

## Photomechanical Effects in Azobenzene-Containing Polymer Systems

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Received February 5, 2004

**Abstract:** Several kinds of photodeformable polymer systems containing azobenzenes, capable of generating photomechanical effects, are reviewed. In polymer amorphous systems including monolayers, gels and solid films, *trans-cis* photoisomerization of the azobenzene moieties accompanied by geometrical and dipolar changes caused contraction and expansion of the systems. Recently, polymer liquid-crystalline elastomers containing azobenzenes, a novel system able to produce the photomechanical effects, have been developed to achieve fast and large photoinduced deformations. It is interesting that not only photoinduced contraction but also photoinduced bending have been achieved. These deformations are ascribed to the subtle variation in microscopic ordering during the photochemical phase transition of the polymer liquid-crystalline elastomers. This new photomechanical system is potential for application in driving micromachines and nanomachines without the aid of batteries, motors and gears.

**Key words:** photomechanical effect, azobenzene, photoisomerization, photochemical phase transition, liquid crystal

## 1. Introduction

Human civilization is profoundly influenced by materials technologies whose historical evolution experiences a distinct transition from structural materials to functional materials, and now "smart" materials.<sup>1)</sup> The smart materials have capability to select and execute specific functions intelligently in response to changes of environmental stimuli. Particularly, the materials that can sense signals and produce a definite dynamic response in the form of a change in shape or volume are central to developments in various scientific fields.<sup>2)</sup> Many materials are under active investigation in this field like shape-memory alloys,<sup>1)</sup> polymer gels,<sup>3)</sup> conjugated polymers,<sup>4-6)</sup> carbon nanotubes<sup>7-9)</sup> and dielectric elastomers,<sup>10)</sup> and many chemical and physical stimuli have been applied to induce the responses of these materials like pH, solvent composition, temperature, electric field, magnetic field and light.

Light is a clean energy, and can be controlled rapidly and remotely. Therefore, photodeformable smart materials that can undergo a shape or volume change in response to light attract much attention of the researchers. By using their deformations, we can convert light energy into mechanical power directly (photomechanical effects). Moreover, since their deformations driven by light require neither batteries nor controlling devices on the materials themselves, it should be simple to miniaturize the photodeformable systems for potential application in driving micromachines and nanomachines.

Most of the photodeformable smart materials capable of generating the photomechanical effects contain photochromic compounds, such as azobenzene, stilbene and spiropyran.<sup>11-18)</sup> Azobenzene photochemistry is a fascinating area of

investigation, on one hand, because it is fairly well-known, and on the other hand, because it has produced and continues to reveal completely unexpected phenomena.<sup>18)</sup> Therefore, the photomechanical effects in azobenzene-containing polymer systems are introduced in this review.

## 2. Photomechanical Effects in Polymer Amorphous Systems Containing Azobenzenes

## 2.1 Photoisomerization of Azobenzene Derivatives

As shown in Fig. 1, azobenzene and its derivatives can undergo *trans-cis* isomerization, and the *trans* form is thermodynamically more stable than the *cis* form.<sup>12,13,19)</sup> The *trans* form is converted into the *cis* form by UV light irradiation, and the resultant *cis* isomer can return to the original *trans* form photochemically upon Vis light irradiation or thermally in the dark. The *trans-cis* isomerization of azobenzene derivatives is characterized by monitoring the intense UV absorption (at 320-nm for azobenzene) due to  $\pi-\pi^*$  transition of the *trans* isomer and the weak band at longer wavelength (at 430-nm for azobenzene) arising from  $n-\pi^*$  transition of the *cis* isomer. The wavelengths of the  $\pi-\pi^*$  and  $n-\pi^*$  transitions depend on the positions and types of substituents on the azobenzene framework. It is important, in relation to the photomechanical effects of the azobenzene-containing

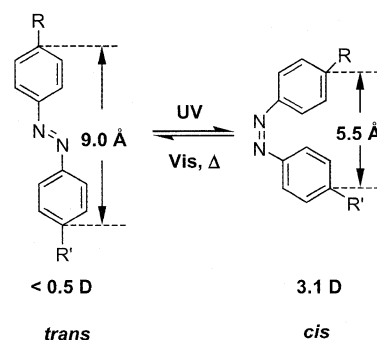


Fig. 1 Geometrical change of azobenzene derivatives upon isomerization.<sup>12,13,19)</sup>

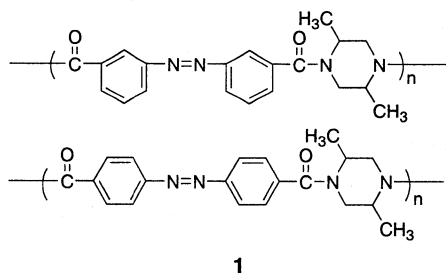
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polymer systems, to note that the photoisomerization of the azobenzene derivatives is accompanied by a significant change in stereochemistry: the *trans* isomers assume a planar configuration, whereas one of the benzene rings of the *cis* isomers occupies a plane tilted 56° from the plane of the other ring; thus, the distance between the *para* carbon atoms in the azobenzene framework decreases from about 9.0 Å in the *trans* form to 5.5 Å in the *cis* form. Likewise, the *trans* form of the azobenzene framework has little dipole moment less than 0.5 D, while the dipole moment of the *cis* form is about 3.1 D.

