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## INVITED ARTICLE

# Photomechanical properties of azobenzene liquid-crystalline elastomers

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We prepared homogeneously aligned azobenzene liquid-crystalline elastomer (LCE) films with low $T_g$ and explored their photomechanical properties. Upon irradiation with UV light, the films bent toward a light source at room temperature. The mechanical force generated upon exposure to UV light was evaluated by thermomechanical analysis. It was found that the mechanical force generated by photo-irradiation increased with an increase in the cross-linking density. In particular, an LCE film containing 80 mol% azobenzene cross-linker produced a force of over 1 MPa by photo-irradiation, which enabled the film to lift an object 20 times heavier than itself. The degree of contraction by photo-irradiation increased with an increase in temperature and light intensity. Bending could be brought about by more than 5000 times with periodic irradiation. Furthermore, it was found that the LCE films exhibited bending and unbending behaviour by irradiation with sunlight.

**Keywords:** liquid-crystalline elastomers; azobenzene; photomechanical property; photomobile materials

## 1. Introduction

Liquid-crystalline elastomers (LCEs) have been intensively investigated over the last two decades due to their unique mechanical properties and potential application as artificial muscles (*1*). LCEs exhibit reversible and large contraction along the alignment direction of mesogens when they are heated to induce their order-disorder phase transition. This phenomenon was first predicted by de Gennes (2) and experimentally confirmed by Küpfer and Finkelmann (*3*). Since then, many studies of the deformation in LCEs have been reported (*4*). The macroscopic deformation is caused by external stimulus, such as electricity (*5*), solvent compositions (*6*), magnetic fields (*7*) and light (*8*). By incorporating azobenzene moieties into liquid crystals (LCs), one can induce their LC-isotropic (I) phase transitions isothermally upon exposure to UV light to cause *trans*-*cis* isomerisation (*9–11*). A large and reversible deformation of LCEs containing azobenzene mesogens is induced by reduction of LC order by light (*12*). Motions of the azobenzene LCE films can be controlled by changing the gradient of the cross-linking density (*13*), polarisation direction of actinic light (*14, 15*) and the initial alignment of mesogens (*16, 17*). Most recently, we have successfully demonstrated sophisticated motions of LCE films laminated with polymer films, such as robotic arm motion, inchworm walk and rotation (*18, 19*). The mechanical property of the LCE films is reinforced by lamination enabling the films to generate large mechanical force without deterioration of the materials by irradiation with UV light at high intensity.

In this work, we investigated the photomechanical properties of LCE films in detail by thermomechanical analysis. In particular, contractions and forces generated by photo-irradiation in the LCE films were studied as a function of the cross-linking density of the LCEs, temperature and light intensity.

## 2. Experimental

### 2.1 Materials

The LC monomers, 9-[4-(4-nonyloxyphenylazo)phenoxy]nonyl acrylate and 4,4′-bis[9-(acryloyloxy)nonyloxy]azobenzene, used in this study are shown in Figure 1. The LCE films were prepared by *in situ* photopolymerisation of a mixture of the compounds. The mixtures containing 2 mol% of a photo-initiator (Irgacure 784, Ciba Specialty) were melted and injected into a glass cell coated with rubbed polyimides (JSR and AL1254) at 110°C. After the mixture was cooled down to an LC phase temperature (87°C), photo-irradiation was carried out at more than 540 nm (2.5 mW cm$^{-2}$ at 547 nm) with a 500-W high-pressure mercury lamp (UI-501HQ, USHIO) through glass filters (AGC techno glass, Y-52 and IRA-25S) for 2.5 hours. The cooling rate of the sample was 0.1°C min$^{-1}$. The LCE film was taken off from the cell in methanol after polymerisation, and dried overnight under reduced pressure.

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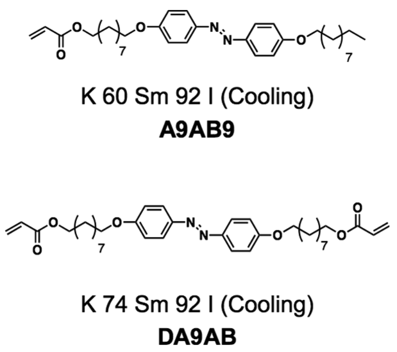

K 60 Sm 92 I (Cooling)
**A9AB9**

K 74 Sm 92 I (Cooling)
**DA9AB**

Figure 1. Chemical structures and phase transition temperatures of the monoacrylate (**A9AB9**) and diacrylate (**DA9AB**) LC monomers used in this study.

