

Fabrication of novel light driven polymeric actuator

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Abstract

New light driven polymeric actuator based on multi-layered films of poly[1-[4-(3-carboxy-4-hydroxyphenylazo) benzenesulfonamido]-1,2-ethanediyl, sodium salt] was fabricated and demonstrated its bending and unbending behaviors. Multi-layered films showed bending and unbending properties upon UV-laser and visible light (435 nm) irradiation respectively. These results were caused due to the molecular orientation and *cis-trans* photoisomerization of azobenzene chromophores. The change in the molecular orientation might cause the disproportion of the molecular packing and the film bent to compensate for the distortion.

Keywords: Azobenzene polymer, Actuator, *Cis-trans* photoisomerization, Multi-layered film.

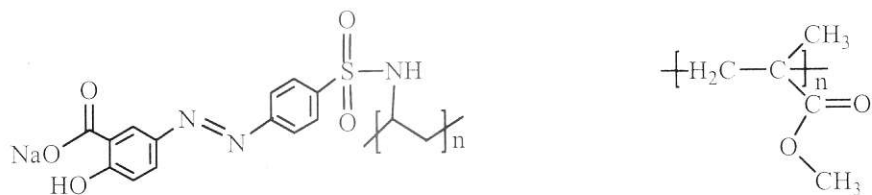
1. Introduction

An actuator is a mechanical device for moving or controlling a mechanism or system. It takes energy, usually transported by air, electric current, or liquid, and converts that into some kind of motion. The development of actuators based on materials that reversibly change shape and/or size in response to external stimuli has attracted interest for some time [1]. A particularly intriguing possibility is offered by light-responsive materials. The photo-response of these materials is based on the photoisomerization of constituent molecules (typically *trans-cis* isomerization of azobenzene chromophores), which gives rise to molecular motions and thereby deforms the bulk material. This effect has been used to create light-deformable polymer films and gels [2-10], but the response of these systems is relatively slow. On the other hand, the development of actuators that show bending movement is of increasing interest. The bending movement is usually induced by an asymmetric contraction or expansion in the materials [11-14]. This type of actuator has more advantages than the actuators that show only two-dimensional movements, such as expansion and contraction, from the viewpoint of precise three-dimensional actuation and long lifetime owing to small deformation for the bending action. Because of these unique properties, the bending actuators are expected to be used for cantilevers, micropumps, and many other micromechanical applications. Various materials have been reported as the bending actuators, such as piezoelectric transducers [15], shape-memory alloys [16], and polymers [12]. In comparison with other materials, the azobenzene polymer actuators are much

softer, lighter, and highly processible, which makes them easily made into various shapes; consequently, studies have been performed on the actuation of azobenzene polymeric materials and many applications have been proposed [17]. In addition, the bending of most polymeric actuators, such as conducting polymers is driven by electrical energy; thus, these materials require wires to acquire electrical power [13]. On the other hand, azobenzene elastomeric polymers, including gels and shape-memory polymers, can undergo mechanical actuation in response to various physical stimuli, such as pH [18], solvent composition [19], heat [20-22], and light [23, 24]. Light can be controlled remotely and rapidly as an external stimulus, so it is of great importance in developing simple, efficient, and compact azobenzene polymeric actuators that can be driven by light. So in this study we attempted to fabricate light driven azobenzene polymeric actuator based on multi-layered film and demonstrated its bending and unbending properties by molecular orientation and *cis-trans* photoisomerization of azobenzene chromophores.

2. Experimental

In this study, two polymers: one is photoresponsive polymer, poly[1-[4-(3-carboxy-4-hydroxyphenylazo) benzenesulfonamido]-1,2-ethanediyl, sodium salt] (PAZO) and other is non photoresponsive, poly (methyl methacrylate) (PMMA) as shown in Scheme 1, were used. Both of these two polymers are commercially available. Poly[1-[4-(3-carboxy-4-hydroxyphenylazo) benzenesulfonamido]-1,2-ethanediyl, sodium salt] was purchased from Sigma-Aldrich and PMMA was purchased from Wako Pure Chemical Industries Ltd. PAZO is soluble in water and PMMA is soluble in toluene.



