

P-104: Aligning Layers Using Azo Dye Derivatives for Liquid Crystal Devices

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Abstract

The photo-induced alignment of an azo dye film and liquid crystal (LC) alignment on it are discussed for the liquid crystal display applications. Considerable dichroism is induced in the azo dye SD1 film not only by polarized UV light but also by obliquely incident non-polarized UV light irradiation. It was found that sulfo groups in the azo dye molecule play an important role in the LC alignment on the film. Large pretilt of LC on the photo-aligned film was achieved simultaneously, because the azo dye molecules can be easily reoriented out of the film plane by obliquely incident non-polarized light irradiation. In order to improve stability of the photo-aligned film, a monomer derived from the azo dye was synthesized. After thermal polymerization, the film of it also exhibit good photo-alignment properties. Improvement of durability against light exposure and moisture was observed in the LC cell using it.

1. Introduction

The photo-induced alignment of liquid crystal on film of azo dyes with peculiar molecular structure has been studied for the liquid crystal display applications [1-3]. The azo dye molecules reorient resulting in their absorption oscillator perpendicular to the polarization of the activating polarized UV light. The azo dye molecule is thought to be photochemically stable and reorient without cis-trans isomerization process [4,5]. This process can be described statistically as a diffusion motion of the dye molecules under the action of the polarized light [6,7]. The order parameter induced in the azo dye film is very large and its anchoring energy to LC molecules is as large as that of the rubbed polyimide film. Furthermore high thermal stability of the alignment and high voltage holding ratio (VHR) in the LC devices using the film suggest potentialities of its practical use.

In this paper, we discuss dependence of photo-alignment properties on molecular structure of these azo dyes. In order to improve durability against light exposure and moisture, we developed an azo dye monomer, which can be polymerized by heating after the photoalignment. We also report their photo-alignment properties.

2. Experimental

The azo dye compound SD1 shown in Figure 1 was synthesized for the study of photo-induced alignment. SD1 was synthesized from corresponding benzidinedisulfonic acid using azo coupling. The product was purified by recrystallization. SD1 was dissolved in N,N-dimethylformamide (DMF) at a concentration of 1 wt%. The solution was spin coated onto glass substrates with ITO electrodes and dried at 100°C for 1 minute. The spin-coated film was uniform and 10 ~ 20 nm thick. UV light was irradiated onto the surface of the film using super-high pressure Hg lamp through an interference filter at 365 nm. The light intensity irradiated on the surface of the film was 15 mW/cm² for polarized light and 40 mW/cm² for non-polarized light. In order to observe LC

alignment, two glass substrates with the photo-aligned film were assembled to form liquid crystal cell with a gap of 10 μm using thermally hardening adhesive and spacer. After heating at 150 °C for 1 hour, liquid crystal mixture 11-3323 (from Dainippon Ink and Chemicals Inc.) was injected into the cell in an isotropic phase by capillary action.

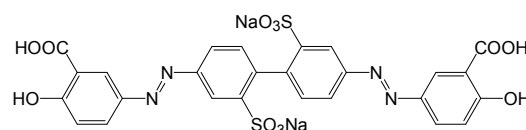


Figure 1. Azo dye SD1 used for the study of photoalignment

3. Photoalignment of the Azo Dyes

Polarized UV spectra of three kinds of azo dyes with similar molecular structure were measured. One of the dyes was SD1, and another one was a dye which has sulfo groups at 3,3' position of the biphenyl moiety instead of 2,2' position of SD1 (3,3'-SD1), and the other was a dye which has trifluoromethyl groups instead of the sulfo groups of SD1 (FD1). Chemical structures of the latter two compounds are shown in Figure 2.

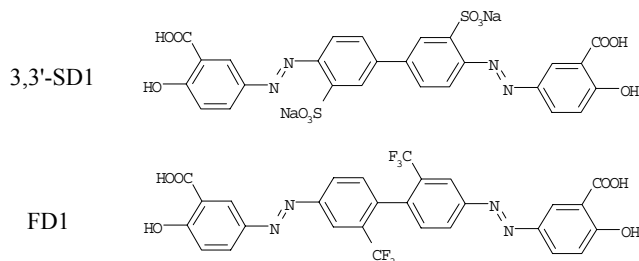


Figure 2. Azo derivatives used for comparison of photo-alignment properties with SD1

Figure 3 shows polarized light absorption spectra of SD1 film. Absorption maximum of SD1 was at 374 nm. After the irradiation of linearly polarized activating UV light, absorption of light with polarization parallel to the polarization of the activating light decreased, while that orthogonal increased. This result means that SD1 molecules reorient with their long axes perpendicular to the polarization direction of the activating UV light, because direction of their absorption oscillator is parallel to the long axes of the molecules.

