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Liquid Crystals

Photomobile Polymer Materials: Photoresponsive Behavior of Cross-Linked Liquid-Crystalline Polymers with Mesomorphic Diarylethenes

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Abstract: Cross-linked liquid-crystalline (LC) polymers with a mesomorphic diarylethene were prepared to demonstrate a versatile strategy for cross-linked photochromic LC polymers as photomobile materials. Upon exposure to UV light to cause photocyclization of the diarylethene chromophore, the cross-linked polymer films bend toward an actinic light source. By irradiation with visible light to cause a closed-ring to open-ring isomerization, the bent films revert to the initial flat state. Without visible-light irradiation, the bent films remain bent even at 120 °C, indicating high thermal stability of the cross-linked diarylethene LC polymers.

Recently, much attention has been paid to soft materials that can convert light energy directly into mechanical work (photomechanical effect) due to their advantages, such as miniaturization, remote control, and quiet operation.[1,2] Polymers are one of the most promising candidates for soft actuator materials because of their flexibility, lightweight, low costs, and simple fabrication processes for devices. Many types of polymers have been developed as actuator materials, such as amorphous polymers,[2] polymer gels,[3,4] and conducting polymers.[5] Light as an external stimulus enables the remote control and rapid deformation of materials, and light-driven polymer actuators have been extensively developed for the use of a wide range of micro- and macroscale devices. These photomobile polymer materials can convert light energy directly into mechanical work without the aid of batteries, electric wires, or gears. However, in amorphous polymer materials, the deformation in response to light occurs in an isotropic way and the degree of deformation is too small to be practically utilized.

A sophisticated way to amplify deformation of materials is to use cross-linked liquid-crystalline (LC) polymers (CLCPs),[1] which show anisotropic contraction resulting from the change in alignment of mesogens by external stimuli, such as temperature[6] and light.[7] In our previous work, we found that CLCP films containing azobenzene moieties showed photoinduced bending toward an actinic light source.[8] A large and reversible deformation of the azobenzene CLCPs is induced by reduction of LC order by light. Deformation of these films can be controlled by such factors as the cross-linking density, polarization direction of actinic light and the initial alignment of mesogens.[8,9] We also have demonstrated new three-dimensional movements of the CLCPs and their composite materials driven only by light: a light-driven plastic motor, an inchworm walk, and a flexible robotic arm motion.[10]

There have been many photochromic molecules developed to date, such as azobenzenes, spiropyrans, fulgides, and diarylethenes, in an attempt to apply these materials to optoelectronic devices, including optical memories and switches.[11] Of them, azobenzenes have been most widely used as a photoresponsive molecule in photomobile materials composed of CLCPs, because 1) azobenzenes show a large change in shape upon *trans*/*cis* photoisomerization, which could lead to a large deformation of materials; and 2) many azobenzenes are mesomorphic by themselves, which is very advantageous in view of miscibility with many LC molecules, and high concentrations of azobenzenes can be used in the LC mixtures, which could lead to high sensitivity of photomobile materials.[7–10] However, azobenzenes show drawbacks: their *trans* forms are very stable, whereas *cis* isomers are thermally unstable, which means that upon exposure to actinic light, CLCP films containing azobenzenes show deformation by *trans*/*cis* isomerization of the azobenzenes, but the deformed films easily revert to the initial state at high temperatures. To represent a more versatile strategy for the photochromic CLCPs as photomobile materials, we have been investigating the photomobile properties of CLCPs with various photochromic moieties.

Diarylethenes undergo thermally irreversible and fatigue-resistant photochromic reactions not only in solution, but also in single crystals.[12] The rod-like crystals of diarylethene derivatives exhibit reversible bending upon photoirradiation.[13] Furthermore, fabrication of diarylethene crystals into various shapes enables a variety of 3-dimensional movements of the

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assemblies.[14] The addition of LC property to diarylethenes could lead to thermally stable photomechanical systems. Diarylethene derivatives exhibiting LC properties have been reported as potentially useful in various fields due to both photochromic and mesomorphic functionalities.[15] We expected that CLCPs incorporating diarylethenes could be new photomobile materials with high thermal stability. Herein, we designed and synthesized new diarylethene derivatives with LC property and investigated the photomobile property of the CLCPs containing the mesomorphic diarylethenes.

