

Photoinduced bending and unbending behavior of liquid-crystalline gels and elastomers*

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Abstract: Liquid-crystalline gels and elastomers were prepared by polymerization of mixtures containing azobenzene monomers and cross linkers with azobenzene moieties. Oriented liquid-crystalline gels and elastomer films were found to undergo anisotropic bending and unbending behavior only along the rubbing direction, when exposed to alternate irradiation of unpolarized UV and visible light. In the case of polydomain liquid-crystalline elastomer films, the bending and unbending were induced exactly along the polarization direction of incident linearly polarized light. By altering the polarization direction of light, a single film could be bent repeatedly and precisely along any chosen direction.

INTRODUCTION

“Intelligent” or “smart” materials continue to fascinate scientists and engineers because they have capability to select and execute specific functions autonomously in response to changes of environmental stimuli, and thus have obvious attractiveness in many applications, for instance, serving as artificial muscles, sensors, microrobots, micropumps, and actuators. In particular, 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. Many materials are under active investigation in this field, such as shape-memory alloys [1], polymer gels [2–9], conjugated polymers [10–14], carbon nanotubes [15–18], and dielectric elastomers [19]. However, the changes of shape and volume of these materials occur isotropically, since they are usually amorphous without microscopic or macroscopic order. If materials with anisotropic order are used, the changes of shape and volume will become anisotropic, and mechanical power that can be utilized will increase significantly.

Liquid-crystalline gels (LCGs) and elastomers (LCEs) show combined unique properties as self-organized liquid-crystalline (LC) systems with strong anisotropy and polymer networks with rubbery elasticity [20–27]. The possibility of using LCGs and LCEs as artificial muscles, depending on their substantial uniaxial contraction in the direction of the optical axis or director axis, was theoretically proposed by de Gennes [28]. The reason for the contraction is in the subtle decrease of microscopic order upon nematic-isotropic (I) phase transition. Previously, experimental investigations of this deformation in response to temperature, generating thermomechanical effects, were reported [29–31]. Accordingly, if the alignment order of LCGs and LCEs can be manipulated by light, a photoinduced large deformation should be generated. Light can be controlled remotely and rapidly as an external stimulus, so that it is of great importance in developing photomechanical effects in LCGs and LCEs.

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It is well known that azobenzene chromophores show *trans*–*cis* photoisomerization accompanied by a large change in the molecular length: the distance between 4- and 4'-carbons decreases from 9.0 Å (*trans*) to 5.5 Å (*cis*) [32]. Furthermore, upon irradiation of UV light, LC systems containing azobenzene chromophores experience a reduction in alignment order and even an LC-I phase transition due to the *trans*–*cis* photoisomerization of azobenzene moieties, because the rod-like *trans* form azobenzene stabilizes the LC alignment, whereas the bent *cis* form lowers the LC order parameter [33,34]. Recently, by using azobenzene-containing LCEs, large photocontraction has been achieved by Finkelmann and other researchers [35–37]. The driving force for the substantial contraction is suggested to arise from the variation of alignment order.

However, in the other promising materials for the investigation of actuators mentioned above, such as polymer gels and conjugated polymers, besides contraction [2–4,8,13], a bending mode of deformation has been produced [5a,6,9,11,12]. The bending mode should be advantageous for artificial “hands” and medical microrobots that are capable of completing particular manipulations [11]. Most recently, we have achieved a uniaxial bending upon irradiation of unpolarized light in oriented LCG films containing azobenzene chromophores in good solvents and in oriented LCE films in air. Moreover, by using linearly polarized light (LPL), we have succeeded in leading a single polydomain LCE film to repeatedly and precisely bend along any chosen direction.

EXPERIMENTAL SECTION

Materials

The structures of LC monoacrylates, **A6AB2** and **A6AB6**, and a diacrylate cross linker, **DA6AB**, used in this study are shown in Fig. 1, all of which possess azobenzene moieties. The oriented LCG 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 [38]. The oriented and polydomain LCE 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 alignment layers that had been rubbed or not.

