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Photoinduced Molecular Alignment of Azo Dye Derivative

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Abstract

Photo-induced molecular alignment behavior of azo dye derivative (sodium 4,4'-bis (4-hydroxy-3-carboxy-phenylazo) benzidine-2,2'- disulphonate : SD1) was investigated using SD1 film prepared by spin-coating method. As-prepared SD1 film was composed of an amorphous layer with smooth surface. Upon linearly polarized UV light irradiation, the film surface was roughened slightly and X-ray diffraction measurement and transmittance electron microscope observation indicated that SD1 molecules crystallized with orientation. Molecular plane of SD1 aligned parallel to the substrate surface along the normal to the polarization direction of irradiated UV light through the *trans–cis* and *cis–trans* isomerizations of the azobenzene chromophore.

Keywords: Azo dye; Photo-induced molecular alignment; Polarized absorption; Anisotropic diffusion model

1. Introduction

Liquid crystal (LC) displays are expanding in application because they offer several advantages such as reduction in thickness, low power consumption and so on. The alignment layers that play a significant role in orientation control of liquid crystal molecules are indispensable in the practical display fabrication. In general, the alignment layers are prepared on polyimide film by rubbing method. However, this method generates frequently the irregular degree of alignment in the layers and the static electricity with friction, resulting deterioration of the image quality. Therefore, new technique taking the place of rubbing method has been strongly desired. Nowadays, various methods such as photo-induced alignment technique [1-15], Langmuir-Blodgett (LB) technique [16-18] and subsequent thermal treatment of liquid crystalline polymer

[19] have been proposed as a rubbing-free technique. Among them, photoinduced alignment technique is a clean and non-contact process utilizing dimerization and/or isomerization of molecule with light irradiation. In this case, linearly polarized light, non-polarized light and coherent light of laser are used as an irradiation light. The photo-induced anisotropy in absorption property has been reported firstly in 1977 using polyvinylcinnamate [20]. However, polyvinylcinnamate was not so much sufficient as induced layer for LC crystals because of its poor thermal stability and poor compatibility with LC crystals. Recently, the potential ability on the molecular rearrangement of azo-benzene materials based on photo-isomerization has been much attention. There are many reports on formation of surface relief gratings (SRG) using azobenzene-based materials [21]. Several models of formation mechanism of SRG have been proposed, but few reports on the molecular alignment.

In this paper, the structure of photo-induced molecular alignment of azo dye derivative is investigated and the alignment mechanism is also discussed.

2. Experimental

Sodium 4,4’-bis (4-hydroxy-3-carboxy-phenylazo) benzidine-2,2’- disulphonate (SD1) shown in Fig. 1 was used as an azo dye. SD1 was synthesized by azo-coupling between 2,2’-benzidine disulfonic acid and salicylic acid according to the literature [22]. SD1 is dissolved in mixed solvent of 2-butoxyethanol, *N*-methyl-2-pyrrolidone and ethanol at a concentration of 1.0 wt%. SD1 film was prepared on a fused silica plate and Si-wafer by spin coating method and was heated at 100 ºC for 1 minute. The thickness of SD1 film was about 50 nm. Light irradiation was carried out using linearly polarized UV light of 365 nm with 0.05 mW/cm^2 power.

Ultraviolet-visible (UV-Vis) absorption and infrared (IR) absorption spectra of the films were recorded using a Shimadzu UV-2200 spectrometer and a Shimadzu IR-8100 spectrometer equipped with a reflection absorption spectrometry (RAS) instrument, respectively. Incident angle of IR light in RAS measurement was 70°. Morphologies and structures of the films were investigated by an atomic force microscope (AFM, Seiko Instruments SPI3700), a transmission electron microscope (TEM, Hitachi H-7100) and a X-ray diffractometer (Regaku Co., ATX-G). ATX-G is specially designed for characterization of thin films. A parabolic multiplayer equipped next to the laboratory X-ray source produces high intensity parallel beam (Cu Kα). The goniometer has not only usual $\omega/2\theta$ axes but also in-plane $\phi/2\theta\chi$ axes for measuring both in-plane and out of plane diffraction [23]. The incident angle of X-ray was 0.2° in $\omega/2\theta$ and

$\phi/2\theta\chi$ measurements. In this condition the penetration depth of X-ray was estimated about 1.0 μm [24].

