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Short Communication

**Photomechanical response observed for azobenzene-based photochromic amorphous molecular films fabricated on the surface of agar gel**

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**Abstract**

As a novel photomechanical behavior, structural changes of azobenzene-based photochromic amorphous molecular films fabricated on the surface of soft materials such as agar gel were found upon irradiation with linearly polarized laser beam. The present photomechanical behavior included two-stage processes, striped pattern formation in the direction perpendicular to the polarization direction of the incident beam and subsequent band-like structure formation aligned in the direction parallel to the polarization direction. Both glass-transition temperature of the photochromic materials and the viscosity of the underlying layers were suggested to be important factors for exhibiting the present photomechanical behavior.

**Keywords:** *photomechanical behavior; azobenzene; photochromic amorphous molecular material; agar gel; glass-transition temperature, viscosity*

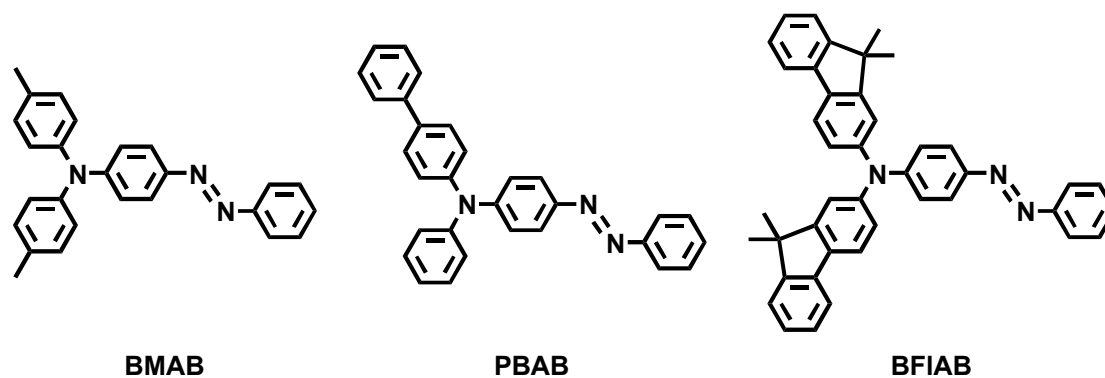
## 1. Introduction

Photomechanical behaviors observed for organic photochromic materials have attracted a great deal of attention. In early stage, photomechanical bending motion of azobenzene-based liquid-crystalline polymer films [1,2], photomechanical shape changes of diarylethene-based molecular crystals [3], and photoinduced surface relief grating (SRG) formation of azobenzene-based polymer films [4,5] have been reported as typical examples.

It is well known that azobenzene-based derivatives often exhibit photochromism based on photochemical trans–cis and cis–trans isomerization reactions. Due to their large changes in molecular structures associated with the photochromic reactions, azobenzene-based materials have great potential as candidates for photomechanical systems with large movements and/or structural changes. In addition to the above mentioned behaviors observed for azobenzene-based polymers, other unique photomechanical behaviors have been reported such as photoinduced deformation of spheres [6,7] and photoinduced phase-transition of azobenzene-based molecular crystals that triggered the photomechanical motions [8,9]. Self-oscillation of the hybrid self-assembled crystals upon continuous irradiation is also the recent attractive topic [10].

We have designed and synthesized several kinds of low-molecular-mass photochromic compounds that readily form amorphous glasses above room temperature, namely photochromic amorphous molecular materials, and have studied their photochromic properties as their amorphous films [11-15]. In addition, we have found that azobenzene-based photochromic amorphous molecular materials, such as BMAB, PBAB, and BFIAB, exhibit a variety of photomechanical behaviors related with photoinduced mass transport, such as photoinduced SRG formation of their amorphous films [16-18], photomechanical bending of their molecular fibers [19,20], photoinduced mass flow at the surface of their amorphous films [21], and photoinduced movements of glass fragments on the substrate [21,22]. It is to

be noted that all these phenomena depended on polarization direction of the incident laser beam. In addition to such single systems of azobenzene-based materials, we have also found that their hybrid systems exhibited other novel photomechanical behaviors such as photoinduced change in phase separated structures of the mixed films of the azobenzene-based materials with poly(vinyl acetate) [23] and photoinduced shape changes of glass particles fixed in agar gel [24,25]. Thus, the azobenzene-based photochromic amorphous molecular materials are expected to exhibit various behaviors by controlling their shapes and surrounding environments. We report here a new photomechanical behavior observed for the BFIAB film fabricated on the surface of soft materials such as agar gel.