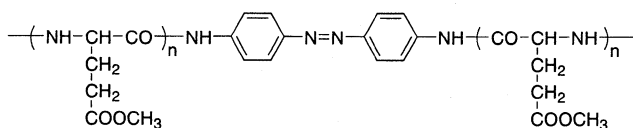
## 2.2 Photomechanical Effects in Monolayers

Monolayer-forming compounds containing azobenzenes can be easily prepared by incorporation of the azobenzene chromophores into polymer backbones or side chains. Blair et al. reported the photomechanical effects of monolayers consisting of polyamides with azobenzene units in the main chain (1).<sup>20</sup> At air/water interface, an increase in stress was observed upon UV light irradiation, indicating a contraction of the monolayers. In the dark, the stress decreased again, and the cycle could be repeated many times. For these main-chain type monolayers, the azobenzene units are considered to lie flat on the water surface. The photomechanical effects are simply due to the *trans-cis* isomerization of the azobenzene units, which occupy a larger area in the interface when they are in the more linear *trans* form than in the *cis* form.



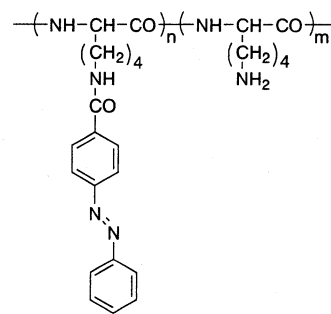
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Moreover, Higuchi et al. prepared a polypeptide monolayer composed of two  $\alpha$ -helical poly( $\gamma$ -methyl L-glutamate) rods linked by an azobenzene unit (2).<sup>21</sup> The *trans-cis* photoisomerization and the consequent variation in geometry of the azobenzene unit produced a bending of the main chain of the molecule and a decrease of the area of the monolayer. On the basis of the decrease in the limiting area per molecule, it was estimated that the bending angle between the two  $\alpha$ -helical rods, produced by irradiation of UV light, was about 140°.



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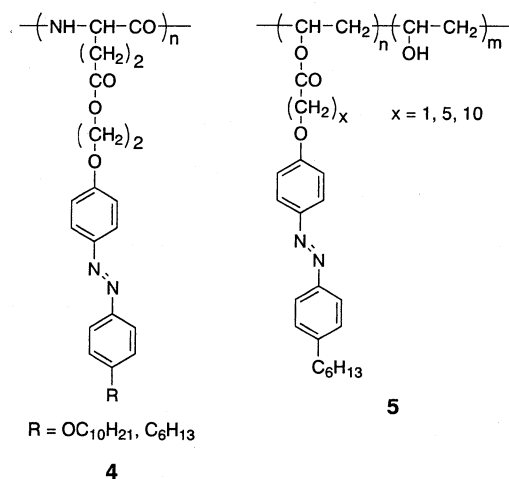
Side-chain type monolayers have also been characterized by using poly(L-lysine) containing about 40 mol% azobenzene units in the side chains (3).<sup>22</sup> When the monolayer was kept at a constant area, alternate irradiation of 365- and 450-nm light produced reversible changes of the surface pressure. At constant pressure, irradiation at the two different



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wavelengths produced reversible contraction and expansion of the monolayer.

On the other hand, Menzel et al. prepared monolayers by using rigid rod polypeptides with flexible side chains, which are photochromic poly(L-glutamate)s with azobenzene units in side chains coupled to the backbone via alkyl spacers (4).<sup>23</sup> The monolayers showed the photomechanical effects that were opposite with respect to those described above. They expanded when exposed to UV light, and shrank when exposed to Vis light. A similar photoresponse was obtained by Seki et al.<sup>24</sup> They reported the photoinduced deformations of monolayers composed of poly(vinyl alcohol) containing azobenzene side chains (5). The monolayers at air/water interface exhibited a three-fold expansion in area upon UV light irradiation and reversibly shrank upon Vis light irradiation. The mechanism of the photoinduced area changes is proposed as follows: the *trans* to *cis* photoisomerization leads to the increase in dipole moment, bringing about an affinity to the water surface and the expansion of the monolayers; furthermore, the reverse isomerization upon Vis light irradiation gives rise to the recovery of the monolayers to the original structure. Recently, this photomechanical effect was also observed in the azobenzene-crown-containing dendrimer monolayers.<sup>25</sup>



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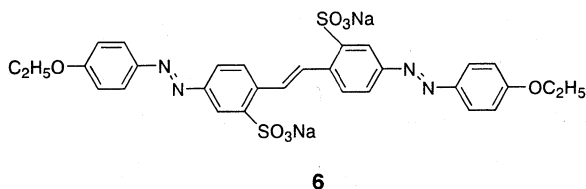
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These results indicate that the photoinduced deformations of the azobenzene-containing monolayers strongly depend on the location of the azobenzene units in the dark: when the units are on or in the water subphase, the structural response of the monolayers is determined by the geometrical change of the photochromic units. On the other hand, the polarity increase of the azobenzene units is a more important factor when the units are free from the water subphase in the dark.

