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ARTICLE

Photoinduced shape change of azobenzene-based molecular glass particles fixed in agar gel †

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Photomechanical behaviours observed for photochromic materials have been attracting a great deal of attention. Here we report a new photomechanical phenomenon, i.e., elongation of azobenzene-based molecular glasses fixed in agar gel as an isotropic environment upon irradiation with linearly polarized laser beam to form string-like structure. Direction of the elongation was three-dimensionally confirmed to be parallel to the polarization direction of the incident beam. The phenomenon could be explained by the photoinduced vibration and/or transport of the molecules parallel to the polarization direction of the incident beam to generate the force of the particles to push the surrounding gel away in the direction parallel to the polarization direction. The increasing in Tg of the material was favourable but the introduction of bulky substituents at both ends of azobenzene moiety was undesirable for the photoinduced elongation. Such elongation could also be induced by using linearly polarized incoherent LED light, suggesting that the coherency of the incident beam was irrelevant to the photomechanical behaviours.

Introduction

Photomechanical behaviours observed for photochromic materials have been attracting a great deal of attention. In early stage, photomechanical bending motions of azobenzene-based liquid-crystalline polymer films and fibres,[1] reversible photomechanical shape changes of needle- and plate-shaped microcrystals of photochromic compounds,[2] and photo-induced surface relief grating (SRG) formation using azobenzene-based polymer films[3] have been demonstrated. Photomechanical shape changes of colloidal spheres composed of azobenene-conjugated polymers have recently been reported.[4] Related photoinduced fluidization phenomena were also reported for azobenzene-based materials.[5] Very recently, unique reversible shape changes of agarose-based film containing photoreactive 1,4-bis(para-hydroxystyryl)benzene have been reported.[6] We have been performing studies of the creation of photochromic molecular glasses, namely amorphous glasses of photochromic materials based on low molecular-mass derivatives,[7-9] and in due course we have found several kinds of their photomechanical behaviours related with photoinduced mass transport. They include photo-induced SRG formation on their amorphous films,[9,10] photomechanical bending motion of the molecular fibres of which the bending direction depended upon polarization direction of the incident beam,[11] photoinduced mass flow at the surface of the amorphous films[12] and photoinduced movements of the glass fragments on the substrate.[12,13] These phenomena could be explained by anisotropic mass transport induced in the direction parallel to the polarization direction of incident laser beam. However, in these cases, the materials were placed in somewhat anisotropic environments that might affect the

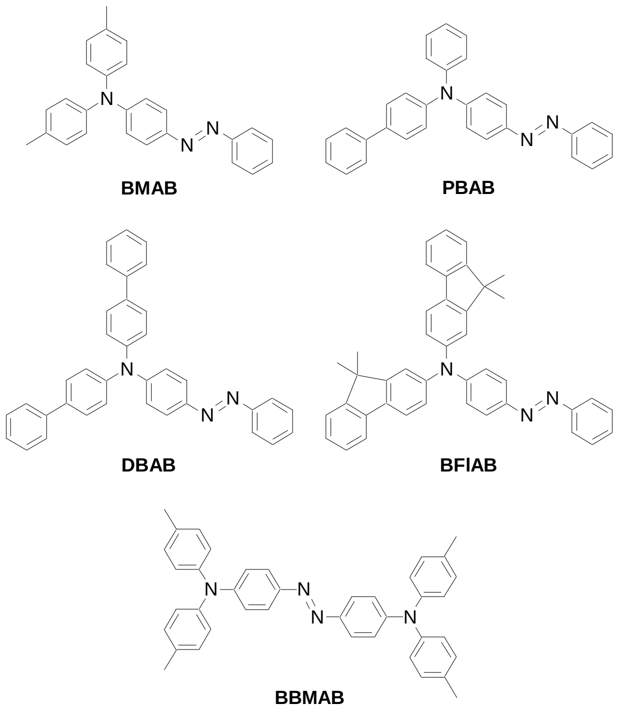

Fig. 1 Molecular structures of the materials used in the present study.

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anisotropic photomechanical behaviours. It is of interest and of importance to investigated the photomechanical behaviours in an isotropic environment, which will provide information about the exact direction of the photomechanical force and might help to elucidate the mechanism of the photomechanical behaviours related to the photoinduced mass transport. In the present study, photomechanical behaviours of the glass particles of azobenzne-based molecular mateials, 4-[bis(4-methylphenyl)amino]azobenzene (BMAB),[7b,10] 4-[phenyl-(biphenyl-4-yl)amino]azobenzene (PBAB),[14] 4-[di(biphenyl-4-yl)amino]azobenzene (DBAB),[7b,10] 4-[bis(9,9-dimethylfluoren-2-yl)amino]azobenzene (BFlAB)[7b,9a,10] and 4,4'-bis[bis(4-methylphenyl)amino]azobenzene (BBMAB)[7b] (Fig. 1), fixed in an agar gel as an isotropic environment have been investigated.