3. Results and discussion

The polarized UV-Vis absorption measurements were performed with normal and parallel setup in which the polarization direction of the incident light was normal and parallel to the direction of the polarized UV light at irradiation, respectively. Figure 2 shows the polarized UV-Vis absorption spectra of the SD1 films before and after UV light irradiation for 60 minutes. As-prepared SD1 film showed a broad absorption corresponding to π-π* transition of trans-form azobenzene moiety in the wavelength region from 320 nm to 500 nm. The absorption intensities of both spectra indicated by $1_{\perp}$ and $2_{//}$, in which subscripts indicate the relative relation between the polarization dirction of the incident light and that of UV light at irradiation, are almost equal. On the other hand, after UV light irradiation, the absorption intensity of spectrum measured in normal setup ($3_{\perp}$) increased, while that in parallel setup ($4_{//}$) decreased. The dichroic ratio of absorption calculated directly from the peak intensity at 365nm was about 6. The transition moment of SD1 molecule is parallel to the longitudinal direction of the molecule. Therefore, it is suggested that SD1 molecules were aligned normal to the polarization direction of the irradiated UV light. The dichroic ratio in absorption increased rapidly until 20 minutes irradiation and then saturated at 60 minutes irradiation. It is found that an excess irradiation gives rise to the photo-degradation of SD1.

Figure 3 shows the AFM images of the films before and after UV light irradiation. As-prepared SD1 film was composed of an amorphous layer with smooth surface. Upon UV light irradiation for 20 minitues, the film surface was roughened slightly. However, it is noteworthy that the height distribution of the film surface is less than 2 nm.

There were no diffraction peaks in the XRD pattern of as-prepared film measured by 3 kinds of methods such as conventional $\theta/2\theta$ scan mode, out-of-plane and in-plane scan modes. Because the penetration depth of X-ray in out-of-plane and in-plane scan modes is about 1.0 μm, as-prepared film with 50nm in thickness is concluded to be amorphous as a whole. Figure 4 shows the XRD pattern of the film after UV light irradiation measured by $\theta/2\theta$ scan mode. Only halo pattern is observed. On the other hand, the XRD patterns measured by out-of-plane and in-plane scan modes showed the weak reflection peaks at $2\theta=6.3$ ° and 5.78 ° corresponding to interplanar distance of 1.40 nm and 1.53 nm, as shown in Fig. 5. Figure 6 shows the high resolution electron diffraction pattern of SD1 film and its schematic diagram after UV light irradiation. Diffuse diffraction arcs with the interplanar distance of 0.74 nm^{-1} are observed. Comparing the result with XRD measurement, it seems that these arcs correspond to the secondary reflection of the diffraction peak observed in in-plane scan pattern. It is noted that diffraction arcs appear along the polarization direction of the irraditated UV light. From XRD measurements and TEM observation, it is concluded that the SD1 molecules crystallize along same direction by UV light irradiation.

In order to clarify the molecular orientation of SD1 in the film , RAS measurement was carried out. Figure 7 shows the transmittance and reflection IR spectra of SD1 films on a Si-wafer after UV irradiation. Many absorption peaks appear in the finger region of both absorption spectra. The absorption bands at 1680 cm^{-1} and 910 cm^{-1} were asigned to the stretching vibration band of carboxyl group and the out-of-plane deformation vibration band of C-H in benzene ring, respectively. The bond axis of C=O in carboxyl group is located in the same plane formed with benzene ring because hydroxyl group and carboxyl group situated at ortho position each other form the cyclic structure by intramolecular hydrogen bonding. Therefore, these bands give information of the molecular orientation of benzene ring. The intensity at 1680 cm^{-1} in the refrection absorption spectrum is weaker than that in the transmittance absorption one. On the other hand, the refrection absorption intensity at 910 cm^{-1} is stronger comparing of the transmittance absorption intensity. These indicate that the benzene rings of SD1 molecule align parallel to the substrate surface. Therefore, it is concluded that the molecular plane of SD1 aligns parallel to the substrate surface along the normal to the polarization direction of irradiated UV light.

On consideration of the molecular alignment mechanism of SD1 induced by UV light irradiation, the formation model of SRG furnishes with much information. Three models; a pressure gradient model [25], an electric-field gradient model [26] and an anisotropic diffusion model [27]; have been proposed for SRG formation. A mechanism of a pressure gradient model is proposed which involves pressure gradients as a driving force, present due to different photochemical behaviors of the azo chromophores. A mechanism of an electric-field gradient model is proposed that the gradient force of the optical electric field and the influence of surface tension are considered as driving forces for photoinduced mass transport. The anisotropic diffusion model assumes that molecules absorbed light move to the direction parallel to the long axis of the azobenzene chromophore through the *trans–cis* and *cis–trans* isomerizations of the azobenzene chromophore. The anisotropic diffusion model is most spacious for the molecular alignment mechanism of SD1 because SD1 molecules aligned normal to the polarization direction of irradiated UV light as described above. Figure 8 shows the schematic diagram of alignment structure in the SD1 film induced by the UV light irradiation. The molecular planes of SD1 orient parallel to the substrate surface taking the longitudinal direction of the molecules normal to the polarization direction of the irradiated UV light.