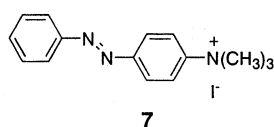
Since the monolayers are restricted in two dimensions, they offer intriguing systems for understanding the macroscopic deformations in terms of the processes taking place at the molecular level. Nevertheless, from the viewpoint of applications, the azobenzene-containing systems of gels and solid films are of greater interest.

### 2.3 Photomechanical Effects in Gels

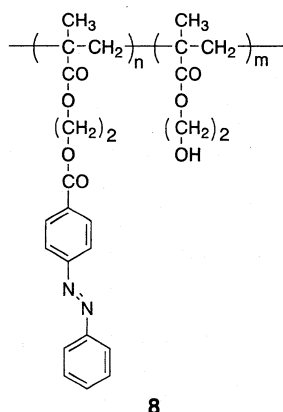
Prins et al. prepared a gel system consisting of a low-molecular-weight chrysofenine dye (**6**) and a water-swollen gel of poly(2-hydroxyethyl methacrylate) cross-linked with ethylene glycol dimethacrylate.<sup>26)</sup> The polymer gel was found to contract upon UV light irradiation. It is because the isomerization from the *trans* to the *cis* form causes a reduction in hydrophilicity of the dye, liberating the hydrophilic dyes from the polymer chain to the surrounding solution. The same manner of the photoinduced deformations was also observed in cross-linked poly(methacrylic acid) on which chrysofenine was adsorbed.<sup>27)</sup>



On the other hand, when a positively charged dye, 4-phenylazophenyl trimethylammonium iodide (**7**), was adsorbed to the cross-linked poly(methacrylic acid) film, the film behavior was reversed from that shown above.<sup>28,29)</sup> Swelling occurred upon irradiation and contraction took place during dark relaxation. It is because the aqueous polymeric acid gel combined with the positively charged *trans* **PTA** gives a more hydrophobic and globular conformation. After irradiation, the more soluble *cis* **PTA** is formed, causing the dye to drop off the polymer. As a result, the polymer relaxes to an extended conformation, leading the sample to swell.



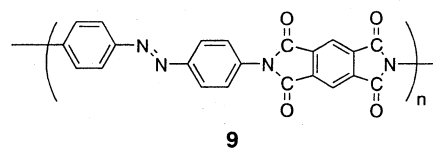
The photoinduced deformation ascribed to the real photochemical effect was observed in a hydrogel by Ishihara et al.<sup>30)</sup> They prepared a gel of poly(2-hydroxyethyl methacrylate) with pendant azobenzene units (**8**), and the gel was



swollen in water. When irradiated with UV light, the gel swelling decreased as much as 7% in 1 h. Upon Vis light irradiation, the gel again swelled slowly in 10 h.

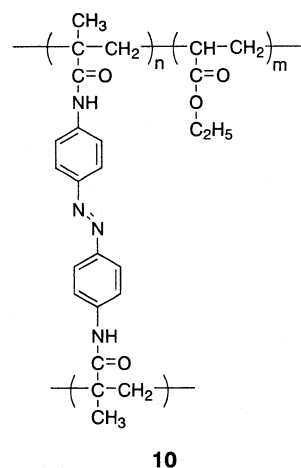
### 2.4 Photomechanical Effects in Solid Films

The use of structural changes of photoisomerizable chromophores for the size changes of polymer solids was proposed for the first time by Merian.<sup>31)</sup> He observed that a nylon filament fabric dyed with an azobenzene derivative shrank upon photoirradiation. This effect is ascribed to the photochemical structural change of the azobenzene derivatives absorbed on the nylon fibers. However, the obtained shrinkage was too small, only about 0.1%. Following this work, efforts were made to find new photomechanical systems and to increase the effect.



A covalently bound chromophore is expected to give a more direct effect on the deformations of polymers. Therefore, Agolini and Gay prepared a polyimide with azobenzene chromophores in the backbone (**9**).<sup>32)</sup> It was reported that 0.5% contraction of the polymer film took place at 200 °C under UV light irradiation. However, the isomerization is not the sole origin of the contraction of the system, because a rapid thermal reverse reaction from the *cis* to the *trans* form should occur at the high temperature.<sup>13)</sup>

Another approach to realize a large photomechanical effect is to incorporate the chromophore as a cross-linking agent into a polymer network. Eisenbach synthesized polymer networks with an azobenzene derivative as cross-linker (**10**).<sup>33)</sup> The film contracted upon UV light irradiation, which causes the *trans* to *cis* isomerization of the azobenzene chromophores, while it expanded by irradiation of Vis light, which induces the *cis* to *trans* isomerization. However, the observed contraction was still small, only about 0.2%.



As mentioned above, the gels and the solid films containing azobenzenes are potential materials for applications. However, the previous study shows that the gels have a serious disadvantage in that the response is slow, and the deformations of the solid films are too small to be practically utilized. Therefore, it is of great importance to find novel photo-

tomechanical systems that can undergo fast and large deformations. In the previous study described above, the gels and the solid films used were amorphous without microscopic or macroscopic order, and thus their deformations occurred isotropically. If the materials with anisotropic order are used, the changes of shape and volume will become anisotropic, and the mechanical power that can be utilized will increase significantly.

