

Photomechanical Effects of Ferroelectric Liquid-Crystalline Elastomers Containing Azobenzene Chromophores

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Photodeformable smart materials that can undergo a shape or volume change in response to light are attracting increasing attention. On the one hand, light is a clean energy and can be controlled rapidly and remotely; on the other hand, by using the deformation of these materials, one can convert light energy into mechanical energy directly (photomechanical effects). Most photodeformable smart materials contain photochromic compounds, such as azobenzene, stilbene, and spiropyran. The chromophores change their molecular structure upon exposure to light; thus, their incorporation into polymer systems gives rise to conformation changes of the polymer chains and concomitant changes in the physical and chemical properties of the polymer solutions and solids through photoisomerization, including photoinduced contractions/expansions of rubbery networks and swollen gels.^[1–12] However, the low elastic modulus and low yield strength of gels provide important limitations in the performance of actuation, while for the solid polymer networks, deformations of less than 10% limit their practical applications.

Large photoinduced contractions/expansions have been acquired by Finkelmann et al. and other research groups by incorporating azobenzene derivatives into liquid-crystalline elastomers (LCEs) as a trigger.^[13–15] LCEs with the rubber elasticity of polymer networks exhibit a simultaneous anisotropic orientational symmetry of liquid-crystalline (LC) phases. The driving force for their large changes in shape is suggested to arise from a variation of LC alignment order: upon irradiation with UV light, LC systems containing azobenzene chromophores experience a reduction in alignment order and even an LC-I phase transition as a result of the *trans*–*cis* photoisomerization of the azobenzene moieties, because the rodlike *trans*-azobenzene moieties stabilize the LC alignment, whereas the bent *cis* forms lower the LC order parameter.

Furthermore, a three-dimensional deformation, photo-induced bending, has been achieved by using nematic LCE films containing azobenzenes swollen in suitable solvents or

heated above their glass transition temperatures in air.^[16] As a consequence of the limitation of absorption of photons, a surface contraction caused by the photoinduced change in alignment of liquid crystals contributes to the bending. Several examples of the three-dimensional deformations have been reported, such as twisting of the azobenzene-containing LCEs.^[17–19] In comparison with the contraction/expansion that is a two-dimensional action, the bending could be advantageous for artificial hands and medical microrobots that are capable of completing particular manipulations. However, the following three factors limit their actual applications: 1) a slow response in the order of minutes^[16a] or seconds;^[16d] 2) difficulty in inducing effective bending at room temperature in air; and 3) the low force generated upon photoirradiation.

In our previous work, we found that the bending speed was different in the nematic LCE films with various cross-linking densities.^[16c] The larger the order parameter and the mobility of polymer segments, the faster the bending. According to these results, if we use films with a higher order of liquid crystals and a lower glass transition temperature (T_g), it should be easy to acquire high-speed bending at room temperature. It is well-known that ferroelectric liquid crystals have two advantages: their high degree of order of mesogens, and the fact that their molecular alignment can be controlled quickly by applying an electric field, because of the presence of spontaneous polarization.

Zentel et al. synthesized ferroelectric LCEs from electric-field-induced oriented LC polysiloxanes by a radical photocross-linking process.^[20] Later, Finkelmann et al. prepared chiral smectic C (SmC*) elastomers by two successive deformation processes,^[21a] and more perfectly by mechanical shear deformation;^[21b] they successfully obtained a monodomain SmC* elastomer by a mechanical shear field.^[21c] Here, we used a photopolymerization method to prepare new ferroelectric LCE films from a mixture of molecules **1** and **2** (Figure 1; 80:20) in the SmC* phase in a rubbing-treated indium tin oxide (ITO) glass cell under an electric field, as it has been reported that highly ordered polymers can be obtained by in situ photopolymerization of oriented LC monomers.^[22] In the obtained ferroelectric LCE films, the long axis of the molecules (director **n**) in each layer is aligned in the same direction in the smectic layers oriented roughly perpendicular to the surface of the glass cell (Figure 2a). Moreover, **n** is not parallel to the rubbing direction of the alignment layer but has a tilt with it.^[23]