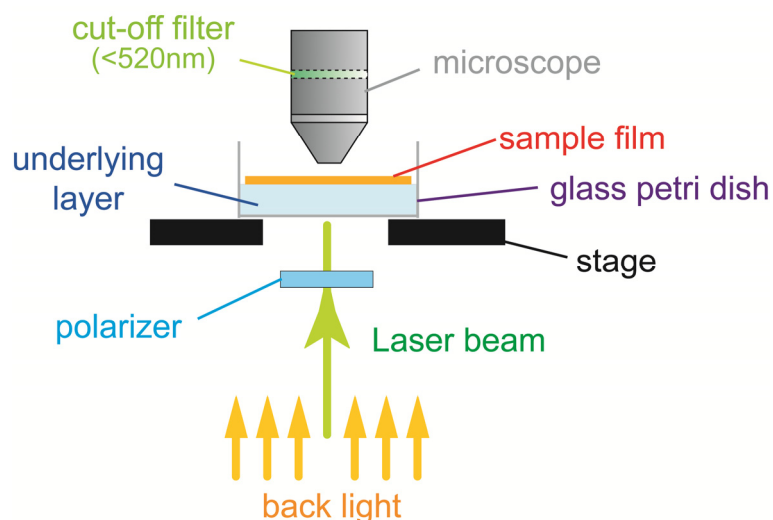


## 2. Experimental

Azobenzene-based photochromic amorphous molecular materials, BMAB, PBAB, and BFIAB, were prepared by the method described in our previous paper [15,26]. Agar (Kanto Chemical Co., Inc.), poly(vinyl alcohol) (PVA: Wako Pure Chemical Industry, Ltd.), and ethylene glycol (EG: Kanto Chemical Co., Inc.) were purchased commercially and used without further purification. Agar was dissolved in deionized water ( $0.5\text{-}2.5\text{ mg}\cdot\text{mL}^{-1}$ ) by heating at ca.  $90\text{ }^{\circ}\text{C}$  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.  $3\text{ }^{\circ}\text{C}$ ) to obtain the underlying layer. When the

concentration of agar was  $0.5 \text{ mg}\cdot\text{mL}^{-1}$ , the resulting underlying layer was viscous aqueous solution of agar. On the other hand, the layer was obtained as a gel when the concentration of agar was  $1.5 \text{ mg}\cdot\text{mL}^{-1}$  and larger. In the case of the concentration with  $1.0 \text{ mg}\cdot\text{mL}^{-1}$ , the incomplete gelation took place. The azobenzene-based materials were gently casted onto the underlying agar layer from their carbon tetrachloride solution ( $6.9 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1}$ ) at ambient atmosphere and leave to stand to obtain the sample film placed on the underlying agar layer. The thickness of the film was a few hundred nanometers estimated from the electronic absorption spectrum of the film. The BF1AB film placed on a mixed film of PVA and EG was fabricated by spin-coating method from carbon tetrachloride solution of BF1AB ( $6.9 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1}$ ) onto the mixed film of PVA and EG which was prepared by casting from aqueous solution of PVA and EG (20:80 w/w) onto a glass substrate. With regard to BF1AB film placed on single EG, the carbon tetrachloride solution of BF1AB ( $6.9 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1}$ ) gently put on the surface of EG in the petri dish and leave to stand to form the BF1AB film onto the surface of EG.

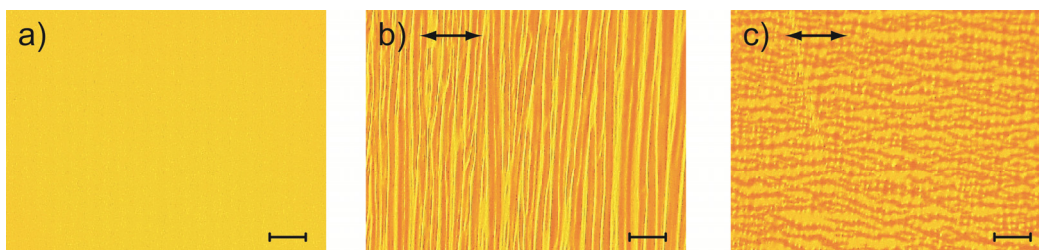
Schematic illustration of experimental set-up for monitoring the photomechanical response was shown in Fig. 1. The photomechanical responses of the films were monitored at ambient atmosphere (ca.  $22 \text{ }^\circ\text{C}$ , 20-40%RH) in situ by means of optical microscope (Optiphot X2, Nikon) upon irradiation with polarized laser beam (488 nm, CYAN-488-100 CDRH, SpectraPhysics Inc.) from the bottom of the sample through an appropriate polarizer. Surface structures after irradiation was examined by means of a confocal microscope (VK-X210, Keyence Co.).