### 3. Photomechanical Effects in Polymer Liquid-Crystalline Systems Containing Azobenzenes

#### 3.1 Liquid Crystals and Photochemical Phase Transition

For a long time it has been known that anisotropic molecules, so called "mesogenic" units, can form liquid crystalline (LC) phases. The remarkable properties of the LC phases stem from their combination of the molecular long-range order of crystals with the mobility of fluids. Since the LC phases are thermodynamically stable phases that exist in a temperature range between the crystalline phase and the isotropic (I) melt, the phase transition of LC compounds from the LC to I phase is generally induced by heating the samples to high temperatures.

In relation to the photomechanical effects, it is important to note that some photochromic molecules such as azobenzene are able to isothermally trigger the phase transition of LC systems through the photochemical reaction of the chromophores (photochemical phase transition).<sup>34)</sup> The working principle of the photochemical phase transition can be interpreted in terms of the changes in geometrical structure of the chromophores. For instance, the *trans*-form azobenzene having a rod-like shape stabilizes the LC phase structure, whereas the bent *cis* form acting as an impurity lowers the LC order parameter (Fig. 2). Thus, the LC to I phase transition temperature of the *cis*-azobenzene/LC mixture is much lower than that of the *trans*-azobenzene/LC mixture. As a result, if the *trans* to *cis* photoisomerization is evoked in the *trans*-azobenzene/LC mixture, the phase transition occurs isothermally. On the other hand, from the viewpoint of the photomechanical effects, the subtle variation in microscopic ordering during this phase transition is possible to cause a significant uniaxial deformation of LCs along the director axis, if the LC molecules are strongly associated by covalent cross-linking to form a three dimensional polymer network.<sup>35)</sup>

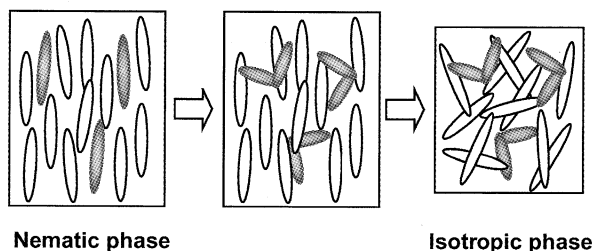


Fig. 2 Schematic illustration of photochemical phase transition in azobenzene-containing LC systems.<sup>34)</sup>

#### 3.2 Photoinduced Contraction of LC Elastomers

Recently, Finkelmann et al. has reported a pioneering work on a photoinduced large contraction in azobenzene-containing LC Elastomers (LCEs) arising from the photochemical phase transition behavior. They synthesized monodomain

nematic LCEs (NLCEs) containing polysiloxane main chain and azobenzene chromophores in cross-links (Fig. 3).<sup>36)</sup> When exposed to UV light at 365-nm, the elastomers contracted about 20%, caused by the decrease in order parameter due to the photochemical phase transition. After the irradiation was switched off, the elastomers returned to the original state thermally due to the *cis* to *trans* back isomerization of the azobenzene units. Subsequently, a range of such NLCEs containing different compositions and cross-linking topologies was studied in their response to UV light.<sup>37)</sup> It was found that the magnitude of the photoinduced contraction was dependent on the proportion and the position of the azobenzene units in the cross-linked polymer network. In addition, the photomechanical effects were also observed in side-on NLCEs (Fig. 4).<sup>38)</sup> When exposed to UV light at 365 nm, the films contracted by up to 12–18%, and the extent of the contraction was found to be dependent on the intensity of the light used.

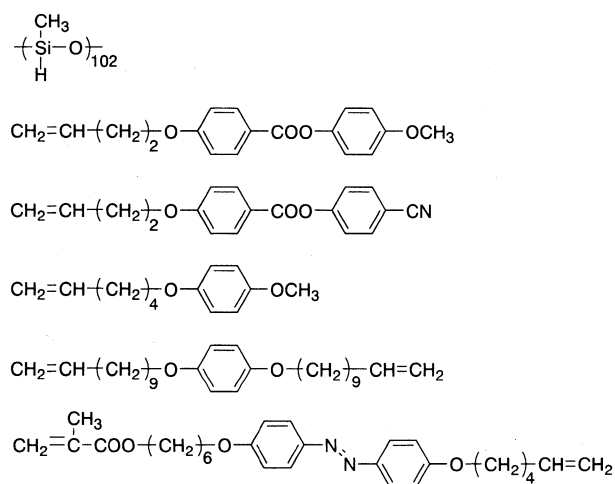


Fig. 3 Chemical structures of the compounds used for the synthesis of nematic LCEs.<sup>36)</sup>

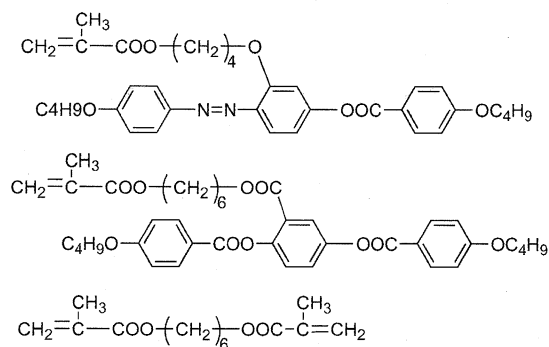


Fig. 4 Chemical structures of the monomers used for the synthesis of side-on nematic LCEs.<sup>38)</sup>