The order parameter S induced by the polarized light irradiation can be defined as $S = (A_2 - A_1) / (A_2 + 2A_1)$, where A_1 and A_2 are

absorbance of light with polarization perpendicular and parallel to the polarization of the activating light, respectively. The maximum absolute value of S is 0.5 when these molecules reorient resulting in their absorption oscillator perpendicular to the polarization of the activating UV light. The induced S in the SD1 film was -0.267 at 374 nm.

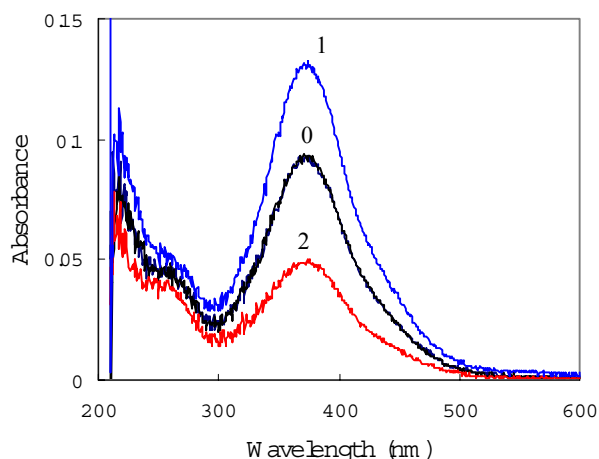


Figure 3. Absorption spectra of SD1 film before the polarized UV irradiation (curve 0). Curve 1 and 2 show the absorption spectra of light with polarization perpendicular and parallel to the polarization of the irradiated activating UV light (1 J/cm^2), respectively.

The dichroism was also induced in the film of 3,3'-SD1 and FD1. The induced S s of 3,3'-SD1 and FD1 at their absorption maximum were -0.173 (at 404 nm) and -0.059 (at 355 nm), respectively. These molecules were also reoriented with their long axes perpendicular to the polarization direction of the activating UV light.

The dichroism was also observed in these films after irradiation of obliquely incident non-polarized UV light. In this case, Non-polarized light was irradiated to the films obliquely at the angle of 45° to the film plane. The polarized light absorption spectra of SD1 film before and after the irradiation are shown in figure 4. After the irradiation, absorption of light with polarization perpendicular to the incidence plane of the activating UV light decreased more than parallel. From these results, it can be concluded that SD1 molecules reoriented with their long axes parallel to the incidence plane.

The order parameter S of SD1, 3,3'-SD1, and FD1 after the non-polarized light irradiation was defined as $S = (A_2 - A_1) / (A_2 + 2A_1)$, where A_1 and A_2 are absorbance of light with polarization parallel and perpendicular to the incidence plane of the activating non-polarized light. S s at their absorption maximum were -0.095, -0.123, and -0.016, respectively.

Angular dependences of optical retardation of the SD1 film irradiated with obliquely incident non-polarized UV light was measured using crystal rotation method [8]. The result is shown in figure 5. Increasing irradiation energy to the film, the maximum of the curve shifted towards the minus direction. This result means that not only reorientation within the film plane, but also

tilt of the molecules out of the plane is induced by irradiation of obliquely incident non-polarized UV light.

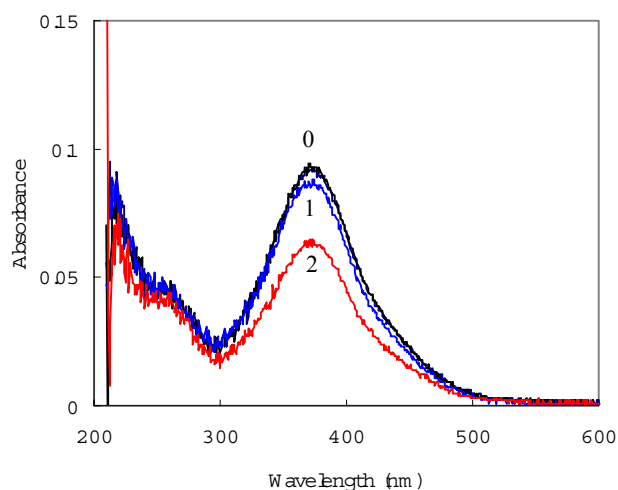


Figure 4. Absorption spectra of SD1 film before the UV irradiation (curve 0). Curve 1 and 2 show the absorption spectra of light with polarization parallel and perpendicular to the incidence plane of the irradiated activating UV light (5 J/cm^2), respectively.

