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Photomobile Polymer Materials: Towards Light-Driven Plastic Motors**

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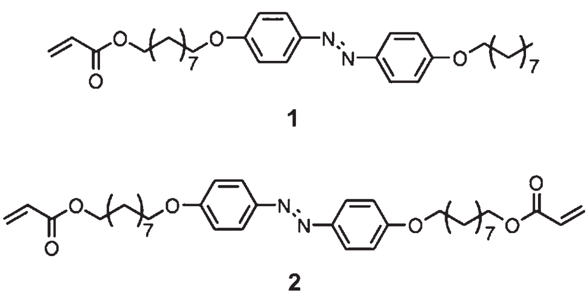
As light is a good energy source that can be controlled remotely, instantly, and precisely, light-driven soft actuators could play an important role for novel applications in wide-ranging industrial and medical fields. Liquid-crystalline elastomers (LCEs) are unique materials having both properties of liquid crystals (LCs) and elastomers,[1–3] and a large deformation can be generated in LCEs, such as reversible contraction and expansion, and even bending, by incorporating photochromic molecules, such as an azobenzene, with the aid of photochemical reactions of these chromophores.[4–12] Herein we demonstrate new sophisticated motions of LCEs and their composite materials: a plastic motor driven only by light.

If materials absorb light and change their shape or volume, they can convert light energy directly into mechanical work (the photomechanical effect) and could be very efficient as a single-step energy conversion. Furthermore, these photomobile materials would be widely applicable because they can be controlled remotely just by manipulating the irradiation conditions. LCEs show an anisotropic order of mesogens with a cooperative effect, which leads them to undergo an anisotropic contraction along the alignment direction of mesogens when heated above their LC-isotropic(I) phase transition temperatures ($T_{\mathrm{LC\text{-}I}}$) and an expansion by lowering the temperature below $T_{\mathrm{LC\text{-}I}}$.[1,13–18] The expansion and contraction is due to the microscopic change in alignment of mesogens, followed by the significant macroscopic change in order through the cooperative movement of mesogens and polymer segments.

It is well known that when azobenzene derivatives are incorporated into LCs, the LC-I phase transition can be induced isothermally by irradiation with UV light to cause *trans–cis* photoisomerization, and the I-LC reverse-phase transition by irradiation with visible light to cause *cis–trans* back-isomerization.[19] This photoinduced phase transition (or photoinduced reduction of LC order) has led successfully to a reversible deformation of LCEs containing azobenzene chromophores just by changing the wavelength of actinic light.[4–12] Although the photoinduced deformation of LCEs previously reported is large and interesting, it is limited to contraction/expansion and bending, preventing them from being used for actual applications. Herein we report potentially applicable rotational motions of azobenzene-containing LCEs and their composite materials, including a first light-driven plastic motor with laminated films composed of an LCE film and a flexible polyethylene (PE) sheet.

The LCE films were prepared by photopolymerization of a mixture of an LC monomer containing an azobenzene moiety (molecule **1** shown in Scheme 1) and an LC diacrylate with an azobenzene moiety (**2** in Scheme 1) with a ratio of 20/80 mol/mol, containing 2 mol% of a photoinitiator in a glass cell coated with rubbed polyimide alignment layers. The photopolymerization was conducted at a temperature at which the mixture exhibited a smectic phase. The glass-transition temperature of the LCE films is at about room temperature, allowing the LCE films to work at room temperature in air, as the films are flexible enough at this temperature.

We prepared a continuous ring of the LCE film by connecting both ends of the film. The azobenzene mesogens were aligned along the circular direction of the ring. Upon exposure to UV light from the downside right and visible light from the upside right simultaneously (Figure 1), the ring



Scheme 1. Chemical structures of the LC monomer (**1**) and LC diacrylate (**2**) used in this study. Upon cooling, **1** changes from an isotropic to a smectic phase at 92 °C, and at 60 °C it becomes crystalline; upon cooling, **2** changes from an isotropic to a smectic phase at 91 °C, and at 74 °C it becomes crystalline; upon cooling, the mixture of **1**/**2** (20/80 mol/mol) changes from an isotropic to a smectic phase 89 °C, and at 60 °C it becomes crystalline.