It is worth mentioning that these researches provide a new mechanism for the photomechanical effects. Furthermore, although the photoinduced contraction of the azobenzene-containing LCEs described above took place on a timescale of minutes and even tens of minutes, they are a promising system able to undergo fast photoinduced deformations. It is because the photochemical phase transition of polymer LCs containing azobenzenes could be induced much

quickly on a timescale of nanoseconds under optimized conditions.<sup>39)</sup>

### 3.3 Photoinduced Bending of LC Gels and LCEs

Almost at the same time when Finkelmann et al. did their research on the photoinduced contraction of LCEs, we focused our attention on developing more interesting photomechanical behavior, photoinduced bending, by using LC gels (LCGs) and LCEs containing azobenzenes. In comparison with the contraction mode that is a two-dimensional action, the bending mode, a three-dimensional movement, should be advantageous for artificial "hands" and medical microrobots that are capable of completing particular manipulations.<sup>5)</sup>

#### 3.3.1 Photoinduced Anisotropic Bending of LCGs in Good Solvents

Fig. 5 shows the structures of an LC monoacrylate, **A6AB6**, and a diacrylate cross-linker, **DA6AB**, both of which possess azobenzene moieties, used in this study.<sup>40,41)</sup> Polymer films were prepared by *in-situ* photopolymerization of the mixture of **A6AB6** and **DA6AB** (mol/mol: 8/2) in a glass cell coated with rubbing-treated polyimide alignment layers. The free-standing LCGs were obtained by placing the polymer films horizontally in a vessel containing good solvents.

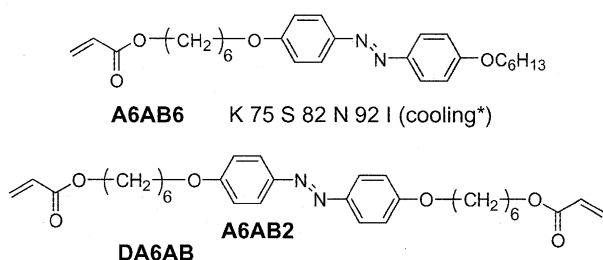


Fig. 5 Structures, properties and abbreviations of the LC monomer and the cross-linker used for the preparation of LCGs. I: isotropic; N: nematic; K: crystal. \***A6AB6** shows a monotropic smectic phase when cooled from a nematic phase.<sup>40,41)</sup>

When an LCG film in toluene was exposed to unpolarized 360-nm light, it was found that the film bent toward the irradiation direction of the incident light (Fig. 6). The bending was completed in 20 s at a light intensity of 3 mWcm<sup>-2</sup>. Moreover, when the bent film was exposed to unpolarized Vis light at 450-nm, unbending behavior was immediately observed and the initial flat film was restored in 30 s at the same light intensity. This bending and unbending behavior could be repeated by alternate irradiation of UV and Vis light. It is interesting to note that the bending of the LCG film occurred anisotropically, only in the direction parallel to the rubbing direction of the alignment layers.

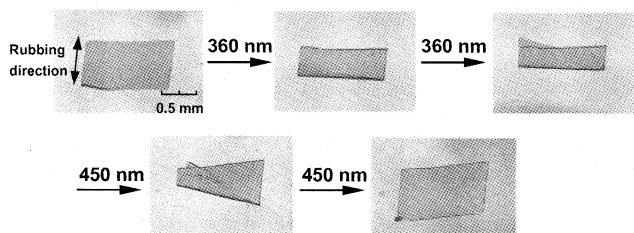


Fig. 6 Photographs of the bending and unbending processes of the LCG film in toluene at room temperature.<sup>40)</sup>

As described above, irradiation of UV light gives rise to the *trans-cis* isomerization of the azobenzene moieties and even the LC-I phase transition of the LC systems, both of which can bring about a volume contraction of the LCG films. However, the extinction coefficient of the azobenzene moieties at ~360-nm is large ( $2.6 \times 10^4$  Lmol<sup>-1</sup>cm<sup>-1</sup>), and more than 99% of the incident photons are hence absorbed by the surface with a thickness less than 1 μm. Since the thickness of the LCG films used was 10 μm, the volume contraction is generated only in the surface region, causing the bending toward the irradiation direction of the incident light (Fig. 7). Furthermore, the azobenzene moieties are preferentially aligned along the rubbing direction, and the decreases in size and alignment order of azobenzene moieties are thus produced just along this direction, contributing to the anisotropic bending behavior. The unbending behavior is ascribed to the recovery of the initial structure and alignment order of azobenzene moieties due to the *cis to trans* back isomerization induced by irradiation of Vis light.