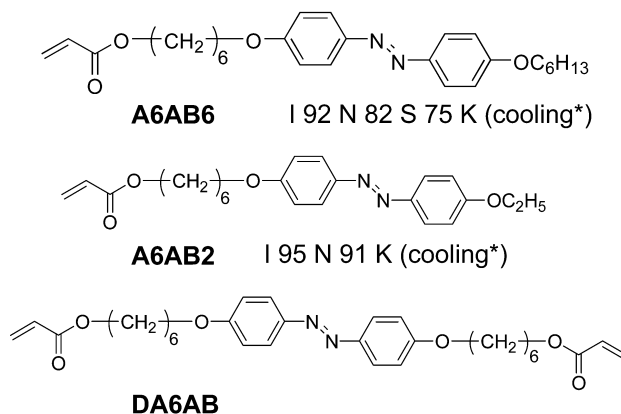


Fig. 1 Structures, properties and abbreviations of the LC monomers and the cross linker used in this study. I: isotropic; N: nematic; K: crystal. ***A6AB6** shows a monotropic smectic phase when cooled from a nematic phase, and **A6AB2** shows a monotropic nematic phase when cooled from an isotropic phase.

Photoinduced bending and unbending behavior

The photoresponsive deformation of the oriented LCG films was investigated by placing a film horizontally in a toluene-containing vessel and irradiating the film with unpolarized 360-nm light from a Xe lamp through a monochromator (Jasco, SM-5). The bent LCG film was exposed to unpolarized visible light at 450 nm from the Xe lamp. The bending and unbending behavior of the oriented LCG film was observed at room temperature by polarizing optical microscopy (Olympus, BH-2).

For the oriented LCE films, a partially freestanding film put on a glass substrate was placed on a Mettler hot stage (models FP-90 and FP-82). The bending behavior of the film was observed upon irradiation of unpolarized UV light at 366 nm from a 500 W high-pressure mercury lamp through glass filters (Toshiba, UV-D36A, UV-35, and IRA-25S). The bent film was exposed to unpolarized visible light at >540 nm (Toshiba, Y-52, and IRA-25S). The photographs of the bending and unbending behavior were taken by a digital camera (Sony, DSC-F505).

The photoresponsive deformation of the polydomain LCE films was investigated upon irradiation of LPL by putting a film on a copper stick, whose temperature was controlled by the Mettler hot stage placed under the copper stick. The bending behavior of the film was observed upon irradiation of LPL at 366 nm from the mercury lamp passed through the cut-off filters and a polarizer. The bent film was exposed to visible light at >540 nm. The photographs of the bending and unbending behavior were taken by the digital camera.

RESULTS AND DISCUSSION

Anisotropic bending and unbending behavior of oriented LCG films in solvents

As Fig. 2 shows, exposure of the oriented LCG film in toluene to unpolarized 360-nm light led the film to bend toward the irradiation direction of the incident light. The bending was completed in 20 s at a light intensity of $3 \text{ mW}\cdot\text{cm}^{-2}$. Moreover, when the bent film was exposed to unpolarized visible 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 visible light. It is worth mentioning that the bending of the oriented LCG films occurred anisotropically, only in the direction parallel to the rubbing direction of the alignment layers. 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 [38]. It is because when the oriented 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.

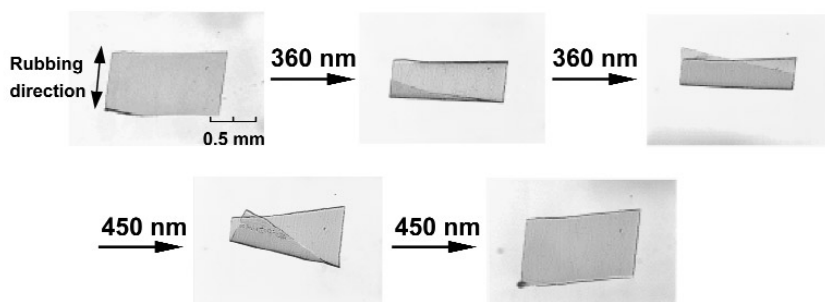


Fig. 2 Photographs of the bending and unbending processes of the oriented LCG film in toluene at room temperature. The oriented LCG film bent toward the irradiation direction of unpolarized UV light (360 nm), and the bent film reverted to the initial flat state completely upon irradiation of unpolarized visible light (450 nm).