**Fig. 1.** Schematic experimental set-up for monitoring the photomechanical behaviors.

### 3. Results and discussion

We have found that the BFIAB film fabricated on agar gel exhibited a novel photomechanical behavior with two-stage processes. Fig. 2 shows the optical microphotographs indicating photomechanical behavior of the BFIAB film fabricated on the agar gel with a concentration of agar of  $2.5 \text{ mg}\cdot\text{mL}^{-1}$ . Before irradiation, the sample was almost smooth and homogeneous as shown in Fig. 2a. When the sample film was irradiated with the laser beam with an intensity of  $15 \text{ mW}$  (ca.  $480 \text{ mW}\cdot\text{cm}^{-2}$ ), 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. Such photomechanical response of the film is shown in Supporting Video. When the irradiation stopped after striped pattern formation, the pattern was found to remain unchanged for at least 24 h in the dark at room temperature.

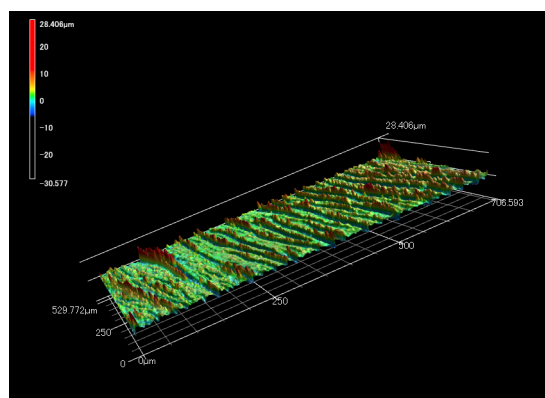


**Fig. 2.** Optical microphotographs of the BF1AB film fabricated on an agar gel (concentration of agar:  $2.5 \text{ mg}\cdot\text{mL}^{-1}$ ). a) Before irradiation. b,c) After irradiation with the laser beam for b) 30 s and c) 1800 s. Arrows indicate polarization directions of the incident beam. Scale bar:  $50 \mu\text{m}$ .

It is to be noted that such photomechanical response could be observed for neither BMAB nor PBAB films. We have previously reported that both photoinduced SRG formation observed for amorphous films [17] and photomechanical shape changes of the glass particles of azobenzene-based photochromic amorphous molecular materials fixed in agar gel [24,25] became more favorable with increasing glass-transition temperature ( $T_g$ ) of the material. These facts seemed to be consistent with the present results since  $T_g$ s of BMAB and PBAB ( $27$  and  $48 \text{ }^\circ\text{C}$ , respectively) were considerably lower than that of BF1AB ( $97 \text{ }^\circ\text{C}$ ). Thus, the  $T_g$  of the photochromic materials were suggested to be an important factor for exhibiting the present photomechanical phenomenon. Photomechanical force might become smaller with decreasing  $T_g$  of the photochromic materials due to increasing fluidity. In addition to these facts, we could observe the similar photomechanical behavior for the BF1AB film fabricated on the mixed film of PVA and EG, while no such phenomenon was observed for the BF1AB film fabricated on a glass substrate. These results suggested that soft materials as underlying layer also played an important role for the present photomechanical phenomenon.

Since the films on soft surfaces exhibit somewhat complicated photomechanical behaviors with two-stage processes as described above, we focused below on the first process, namely,

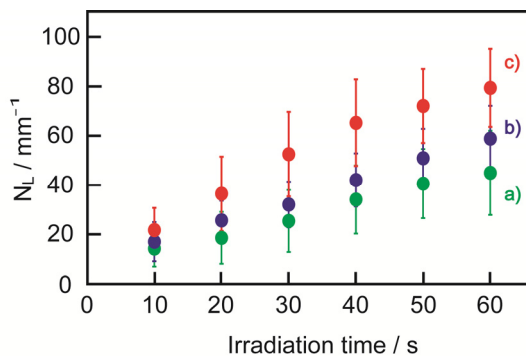
the striped pattern formation. Confocal microscopy of the BFlAB film fabricated on the surface of agar gel (concentration of agar:  $2.5 \text{ mg}\cdot\text{mL}^{-1}$ ) after irradiation for 30 s indicated the formation of wrinkle with their ridges aligned perpendicular to the polarization direction of incident laser beam as shown in Fig. 3. Thus, the striped pattern formation observed in the first process by means of optical microscope was suggested to be due to wrinkling of the film. It is to be noted that obvious molecular alignments could not be observed for photoinduced wrinkling confirmed by polarizing microscopy, that is, the optical views of the film under crossed Nichol condition were in dark before and after irradiation.



