Photomechanical Behaviors of Azobenzene-based Amorphous Molecular Materials: Photoinduced Structural Changes of Amorphous Films of 4-[Bis(9,9-dimethylfluoren-2-yl)amino]azobenzene Analogues Fabricated on the Surface of Agar Gel

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Photomechanical behaviors of the films of 4-[bis(9,9-dimethylfluoren-2-yl)amino]-4'-cyanoazobenzene (CN-BFlAB) and 4-[bis(9,9-dimethylfluoren-2-yl)amino]-4'-nitroazobenzene (NO2-BFlAB) fabricated on the surface of agar gel have been investigated. Two-stage process including striped pattern formation and the subsequent band-like structure formation was observed upon irradiation with a linearly polarized laser beam with 488 nm, being similar to the result for the film of the parent compound, 4-[bis(9,9-dimethylfluoren-2-yl)amino]azobenzene (BFlAB). The rate of such structural change for CN-BFlAB was almost similar to or somewhat slower than that for BFlAB film. On the other hand, the rate for NO2-BFlAB was considerably slower than those for BFlAB and CN-BFlAB. The results suggested that the photochromic reactivity of the molecule in the amorphous film plays a role for the present photomechanical behaviors.

Keywords: Photomechanical behavior, Photochromic amorphous molecular materials, Azobenzene, Agar Gel, Reactivity

1. Introduction

Azobenzene-based organic films are attracting materials because of their unique photoinduced structural changes as photomechanical behaviors. In early stage, photomechanical bending motions of azobenzene-based liquid-crystalline polymer films have been reported [1,2]. Photoinduced surface relief grating (SRG) formation of azobenzene-based polymers have also attracted a great deal of attention [3-8]. The phenomena of the photoinduced SRG formation were believed to be due to mass transport in the films induced by interference irradiation with two coherent laser beams. SRG-forming ability was found to strongly depend on the polarization directions of incident beams. Several mechanisms of photoinduced SRG formation have been proposed [5-8]; however, the details have not been clear yet. Other unique photomechanical behaviors have been reported such as photoinduced deformation of spheres [9,10] and photoinduced phase-transition of azobenzene-based molecular crystals that triggered the photomechanical motions [11,12]. Self-oscillation of the hybrid self-assembled crystals upon continuous irradiation is also the recent attractive topic [13].

We have performing studies on the creation of low molecular-mass photochromic materials that readily form amorphous glasses, namely photochromic amorphous molecular materials [14-20] and in due course, we have found that azobenzene-based photochromic amorphous molecular materials exhibited several unique photomechanical behaviors related to photoinduced mass transport. At the initial stage, photoinduced SRG formation taking place for amorphous film of 4-[bis(9,9-dimethylfluoren-2-yl)amino]azobenzene (BFlAB) was observed upon irradiation with coherent laser beams [21]. Relationship between molecular structures and SRG forming properties have been investigated and it was concluded that the
glass-transition temperatures ($T_{gs}$) and photochromic reactivity of the materials play an important role for photoinduced SRG formation observed for the azobenzene-based photochromic amorphous molecular materials [22-24]. Not only photoinduced SRG formation but also other photomechanical behaviors have been found including photomechanical bending motions of azobenzene-based amorphous molecular fibers depending upon the polarization direction of incident beam [25,26], photoinduced mass flow at the surface of the azobenzene-based amorphous molecular films by angled irradiation with p-polarized laser beam [27], photoinduced movements of the glass fragments of the azobenzene-based amorphous molecular materials by angled irradiation with p-polarized laser beam from the bottom [27,28], photoinduced changed in phase-separated structures of composite films of azobenzene-based amorphous molecular materials together with poly(vinyl acetate) [29,30], and photoinduced structural changes of the glass particles of azobenzene-based amorphous molecular materials fixed in agar gel [31,32]. All these phenomena could be explained by the photoinduced vibration and/or transport of molecules parallel to the polarization direction of the incident beam.

Very recently, we have found a new photomechanical behavior of the azobenzene-based photochromic amorphous molecular material, that is, the photoinduced structural changes of the film of BFIAB fabricated on agar gel [33]. The phenomenon included two-stage process, striped pattern formation and the subsequent band-like structure formation depending on the polarization direction of the incident laser beam. Unfortunately, such phenomenon was not observed for several other azobenzene-based amorphous molecular materials with lower $T_{gs}$ maybe due to their higher fluidity upon photoirradiation. The phenomena were expected to be observed for films of azobenzene-based amorphous molecular materials with higher $T_{gs}$. It is of interest and of importance to elucidate the relationship between molecular structures and abilities of the phenomena, which might help understanding of the mechanism of the phenomenon. In the present study, we have investigated photoinduced structural changes of amorphous films of 4-[bis(9,9-dimethylfluoren-2-yl)amino]-4’-cyanoazobenzene (CN-BFIAB) and 4-[bis(9,9-dimethylfluoren-2-yl)amino]-4’-nitroazobenzene (NO$_2$-BFIAB) fabricated on the surface of agar gel. $T_{gs}$ of CN-BFIAB and NO$_2$-BFIAB are 117 and 116 °C, respectively [23], being somewhat higher than that of the parent material, BFIAB (97 °C).