### 2.2 *Characterisation*

The thermodynamic property of the polymers was determined by differential scanning calorimetry (DSC) (DSC6220G, Seiko I&E Ltd, Tokyo, Japan) at heating and cooling rates of 10° C min$^{-1}$. Bending of the films was induced upon irradiation with UV light at 366 nm from a UV-LED (UV-400 with UV-50H and L-8, Keyence) and recorded with a digital video camera (VH-Z0R and VW-6000, Keyence). After measurement, the bent film was exposed to visible light from a halogen fibre lamp (FLH-50, Shimadzu, Kyoto, Japan) or a 530-nm LED irradiator (PJ-1505-2CA with HLV-24GR-3W, CCS, Waukesha, WI, USA) to revert to the initial shape. The degree of contraction and the mechanical force induced by photo-irradiation of the LCE films were measured with a thermomechanical analyser (TMA-60, Shimadzu). The spectrum of the sunlight through the glass filter was checked with a multichannel spectrometer (Maya 2000 Pro, Ocean Optics Inc., Dunedin, FL, USA).

## 3. Results and discussion

We evaluated the effect of the cross-linking density on the photomechanical properties. Table 1 shows the abbreviations and the feed ratio of the samples used in this study. The former number of the abbreviation describes the feed ratio of an azobenzene monomer, **A9AB9**, and the latter one denotes an azobenzene cross-linker, **DA9AB**. The glass transition temperature of the LCEs appeared at approximately 30°C in DSC thermograms, allowing the LCE films to work at room temperature. Figure 2(a) shows an experimental setup for thermomechanical analysis: both ends of the film were clamped and a load of 10 mN was initially applied to the LCE films along the rubbing direction.

Table 1. Nomenclature and feed ratio of compounds.

| Sample | A9AB9 (mol%) | DA9AB (mol%) |
|---|---|---|
| **E82** | 80 | 20 |
| **E64** | 60 | 40 |
| **E46** | 40 | 60 |
| **E28** | 20 | 80 |

Here, we define the degree of contraction upon exposure to UV light, Δl, for evaluation of the photomechanical properties as follows:

$$\Delta l = (l_0 - l)/l_0 \tag{1}$$

where $l_0$ and $l$ represent the length of the film before and after photo-irradiation, respectively. Figure 2(b) shows the change in $\Delta l$ of the samples with different cross-linking densities at 30°C. The films contracted along the alignment direction of the azobenzene mesogens at room temperature, and the value of $\Delta l$ increased with an increase in the cross-linking density although the values were low. We measured the change in force upon photo-irradiation by keeping the length of the film unchanged. The mechanical force generated by irradiation with UV light, $\Delta F$, is defined as follows:

$$\Delta F = F - F_0 \tag{2}$$

where $F_0$ and $F$ denote the force before and after

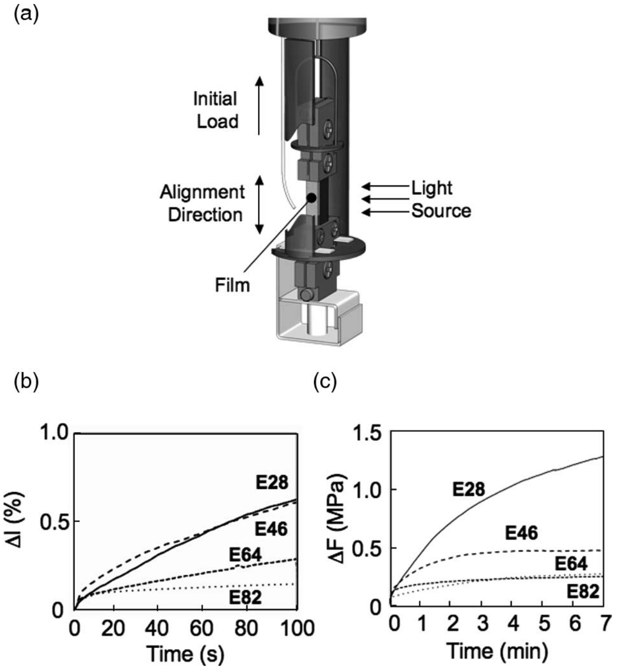

Figure 2. Schematic illustration of an experimental setup for (a) thermomechanical analysis, (b) contraction and (c) mechanical force of LCE films with different cross-linking densities upon irradiation with UV light. Size of the films: 5.5 mm × 5 mm × 20 $\mu$m.

