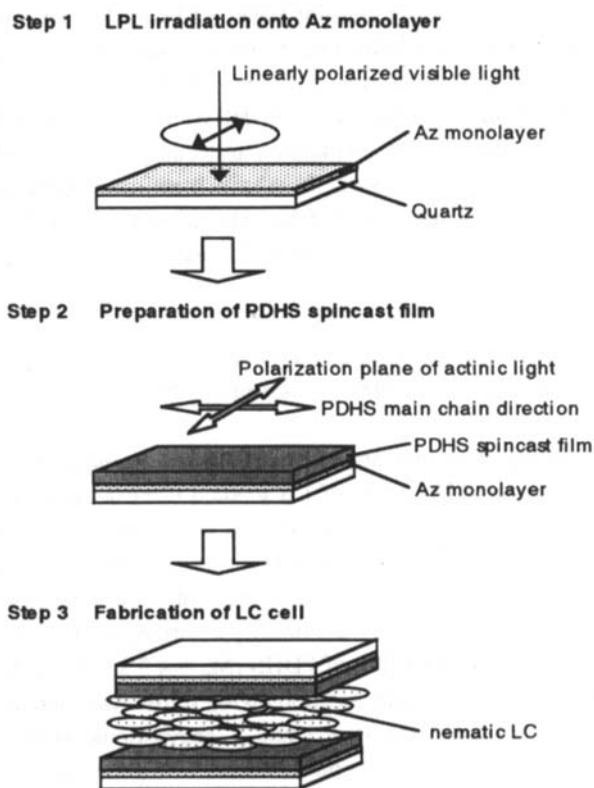
successive reaction of the Az monolayer underneath. The goal of the present work was to study the alignment of nematic LCs on polysilane thin film, alignment that was obtained via a two-step orientational transfer involving Az monolayer  $\rightarrow$  PDHS film  $\rightarrow$  LC molecules. Here are presented the sample preparation procedures and the results of experimental studies following the above mentioned approach of an indirect transfer of alignment from photochromic monolayer to a nematic LC via intermediate thin layer of linear polysilane chain.

### **EXPERIMENTAL**

A schematic illustration of the entire procedure of preparation of glass substrates and thereafter the assembling of LC cells is illustrated in Scheme 1.

According to the preparation procedure, the monolayer of 6Az10-PVA<sup>4</sup> was prepared by means of LB method using a Lauda FW2 film balance. The spread monolayer in the cis form was compressed to an area of 0.4 nm<sup>2</sup> per Az and transferred onto a fused silica plate. This 6Az10-PVA monolayer was irradiated first with non-polarized 365 nm (0.3 J cm<sup>-2</sup>), and then with 436 nm linearly polarized light (LPL) (3.0 mJ cm<sup>-2</sup>) (Step 1). A spincoat film of PDHS ( $M_w = 4.3 \times 10^4$ ,  $M_w/M_n = 2.6$ ) was deposited from a hexane solution on top of the Az monolayer (Step 2). The film thickness was  $45 \pm 3$  nm. A conventional sandwich cells were prepared using such silica plates coated with photo-oriented PDHS film on their inner side. The cell gap was fixed by a PET film spacer to be 25  $\mu$ m. A nematic LC (DON-103 or NPC-02 donated by Rodic Co.) was injected in the cell. The filling of the cell with LC was done in such way that the direction of the LC flow was different from the one of the light polarization in order to avoid any influence of the flow on the LC alignment.

UV-visible absorption spectra were taken by means of a HP8452A. The LC alignment induced by the photo-oriented PDHS film was inspected by means of polarizing microscope and evaluated from the measurements of light intensity of a probing polarized He-Ne laser beam transmitted through the cell.



Scheme 1 Procedure of cell fabrication

## **RESULTS AND DISCUSSION**

### **Photo-orientation of the PDHS film**

Immediately after preparation of the spincast film on the LPL irradiated 6Az10-PVA monolayer, no in-plane anisotropy was observed in the PDHS film. The orientation of the PDHS backbone in the film was promoted as the crystallization proceeded. After sufficient degree of crystallization of the film at room temperature, typically for 2 days,

the film exhibited a highly anisotropic behavior. The typical order parameter of the polysilane chains was ca. 0.4. Their orientational order enhanced upon annealing. Heating at 100 °C for 3 h followed by a successive storage at room temperature for 2 days led to significant improvement of the orientational order to ca. 0.6.

The polarized UV-visible absorption spectra of the PDHS film deposited on a pre-irradiated 6Az10-PVA monolayer are shown in FIGURE 1. As indicated, the orientation of the Si backbone is orthogonal to the polarization plane of the actinic LPL with high orientational order.

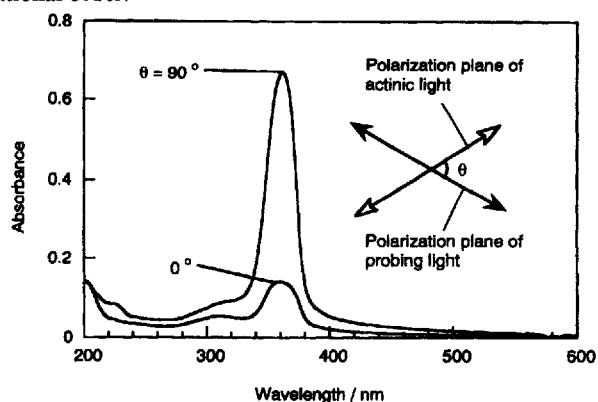


FIGURE 1. Typical polarized absorption spectra of PDHS film oriented on a 6Az10-PVA monolayer pre-irradiated with LPL at 436 nm.