Results and discussion

As we have already reported, azobenzene-based materials, BMAB, PBAB, DBAB, BFlAB and BBMAB, form readily amorphous glasses with glass transition temperatures (Tg) of 27, 48, 68, 97 and 79 °C, respectively, and exhibit photochromism based on trans-cis and cis-trans isomerization reactions as their amorphous films.[7b,14] Experimental set-up for monitoring the photomechanical behaviours was illustrated in Fig. 2. Crashed powders of these materials were fixed in agar gel (concentration of agar: 2.5 mg cm^{-3}) in a transparent sample cell and the cell was placed on the stage of the optical microscope. Photomechanical behaviours of the particles with dimensions of ca. 5-15 μm were monitored at room temperature (ca. 21 °C) upon irradiation with the polarized laser beam (488 nm) from either bottom or side of the sample.

Upon irradiation of the BFlAB particles in the agar gel with linearly polarized laser beam, a new photomechanical behaviour was found. As shown in Fig. 3a, when the sample particles in the agar gel were irradiated from the bottom with the laser beam (15 mW[‡]), the shapes of the particles were gradually and drastically changed, being elongated parallel to the polarization direction of the incident laser beam to form string-like structure. The resulting structure maintained at room temperature after stopping the irradiation. When the resulting string-like particles were irradiated with the laser beam with another polarization direction, the particles immediately shrank and then elongated in the direction parallel to the new polarization direction. Such phenomena also can be seen in supplementary Videos 1 and 2.[†] It has been reported that the colloidal spheres with submicron dimensions composed of azobenzene-conjugated polymers placed on the surface of a silicon wafer were deformed upon irradiation with linearly polarized laser beam to form ellipsoids structures.[4] The phenomenon was somewhat resemble to the present photomechanical behaviours but the obtained structures were quite different from each other.

When the pristine sample was irradiated from the side, similar elongation of the particles parallel to the polarization direction was observed without elongation in the direction parallel to the path of the laser beam (Fig. 3b). Thus, the photomechanical elongation was three-dimensionally confirmed to take place just in the direction parallel to the polarization direction of the incident laser beam in the isotropic environment. Similar photomechanical elongations were observed for BMAB, PBAB, DBAB and BBMAB particles fixed in agar gel. It is notable that such photoinduced elongation could not been observed for crystalline samples of Disperse Red 1 and 4-iodoazobenzene without glass-forming ability, suggesting that glass-forming ability at around room temperature is needed to exhibit the photoinduced elongation behaviour.

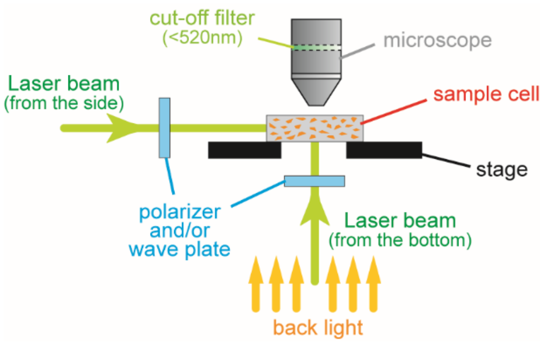

Fig. 2 Experimental set-up for monitoring the photomechanical behaviours.