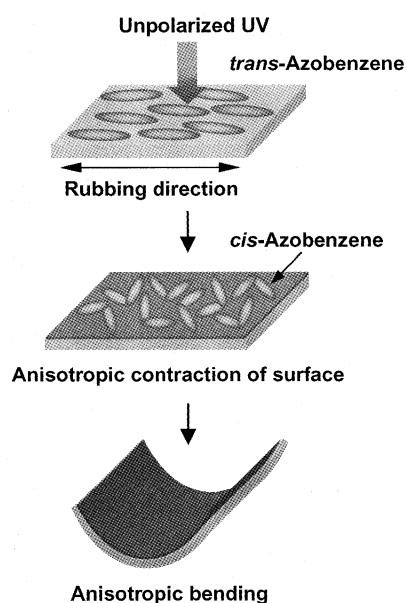


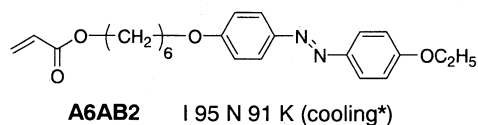
Fig. 7 Schematic illustration of plausible mechanism of the anisotropic bending behavior.

In addition, the bending and unbending were observed in good solvents such as toluene and chloroform, but not induced in poor solvents such as methanol and n-hexane. It is because when the LCG films are swollen in good solvents, free volume and mobility of the polymer segments increase, providing the possibility of visualizing at a macroscopic level the conformational change occurring at a molecular level through the cooperative movement of the polymer segments.

#### 3.3.2 Photoinduced Anisotropic Bending of Oriented LCEs in Air

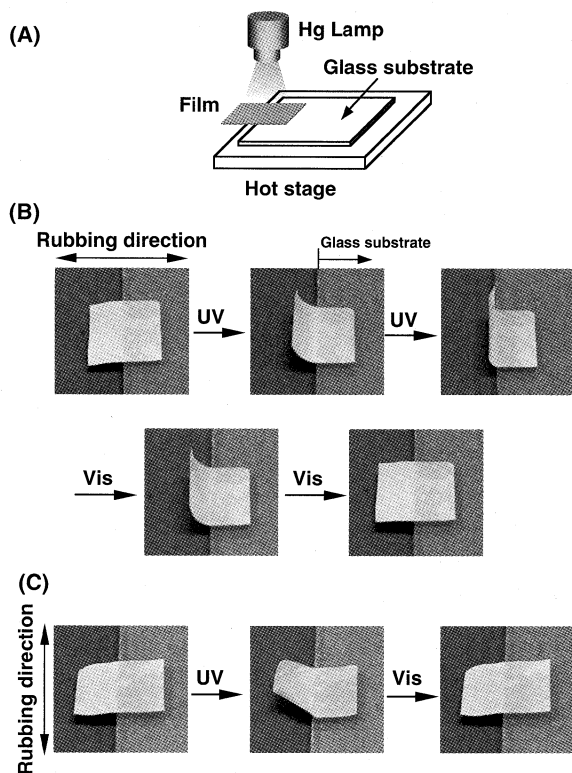
It is well known that the relaxation of the polymer segments can be achieved by heating the polymers to above their  $T_g$  instead of suspending them in good solvents; therefore, we also investigated the photoinduced bending and unbending behavior in air.<sup>42)</sup> Here, the oriented LCE (OLCE) films were prepared by thermal polymerization of the mixture of another LC monoacrylate, **A6AB2** (Fig. 8), and **DA6AB** (mol/mol: 9/1) in the glass cell coated with the rubbing-treated align-

ment layers. The OLCE films obtained showed a much lower  $T_g$  (50 °C) than the LCG films.



**Fig. 8** Structure, property and abbreviation of the LC monomer used for the preparation of LCEs.  
\*A6AB2 shows a monotropic nematic phase when cooled from an isotropic phase.<sup>42,43)</sup>

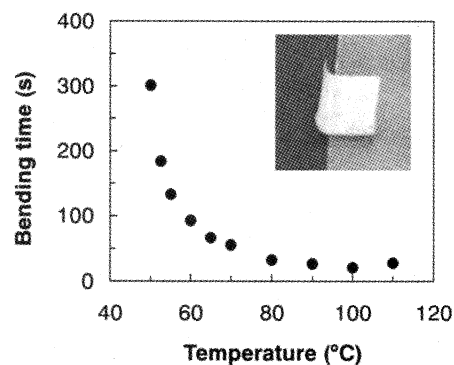
Normal irradiation of the unpolarized light was performed on the film, when an OLCE film was partially pasted on the glass substrate heated by a hot stage (**Fig. 9A**). **Fig. 9B** shows the bending and unbending processes induced by irradiation of UV and Vis light, respectively, when the film was heated to 70 °C. It was observed that the OLCE film bent toward the irradiation direction of the incident UV light along the rubbing direction, and the bent film reverted to the initial flat state after exposure to Vis light. The bending was completed in 60 s upon irradiation of 366-nm light with an intensity of 1.5 mWcm<sup>-2</sup>, and the unbending was completed in 30 s upon irradiation of Vis light at (540-nm (547-nm, 13 mWcm<sup>-2</sup>; 577-nm, 15 mWcm<sup>-2</sup>). This bending and unbending behavior was reversible just by changing the wavelength of the incident light. In addition, after the film was rotated by 90° in such a way that the rubbing direction became parallel to one side of the glass substrate, the bending was again observed along the rubbing direction (**Fig. 9C**). This anisotropic bending behav-



**Fig. 9** Anisotropic bending and unbending behavior of the oriented LCE film at 70 °C in air. (A) Schematic illustration of the setup used for the experiment. (B) The rubbing direction was set perpendicular to one side of the glass substrate. (C) The rubbing direction was set parallel to one side of the glass substrate. Size of the film: 5 mm × 5 mm × 20 μm.<sup>42)</sup>

ior of the OLCE films is identical to that observed in the LCG films in good solvents.