### LC Alignment

Nematic LC (DON-103; C-17°C-N-73°C-I) was introduced in the sandwich cell consisting of two parallel plates covered with the photo-oriented PDHS film. FIGURE 2 shows the polarizing microscope photographs of the LC cell that have been taken at angle of 0, 15, 30 and 45 degrees, respectively, from the preferred direction of orientation of the Si-backbone. As shown, the LC exhibited uniform planar alignment. For LC cell fabricated with PDHS films that were not photoligned, no homogeneous texture of LC was obtained.

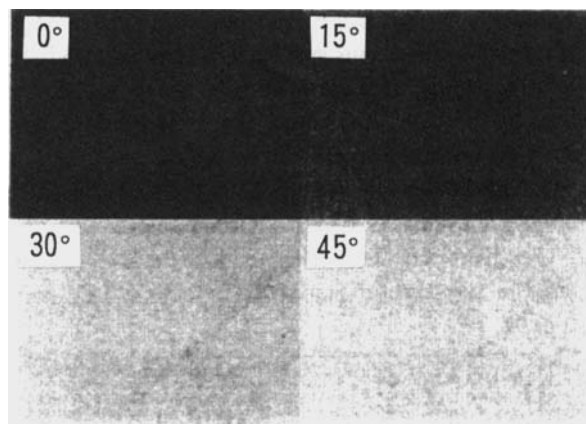


FIGURE 2 Images of the LC cell from the polarizing microscopic. The angles from the direction of PDHS main chain are shown in the images.

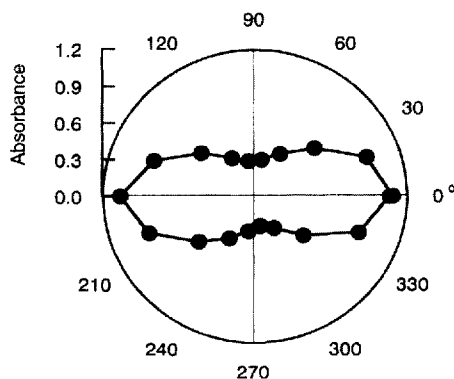


FIGURE 3 Angular dependence of absorbance at 633 nm of dichroic dye doped in the LC cell.  $0^\circ$  and  $180^\circ$  correspond to the direction of PDHS main chain direction.

In order to study the azimuthal orientation of the nematic LC in the cell with photoaligned PDHS films, a dichroic dye LCD-118 (Nihon Kayaku Co.) was doped into the LC material, and the angular dependence of the light absorption of Ne-Ne laser beam (633 nm) was



evaluated (FIGURE 3). The strongest light absorption was obtained at angles of  $0^\circ$  and  $180^\circ$  which indicates that the orientation of LC molecules is along the main chains direction of PDHS. However, the uniform LC alignment was not stable. After a long term storage, several hours to a couple of days, it underwent substantial changes due to the changes in the PDHS alignment layer. This layer was not simply dissolved in the nematic liquid crystal, as observed by the polarizing microscope. It seemed that the liquid crystal resulted in a detachment of the PDHS film from the Az monolayer lying underneath without destroying the polysilane film. For comparison, a cell with photo-oriented PDHS film filled with another nematic LC NPC-02 was prepared and studied. The preliminary results showed that in this case the polysilane alignment film appeared to be more stable. Further study is under way. The difference in the stability of the PDHS film in these two cases can be explained in the following way. The polarity of Az monolayer is enhanced after the photoisomerisation thus attracting more strongly the polar LC molecules. The LC molecules penetrate the polysilane layer entering slowly in between the azobenzene monolayer and polysilane film and, thus, resulting in detachment of the polysilane film from the substrate. Due to the different degree of polarity of these two LC, their molecules penetrate through the PDHS layer with different speed. Since the nematic LC DON-103 appears to be more polar and therefore more active in adsorbing on the azobenzene monolayer, the detachment of the PDHS layer from the substrate is much faster. The poor adhesion of the PDHS film on the Az monolayer did not allow us to carry out studies of the anchoring strength. Nevertheless, the optical study of the samples revealed that at room temperature, far away from the N-I phase transition of the liquid crystal, the planar anchoring is weak which was clearly indicated by the presence of intensive thermal fluctuations of the nematic molecules.

### CONCLUSION

In this work, the two step orientational transfer involving Az monolayer  $\rightarrow$  polysilane film  $\rightarrow$  nematic LC was successfully achieved.

The preferred direction of the LC alignment was found to be parallel to the photo-oriented main chain of PDHS. This approach provides a new way for photoalignment of nematic LC. Although the adhesion of the polysilane at solid substrate has been found to be rather weak, such kind of aligning films are certainly of interest since they offer weak planar anchoring of LC. Weak planar or quasi-planar anchoring is important for obtaining surface bistability in ferroelectric as well as in nematic liquid crystal displays and devices. Such weak anchoring conditions are important also for reducing the Fredericks threshold voltage in TN displays and devices.<sup>6,7</sup> Attempt to improve stability of the photo-oriented PDHS aligning films is a subject of future work.

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