Poly[1-[4-(3-carboxy-4-hydroxyphenylazo) benzene sulfonamido]-1,2-ethanediyl, sodium salt]

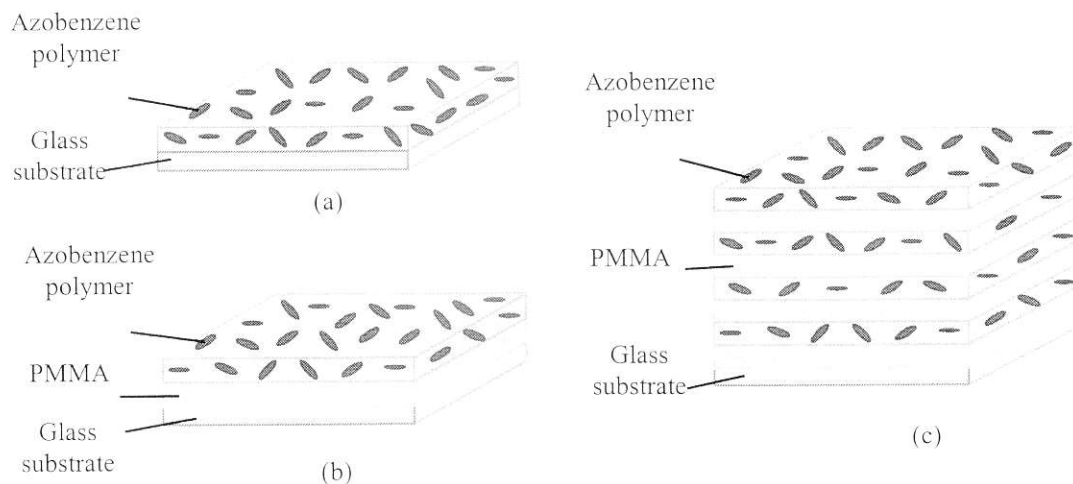
Poly(methyl methacrylate)

Scheme 1: Polymers used in this study

3. Fabrication of multi-layered films

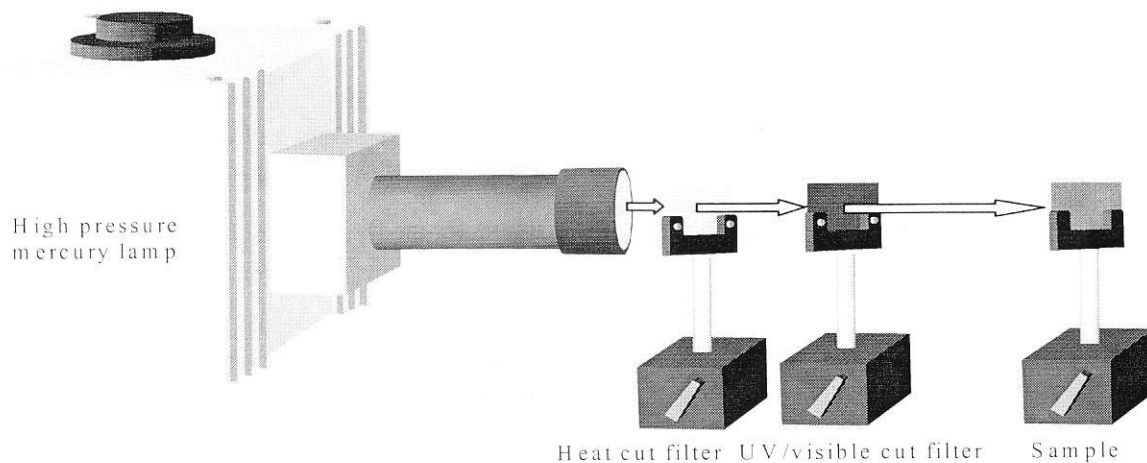
Multi-layered films were fabricated by alternative spin coating of solutions containing PAZO and PMMA on a glass substrate (25 x 20 mm, micro slide glass, Matsunami). Typical coating was performed as follows: speed of rotation 3000 rpm and time of rotation 30 sec with 4 wt% of PAZO

in water and 3 wt% of PMMA in toluene. After spin coating each layer was dried for 5 min at room temperature and water and toluene were evaporated (Scheme 2). Multi-layered films were annealed at 80°C for about 1 h, slowly cooled to room temperature and separated from glass substrate. Thickness of the film was around 3000 nm.



