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Brief Communication

Liquid-Crystal Photoalignment by Super Thin Azo Dye Layer

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A novel liquid crystal (LC) photoalignment method, based on a super thin azo dye molecular layer is proposed. The basic idea of this method is to form a very neat textile knitwear and uniform alignment by azo dye layer without spin coating and rubbing processes. The thickness of the alignment layer is smaller than 3 nm, which is much thinner than traditional PI alignment film. In addition to the advantages of a conventional photoalignment method, the use of super thin layer simplifies the alignment procedure, making possible a high electrooptical performance, good photo-tolerance and thermal stability, better adhesion on indium tin oxide (ITO) surface and compatibility with roll-to-roll process. [DOI: 10.1143/JJAP.45.203]

KEYWORDS: photoalignment, liquid crystal, azo dye layer

Liquid crystal (LC) photoalignment is a promising technology for manufacturing a variety of liquid crystal displays. This technique avoids many drawbacks of traditional rubbing technique for LC alignment, such as a sample contamination, static charge generation and mechanical damage.[1] The technique is attractive as a promising alternative to the rubbing process to be used in the next generation of displays, such as multidomain, vertically aligned, and/or in plane switching mode displays.

As an organic thin film to be used in the LC industry, a photoalignment layer is required to have a wide range of optimized properties. To facilitate rapid processing, the film must be formed easily with a high photosensitivity. The resulting photoaligned film must be insoluble and thermally, electrochemically, and photochemically stable. At present, a new photochemical stable azobenzene sulfuric dye, SD-1, has been synthesized[2,3] and polarization-sensitive photo-anisotropic layers on the basis of this dye were successfully tested for the LC alignment. A remarkable property of this azo-dye is the pure orientation of the molecular absorption oscillators perpendicular to the UV light polarization, which is practically not accompanied with photochemical transformations like other photoalignment materials such as CMPHs-SAM.[4] So SD-1 alignment layer has very good photo-tolerance.[5] In our latest experiments, the dose of UV irradiation of 175 MJ/m^2 from Xe lamp does not destroy LC alignment on polymerized azo dye SD-1 layers. And the polymerized azo dye layers can tolerate the temperature up to 250°C for two hours, which shows excellent thermal stability. Figure 1 shows the chemical structure of SD-1.

On the other hand, the spin coating is needed in liquid crystal display (LCD) fabrication process to be sure that the ITO surface is covered by a uniform layer. However, spin coating process is not suitable in many special cases, such as large area, flexible or curved surface. Moreover, the uniformity and mechanical stability of any alignment layer on indium tin oxide (ITO) surface depends on its thickness, which affects the optical quality of LCD.[2] Furthermore, on some surfaces, there exist certain adhesion problems of azo dye layers such as SD-1. Finally, the roughness of ITO surface is usually larger than the thickness of alignment layer, thus the island or porous defects in LC cells will appear, which distinctly deteriorates the optical quality.

The aim of this paper is to demonstrate a type of LC photoalignment based on super thin azo dye SD-1 layer. This

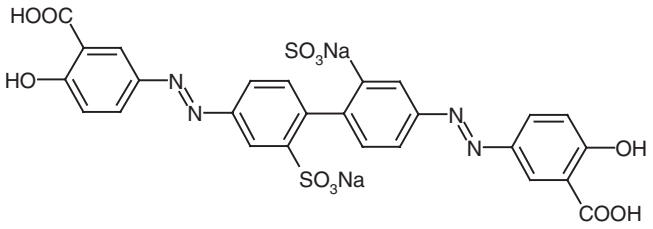


Fig. 1. Chemical structure of SD-1.

new method includes the formation of a very neat "textile knitwear" and can avoid island structures of alignment layers on ITO surface. The original thickness and quality of the pre-photo-alignment dye layers is not important in forming final alignment films. The super thin azo dye layer can be obtained by any accessible methods: draw from solution, roll deposited or orifice drawing, spin coating, vacuum or doctoring deposited, screen printing, tampon printing, etc. Our new method is very simple and suitable for large quantity fabrication of LC alignment, such as flexible displays or optical fibers. And all the good properties, such as good thermal stability and photo-tolerance, still exist if super thin layer is used for alignment.