The influence of temperature on the bending time was examined by measuring the time for a film to bend by 90°, as the photograph in the inset of **Fig. 10** shows. The unpolarized 366-nm light with the intensity of 1.5 mWcm<sup>-2</sup> was used and the results are shown in **Fig. 10**. It was observed that the bending could be induced only when the film was heated to above  $T_g$ , because the relaxation of the polymer segments is necessary. It is known that the higher the temperature, the larger the mobility of the polymer segments becomes; therefore, above  $T_g$ , the bending time decreased to a great extent with the initial increment of temperature. Moreover, the *cis-trans* back isomerization of azobenzene moieties, resulting in the unbending of the films, can be induced thermally and its rate is increased with increasing temperature. This makes the bending time unable to decrease to more extent when the temperature is increased higher. It was even observed that the bending time at 110 °C was longer than that at 100 °C, and the bending to 90° could not be completed at all when the temperature was raised higher.



**Fig. 10** Bending time for the oriented LCE film to bend by 90° as a function of temperature upon irradiation of 366-nm light (1.5 mWcm<sup>-2</sup>) and the photograph of the film bending by 90° (inset).<sup>42)</sup>

Upon exposure to 366-nm light with different intensities at 70 °C, the bending time defined as above was measured (**Fig. 11**). In the low intensity region, the bending time decreased significantly with an increase of the light intensity, because actinic light with higher intensity produces a higher concentration of *cis*-azobenzene moieties, bringing about a larger volume contraction and faster bending. In the high intensity region, the amount of *trans*- and *cis*-azobenzene moieties quickly reaches a thermodynamic equilibrium state, and the relaxation process becomes a rate-determining step for the bending rather than the changes in structure and alignment of azobenzene moieties. Because the relaxation of the polymer segments, as a function of temperature, has no relation to the light intensity, the bending time is insensitive to the increment of the light intensity.

In addition, the effect of the film thickness ( $\leq 20 \mu\text{m}$ ) on the bending time was investigated, when the films were irradiated with 366-nm light at 70 °C (**Fig. 12**). It is worth noting that the bending time increased remarkably with the increment of the film thickness. When the film becomes thick, the thickness of bulk region without the volume contraction increases. Namely, the quantity of the polymer segments in

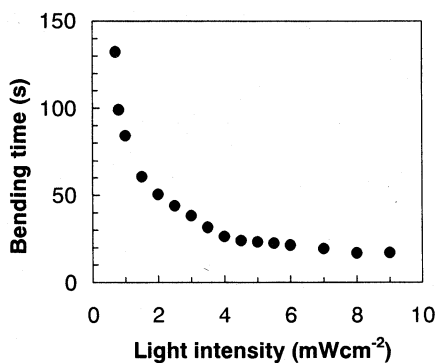


Fig. 11 Bending time for the oriented LCE film to bend by 90° as a function of the intensity of 366-nm light at 70 °C.<sup>42)</sup>

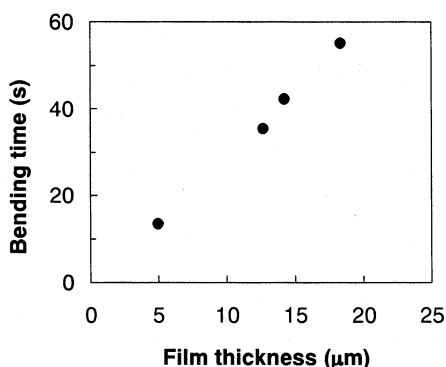


Fig. 12 Bending time for the oriented LCE film to bend by 90° as a function of the film thickness upon irradiation of 366-nm light (1.5 mWcm<sup>-2</sup>) at 70 °C.<sup>42)</sup>

the bulk region becomes large. Since the relaxation of the polymer segments is necessary for the occurrence of the bending, the time for the relaxation of the total polymer segments increases with the increment of the film thickness. Furthermore, we also prepared much thicker films, 60 and 110 μm, and found that the bending could not be induced in either of the films. It is proposed that the maximum driving force for the bending generated from the volume contraction in the surface region of the film is definite and not able to propel the cooperative movement of the total polymer segments in such thick films. This implies that there is a limit of film thickness for the occurrence of the bending behavior.

### 3.3.3 Photoinduced Direction-Controllable Bending of Polydomain LCEs in Air

In the LCG and OLCE films, the azobenzene mesogens are preferentially aligned along one direction, and the incident unpolarized light is a homogeneous external stimulus. In this case, the anisotropic bending is photoinduced, whose direction is determined fully by the alignment direction of the azobenzene mesogens and cannot be freely varied. Here, we changed to use polydomain LCE (PLCE) films and linearly polarized light (LPL).<sup>43)</sup> The PLCE films were prepared by thermal polymerization of the mixture of A6AB2 and DA6AB (mol/mol: 9/1) in the glass cell coated with the polyimide layers that had not been rubbed.