Scheme 2: Construction of multi-layered film by spin coating method, (a) PAZO single layer film, (b) PMMA/PAZO 1 bi-layer film and (c) PMMA/PAZO multi-layered (20 bi-layered) film.

Photoirradiation was performed by using a 500W high-pressure Hg lamp (USHIO) with adequate cut filter for UV and Vis light at room temperature. The experimental set up for photoirradiation is shown in Scheme 3.



Scheme 3: Schematic diagram of the experimental set up for photoirradiation.

The orientational order was studied using polarized UV-Vis spectroscopy (Perkin Elmer Lambda 650 UV/Vis Spectroscopy), because the transition moment of the *trans* isomer of azobenzene moiety is directed along the long axis of this group. For this purpose the angular dependence of the absorbance was measured.

4. Results and Discussion

Bending and unbending of multi-layered film

As shown in Figure 1, the multi-layered film showed bending and unbending (also shape changes) behaviors upon irradiation of UV-laser and visible light respectively. When UV-laser (375 nm) light was irradiated upon multi-layered

film, it became bended gradually to the opposite of irradiation direction. And after prolonged irradiation the film bended to a certain level. After observing the bending behavior of multi-layered film, visible light of 435 nm was also irradiated. Upon irradiation of visible light the multi-layered film became unbending gradually. After 30 min visible light irradiation the film shifted to its original position. Before UV light irradiation, the film was annealed at 80°C for 1 hour. In multi-layered film, before annealing the azobenzene chromophores were aligned randomly on glass substrate and after annealing the azobenzene chromophores may be aligned vertically on glass substrate.

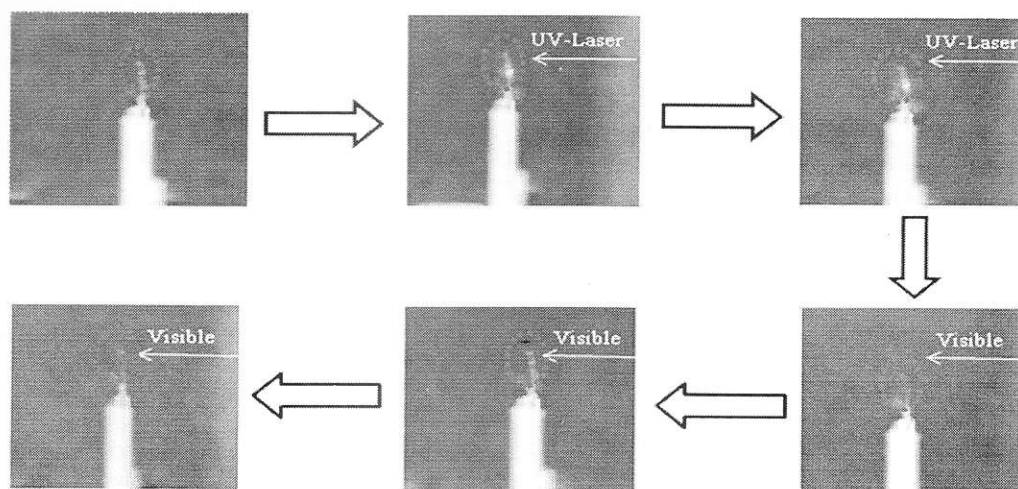


Fig. 1: Reversible shape changes (bending and unbending) of multi-layered film of PMMA and PAZO upon alternative irradiation with UV-laser (375 nm) and visible light (435 nm) at room temperature.

Photoisomerization of PMMA and PAZO bi-layer film

UV-visible absorption spectroscopy was employed in order to investigate the photoisomerization behavior of PMMA and PAZO bi-layer films. In these experiments, the samples were irradiated with the photoactive light propagating perpendicular to the sample plane. The photoisomerization

reaction was studied by irradiating the sample with UV and visible light and recording the spectra over different time intervals until photostationary states were reached. The spectra obtained during the photoisomerization of a one bi-layer PMMA/PAZO sample are presented in Figure 2.