As described in the introduction, irradiation of UV light gives rise to the *trans*–*cis* isomerization of azobenzene moieties and even the LC-I phase transition of the LC systems; therefore, not only the size, but also the alignment order of azobenzene moieties is reduced, both of which can bring about a volume contraction of the oriented LCG films according to the previous studies [32,35–37]. However, the extinction coefficient of the azobenzene moieties at ~360 nm is large ($2.6 \times 10^4 \text{ l}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$), 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 oriented LCG films used was 10 μm , as Fig. 3 shows, the photochemical changes in size and alignment order of azobenzene moieties occur only in the surface region facing the incident light, but in the bulk of the film the *trans*-azobenzene moieties remain unchanged. As a result, the volume contraction is generated only in the surface region, causing the bending toward the irradiation direction of the incident light. Furthermore, the azobenzene moieties are preferentially aligned along the rubbing direction of the alignment layers, and the decreases in size and alignment order of azobenzene moieties are thus produced just along this direction, contributing to the anisotropic bending behavior. Additionally, the unbending behavior is ascribed to the recovery of the initial structure and alignment order of azobenzene moieties due to *cis*–*trans* back isomerization induced by irradiation of visible light.

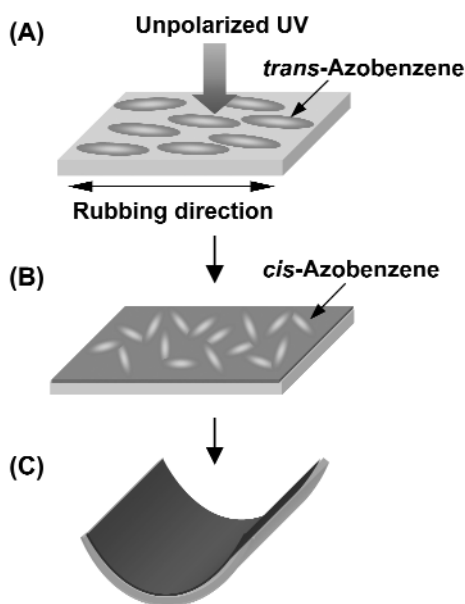


Fig. 3 Schematic illustration of plausible mechanism of the anisotropic bending behavior. (A) Azobenzene moieties are preferentially aligned in one direction in the film. (B) Irradiation of UV light gives rise to the *trans*–*cis* isomerization and the alignment change of azobenzene moieties in the surface region, causing an anisotropic contraction of the film surface. (C) Anisotropic bending behavior takes place in the film.

In order to study the change in the surface region of the oriented LCG films upon irradiation of UV light, the measurement of atomic force microscopy (AFM) was carried out. Figure 4A shows the AFM image of the surface of the film before irradiation of UV light. It was observed that fiber-like structures aligned in one direction parallel to the rubbing direction of the alignment layers were formed in the film, and the size of the structures was 5–10 μm with a height of >1 μm [39]. As Fig. 4B shows, after irradiation of UV light, the microscopic surface morphology of the fibers changed: anisotropic grooves appeared in the direction perpendicular to the fibers. It is due to the volume contraction in the surface region along the rubbing direction of the alignment layers induced by the photochemical