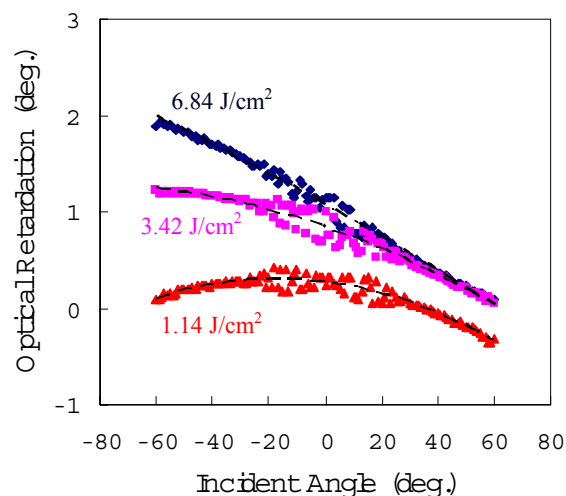


Figure 5. Angular dependences of optical retardation of the SD1 film irradiated with obliquely incident non-polarized UV light by function of the irradiation energy.

The azo dye molecules are reoriented by polarized light irradiation resulting in their long axes perpendicular to the polarization of the incident light. However, when irradiated with obliquely incident non-polarized light, they reorient resulting in their long axis parallel to the direction of incidence, because it is the only direction where their long axes is perpendicular to electric vector of the incident light. This is thought to be the reason these azo dye

molecules are photoaligned with tilt from the plane by obliquely incident non-polarized light irradiation.

4. LC Alignment on the Photo-aligned Azo Dye Films

LC alignment on the films of the azo dye derivatives was observed. In order to check the LC alignment directions, LC doped with dichroic dye M-317 (from Dainippon Ink and Chemicals Inc.) was injected into the cells. LC on the photo-aligned SD1 and 3,3'-SD1 films were aligned perfectly and homogeneously, while that on FD1 was aligned imperfectly. But, direction of the LC alignment is different between SD1 and 3,3'-SD1 film (see figure 6). Azo dye molecules in the all LC cells were photoaligned in the direction marked in the figure. It is judged from the figure that LC molecules on the SD1 films were aligned in parallel with the alignment direction of SD1 molecules, while those on 3,3'-SD1 films aligned perpendicularly, when UV light was irradiated using methods (a) and (b). Alignment of LC on 3,3'-SD1 film was not uniform in case of method (c).

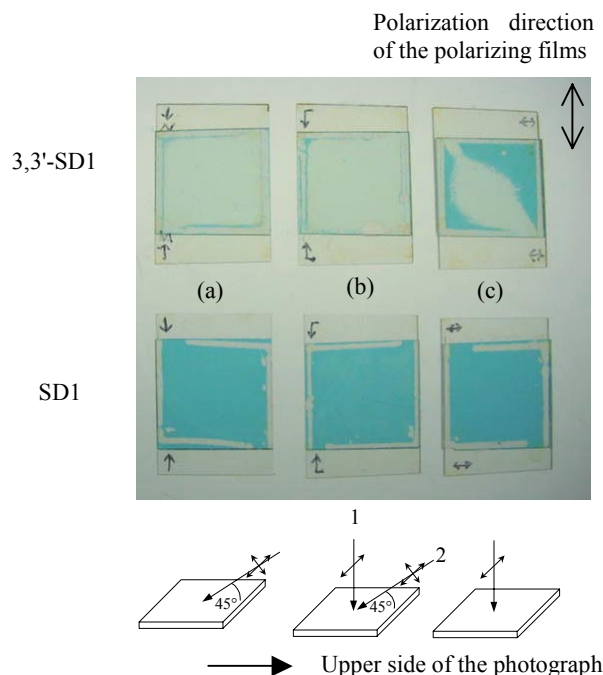


Figure 6. Observation of LC alignment by the photo-aligned azo dyes

The cells injected with LC were placed between two polarizing films. The UV irradiation methods used for the photoalignment are shown under the photograph. Azo dye films of (a) and (c) are irradiated with obliquely incident non-polarized and vertically incident polarized UV light, respectively. Method (b) is polarized light irradiation followed by non-polarized light irradiation.