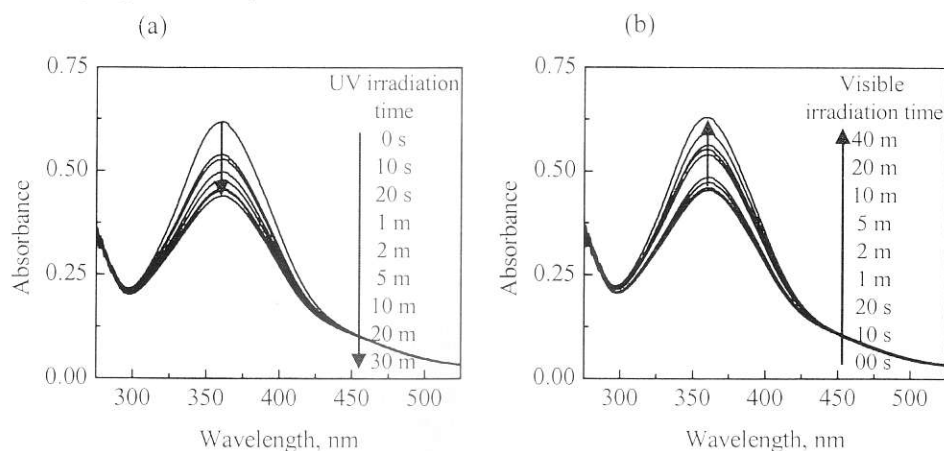


Fig. 2: Changes in UV-vis. absorption spectra of PMMA and PAZO one bi-layer film during (a) UV irradiation (365 nm) and (b) visible light irradiation (435 nm). The intensity of UV and visible light was 13.0 mWcm^{-2} and 120 mWcm^{-2} respectively.

As the photoisomerization reaction was induced by UV light, a spectral change occurred, with a progressive decrease in the π - π^* band maximum intensity. This band does not disappear even after the longest irradiation interval, indicating that the photoreaction does not reach completion. After a certain period of UV irradiation the decrease in absorbance in the π - π^* transition region became very slow, reached into photostationary state. As a result of the subsequent irradiation with visible light, the reverse changes occur establishing a steady state with a high concentration of *trans* isomers. However, the recovery of the initial spectrum is not complete: even upon a prolonged irradiation. The rate of increase in absorbance in the region of π - π^* transition upon the irradiation with visible light is much lower than the rate of decrease in absorbance in the region of π - π^* transition upon UV irradiation. In case of PAZO multi-layered film, similar type of *cis-trans* photoisomerization was reported by Dante et al. [25]. Consequently, *trans-cis-trans* photoisomerization cycle of PAZO single layer film, PMMA/PAZO bi-layer film as well as multi-layered film will be brought about by irradiation of the light in region of 365 nm and 435 nm [26, 27].

5. Back-isomerization in PAZO single layer film

After irradiation by UV light, we investigated the thermal *cis-to-trans* isomerization of the sample as shown in Figure 3. For this purpose, the samples were left in the dark and the UV-visible absorption spectra were measured after 1 hour. After 1 hour, UV-vis. absorption spectra showed considerable increase in absorbance, indicating the thermal back isomerization of azobenzene chromophores.

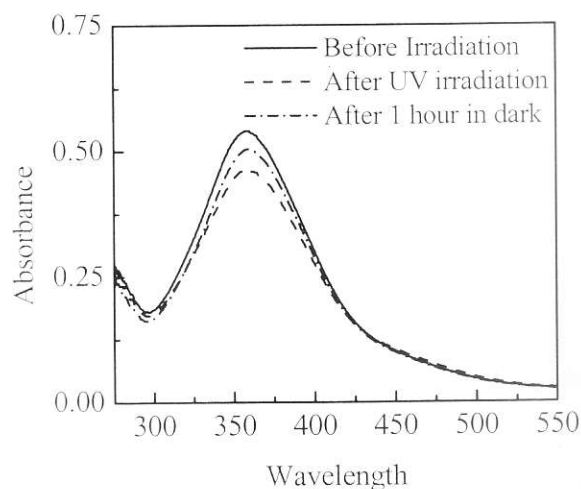


Fig. 3: UV-vis. absorption spectra of thermal back isomerization after UV irradiation on PAZO single layer film.