It is known that light absorption to give excited states of molecules meets exclusive requirements including the coincidence of the electric field vector of light with the direction of

a transition moment of the molecules (photoselection), thereby *trans*-azobenzene molecules with  $\pi$ - $\pi^*$  transition moments approximately parallel to the molecular long axis show angular-dependent absorption of LPL: the *trans*-azobenzene molecules with their transition moments parallel to the polarization direction of LPL are activated very effectively to their excited states, followed by the *trans*-*cis* isomerization, while the molecules with their transition moments perpendicular to the polarization direction of actinic light are inactive towards the isomerization.<sup>18,34)</sup> By utilizing the selective absorption of LPL in the PLCE films, we succeeded in realizing an photoinduced direction-controllable bending in that a single LPL film can be bent repeatedly and precisely along any chosen direction.<sup>43)</sup>

This attractive bending and unbending behavior is shown in Fig. 13. The PLCE film was laid on a copper stick fixed to a copper plate, and the hot stage under the plate was set at 85 °C to control the temperature of the film, which was covered by a piece of blue paper. Fig. 13A shows the film before light irradiation, and Fig. 13B shows how the film curls up after exposure to 366-nm LPL that has a polarization direction at zero degree. The film bent toward the irradiation direction of the incident light with the bending occurring parallel to the direction of light polarization (white arrows). When the bent film was exposed to Vis light at > 540-nm, it completely reverted to its initial flat state. The effect on the film of altering the polarization direction of 366-nm LPL to -45°, -90° and -135° is shown in Fig. 13C, 13D and 13E, respectively. It can be seen that the bending direction of the film moves anticlockwise by 45°, 90° and 135°, respectively, keeping parallel to the direction of light polarization. The film could be restored from each bent state to its initial flat form by irradiation of Vis light at > 540-nm.

The bending time for the four different directions was within 10 s, when the light intensity of 366-nm LPL was 3.5 mWcm<sup>-2</sup>. After exposure to Vis light at > 540 nm (547 nm, 24.2 mWcm<sup>-2</sup>; 577 nm, 26.8 mWcm<sup>-2</sup>), the bent film reverted

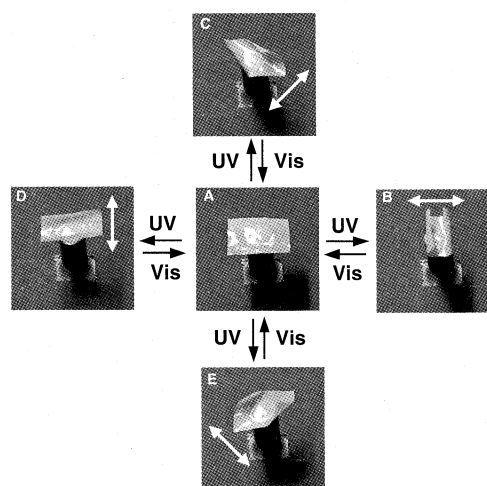
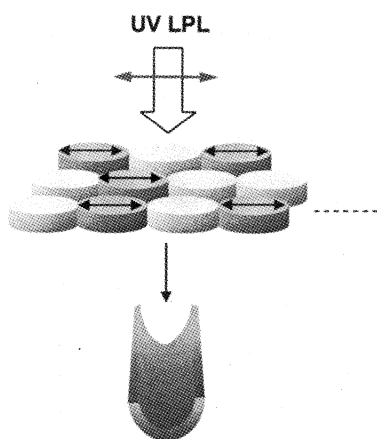


Fig. 13 Photographs of the polydomain LCE film before irradiation (A) and after irradiation of 366-nm LPL with different polarization directions indicated by the white arrows (B), (C), (D), (E). The film bent in different directions after exposure to UV LPL, and could be restored from each bent state to its initial flat form by irradiation with Vis light. Size of the film: 4.5 mm × 3 mm × 7 μm.<sup>43)</sup>

to the flat state in about 10 s. Moreover, the bending–unbending cycle of these four modes could be repeated without apparent fatigue. These results show that the bending direction of a single film can be precisely controlled by altering the polarization direction of the incident UV LPL, and that such a film can be bent repeatedly.

The PLCE film used here consists of a large number of micro-size domains of azobenzene mesogens, in which the mesogens are aligned in one direction in each domain but macroscopically the direction of alignment is random. Upon irradiation of UV LPL, the selective absorption of light in a specific direction, light polarization, leads to the *trans-cis* isomerization of azobenzene mesogens in specific domains where the azobenzenes mesogens are aligned along the direction of light polarization (Fig. 14). As a result, the subtle reduction in microscopic size and order of the mesogens gives rise to a substantial macroscopic volume contraction at the film surface and a bending of the whole film through the cooperative movement of the mesogens and the polymer segments.



**Fig. 14** Schematic illustration of plausible mechanism of the direction-controllable bending behavior induced by UV LPL in the polydomain LCE films. When the film is exposed to UV LPL, the azobenzene mesogens in some specific domains (orange ellipsoids with blue arrows), where the mesogens are aligned parallel to the light polarization (red arrow), absorb the photons and undergo the photochemical change.

This directed bending is a novel deformation mode that has not been reported in other photodeformable smart materials. The changeability of the bending direction and the repeatability of the bending behavior make this new kind of the smart materials to be potential in the development of high-speed actuators for microscale or nanoscale applications, for example in microrobots in medicine or optical microw tweezers.

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