Figure 1 shows the chemical structures of bifunctional monomers, 1,2-bis[6-(4′-(acryloyloxyhexyloxy)-4-biphenyloxycarbonyl)-2-methylbenzo[*b*]thiophen-3-yl]hexafluorocyclopentene (**1**) and its derivative (**2**) used in this study. Biphenyl mesogens were incorporated into both sides of the diarylethene core.

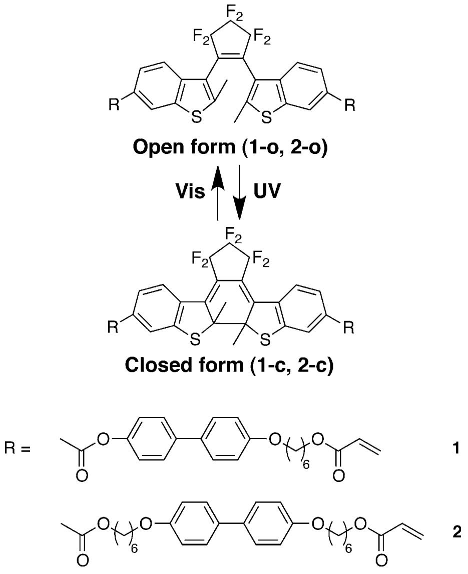

Figure 1. Structures of the diarylethene LC derivative (**1**) and (**2**) used in this study and their photochromic reactions.

The photochromic property of **1** in chloroform was investigated by UV/Vis absorption spectroscopy as shown in Figure 2a. Upon irradiation with UV light at 313 nm, the solution turned from colorless to purple. This change in color indicates that the open form (**1-o**) transforms to a more conjugated closed-ring isomer (**1-c**) characterized by a broad visible band with a maximum at $\lambda = 550$ nm upon UV irradiation. The purple color of the solution disappeared upon irradiation with visible light at $\lambda > 540$ nm with a simultaneous change in the absorption spectrum. The photocyclization/photocycloreversion of the diarylethene derivative could be repeated more than 30 times by alternative irradiation with UV and visible light. Both isomers, **1-o** and **1-c**, were thermally stable in the dark. The diarylethene derivative **2** also showed a similar photocyclization/cycloreversion reaction by irradiation with UV and visible light.

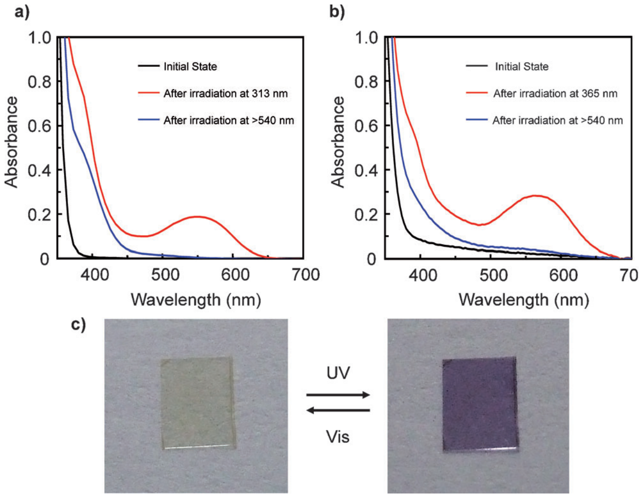

Figure 2. Change in absorption spectra of **1** by irradiation with UV light. (a) In chloroform (2×10^{-5} mol L^{-1}); (b) in the cross-linked polymer film (size of the film: 10 mm×5 mm; thickness of the film: 2 μm). (c) Photographs of the cross-linked diarylethene LC polymer films before and after photoirradiation.

The LC property of the diarylethenes was investigated by differential scanning calorimetry (DSC) and polarizing optical microscopy (POM). It was found that **1** exhibited a glass transition at around 50 °C and two different LC phases upon cooling: a nematic phase between 117 and 110 °C and a smectic phase between 110 and 50 °C (Figure S1 in the Supporting Information). Compound **2** with alkyl spacers between a diarylethene core and biphenyl mesogens showed similar mesomorphic behavior but at lower temperatures compared to **1** (Figure S2 in the Supporting Information). Introduction of alkyl spacers between the diarylethene core and biphenyl mesogenic parts leads to an increase in flexibility of the whole molecule, resulting in a decrease of LC phase temperatures. Next, **1** and **2** were irradiated at $\lambda = 365$ nm for 30 min in chloroform, and the solvent was removed for evaluation of the mesomorphic property of the compounds in the photostationary state. However, no sharp peak associated with the phase transition was observed in DSC thermograms (Figure S3 in the Supporting Information). In ^{1}H NMR spectra of **1**, two peaks were observed at $\delta = 2.31$ and 2.55 ppm due to the existence of two conformers before photoirradiation (Figure S4a in the Supporting Information). Upon irradiation at $\lambda = 365$ nm, a new peak appeared at $\delta = 2.17$ ppm along with a decrease in the intensity of the two peaks (Figure S4b in the Supporting Information). The new peak is assigned to a methyl proton of the closed-ring form. The conversion of the open-ring to closed-ring isomer in the photostationary state under irradiation at $\lambda = 365$ nm was estimated as 33 % from the NMR spectrum. Because **1** showed three conformers after irradiation with UV light, antiparallel-open-ring, parallel-open-ring, and closed-ring, no obvious peaks associated with LC phase transition were observed in the photostationary state. We need further studies to identify the mesophases of the diarylethenes before and after photoirradiation in detail.