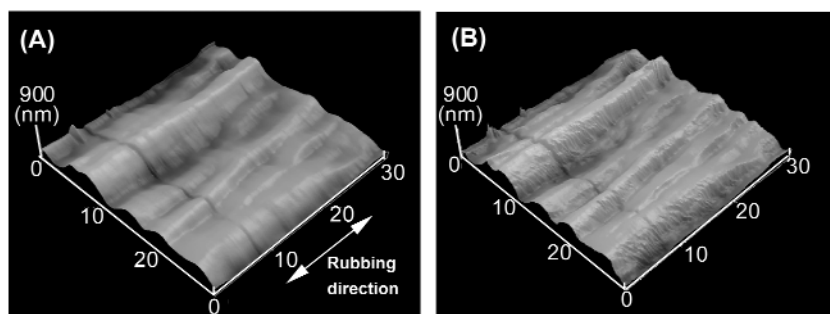


Fig. 4 AFM images of the surface structures of the oriented LCG film measured in the absence of solvents at room temperature. Before (A) and after (B) irradiation of UV light.

changes in size and alignment order of azobenzene moieties. Here, because the AFM measurement was performed at room temperature, which is lower than the glass transition temperature ($T_g = 85\text{ }^\circ\text{C}$) of the oriented LCG film, when the film was put in air instead of swollen in solvents, the mobility of the polymer segments is restricted, and the volume contraction in the surface region cannot evoke any appreciable macroscopic changes of the film (e.g., bending), but only microscopic changes (e.g. the formation of grooves).

Anisotropic bending and unbending behavior of oriented LCE films in air

As described above, for the occurrence of the photoinduced bending and unbending behavior, the relaxation of the polymer segments is necessary, which can be achieved by suspending the films in good solvents or heating them to above T_g . Thus, we also investigated the photoinduced bending and unbending behavior in air by using the oriented LCE films that show a much lower T_g ($50\text{ }^\circ\text{C}$) than the oriented LCG films.

As shown in Fig. 5A, an oriented LCE film was partially pasted on a glass substrate heated by the hot stage, and normal irradiation of unpolarized light was performed when the film was heated to $70\text{ }^\circ\text{C}$. Figure 5B shows the processes of bending and unbending induced by irradiation of UV and visible light, respectively, when the rubbing direction was set perpendicular to one side of the glass substrate. It was observed that the 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 visible light. The bending was completed in 60 s upon irradiation of 366-nm light with an intensity of $1.5\text{ mW}\cdot\text{cm}^{-2}$, and the unbending was completed in 30 s upon irradiation of visible light at $>540\text{ nm}$ (547 nm, $13\text{ mW}\cdot\text{cm}^{-2}$; 577 nm, $15\text{ mW}\cdot\text{cm}^{-2}$). 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. 5C). These results clearly demonstrate that the bending is anisotropically induced, only along the rubbing direction of the alignment layers. This bending behavior is identical to that observed in the oriented LCG films in good solvents.