4. Conclusions

Photo-induced molecular alignment behavior of azo benzene dye was investigated using SD1 film prepared by spin-coating method. Upon UV light irradiation, the anisotropic absorption feature of SD1 film was observed. Out-of-plane and in-plane XRD scanning pattern of the film after UV light irradiation showed weak reflection peaks. Height distribution of the SD1 film surface after UV light irradiation was estimated to be less than 2 nm. Molecular plane of SD1 aligned parallel to the substrate surface along the normal to the polarization direction of irradiated UV light through the *trans–cis* and *cis–trans* isomerizations of the azobenzene chromophore. The alignment mechanism of SD1 was explained by anisotropic diffusion model.

Acknowledgements

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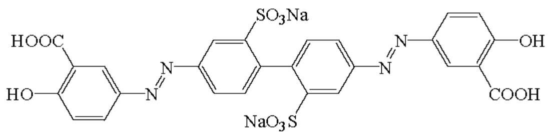

Fig. 1. Chemical structure of SD1

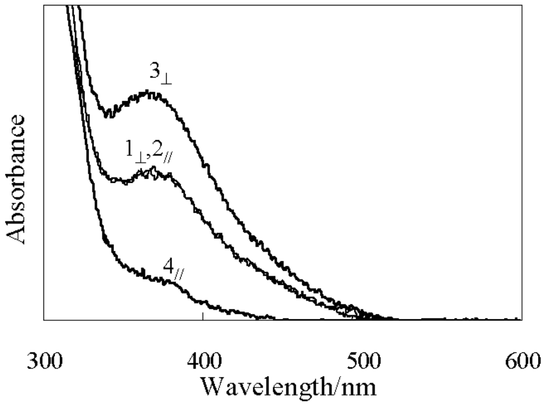

Fig. 2. Polarized absorption spectra of SD1 films before (curves 1⊥ and 2//) and after UV light irradiation (curves 3⊥ and 4//) in the direction normal and parallel to that of polarized UV light irradiated.

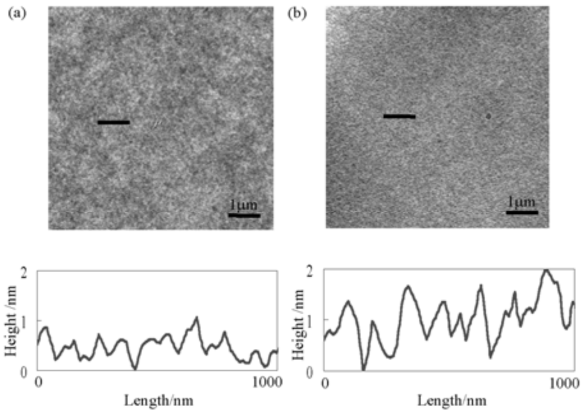

Fig. 3. AFM images and height profiles of SD1 film before (a) and after UV light irradiation (b). The black lines show scan line of height profiles.

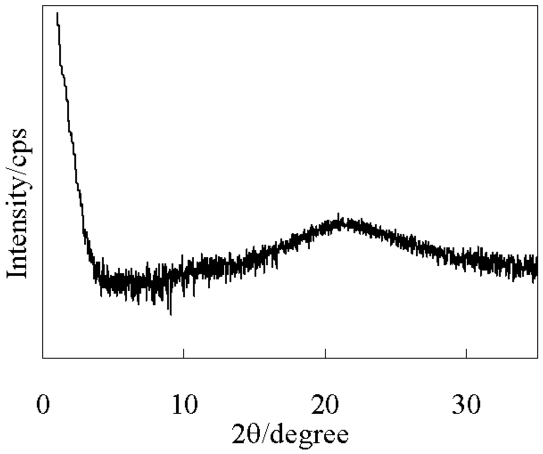

Fig. 4. θ/2θ XRD pattern of SD1 film after UV light irradiation.