**Fig. 3.** Three-dimensional confocal microscope image of the BFlAB film fabricated on the surface of agar gel (concentration of agar:  $2.5 \text{ mg}\cdot\text{mL}^{-1}$ ) after irradiation with the laser beam for 30 s.

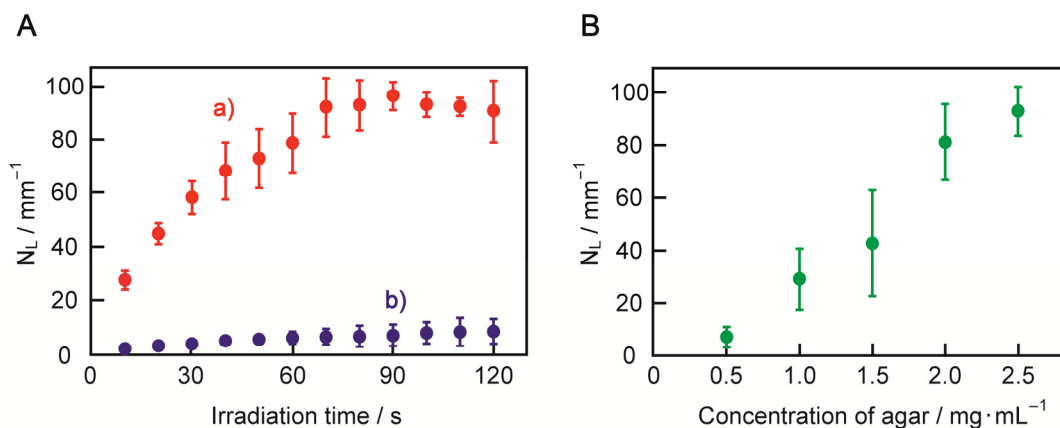
The striped pattern formation of the BFlAB films fabricated on the surfaces of agar gel were found to depend on the intensity of the incident laser beam. As shown in Fig. 4, the number of dark orange lines per mm ( $N_L$ ) observed in the above optical microscopies increased with the increasing irradiation time and the rate increased with increasing the intensity. The result suggested that the present striped pattern formation was associated with mechanical motions induced by photoirradiation.





**Fig. 4.** Growth of the  $N_L$  values observed for the BFIAB film upon irradiation with different intensity of incident beam. a) 5 mW, b) 10 mW, c) 15 mW. Concentration of agar in underlying layer:  $2.5 \text{ mg}\cdot\text{mL}^{-1}$ .

Next, the striped pattern formation of the BFIAB films fabricated on the surfaces of several underlying layers with different concentrations of agar were investigated. As shown in Fig. 5A, the  $N_L$  value increased with the increasing irradiation time in the region within a few minutes. With regard to the film fabricated on the gel with a concentration of  $2.5 \text{ mg}\cdot\text{mL}^{-1}$  (Fig. 5Aa), the increase in the  $N_L$  value seemed to be saturated within ca. 80 s. After that, the second stage process began to destroy the striped pattern gradually to form band-like structure. With regard to the film fabricated on the underlying agar layer with a concentration of  $0.5 \text{ mg}\cdot\text{mL}^{-1}$  (Fig. 5Ab), the  $N_L$  value was lower and increased slower. In this case, the increase in the  $N_L$  value also seemed to be saturated within ca. 80 s. Thus, the present photomechanical behavior depended upon the concentration of agar in the underlying layer. Fig. 5B shows the  $N_L$  values after irradiation for 80 s. It was found that the  $N_L$  value of stripes increased with increasing concentration of agar.