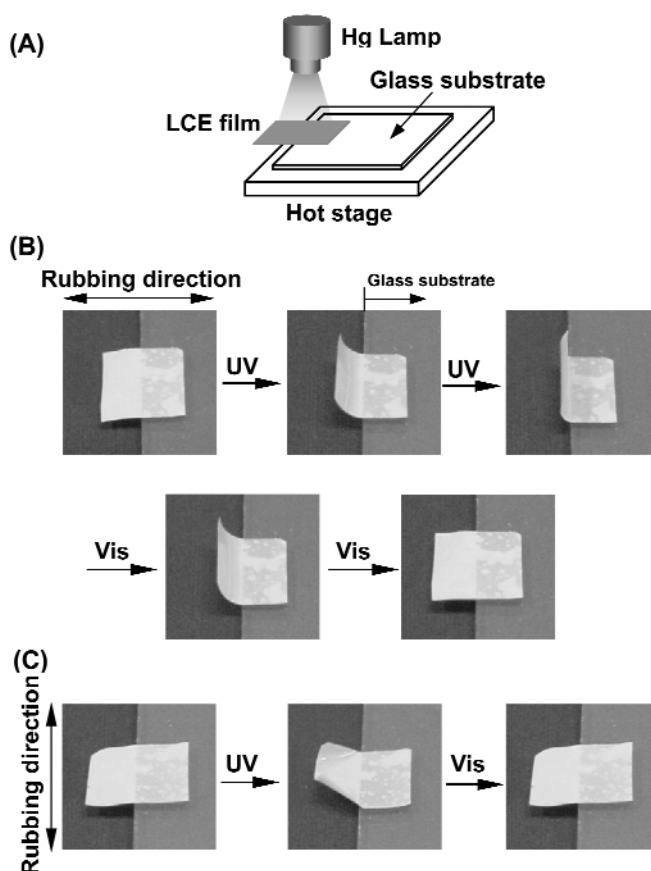


Fig. 5 Anisotropic bending and unbending behavior of the oriented LCE film at 70 °C in air. The oriented LCE film bent toward the irradiation direction of unpolarized UV light (366 nm), and the bent film reverted to the initial flat state completely upon irradiation of unpolarized visible light (>540 nm). The bending was always induced along the rubbing direction of the alignment layers. (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.

Temperature dependence of bending behavior

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. 6 shows. The 366-nm light with the intensity of 1.5 mW·cm⁻² was used, and the results are shown in Fig. 6. It was observed that the bending could be induced only when the films were heated to above T_g , because the relaxation of polymer segments is necessary to transfer the changes in structure and alignment of azobenzene moieties at the film surface to the transformation of the conformation in the entire polymer network. It is known that the higher the temperature, the larger the mobility of 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. Consequently, increasing temperature has two effects on the bending process: one is to improve the mobility of the polymer segments, accelerating the bending rate, and the other is to stimulate the *cis*–*trans* isomerization, reducing the bending rate and compressing the bending of the film to 90°. 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

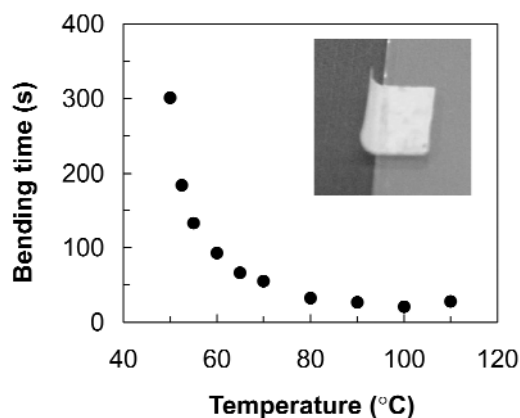


Fig. 6 Bending time for the oriented LCE film to bend by 90° as a function of temperature upon irradiation of 366-nm light ($1.5 \text{ mW}\cdot\text{cm}^{-2}$) and the photograph of the film bending by 90° (inset).

was longer than that at 100 °C, and the bending to 90° could not be completed at all when the temperature was raised higher.

Light-intensity dependence of bending behavior

Upon exposure to 366-nm light with different intensities at 70 °C, the bending time defined as above was measured and the results are shown in Fig. 7. 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. On the other hand, as referred above, the relaxation of polymer segments is of great importance to the occurrence of the bending behavior. In the high intensity region, the amount of *trans*- and *cis*-azobenzene moieties reaches quickly to 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 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 when the intensity is high.

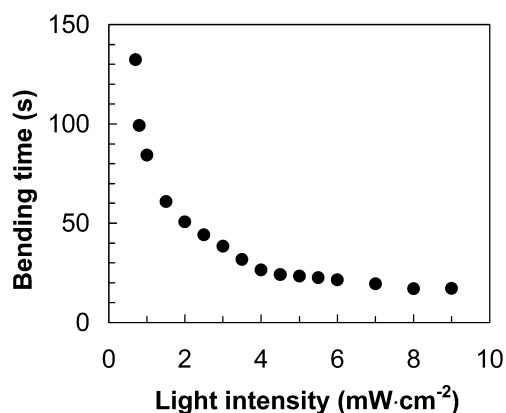


Fig. 7 Bending time for the oriented LCE film to bend by 90° as a function of the intensity of 366-nm light at 70 °C.

Film-thickness dependence of bending behavior

Figure 8 shows the effect of the film thickness ($\leq 20 \mu\text{m}$) on the bending time, when the films were irradiated with 366-nm light at 70°C . In this experiment, we used the films with the same size and the same area of the freestanding part. It is worth mentioning that the bending time increased remarkably with the increment of the film thickness. When the film becomes thick, the thickness of the bulk region without the volume contraction increases. Namely, the quantity of polymer segments in the bulk region becomes large. Since the relaxation of 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.