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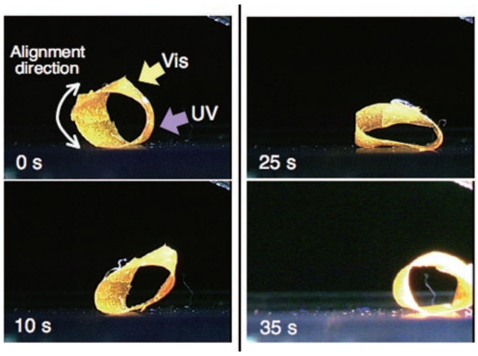

Figure 1. Photoinduced rolling motion of a continuous ring of LCE film. Series of photographs showing time profiles of the photoinduced rolling motion of the LCE ring by simultaneous irradiation with UV (366 nm, 200 $\mathrm{mW\,cm^{-2}}$) and visible light (>500 nm, 120 $\mathrm{mW\,cm^{-2}}$) at room temperature. Size of the LCE ring: 18 mm × 3 mm (diameter: 6 mm). Thickness of the LCE ring: 20 μm.

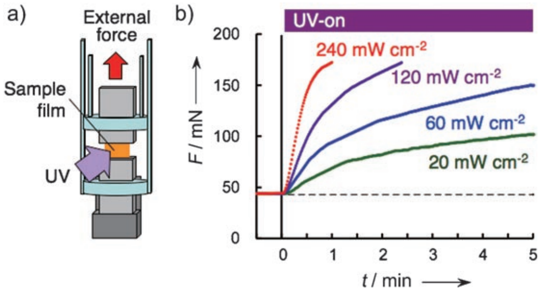

Figure 2. Mechanical force generated in the LCE laminated film by UV light irradiation. a) The experimental setup. b) Change in the generated force in the LCE laminated film upon exposure to UV light on one side with different intensities (366 nm; 20, 60, 120, and 240 $\mathrm{mW\,cm^{-2}}$) at 30 °C. The LCE layers were coated on the both sides of the PE film to make the initial sample flat, thus allowing the generated force to be measured accurately. Film size: 2.5 mm × 5 mm, thickness of LCE laminated film layers: PE, 50 μm; LCE layers, 15 μm. An external force of 44 mN was loaded initially on the film to keep its length unchanged.

rolled intermittently toward the actinic light source, resulting almost in a 360° roll at room temperature. This is the first example of this kind of photoinduced motion in a single layer film, although the rolling of the LCE ring used herein was slow, and stopped when the ring was broken by irradiation.

The photoisomerization of the azobenzene moieties, which is a trigger of the photoinduced deformation of LCE films, occurs only in the surface region of the films facing the incident light, and in the bulk of the films the *trans*-azobenzene moieties remain unchanged owing to the limitation of light absorption by the azobenzene mesogens. Thus, we assume that a bilayer structure may be simply produced by light irradiation in a single LCE film: The first layer in the surface region of the LCE film contracts by photoirradiation while the second layer in the bulk of the film shows no photochemical reactions but changes its shape just by following the first layer. On the basis of this assumption, photoactive LCE layers are needed only in the surface region of the films facing light sources, and the rest of the films can be replaced by other materials.

By preparing a laminated structure composed of an LCE layer and a flexible plastic sheet, both photoresponsive and good mechanical properties can be provided simultaneously in a simple laminated film, enabling us to induce various movements of these films by light without deterioration or breakages of the materials. We fabricated the laminated films composed of an LCE layer and an unstretched low-density PE film having good flexibility and mechanical properties at room temperature.

To evaluate the driving force of the LCE laminated films to change their shapes by photoirradiation, we measured the internal stress generated in the films upon exposure to UV light with a thermomechanical analyzer. Both ends of a film were clamped (Figure 2a), and a force of 44 mN was initially loaded on the film at 30 °C. Figure 2b shows the change in the load on the film upon irradiation with UV light at different light intensities. As the length of the film was kept unchanged, the increase in the load indicates the generation of mechanical force by photoirradiation. These results clearly indicate that the maximum force and the increment rate of the generated force are enhanced with an increase of the light intensity. It should be mentioned that the LCE laminated films continued to generate the force during photoirradiation without breaking, whereas the LCE single-layer films cracked after short light irradiation at high intensities, owing to insufficient mechanical strength. The above results demonstrate the possibility of inducing three-dimensional motion with the LCE laminated films by light irradiation at room temperature.