irradiation with UV light. As shown in Figure 2(c), $\Delta F$ was strongly affected by the cross-linking density of the LCE films. When the cross-linking density became higher, a large contraction force was generated by photo-irradiation. In particular, the $\Delta F$ of the **E28** film, containing 80 mol% of the azobenzene cross-linker, reached over 1 MPa after irradiation with UV light for 5 minutes. Additionally, it was found that the $\Delta F$ of the LCE films with high cross-linking density changed slowly. These results are explained by the coupling between azobenzene moieties and polymer backbones. Since the azobenzene cross-linkers are attached to the polymer backbones at two points, the LCE film with high cross-linking density effectively converts the change in molecular order into the macroscopic motion. On the other hand, cross-links in the LCE films restrict the movement of mesogens. Therefore, the LCE films show larger and slower changes in $\Delta F$, when the cross-linking density becomes higher.

We observed the photo-induced bending of the LCE films. Part of the freestanding LCE film was clamped with an aluminium block and normal irradiation with UV light was performed at room temperature. It was found that the films exhibited photo-induced bending upon exposure to UV light at 25 mW cm$^{-2}$. The bent film reverted to the initial shape by irradiation with visible light or when kept in the dark overnight. Furthermore, we investigated the effect of the cross-linking density on the photo-induced macroscopic actuation of the LCE films with an experimental setup indicated in Figure 3(a). An LCE film was covered completely with a glass substrate and irradiated with UV light from above. The weight of the glass substrate was approximately 20 mg, much heavier than that of the LCE films (<1 mg). The **E28**, **E46** and **E64** films bent toward the light source and lifted the glass substrate upon exposure to UV light at 25 mW cm$^{-2}$, while the **E82** films showed no macroscopic actuation under the experimental condition (Figure 3(c)). When the glass substrate was removed, all the films bent and curled up as shown in Figure 3(d), indicating that the film with high cross-linking density exhibited larger actuation resulting from larger contraction force. In addition, all the bent film reverted to the initial shape by irradiation with visible light. These results mean that the LCE films with high cross-linking density generate large mechanical work by photo-irradiation and exhibit shape memory effect by densely cross-linked structures. From these results, we used the **E28** films as a sample for evaluation of the photomechanical property of LCE films.

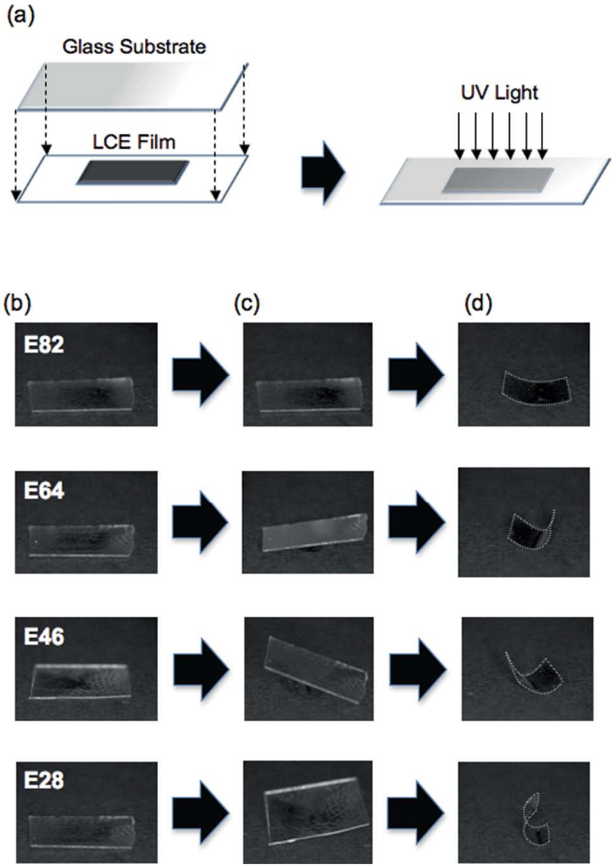

Figure 3. Schematic illustration of an experimental setup (a) and photographs of photo-induced lifting of LCE films with different cross-linking densities before (b) and after irradiation with UV light for 100 seconds at 25 mW cm$^{-2}$ (c). (d) Photographs of the LCE films after irradiation with UV light and removal of the glass substrate. The white dash line in (d) describes the edges of the film. Size of the films: 5 mm × 5 mm.