In addition, we also prepared much thicker films, 60 and $110 \mu\text{m}$, 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.

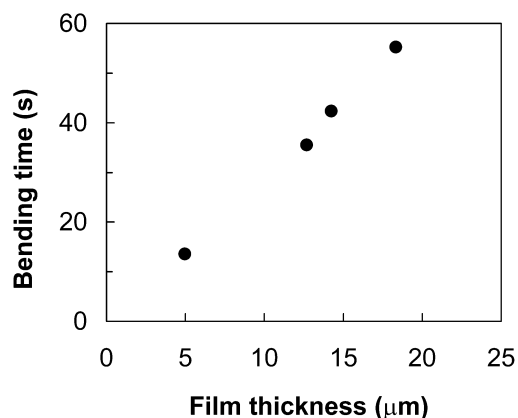


Fig. 8 Bending time for the oriented LCE film to bend by 90° as a function of the film thickness upon irradiation of 366-nm light ($1.5 \text{ mW}\cdot\text{cm}^{-2}$) at 70°C .

Direction-controllable bending and unbending behavior of polydomain LCE films

The photoinduced bending and unbending behavior of the oriented LCG and LCE films shown above takes place anisotropically, whose direction is determined fully by the alignment direction of azobenzene mesogens in the films and cannot be freely varied. On the other hand, we found that a single polydomain LCE film could be bent repeatedly and precisely along any chosen direction by using LPL [40]. This attractive bending and unbending behavior is shown in Fig. 9. The polydomain LCE 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. Figure 9A shows the film before light irradiation, and Fig. 9B 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 visible light at $>540 \text{ nm}$, 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 Figs. 9C, 9D, and 9E, 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 with visible light at $>540 \text{ nm}$.

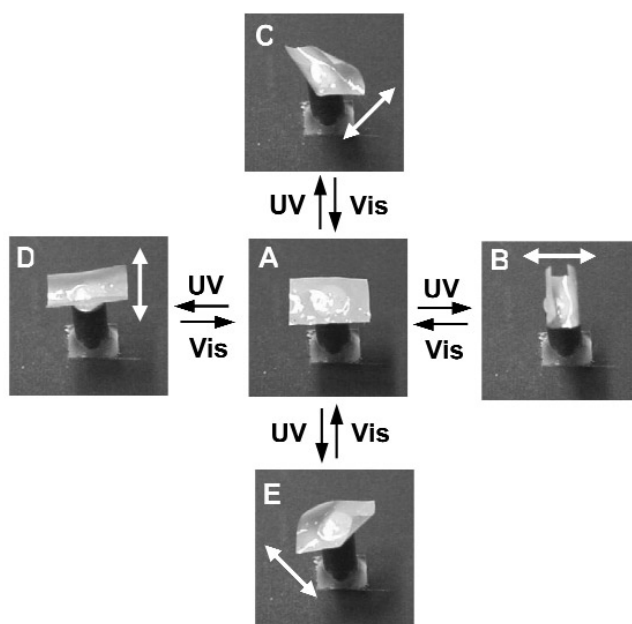


Fig. 9 Photographs of the polydomain LCE film before irradiation (A) and after irradiation of 366-nm LPL with different polarization directions indicated by the white arrows (B), (C), (D), (E). The film bent in different directions after exposure to 366-nm LPL, and could be restored from each bent state to its initial flat form by irradiation with visible light at >540 nm. Size of the film: $4.5 \text{ mm} \times 3 \text{ mm} \times 7 \text{ }\mu\text{m}$.

The bending time for the four different bending directions was within 10 s, when the light intensity of 366-nm LPL was $3.5 \text{ mW}\cdot\text{cm}^{-2}$. After exposure to visible light at >540 nm (547 nm, $24.2 \text{ mW}\cdot\text{cm}^{-2}$; 577 nm, $26.8 \text{ mW}\cdot\text{cm}^{-2}$), the bent film reverted 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 polydomain LCE film used here consists of a large number of microsize domains of azobenzene mesogens, in which 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. 10). As a result, the subtle reduction in microscopic size and order of 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 mesogens and polymer segments.