A motor device is one of the most useful energy conversion systems that can convert input energy directly into a continuous rotation. Although chemomechanical motors[20,21] and light-switchable molecular machines that can move objects by light[22,23] have been demonstrated, light-driven plastic motors converting light energy directly into a rotation have not yet realized. We prepared a plastic belt of the LCE laminated film by connecting both ends of the film, and then placed the belt on a homemade pulley system as illustrated in Figure 3a. By irradiating the belt with UV light from top right and visible light from top left simultaneously, we induced a rotation of the belt to drive the two pulleys in a counterclockwise direction at room temperature, as shown in Figure 3b (see also Movie 1 in the Supporting Information). A plausible mechanism of the rotation is as follows: Upon exposure to UV light, a local contraction force is generated at the irradiated part of the belt near the right pulley along the alignment direction of the azobenzene mesogens, which is parallel to the long axis of the belt. This contraction force acts on the right pulley, leading it to rotate in the counterclockwise direction. At the same time, the irradiation with visible light produces a local expansion force at the irradiated part of the belt near the left pulley, causing a counterclockwise rotation of the left pulley. These contraction and expansion forces produced simultaneously at the different parts along the long axis of the belt give rise to the rotation of the pulleys and the belt with the same direction. The rotation then brings new parts of the belt to be exposed to UV and to visible light, which enables the motor system to rotate continuously. Reverse rotation of this belt could also be induced just by changing the irradiation positions of the UV and visible light.

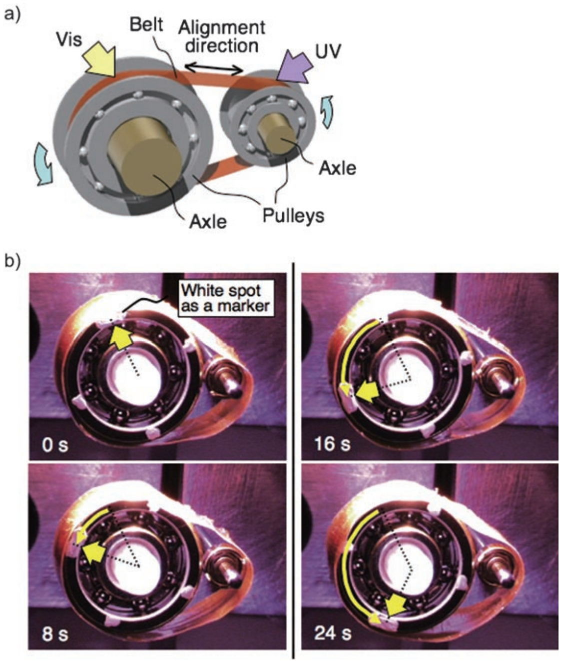

Figure 3. A light-driven plastic motor with the LCE laminated film. a) Schematic illustration of a light-driven plastic motor system used in this study, showing the relationship between light irradiation positions and a rotation direction. b) Series of photographs showing time profiles of the rotation of the light-driven plastic motor with the LCE laminated film induced by simultaneous irradiation with UV (366 nm, 240 mW cm^{-2}) and visible light (> 500 nm, 120 mW cm^{-2}) at room temperature. Diameter of pulleys: 10 mm (left), 3 mm (right). Size of the belt: 36 mm × 5.5 mm. Thickness of the layers of the belt: PE, 50 μm; LCE, 18 μm.

With the LCE films and their composite materials, we have successfully developed new photomechanical devices, including the first light-driven plastic motor. They can convert light energy directly into mechanical work without the aid of batteries, electric wires, or gears. The size of the samples is in the range of millimeters for the demonstration, but is not in principle material-limited, so numerous applications even on the nanoscale are possible, especially where efficient power supply to mechanical system is battery-free and noncontact.

Experimental Section

The preparation of molecules **1** and **2** is given in the Supporting Information. The LCE films were prepared by in situ photopolymerization of a mixture of molecule **1** and **2** (20/80 mol/mol) containing 2 mol% of a photoinitiator (Ciba Specialty, Irgacure 784). First, the melt of the mixture was injected into a glass cell coated with rubbed polyimide alignment layers at 110 °C. After the sample was cooled down slowly (0.1 °C min^{-1}) to a polymerization temperature at 89 °C, at which it showed a smectic phase, photoirradiation was carried out at > 540 nm (3 mW cm^{-2} at 547 nm) with a 500 W high-pressure mercury lamp through glass filters (Asahi Techno Glass, Y-52, and IRA-25) for 2.5 h. The LCE films were taken off from the cells after polymerization.

The LCE laminated films composed of an LCE layer and a PE film were prepared by thermal compression bonding. First, an adhesive mixture (weight ratio of solid content: 70/30) of acid denaturation polyethylene emulsion (Unitika, ARROWBASE SB-1200) and a solution of waterborne polyurethane (Adeka, BONTIGHTER HUX380) was coated on an unstretched low-density PE film with 50 μm thickness (Tohcello, TUX-FCS) with a bar coater and dried in an oven at 105 °C for 60 s, forming the adhesion layer on the PE film. An LCE film and the coated PE film were then laminated between two glass plates under pressure (approximately 0.5 kgf cm^{-2}) at 105 °C for 60 s. The LCE laminated film was obtained by separating the film from the glass plates.

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