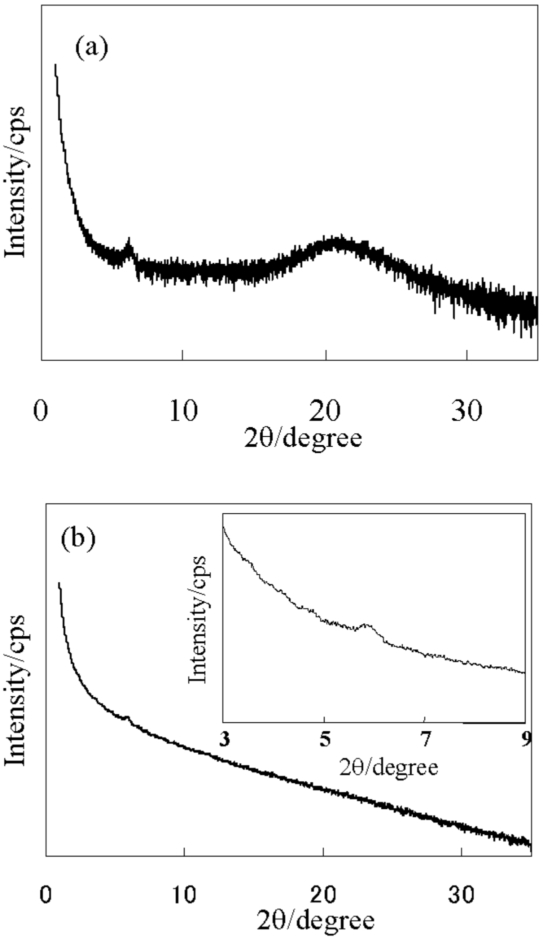

Fig. 5. ω/2θ (a) and ϕ/2θ (b) XRD patterns of SD1 film after UV light irradiation.

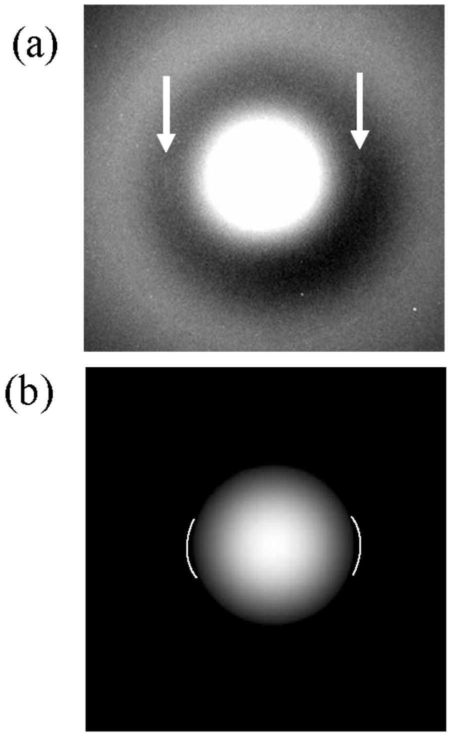

Fig. 6. High resolution electron diffraction pattern of SD1 film and its schematic diagram after UV light irradiation.

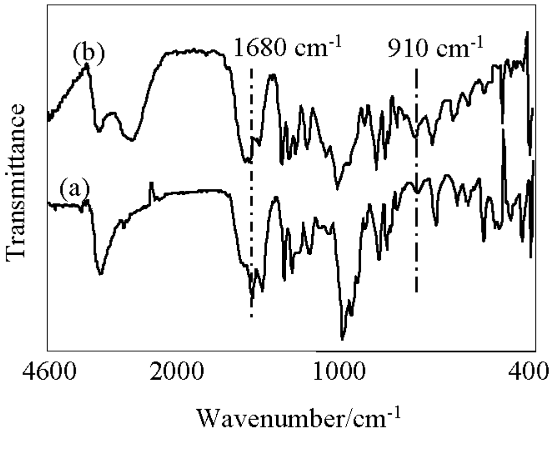

Fig. 7. Transmittance (a) and reflection IR spectra (b) of SD1 films after UV light irradiation.

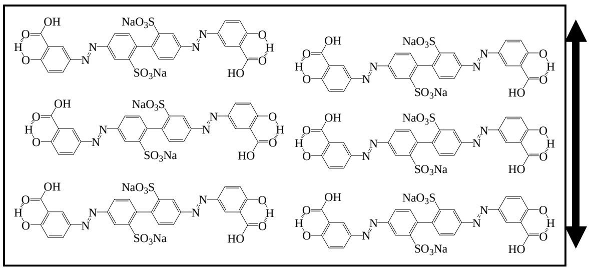

Fig. 8. Schematic diagram of the structure of SD1 film after UV light irradiation top view. The arrow indicates the direction of electrical field of irradiated UV light.