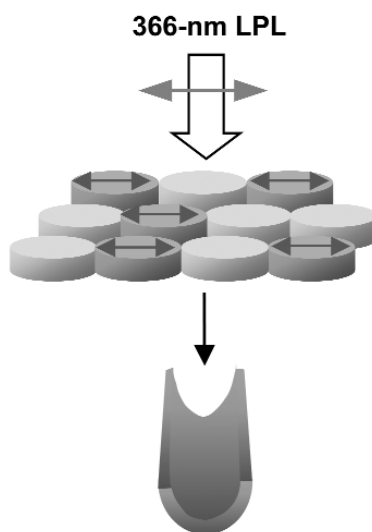


Fig. 10 Schematic illustration of plausible mechanism of the direction-controllable bending behavior induced by UV LPL in the polydomain LCE films. When the film is exposed to UV LPL, the azobenzene mesogens in some specific domains (ellipsoids with arrows), where the mesogens are aligned parallel to the light polarization (transverse arrow), absorb the photons and undergo the photochemical change.

CONCLUSIONS

Anisotropic bending and unbending were achieved in the oriented LCG and LCE films upon alternate irradiation of unpolarized UV and visible light. It is suggested that the photochemical changes in size and alignment order of azobenzene moieties along one direction only at the film surface results in this behavior. For the oriented LCG films, the bending was observed only in good solvents, and for the oriented LCE films, the bending occurred only when the films were heated to above T_g . The cooperative movement of polymer segments is thus of great importance for this photoresponsive behavior. Moreover, the temperature, the intensity of 366-nm light, and the film thickness have great influence on the bending time of the oriented LCE films. In addition, a single polydomain LCE film could be bent repeatedly and precisely along any chosen direction by using LPL because of the photoselective volume contraction. The photoinduced bending and unbending behavior supplies a novel method for converting light energy to mechanical work and is hoped to be applied for the microscopical soft machines.

REFERENCES

1. M. V. Gandhi and B. S. Thompson. In *Smart Materials and Structures*, Chapman & Hall, London (1992).
2. A. Mamada, T. Tanaka, D. Kungwachakun, M. Irie. *Macromolecules* **23**, 1517 (1990).
3. A. Suzuki and T. Tanaka. *Nature* **346**, 345 (1990).
4. R. Yoshida, K. Uchida, Y. Kaneko, K. Sakai, A. Kikuchi, Y. Sakurai, T. Okano. *Nature* **374**, 240 (1995).
5. (a) Y. Osada, H. Okuzaki, H. Hori. *Nature* **355**, 242 (1992); (b) Y. Osada and J. P. Gong. *Adv. Mater.* **10**, 827 (1998).
6. (a) X. Zhang, Y. Li, Z. Hu, C. L. Litter. *J. Chem. Phys.* **102**, 551 (1995); (b) Z. Hu, X. Zhang, Y. Li. *Science* **269**, 525 (1995).
7. A. Suzuki, T. Ishii, Y. Maruyama. *J. Appl. Phys.* **80**, 131 (1996).
8. Z. Liu and P. Calvert. *Adv. Mater.* **12**, 288 (2000).