From these results, it can be concluded that the LC alignment is strongly influenced by the sulfo groups in these azo dyes, not by the bis-azo structure.

Large pretilt of LC on SD1 was achieved simultaneously by obliquely incident non-polarized UV light irradiation (see figure 7). Considering the result of figure 5, it is deduced that pretilt of LC is caused by out-of-plane reorientation of the azo dye molecules.

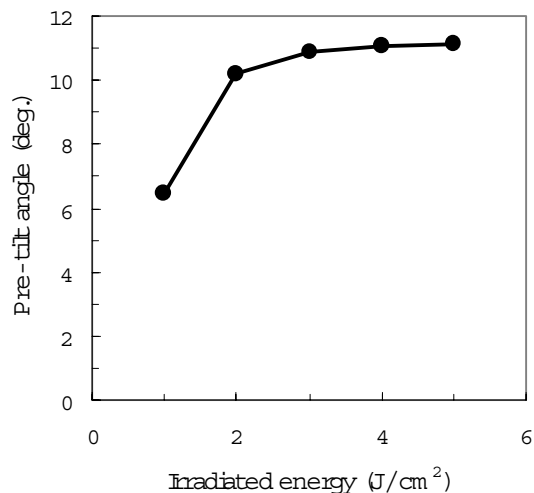


Figure 7. Dependence of the pre-tilt angle on the irradiation energy of the obliquely (45°) incident non-polarized light

5. Azo dye monomer

These photo-aligned azo dye molecules still have the ability to reorient by light irradiation unnecessarily. Besides, improvement of alignment durability against moisture is required, because these azo dyes are soluble to water. In order to improve the durability against light exposure and moisture, polymerization of the azo dyes after the photoalignment was investigated, synthesizing azo dye monomer SDA1 shown in figure 8.

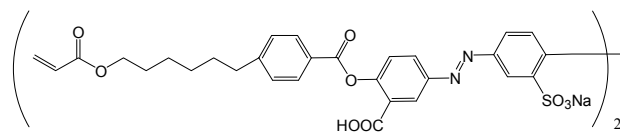


Figure 8. Azo dye monomer SDA1

It was dissolved in DMF and doped by 0.02 % of thermal polymerization initiator V-65 (from Wako Pure Chemicals Industries, Ltd.). The mixture was spin-coated onto glass substrates and photoaligned in the same manner as SD1. After the photoalignment, the SDA1 film was heated at 150°C during 1 hour for the purpose of thermal polymerization.

Optical anisotropy was also induced in the SDA-1 film by either polarized or obliquely incident non-polarized light irradiation (see figure 9). LC on the SDA1 film was aligned in the same direction as SD1. Pretilt of LC was achieved by the obliquely incident non-polarized light irradiation, too.

Improvement of durability against light exposure in the LC cell using SDA1 photo-aligned film after the thermal polymerization was confirmed. It can be concluded that LC alignment properties of the azo dye layer are preserved and the durability in the alignment is improved after the polymerization of SDA1.

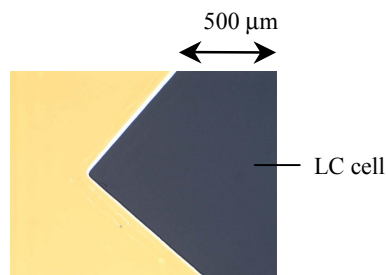


Figure 9. Polarized microscope photograph of LC alignment on photoaligned SDA1 film

6. Conclusion

Azo dye SD1 is photoaligned not only by linearly polarized light but also by obliquely incident non-polarized light irradiation. SD1 molecules reorient with their long axes perpendicular to the polarization direction of the polarized light, or parallel to the incidence plane of the obliquely incident non-polarized light. But the alignment of LC is influenced by the sulfo groups in SD1 molecule, not by the oriented direction of the bis-azo structure. Pretilt of LC is caused by out-of-plane alignment of the SD1 molecule induced by obliquely incident non-polarized UV light irradiation.

Alignment durability against light exposure and moisture can be improved by polymerization of the azo dye monomer which has the same structure as SD1 in the molecule.

The azo dyes, which exhibit the effect of the induced ordering due to the reorientation of the molecules by UV-light irradiation, are promising candidates for the photo-alignment layer for LC devices.

7. References

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