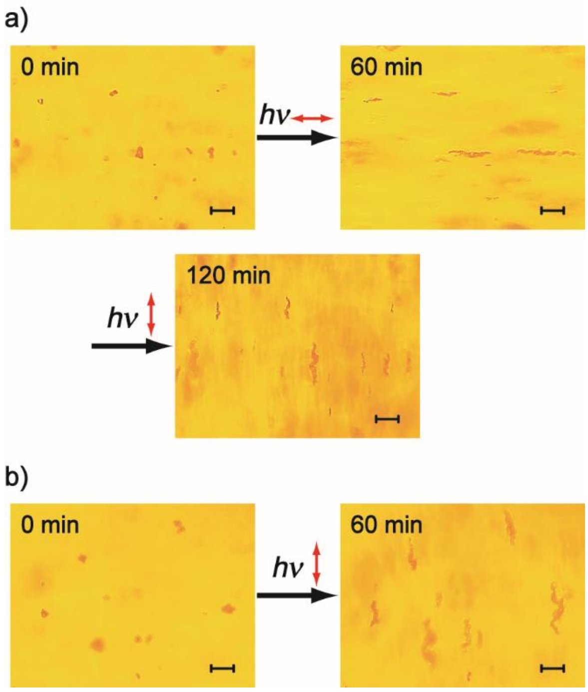

Fig. 3 Shape changes of BFlAB particles in agar gel upon irradiation with the linearly polarized laser beam (a) from the bottom and (b) from the left side of the sample cell. Red arrows indicate the polarization direction of the incident laser beam. Scale bar: 20 μm.

Here, the rates of elongation were evaluated by monitoring the change in relative length of long axis of the particle parallel to the polarization direction of the incident beam during irradiation of the laser beam under different conditions. Fig. 4 shows the change in the relative length of BFlAB particles upon irradiation with the laser beam with different intensities. Although the data have somewhat large distributions, the rates of such photoinduced elongation were found to depend upon the intensity of the incident laser beam, increasing with the increasing in intensity of the incident laser beam. It was also found that the rate decreased in harder gel; that is, by increasing the concentration of agar from 2.5 to 12.5 mg cm^{-3}, the relative lengths of long axis of the BFlAB particles after 60 min-irradiation of 15 mW laser beam decreased from 4.4±0.8 to 2.8±0.3.

It has been reported that photoinduced SRG formation observed for the amorphous films of azobenzene-based polymers and the amorphous molecular glasses upon interference irradiation strongly depend upon the polarization directions of the writing beams, and the mass transport was suggested to be induced in the direction parallel to the polarization direction of the laser beam.[3,10] Related phenomena observed for azobenzene-based molecular materials such as photomechanical bending motion of the molecular fibres, photoinduced mass flow at the surface of the amorphous films and photoinduced movements of the glass fragments on the substrate also depended upon the polarization direction of the incident beam and could be explained by the vibration and/or transport of the molecules parallel to the polarization direction of the incident beam.[12] Although the cause of such polarization-dependent vibration and/or transport of the molecule has not been clear yet, the present photomechanical elongation of the particles can be explained as follows. When the particles are irradiated with a linearly polarized laser beam, photoinduced trans-cis and cis-trans isomerization reactions of the molecules take place, resulting in softening the particles. Simultaneously, the molecules in the particles vibrate and/or transport in the direction parallel to the polarization direction of the incident beam. As a result, the force of the particles to push the surrounding gel away is generated in the direction parallel to the polarization direction, resulting in elongation of the particles. The force became stronger with the increase in intensity of the incident laser beam and harder gel suppressed the elongation stronger.

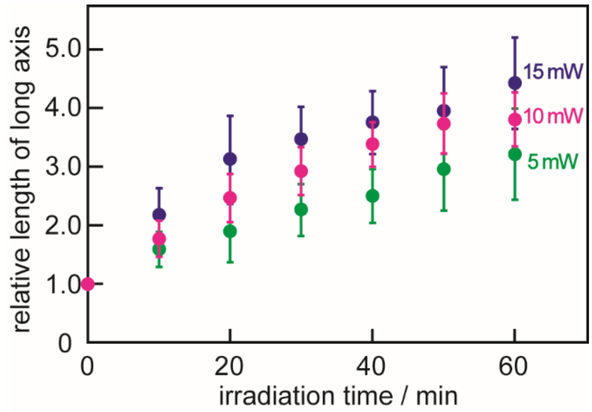

Fig. 4 Change in relative length of long axis of BFlAB particles during irradiation of the laser beam with different Intensities

The rates of photoinduced elongation were also found to depend upon the materials used as shown in Fig. 5. With regard to mono-substituted azobenzenes, the rate increased in the order BMAB < PBAB < DBAB < BFlAB under the same conditions. It is thought that the present photomechanical elongation of the particles related with both the frequency of trans–cis and cis–trans isomerization cycles and the fluidity of the material upon irradiation. That is, the increasing frequency of trans–cis and cis–trans isomerization cycles facilitates the vibration and/or transport of the molecules while the increasing fluidity of the material prevents the elongation due to surface tension to make the particles shrink. Since photochromic properties of