9. M. Zrinyi, J. Feher, G. Filipcsei. *Macromolecules* **33**, 5751 (2000).
10. R. H. Baughman. *Synth. Met.* **78**, 339 (1996).
11. E. W. H. Jager, E. Smela, O. Ingnas. *Science* **290**, 1540 (2000).
12. T. F. Otero and M. T. Cortes. *Adv. Mater.* **15**, 279 (2003).
13. L. Bay, K. West, P. Sommer-Larsen, S. Skaarup, M. Benslimane. *Adv. Mater.* **15**, 310 (2003).
14. E. Smela. *Adv. Mater.* **15**, 481 (2003).
15. R. H. Baughman, C. Cui, A. A. Zakhidov, Z. Iqbal, J. N. Barisci, G. M. Spinks, G. G. Wallace, A. Mazzoldi, D. De Rossi, A. G. Rinzler, O. Jaschinski, S. Roth, M. Kertesz. *Science* **284**, 1340 (1999).
16. P. Kim and C. M. Lieber. *Science* **286**, 2148 (1999).
17. Y. Zhang and S. Iijima. *Phys. Rev. Lett.* **82**, 3472 (1999).
18. G. M. Spinks, G. G. Wallace, L. S. Fifield, L. R. Dalton, A. Mazzoldi, D. De Rossi, I. I. Khayrullin, R. H. Baughman. *Adv. Mater.* **14**, 1728 (2002).
19. R. Pelrine, R. Kornbluh, Q. Pei, J. Joseph. *Science* **287**, 836 (2000).
20. R. Zentel. *Angew. Chem. Adv. Mater.* **101**, 1437 (1989).
21. G. G. Barclay and C. K. Ober. *Prog. Polym. Sci.* **18**, 899 (1993).
22. H. Finkelmann and H. R. Brand. *Trends Polym. Sci.* **2**, 222 (1994).
23. M. Warner and E. M. Terentjev. *Prog. Polym. Sci.* **21**, 853 (1996).
24. S. M. Kelly. *Liq. Cryst.* **24**, 71 (1998).
25. E. M. Terentjev. *J. Phys.: Condens. Matter* **11**, R239 (1999).
26. R. A. M. Hikmet. *J. Mater. Chem.* **9**, 1921 (1999).
27. Y. Osada and D. E. DeRossi. In *Polymer Sensors and Actuators*, pp. 259–272, Springer, Berlin (2000).
28. P.-G. de Gennes, M. Hebert, R. Kant. *Macromol. Symp.* **113**, 39 (1997).
29. (a) J. Kupfer and H. Finkelmann. *Makromol. Chem., Rapid Commun.* **12**, 717 (1991); (b) H. Wermter and H. Finkelmann. *e-Polymers* 013 (2001).
30. D. L. Thomsen III, P. Keller, J. Naciri, R. Pink, H. Jeon, D. Shenoy, B. R. Ratna. *Macromolecules* **34**, 5868 (2001).
31. S. M. Clarke, A. Hotta, A. R. Tajbakhsh, E. M. Terentjev. *Phys. Rev. E* **64**, 061702 (2001).
32. M. Irie. *Adv. Polym. Sci.* **94**, 27 (1990).
33. (a) T. Ikeda and O. Tsutsumi. *Science* **268**, 1873 (1995); (b) T. Ikeda. *J. Mater. Chem.* **13**, 2037 (2003).
34. (a) S. Kurihara, A. Sakamoto, T. Nonaka. *Macromolecules* **31**, 4648 (1998); (b) S. Kurihara, A. Sakamoto, D. Yoneyama, T. Nonaka. *Macromolecules* **32**, 6493 (1999); (c) S. Kurihara, D. Yoneyama, T. Nonaka. *Chem. Mater.* **13**, 2807 (2001).
35. H. Finkelmann, E. Nishikawa, G. G. Pereira, M. Warner. *Phys. Rev. Lett.* **87**, 015501 (2001).
36. P. M. Hogan, A. R. Tajbakhsh, E. M. Terentjev. *Phys. Rev. E* **65**, 041720 (2002).
37. M.-H. Li, P. Keller, B. Li, X. Wang, M. Brunet. *Adv. Mater.* **15**, 569 (2003).
38. T. Ikeda, M. Nakano, Y. Yu, O. Tsutsumi, A. Kanazawa. *Adv. Mater.* **15**, 201 (2003).
39. M. Nakano, Y. Yu, A. Shishido, O. Tsutsumi, A. Kanazawa, T. Shiono, T. Ikeda. *Mol. Cryst. Liq. Cryst.* **398**, 1 (2003).
40. Y. Yu, M. Nakano, T. Ikeda. *Nature* **425**, 145 (2003).