The LC photoalignment composites were prepared as mixtures of SD-1 azo dye and DMF solvent by weight. The original thick azo-dye layer, e.g., 3% SD-1 solution, was drawn on glass substrates covered by ITO coatings for about 15 min in room temperature (~25°C). The coated films were annealed up to high temperature (~140°C) for 20 min to increase the quantity of azo dye molecules, which generated chemical bonding with a surface. Pure solvents, e.g., *N*,*N*-dimethylformamide (DMF), were used in 80° for 5 min to remove SD-1 molecules in the bulk, so that only the super thin layer remains, which is chemically adsorbed on the surface. The SD1 azo dye layer will continually and smoothly cover the ITO surface to form a very neat "textile knitwear". The anisotropy of the aligning substrates was induced by irradiating with a polarized UV-light (500 W Hg lamp with interferometric filter, $\lambda_{exp} = 365$ nm, $P_{exp} = 3.8$ mW/cm^2) to form the alignment layer. This process brings asymmetry to the orientational distribution of the azo dye molecules, which become efficiently perpendicular to the direction of the polarized light. The alignment layer was annealed again (140°C, 20 min) to increase the order parameter of the azo dye molecules. Figure 2 illustrates

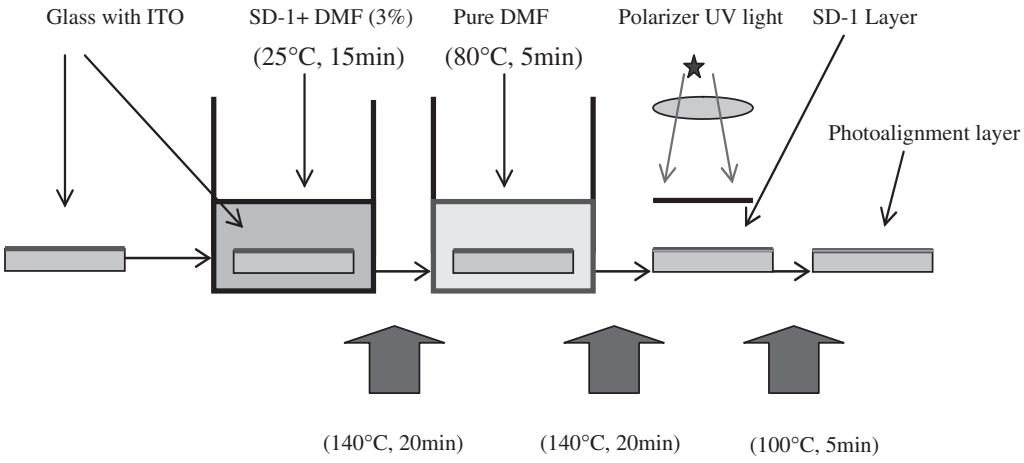
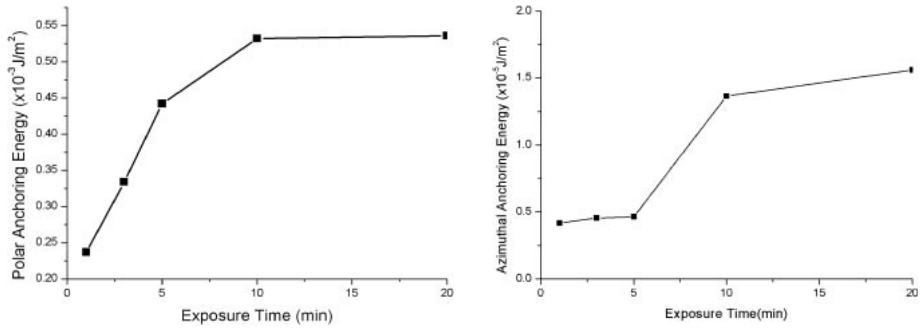


Fig. 2. Illustration of forming super thin photo-alignment layer.



(a) (b)

Fig. 3. (a) Polar anchoring energy of super thin layer with different exposure time. (b) Azimuthal anchoring energy of super thin layer with different exposure time.

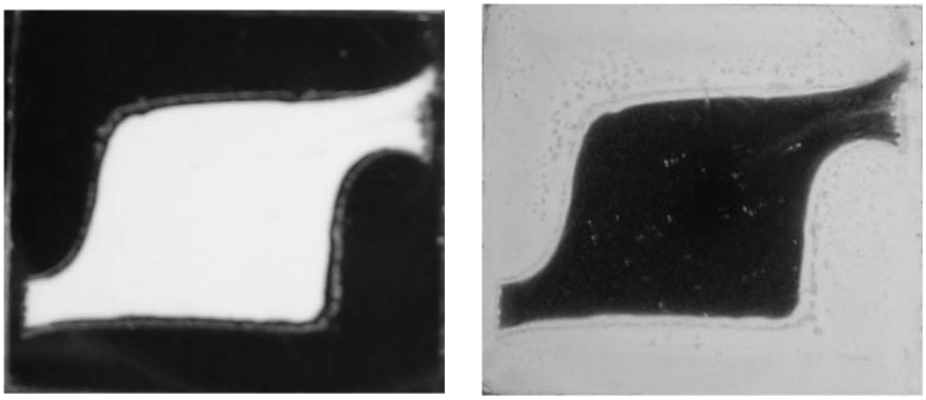
the formation of a super thin azo dye layer onto ITO glass substrates.