The photoresponsive behavior of the ferroelectric LCE films was investigated by irradiation with non-polarized light. The first frame in Figure 2b shows the ferroelectric LCE film before photoirradiation; counting clockwise, the second and

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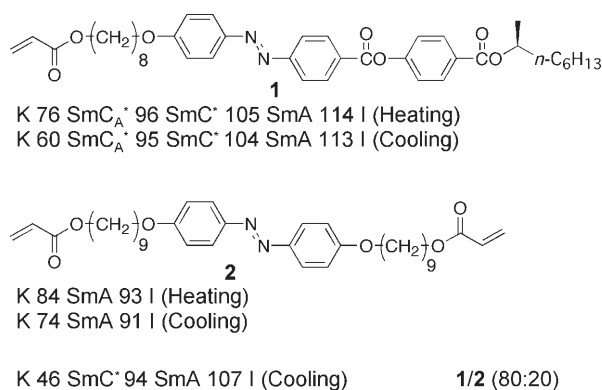


Figure 1. Chemical structures and phase transition temperatures of the LC monomer (**1**), the cross-linker (**2**), and the monomer mixture used for preparation of the ferroelectric LCE film. SmA, smectic A; SmC*, chiral smectic C; SmC_A*, chiral smectic C_A.

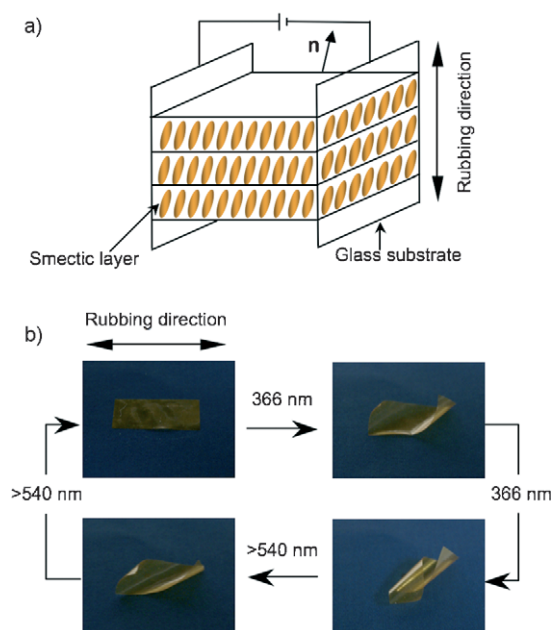


Figure 2. Bending and unbending of the ferroelectric LCE film upon alternate irradiation with UV and visible light at room temperature. a) Azobenzene mesogens are aligned parallel to each other to form layers with a tilt between the director (**n**) and the normal to the smectic layer that is parallel to the rubbing direction. b) Photographic frames of the film bending toward the actinic light source along the alignment direction of mesogens in response to irradiation at 366 nm (17 mWcm^{-2}), and being flattened again by visible light at wavelengths above 540 nm (110 mWcm^{-2} at 547 nm). The size of the film is $10 \text{ mm} \times 4 \text{ mm} \times 10 \text{ }\mu\text{m}$.

third show how the film curls up after irradiation at 366 nm at a light intensity of 17 mWcm^{-2} for 5 and 10 s, respectively. Notably, the film bends toward the actinic light source with a tilt to the rubbing direction of the alignment layer: along **n**. As the third frame in Figure 2b shows, the film even curls up to a corkscrew spiral shape. More importantly, the bending was induced at room temperature, because the ferroelectric LCE films has a low T_g of 20°C . The fourth frame in Figure 2b shows the state of the bent film after exposure to visible light

at wavelengths above 540 nm for 5 s. Then, after further irradiation for 25 s, it is clear that the bent film recovers its initial flat state completely (the first frame in Figure 2b). This bending and unbending behavior was reversible just by changing the wavelength of the incident light.

As mentioned above, the ferroelectric LCE films hold a smectic layer structure with **n** in the layers aligned in the same direction; therefore, irradiation by UV light reduces the alignment order of the azobenzene mesogens along **n** in each layer.^[23] Moreover, the extinction coefficient of the azobenzene moieties around 360 nm is large, which leads to a contraction in the film surface and finally bending of a whole film along **n**.