The CLCP films were prepared by in situ photopolymerization of the bifunctional diarylethenes in the presence of a photoinitiator (2 mol%) in a glass cell coated with rubbed polyimides. POM observation revealed that the CLCP film with the diarylethene core, placed between crossed polarizers, showed a contrast inversion upon rotating the sample every 45° with respect to the analyzer (Figure S5 in the Supporting Information). This result indicates that the mesogens in the cross-linked films are preferentially aligned along the rubbing direction. The photochromism of the CLCP films was examined by the change in absorption spectra (Figure 2b). Upon irradiation with UV light, a band around $\lambda = 570$ nm attributable to the closed-ring structure of **1** appeared with a change in color of the film from colorless to purple, and the purple film reverted to a colorless one by irradiation with visible light at $\lambda > 540$ nm, as shown in Figure 2c. The CLCP films prepared from **2** showed similar photochromic behavior.

DSC measurements were performed to study the thermal property of the CLCP films. A shift in the baseline due to glass transition was observed at 140 °C in the sample prepared from **1** (Figure S6 in the Supporting Information) and at 80 °C in the film prepared from **2** (Figure S7 in the Supporting Information). We next evaluated the photomobile property of the CLCP films. Irradiation with UV light at $\lambda = 365$ nm caused an immediate change in color of the films from colorless to purple, followed by bending of the films toward an actinic light source along the alignment direction of the mesogens at 120 °C (Movie 1 in the Supporting Information). Upon exposure to visible light, the bent film immediately changed the color from purple to colorless and reverted to the initial flat state when it was left in the dark at 120 °C for 24 h (Figure 3). We observed similar photomobile properties in the film prepared from **2**.

Compared to the azobenzene analogues, the diarylethene CLCPs used in this study showed less effective deformation. Although azobenzenes exhibit a large change in their structures upon *trans*/*cis* isomerization, diarylethenes undergo only a small change in their structures upon photocyclization/photocycloreversion, and this small change causes a small reduction in molecular order of mesogens, which could lead to a small macroscopic deformation of the cross-linked polymers. This is the first example of the photomobile polymer materials containing diarylethene LCs, in which we have successfully amplified the small structural changes by photochromic reactions of the diarylethene moieties to macroscopic deformations.

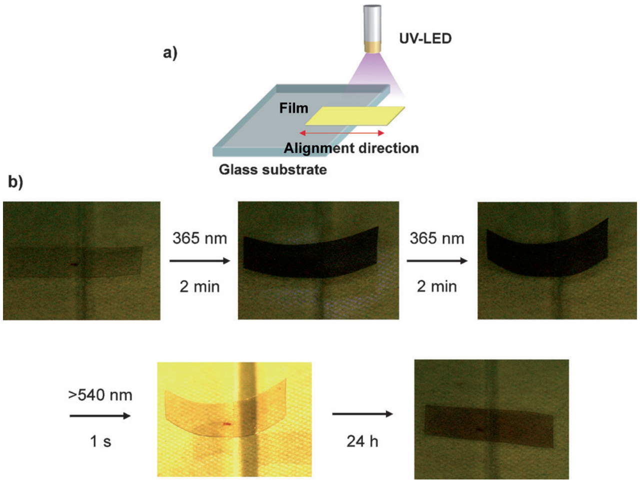

Figure 3. Photoinduced bending behavior of the diarylethene CLCP film prepared from **1**. (a) Schematic illustration of the experimental setup; (b) photographs of the bending of the film upon irradiation with UV and visible light at 120 °C. Size of the film: 10 mm×5 mm. Thickness of the film: 20 μm.