### 2. Experimental

CN-BFIAB and NO$_2$-BFIAB were prepared by the methods reported in our previous paper [23]. Agar was purchased commercially (Kanto Chemical Co., Inc.) and used without further purification. Agar was dissolved in deionized water with a concentration of 2.5 mg‧mL$^{-1}$ by heating at ca. 90 °C and 4 mL of the solution was poured into the transparent glass petri dish with a diameter of 4.2 cm. Then the solution was cooled gradually at ambient atmosphere, followed by storing in refrigerator (ca. 3 °C) to obtain the underlying layer. The azobenzene-based materials, CN-BFIAB and NO$_2$-BFIAB, were gently casted onto the underlying agar gel layer from their carbon tetrachloride solution (6.9×10$^{-3}$ mol‧dm$^{-3}$) at ambient atmosphere and leave to stand to obtain the sample film placed on the underlying agar gel layer.

Schematic illustration of experimental set-up for monitoring the photomechanical response was shown in Fig. 1. The behaviors were monitored at ambient atmosphere (ca. 22 °C, 20–40%RH) in situ by means of optical microscope (Optiphot X2, Nikon) upon irradiation with polarized laser beam (488 nm, 15 mW; CYAN-488-100 CDRH, SpectraPhysics Inc.) from the bottom of the sample through an appropriate polarizer.

![Fig. 1. Experimental setup for observation of photoinduced structural changes of the film.](image_url)
3. Results and discussion

As well as BFlAB, we have found that the films of CN-BFlAB and NO$_2$-BFlAB fabricated on agar gel exhibited obvious photoinduced structural changes. Figure 2 shows optical microphotographs indicating photomechanical behavior of the CN-BFlAB film fabricated on the agar gel. When the film with almost smooth and homogeneous structure (Fig. 2a) was irradiated with the laser beam, the striped pattern formation took place immediately as shown in Fig. 2b. The direction of the stripes was perpendicular to the polarization direction of the incident laser beam. On further irradiation, the pattern gradually changed to form band-like structure aligned parallel to the polarization direction as shown in Fig. 2c. The present phenomenon with two-stage processes was quite similar to that observed for BFlAB film [33]. The striped pattern formation observed in the first process by means of optical microscope was suggested to be due to wrinkling of the film. With regard to NO$_2$-BFlAB film, similar photoinduced structural change with two-stage processes as shown in Fig. 3. These results suggested that higher $T_{gs}$ allowed to suppress the deformation of wrinkles caused by interface tension. Thus, the photoinduced structural changes of the films fabricated on agar gel were suggested to be general phenomena for azobenzene-based photochromic amorphous molecular materials with relatively high $T_{gs}$.

However, Fig. 3 indicated that the time needed for structural change of the NO$_2$-BFlAB film seemed to be quite longer than those for BFlAB and CN-BFlAB films. It took more than 10 times longer for striped pattern formation (Fig. 3b). Band-like structure formation seemed to be incomplete after irradiation for 60 min (Fig. 3c). Then, the rate of striped pattern formation in the first process was compared between them in more detailed. Figure 4 shows the changes in the number of stripes per 1 mm width ($N_L$) upon irradiation. It was found that the growth rate for CN-BFlAB (Fig. 4b) seemed to be similar to or somewhat slower than that for the parent BFlAB (Fig. 4a). On the other hand, the growth rate for NO$_2$-BFlAB was found to be considerably smaller than BFlAB and CN-BFlAB (Fig. 4c). We have already reported the photochromic reactions in amorphous states and photoinduced SRG formations of CN-BFlAB and NO$_2$-BFlAB in comparison of BFlAB [23]. It has been found that the fraction of the photogenerated cis-isomer at the photostationary state ($Y_{pss}$) upon irradiation with 450 nm light were 0.48, 0.33, and 0.14 for BFlAB, CN-BFlAB, and NO$_2$-BFlAB, respectively, and that SRG-forming ability of CN-BFlAB was similar to or somewhat smaller than that for BFlAB whereas the ability for NO$_2$-BFlAB was considerably smaller than those for BFlAB and CN-BFlAB. Thus we concluded that photochromic reactivity in amorphous states was reduced by introduction of bulky substituent that affected the SRG-forming ability. These results were consistent with the present photoinduced structural change of the films fabricated on agar gel. Then the rate of growth of stripe patterns observed in the present study was also suggested to be affected by the photochromic reactivity of the material. Because of the size of nitro-group is considerably larger than cyano-group, the photochromic reaction was more suppressed in amorphous states for NO$_2$-BFlAB, resulting in considerably lower ability of photomechanical stripe-pattern formation for the NO$_2$-BFlAB film.
fabricated on agar gel.

4. Conclusion
Photomechanical behaviors of amorphous films of CN-BFlAB and NO₂-BFlAB fabricated on agar gel were investigated. As well as the parent BFlAB, two-stage process including striped pattern formation and the subsequent band-like structure formation was observed upon irradiation with a linearly polarized laser beam with 488 nm. Thus, the phenomena of photoinduced structural changes of the films fabricated on agar gel were suggested to be general ones for azobenzene-based photochromic amorphous molecular materials with relatively high $T_g$s. The rate of such structural changes were found to depend on the molecular structure. Especially, the rate of photoinduced stripe-pattern formation for NO₂-BFlAB was considerably slower than those for BFlAB and CN-BFlAB. Substitution of large group was suggested to suppress the photochromic reactivity in the amorphous states, reducing the ability of the present photomechanical behaviors. Thus, the photochromatic reactivity of the molecule in the amorphous films was suggested to play a role for the present photomechanical behaviors.

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