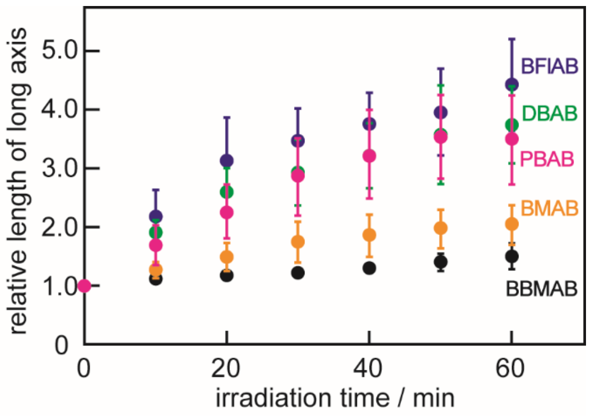

Fig. 5 Change in relative length of long axis of the particles of azobenzene-based molecular glasses during irradiation of the laser beam. Intensity of the laser beam: 15 mW.

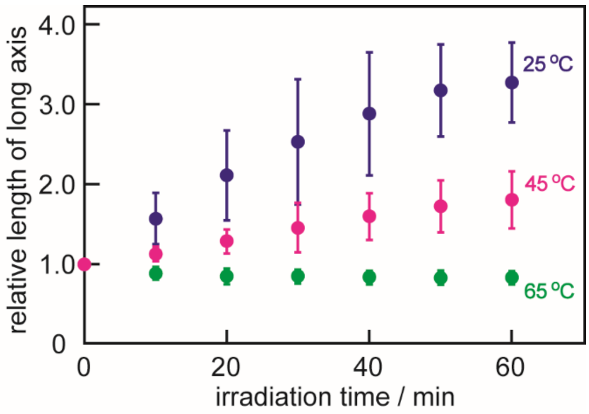

Fig. 6 Change in relative length of long axis of the PBAB particles during irradiation of the laser beam at different temperatures. Intensity of the laser beam: 10 mW.

BMAB, DBAB, PBAB and BFlAB as amorphous films are assumed to be more or less similar to one another,[7a,10] the fluidity was suggested to be dominant to affect the photomechanical properties. The fluidity of the materials at a certain temperature upon irradiation was assumed to relate to Tg of the materials as discussed in our previous paper.[10] That is, the fluidity upon irradiation was thought to be reduced by increasing Tg of the material before photoirradiation. Thus, the rate increased with the increasing in Tg of the material (BMAB < PBAB < DBAB < BFlAB). Fig. 6 shows the change in relative length for PBAB particles at a variety of temperatures. The results shows that the rate decreased with the increasing in temperature. Since the fluidity is assumed to be increase with increasing in temperature, the photomechanical elongation was more favourable at lower temperature. With regard to BBMAB, the rate was smaller than that for BMAB although the Tg of BBMAB is considerably higher than that of BMAB. Since the photochromic reactions of BBMAB were supressed in the amorphous solid due to bulky substituents at both ends of azobenzene moiety,[7b] just small photomechanical force could be induced. We have reported that the increasing in Tg of the material was favourable but the introduction of bulky substituents at both ends of azobenzene moiety was undesirable for photoinduced SRG formation using photochromic amorphous molecular glasses.[10] Thus, the results in the present study were consistent with those regarding the photoinduced SRG formation of the azobenzene-based molecular glasses depending upon the material.

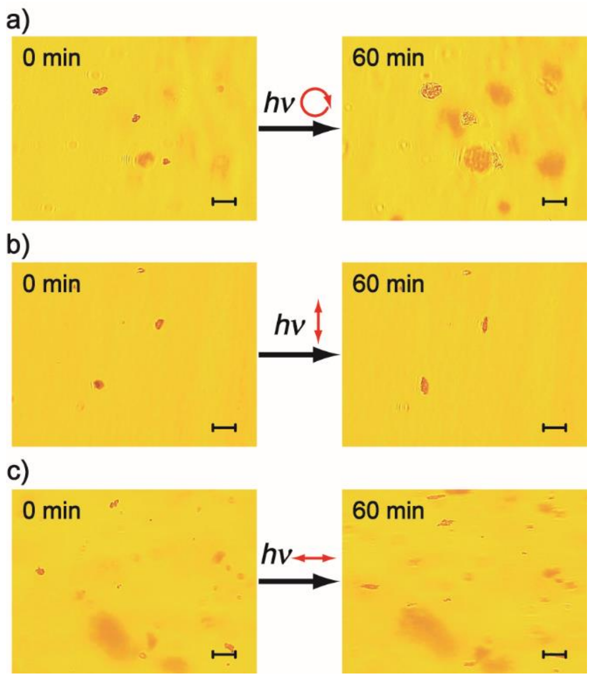

Fig. 7 a,b) Shape changes of BFlAB particles in agar gel upon irradiation with the circularly polarized laser beam (a) from the bottom and (b) from the left side of the sample cell. c) Shape changes of BFlAB particles in agar gel upon irradiation with the linearly polarized LED light from the bottom of the sample cell. Red arrows indicate the polarization direction of the incident laser beam. Scale bar: 20 μm.