Figure 4 shows the change in $\Delta l$ of the **E28** film upon exposure to UV light at different temperatures. It was found that the change of $\Delta l$ in the LCE films became larger and faster with increasing temperature in the initial stage. It is known that the higher the temperature, then the larger the mobility of the polymer segments (*20*). Therefore, the degree of contraction is enhanced to a great extent with an increase in temperature. On the other hand, maximum values of $\Delta l$ increased with an increase in temperature up to 70°C and then decreased. In addition, we measured the change in length of the film after the actinic light was turned off. Here, we define the degree of reversion ($\Delta r$) as follows:

$$\Delta r = (l_r - l)/(l_0 - l) \tag{3}$$

where $l_r$ is the length of the film after the UV light was turned off. Figure 5 shows the value of $\Delta r$ at different

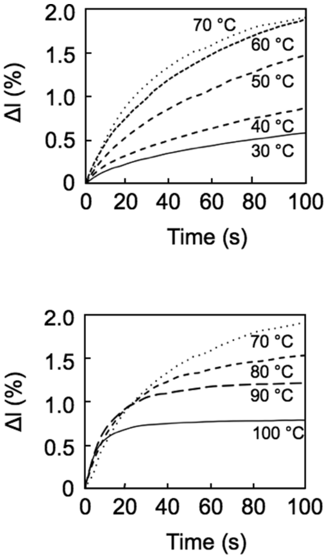

Figure 4. Change in the degree of contraction ($\Delta l$) of the films as a function of time upon exposure to UV light at various temperatures.

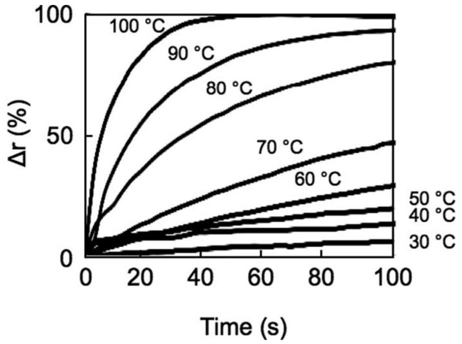

Figure 5. Spontaneous thermal reversion ($\Delta r$) of the contracted films after irradiation with UV light at various temperatures.

temperatures. It was clearly observed that reversion of the film became faster when the temperature increased. In particular, when heated to 100°C the film reverted to the initial length in 40 s. It is presumed that the *cis-trans* back isomerisation of azobenzenes takes place effectively at high temperature, resulting in fast reversion of the films. Consequently, increasing temperature of the LCEs has two effects on the bending process: one is to improve the mobility of the polymer segments, enhancing the degree of contraction, and the other is to stimulate the *cis-trans* isomerisation, decreasing the contraction of the films.

We performed a durability test of LCE films for photo-induced bending at 100°C where fast reversion occurs. Figure 6(a) shows a unit signal of the actinic light. The sample was irradiated with UV light (2.7 mW cm$^{-2}$) for 7 seconds and then kept in the dark for 36 seconds. This cycle was repeated at 100°C, where *cis-trans* thermal isomerisation is induced quite effectively. Figure 6(b) shows the mechanical force generated in the LCE films after 7 minutes. $\Delta F$ increased to approximately 90 kPa upon irradiation with UV light and decreased to the initial values when the sample was kept in the dark for 36 seconds. As shown in Figure 6(c), $\Delta F$ values associated with the photo-induced contraction of the films after 50 hours were almost the same as those observed in the initial state. This result indicates that no obvious fatigue occurs in the LCE films under the present experimental conditions for 50 hours. Therefore, the photo-induced bending of the LCE films can be repeated for more than 5000 cycles.

Figure 7(a) presents the change in $\Delta l$ of the LCE films by irradiation with UV light at different intensities. The degree of contraction increased significantly with an increase in light intensity. The actinic light with higher intensity produces a higher concentration of *cis*-azobenzene, and a large change in the molecular alignment of the mesogens occurs by *trans-cis* photoisomerisation. As a result, a larger contraction of the LCE films is brought about.