For traditional SD-1 alignment layer, Dr. Pozhidaev *et al.* have already been investigated the dependence of layer thickness on concentrations of SD-1 solutions in DMF spin-coated onto ITO surface at 3500 rpm.[6] They found that the SD-1 layer thickness increased from 0 to 12 nm (1.3%) when the concentration of SD-1 in DMF became larger. But no difference can be observed between the ITO surface coated with SD-1 layer and the surface without SD-1 layer if they are scanned by atomic force microscope (AFM) using a tapping mode. That means it is impossible to measure the thickness of super thin layer using the same method as before. We can only estimate the thickness of super thin layer should be smaller than 3 nm, which is the thickness of 0.4% SD-1 after spin coating, because the color of super thin layer is much closer to the pure ITO surface.

The polar anchoring energy of this super thin alignment layer was investigated. We use RV high voltage technique[7] and differential method for the measurement of polar anchoring properties of the super thin layer of azo-dyes. Liquid crystal MLC 5700-100 was filled into the cell. By carefully adjusting the exposure time of a linear polarized UV light (500 W Hg lamp with interferometric filter, $\lambda_{exp} =$ 365 nm, $P_{exp} = 3.8\,mW/cm^2$), a controllable polar anchoring strength can be obtained. Figure 3(a) shows the varied polar anchoring energy of this layer. The results are comparable with the conventional SD1 layer ($\sim 4.7 \times 10^{-4}$ J/m^2) when the exposure time is longer than 10 min, which can make LC properly aligned.

In order to obtain a good alignment quality, sufficiently strong azimuthal anchoring energy of this photo-aligned layer must be obtained.[3] Azimuthal anchoring energy was measured by making transverse nematic (TN) LC cells. Two substrates with superthin photoaligned layer were assembled with a 90° TN configuration. The resulting twist angle could be equal to 90° only in the case of a sufficiently high anchoring energy on the photo-aligned substrates, otherwise it decreased due to the elastic torque.[3] The MLC 5700-000 was injected into the cells with a cell gap of 5 μm. Figure 3(b) shows the measured azimuthal anchoring strength, which increases with the exposure time. The results show that the azimuthal anchoring energy is much smaller than the conventional SD1 layer ($\sim 10^{-4}\,J/m^2$) even after very long UV exposure time.

Using the super thin-molecular alignment layer, we successfully demonstrated 5 μm TN and 18 μm electrically controlled birefringence (ECB) cells. Figure 4 shows the product of 5 μm TN using super thin alignment layer, which exhibits very uniform and excellent alignment. The pictures on the left and right are the bright state and dark state respectively. Both of them give contrast ratio about 140 : 1 measured at the wavelength of 632 nm. It shows that when the super thin-molecular layer is used, even better contrast



(a) (b)

Fig. 4. (a) Bright state of 5 μm TN cell using super thin alignment layer. (b) Dark state of 5 μm TN cell using super thin alignment layer.

ratio can be obtained since the bright state is higher than ordinary thick SD1 layer. It can be possibly explained by the smaller thickness of the super thin layer is comparison with ordinary SD1 layer.

In summary, we have demonstrated LC display cell based on a super-thin photo-aligned layer. This new method includes the formation of a very neat "textile knitwear" and uniform alignment by a super-thin SD-1 layer and allows to avoid the spin-coating procedure. Moreover, the photo-sensitivity of azo-dye after photo-alignment can be further reduced and "island" azo-dye structures onto the rough ITO surface can be prevented due to better adhesion of SD-1 molecules. Using this super-thin SD-1 layer as an alignment agent, the sufficiently high polar and azimuthal anchoring energy and an excellent electrooptical performance in TN and ECB LC cells can be obtained. The method allows to obtain a perfect LC photo-alignment in large or curved cells and compatible with roll to roll process, thus is very attractive for mass production. We hope, that the results of our work can also be used to develop new LC devices, where very thin or curved surfaces are used.

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