It is expected that a variety of structures can be fabricated by controlling the photoirradiation conditions. Fig. 7a and 7b shows the shape changes of BFlAB particles in agar gel upon irradiation with the circularly polarized laser beam from the bottom and from the left side of the sample cell, respectively. The results showed that the particle extended radially perpendicular to the path of the incident beam to form somewhat disk-like structures. Since the circularly polarized beam was assumed to be assembly of linearly polarized beams with all polarization directions perpendicular to the path of the beam, the particles were suggested to expand to form such disk-like structures.

It is of interest to note that the photoinduced elongation behaviour could be observed when the linearly polarized incoherent LED light was used as a light source. When BFlAB particles fixed in agar gel were irradiated with incoherent LED light (450 nm, FWHM: 20 nm, intensity: 35 mW[§]) through polarizer, shape change with elongation in the direction parallel to the polarization direction of the incident light was also found to take place as shown in Fig. 7c. The relative lengths of long axis after 60 min-irradiation was 2.1±0.3, being comparable to that upon irradiation with the coherent laser beam with similar intensity. Thus, the coherency of the incident beam was suggested to be irrelevant to the photomechanical behaviours. The fact was of importance for considering the mechanism of the photomechanical behaviours.

Experimental

Materials.

All azobenzene-based materials, BMAB, PBAB, DBAB, BFlAB and BBMAB were prepared by the methods described in our previous papers.[7b,9a,14] Agar was purchased commercially (Kanto Chemical Co., Inc.) and used without further purification.

Sample preparation.

Agar was dissolved in deionized water (2.5 or 12.5 mg cm^{-3}) by heating at ca. 90 °C and the solution was poured into the transparent glass cell with a path length of 2 mm or 10 mm. The particles obtained by grinding the powder of the azobenzene-based materials were dispersed into the solution in the cell and then the cell was cooled gradually at ambient atmosphere, followed by storing in refrigerator (ca. 3 °C) to obtain the sample of the particles fixed in agar gel.

Methods for monitoring the photoinduced elongation and apparatus.

The sample cell was placed on the stage of the optical microscope (Optiphot X2, Nikon) and the photomechanical behaviours of the particles with dimensions of ca. 5-15 μm were monitored at room temperature (ca. 21 °C) upon irradiation with the polarized laser beam (488 nm, CYAN-488-100 CDRH, SpectraPhysics Inc.) from either bottom or side of the sample through appropriate polarizers and/or wave plates as shown in Fig. 2. In order to investigate the temperature dependence of photomechanical behaviours, the temperature of the sample cell was controlled by a TH-600PM hot stage (Linkam) fitted on a stage of the microscope. As an incoherent light source, UHP-LED-450 (Prizmatix) was used.

Conclusions

As a new photomechanical phenomenon, elongation of azobenzene-based molecular glasses fixed in agar gel was found upon irradiation with linearly polarized laser beam. It was three-dimensionally confirmed that the elongation took place parallel to the polarization direction of the incident beam. The phenomenon was suggested to be due to vibration and/or transport of the molecules induced parallel to the polarization direction of the incident beam, generating the force to push the surrounding gel away in the direction resulting in photomechanical elongation. The increasing in Tg of the material was favourable but the introduction of bulky substituents at both ends of azobenzene moiety was undesirable for the photoinduced elongation. The results could be explained by the fluidity of the material upon irradiation and the photochromic reactivity in the amorphous glass. It was also found that the photoinduced elongation of the particles can be induced by using incoherent LED light. The result suggested that the the coherency of the incident beam was irrelevant to the photomechanical behaviours. Present study provided important information for elucidating the mechanism of the photomechanical behaviours related to photoinduced mass transport and will help to develop a variety of photomechanical behaviours for use in practical applications such as photo-controllable micro-motors and actuators in the near future.

Acknowledgements

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Notes and references

‡ ca. 1.7 Wcm^{-2}

§ ca. 270 mWcm^{-2}

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