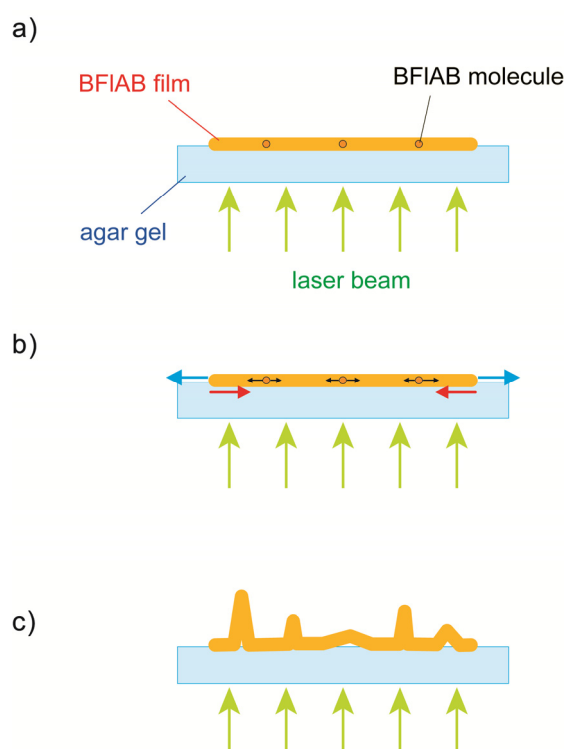


**Fig. 5.** A) Growth of the  $N_L$  values observed for the BFIAB film upon irradiation with an intensity of incident beam of 1.5 mW. Concentration of agar in underlying layer: a) 2.5  $\text{mg}\cdot\text{mL}^{-1}$ , b) 0.5  $\text{mg}\cdot\text{mL}^{-1}$ . B)  $N_L$  values after irradiation for 80 s with a laser beam vs. concentration of agar in underlying layer.

It was supposed that the viscosity of the underlying layer might correlate with the striped pattern formation. Thus, we have examined the  $N_L$  value formed on the surface of single EG. Viscosity of the EG was estimated to be 18 cp by means of Ubbelohde viscometer, being larger than that of aqueous agar solution with a concentration of 0.5  $\text{mg}\cdot\text{mL}^{-1}$  (2.0 cp). The viscosity of the incomplete gel with a concentration of 1.0  $\text{mg}\cdot\text{mL}^{-1}$  was assumed to be larger than EG. When the BFIAB film fabricated on EG was irradiated, the  $N_L$  value after 80 s was found to be  $22 \pm 8 \text{ mm}^{-1}$ , being between the densities of stripes formed on the underlying layers with concentrations of 0.5  $\text{mg}\cdot\text{mL}^{-1}$  ( $6.9 \pm 3.9$ ) and 1.0  $\text{mg}\cdot\text{mL}^{-1}$  ( $29 \pm 12$ ). The results suggested that the  $N_L$  value increased with increasing viscosity of the underlying layer.

The photoinduced striped pattern formation observed as the first process in the present study could be explained as follows (Fig. 6). When the BFIAB film was irradiated with linearly polarized laser beam (Fig. 6a), photoinduced trans-cis and cis-trans isomerization reactions of the molecules took place to soften the film. Subsequently, BFIAB molecules

vibrated and/or moved in the film in the direction parallel to the polarization direction of the incident beam (black arrows in Fig. 6b) to produce force to expand the film in the direction parallel to the polarization direction (blue arrows in Fig. 6b). However, the film was restricted from expansion due to repulsion force caused by interaction with viscous underlying layer (red arrows in Fig. 6b). As a result, wrinkling of the film took place (Fig. 6c), that was observed as striped pattern formation in the direction perpendicular to the polarization direction of the incident beam. When the viscosity increased with increasing concentration of agar in the underlying layer, the repulsion force became larger to increase the  $N_L$  value. With regard to the second process, it is speculated that the molecules existing near the ridges of wrinkles formed through the first process moved and/or vibrated in the direction parallel to the polarization direction of the incident beam and connected to the molecules at neighbor ridges to form band-like structure. Further studies are in progress.



**Fig. 6.** Schematic illustration of the plausible mechanism of photoinduced wrinkling.

#### **4. Conclusion**

A novel photomechanical behavior was observed for the BF1AB film fabricated on the surface of soft materials such as agar gel. The phenomenon included two-stage processes, striped pattern formation and the subsequent band-like structure formation depending on the polarization direction of incident laser beam. T<sub>g</sub> of the photochromic materials and viscosity of underlying layers were suggested to be important factors for exhibiting the phenomenon. Although it has not been clear why the molecules tend to move in the direction parallel to the polarization direction of incident beam, the present study promised that a variety of photomechanical behaviors can be induced by controlling the shape of the material, the environment of surroundings, and irradiation conditions.

#### **Acknowledgement**

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