Finally, we irradiated the films with sunlight and examined their photoresponsive behaviour. Light is a clean energy source although a light source is usually driven by electricity. On the other hand, sunlight is a zero-emission light source and it can supply UV and visible light simultaneously. If the films move by

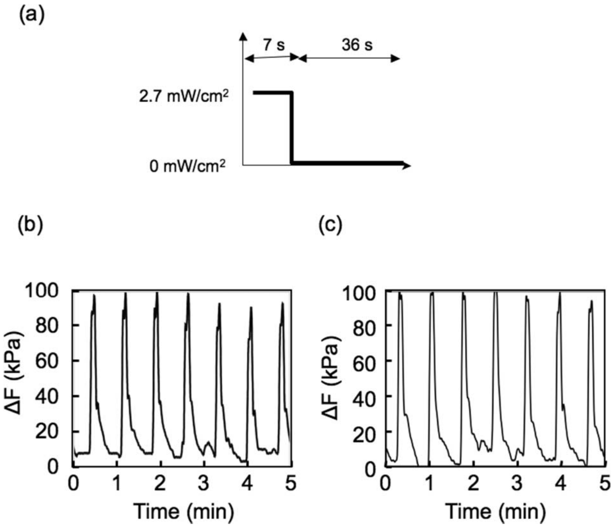

Figure 6. A unit signal of photo-irradiation for durability test on photo-induced bending of the **E28** film (a) and the change in contraction force of the **E28** film after 7 minutes (b) and 50 hours (c).

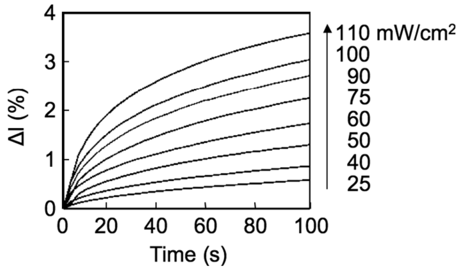

Figure 7. Change in $\Delta l$ of the **E28** film upon irradiation with UV light at different light intensity.

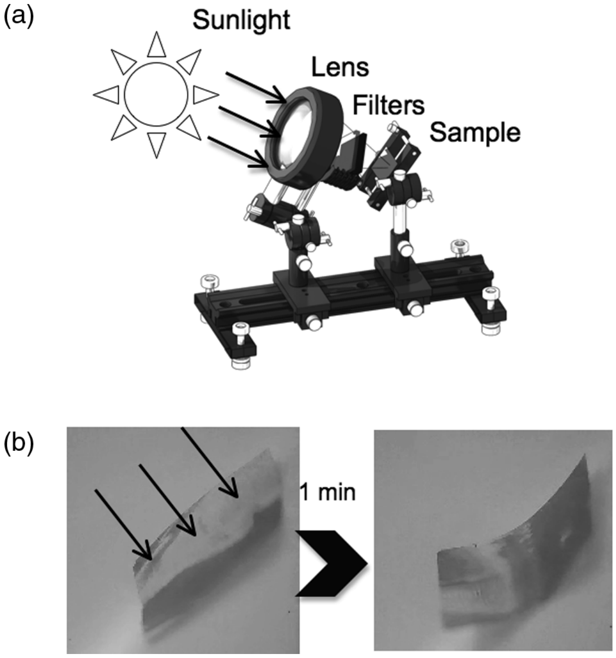

Figure 8. Schematic illustration of (a) an experimental setup and(b) photographs of the **E28** film exhibiting bending upon exposure to focused sunlight through glass filters. Size of the films: 5.5 mm × 5 mm × 20 $\mu$m. The glass filters: UV-36B and IRA-25S. Light intensity: 170 mW cm$^{-2}$ at 366 nm.

sunlight, a prototype for solar mechanical devices can be fabricated (*21*). The LCE film was irradiated with sunlight under an experimental setup illustrated in Figure 8(a) because the intensity of UV light from the sunlight was low. Upon exposure to sunlight focused through glass filters, the film bent sunward, indicating that the LCE films can be actuated by energy in nature alone (Figure 8(b)). The bent film reverted to the initial state immediately by illuminating the sunlight without glass filters.

## 4. Conclusion

We prepared LCE films with low $T_g$ and explored their photomechanical properties. Upon exposure to UV light, the LCE films contracted along the alignment direction of azobenzene mesogens at room temperature. Powerful actuation of the LCE films with high cross-linking density was induced by photo-irradiation. It was found that an increase of the feed ratio of the azobenzene cross-linker made the film stiff. In particular, the LCE films containing 80 mol% azobenzene cross-linkers generated a mechanical force of over 1 MPa by photo-irradiation. Bending of the LCE films could be induced by more than 5000 cycles without fatigue by periodic irradiation. Additionally, the LCE films exhibited bending and unbending by irradiation with sunlight.

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