In our previous work on nematic LCE films, we found that the bending time decreased significantly with an increase in light intensity, because actinic light with a higher intensity produces a higher concentration of *cis*-azobenzene moieties, and thus a larger surface contraction.^[16b] This effect of the light intensity on the bending behavior was also observed in the ferroelectric LCE films. Notably, when exposed to an argon-ion laser at 364 nm with a light intensity of 280 mWcm^{-2} , the film underwent fast bending within 500 ms (for a movie, see the Supporting Information), which is one order of magnitude faster than the bending of the nematic LCE films.^[16]

The mechanical force generated in the ferroelectric LCE films upon photoirradiation was measured with a thermomechanical analyzer (Simadzu, TMA-60) as follows: both ends of a film were clamped and 20 mN was initially loaded on the film; then the film was heated to 50°C and exposed to UV light. Figure 3 shows the change of the load on the film upon photoirradiation at different light intensities. As the length of

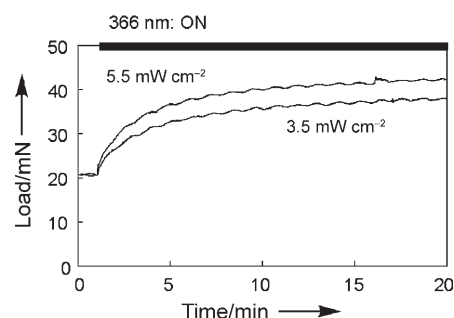


Figure 3. Change of the load on the ferroelectric LCE film when exposed to UV light at 366 nm with different intensities at 50°C . The cross-sectional area of the film was $5 \text{ mm} \times 20 \text{ }\mu\text{m}$. An external force of 20 mN was loaded initially on the film to keep its length unchanged.

the film was kept unchanged, the increase of the load indicates the generation of the mechanical force upon photoirradiation. The maximum loads reached 38 and 42 mN when the light intensity was 3.5 and 5.5 mWcm^{-2} , respectively, which indicates that a mechanical force of 18 and 22 mN is generated. The cross-sectional area of the film was $5 \text{ mm} \times 20 \text{ }\mu\text{m}$, and the force was calculated to be 180–220 kPa, similar to the contraction force of human muscles (around 300 kPa).

It is also clear that the maximum load increases with an increase in light intensity (Figure 3). This finding results from the increment of the concentration of *cis*-azobenzene moieties on increasing the light intensity. Therefore, when we need to enhance the mechanical force generated in this photomechanical system, a laser beam with a higher intensity would be rather simple and effective.

In conclusion, ferroelectric LCE films containing azobenzenes with a high LC order and a low glass transition temperature were prepared by photopolymerization under an electric field. Irradiation with 366-nm light caused the films to bend at room temperature toward the actinic light source along the alignment direction of mesogens, and the bent films recovered their initial flat state completely after exposure to visible light. The bending took place within 500 ms upon irradiation by a laser beam. In addition, the mechanical force generated by photoirradiation reached about 220 kPa, similar to the contraction force of human muscles (around 300 kPa). This fast and strong mechanical response to light may lead to potential applications of the ferroelectric LCEs in artificial muscles, micro-optomechanical systems, and other photo-driven mechanical devices.

Experimental Section

The preparation of **1** and **2** is shown in the Supporting Information. The ferroelectric LCE films were prepared by photopolymerization of a monomer mixture of **1** and **2** (80:20) containing 1 mol% of a photoinitiator (Irgacure 784) in the SmC* phase. First, the molten mixture was injected into an ITO glass cell at 117°C (in an isotropic phase), which was coated with rubbing-treated polyimide alignment layers. Then, after the sample was cooled slowly (2 K min⁻¹) to a polymerization temperature of 90°C (in the SmC* phase), an electric field of 1 V μm⁻¹ (applied voltage/cell thickness) was applied and photoirradiation was performed for 2 h at > 540 nm (3 mW cm⁻² at 547 nm) with a 500-W high-pressure mercury lamp through glass filters (Toshiba, Y-52, and IRA-25S). After polymerization, the ITO cells were opened and the LCE films were removed with a cutter. The detailed measurement methods and the properties of **1** and **2**, the monomer mixture, and the ferroelectric LCE films are described in the Supporting Information.

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