6. Alignment behavior of azobenzene chromophores in PAZO film on visible light Irradiation

To explore the orientational behavior of azobenzene chromophores in polymeric film, we measured the UV-vis. polarized absorption spectra before and after non-polarized visible light irradiation. For polarized absorption spectra, spectral measurements were made at 45° to film normal and significant spectral changes were observed for polymeric films exposed to the irradiation with non-polarized visible light. In the region of the π - π^* transition, the absorbance considerably decreased as shown in Figure 4. From polarized absorption spectra, it is clear that the absorbance in the region of π - π^* transition, are angular dependent. Before non-polarized visible light irradiation, the angular dependency was not significant but after irradiation significant angular dependency was observed. This behavior was accompanied by a well-pronounced development of an out-of-plane order of azobenzene chromophores upon visible light irradiation [28].

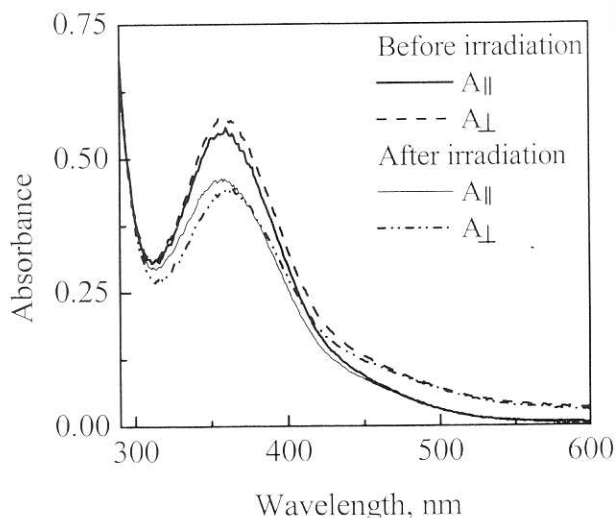
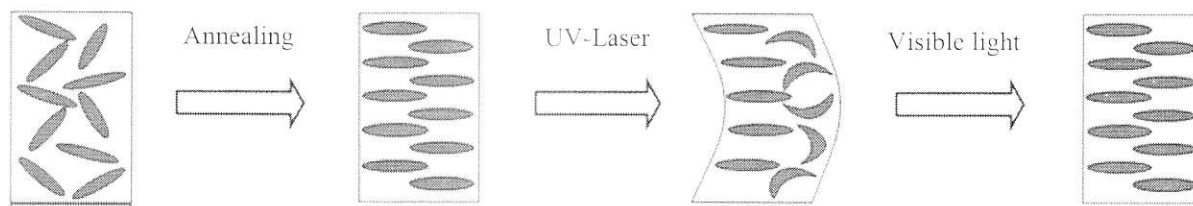


Fig. 4: Polarized UV-vis. absorption spectra of PAZO single layer film before and after visible light irradiation. A_{\parallel} denotes the absorption where the polarization direction is parallel to the film plane and A_{\perp} denotes the absorption where the polarization direction is set at 45° to both film normal and film plane.

So from above discussion, it is clear that the bending and unbending behaviors of multi-layered film were the combination of *cis-trans* photoisomerization and molecular alignment behavior of azobenzene chromophores. At first in fresh film, the azobenzene chromophores were aligned randomly and after annealing, aligned vertically showing unbending/normal situation. But upon UV-laser irradiation, *cis-trans* photoisomerization took place and contraction of azochromophres occurred. Following non-polarized visible light irradiation again increased the order parameter value, indicating the transformation of molecular orientation of azobenzene molecules from random state to out-of-plane order due to photo-orientation (Scheme 4).



Scheme 4: Changes in alignment behavior of azobenzene molecules on annealing, UV-laser and visible light irradiation.

7. Conclusion

In this study, new light driven polymeric actuator based on multi-layered films of poly [1-[4-(3-carboxy-4-hydroxyphenylazo) benzenesulfonamido]-1,2-ethanediyl, sodium salt] was fabricated successfully and demonstrated its bending and unbending behaviors. Multi-layered films showed bending and unbending properties upon UV-laser and visible light (435 nm) irradiation respectively. Bi-layer film of PMMA and PAZO showed reversible *cis-trans* photoisomerization and also upon non-polarized visible light irradiation, PAZO showed out-of-plane molecular orientation. So the bending and unbending of multi-layered films were caused due to the molecular orientation and *cis-trans* photoisomerization of azobenzene chromophores. The change in the molecular orientation might cause the disproportion of the molecular packing and the film bent to compensate for the distortion.

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