To investigate the thermal stability of the CLCPs, the bent films were left in the dark at 120 °C after irradiation with UV light. In the azobenzene CLCP films, the initial flat state was recovered at 120 °C because of thermal *cis*/*trans* back isomerization and reorientation of the azobenzenes.[8d] On the other hand, the color and shape of the diarylethene CLCP films remained unchanged even after 36 h thank to the thermally irreversible isomerization of diarylethenes. This result indicates that the CLCPs prepared from the diarylethene LCs show high thermal stability (Figure 4).

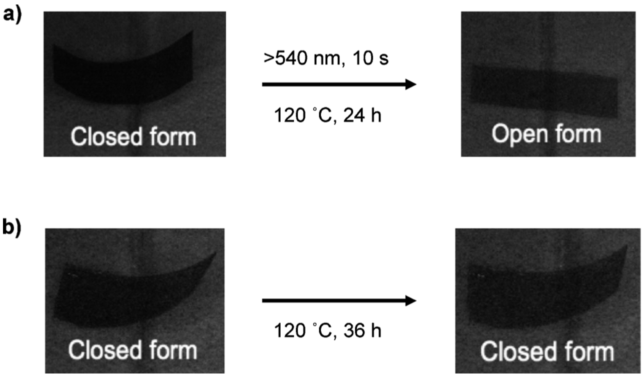

Figure 4. Thermal stability of the diarylethene CLCP films prepared from **1**. (a) Left at 120 °C after irradiation with visible light; (b) left at 120 °C without photoirradiation. Size of the film: 10×5 mm. Thickness of the film: 20 μm.

In conclusion, diarylethene derivatives having photochromic and mesomorphic functionalities were designed and synthesized, and new diarylethene CLCP films were prepared from these mesomorphic diarylethenes. The films bent toward an actinic light source along the alignment direction of mesogens upon irradiation with UV light, and the bent films reverted to the initial flat state completely after exposure to visible light. However, in the dark, the color and shape of the films remained unchanged even at 120 °C, demonstrating high thermal stability of the diarylethene CLCPs.

Experimental Section

The preparation of **1** and **2** is described in the Supporting Information. The diarylethene CLCP films were prepared by photopolymerization of **1** containing 2 mol% of a photoinitiator (Ciba Specialty, Irgacure 784). First, a melt of **1** containing a photoinitiator was injected at 130 °C into a glass cell coated with polyimide alignment layers that had been rubbed. After the sample was cooled slowly (0.3 °C min^{-1}) to a polymerization temperature (113 °C) at which **1** showed a nematic phase, photopolymerization was performed by photoirradiation at $\lambda > 540$ nm (547 nm, 5 mW cm^{-2}) with a high-pressure mercury lamp through glass filters (Toshiba, Y-52 + IRA-25) for 8 h. The cross-linked polymer films were taken off from the cells after polymerization. CLCP films were also prepared similarly from **2** by photopolymerization in a glass cell.

The thermodynamic properties were determined by DSC (Seiko I&E, SSC-5200 and DSC220C) at heating and cooling rates of 3 °C min^{-1} for **1** or **2** and 20 °C min^{-1} for the polymer films. The mesomorphic properties were examined with a polarizing optical microscope (POM; Olympus, BH-2) equipped with a Mettler hot stage (models FP-90 and FP-82). The UV spectra of the films were recorded at RT with a UV/Vis absorption spectrometer (Jasco, V-550).

Keywords: actuators · liquid crystals · photochromism · photomechanical effects · polymers

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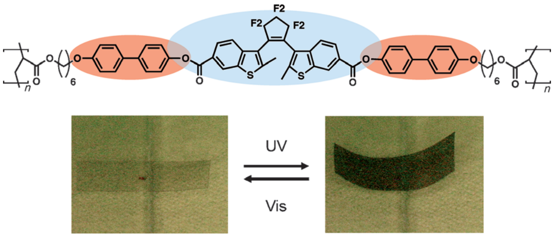
Photomobile Polymer Materials: Photoresponsive Behavior of Cross-Linked Liquid-Crystalline Polymers with Mesomorphic Diarylethenes



Photomechanical effect: Mesomorphic diarylethenes containing two polymerizable groups led to a new photomechanical system of cross-linked liquid-crystalline polymers. Photochromism of the diarylethene was amplified to a macroscopic deformation of the cross-linked polymers. Versatility of the photomobile materials is demonstrated by using the cross-linked photochromic liquid-crystalline polymers (see scheme).