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### Photoresponsive Behavior of Laminated Films Composed of a Flexible Plastic Sheet and a Crosslinked Azobenzene Liquid-Crystalline Polymer Layer with Different Initial Alignment of Mesogens

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## Photoresponsive Behavior of Laminated Films Composed of a Flexible Plastic Sheet and a Crosslinked Azobenzene Liquid-Crystalline Polymer Layer with Different Initial Alignment of Mesogens

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*Laminated films composed of a flexible plastic sheet and a crosslinked azobenzene liquid-crystalline polymer (CLCP) layer with different initial alignment of azobenzene mesogens were prepared by thermal compression bonding of a CLCP film and an unstretched low-density polyethylene (PE) film with an adhesion layer. In both laminated films with a homogeneous alignment of mesogens and a homeotropic one, large movements could be induced by irradiation with UV light at room temperature. A partly laminated film with homogeneous CLCP bent from both ends of the whole film, while one with homeotropic CLCP bent up from the center of the film toward the light source. These results indicate that we enable plastic films with no photoresponsive property to move flexibly upon photoirradiation just by laminating the CLCP layers partly, and the photoinduced motions of the laminated films are completely dependent on the alignment direction of the mesogens in the CLCP layers. In addition, it was found that the maximum stress generated in the films and the stress increment are also different between the homogeneous CLCP laminated films and the homeotropic ones.*

**Keywords:** crosslinked azobenzene liquid-crystalline polymer; flexible plastic sheet; laminated film; light-driven actuator; photoresponsive behavior

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## INTRODUCTION

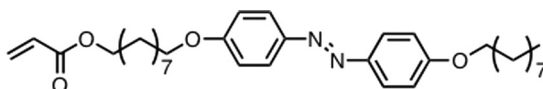
Light-driven actuators have attracted much attention recently because light is a good energy source that can be controlled remotely, instantly and precisely. One emerging class of materials receiving great interest is photomechanical polymers. If polymer materials absorb light and change their shapes or volumes, they can be used as main driving parts of the light-driven actuators. Polymers incorporating photochromic molecules like an azobenzene which photoisomerizes reversibly between a rod-like *trans* and a bent *cis* isomer upon photoirradiation, respond to light irradiation by either expanding or contracting, but just by a few percent [1,2]. CLCPs are unique materials having both properties of liquid crystals (LCs) and elastomers [3–5]. If CLCPs are heated above their LC-isotropic(I) phase transition temperatures ( $T_{LC-I}$ ), contraction of these materials is induced along the alignment direction of mesogens, and by lowering the temperature below  $T_{LC-I}$ , expansion of the materials is brought about [3,6,7]. A large deformation of up to ~400% of CLCPs has been observed [7], which is due to the change in alignment of mesogens associated with the LC-I phase transition. If azobenzene moieties 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 [8]. By incorporating azobenzene moieties into CLCPs, a large deformation can be induced by photochemical reactions of these azobenzene chromophores [9,10]. Previously, we found that CLCP films composed of azobenzene mesogens showed bending by light irradiation [11,12]. Most recently, it has been found that plastic films coated with azobenzene CLCP layers also show bending by irradiation with light and their bending behavior strongly depends on the alignment of the azobenzene moieties of the CLCP surface layer [13].

In this work, we prepared laminated films composed of a flexible plastic sheet and an azobenzene CLCP layer with a different initial alignment of azobenzene mesogens in the CLCP layer, and investigated the photoresponsive behavior of the laminated films at room temperature.

## EXPERIMENTAL

### Materials

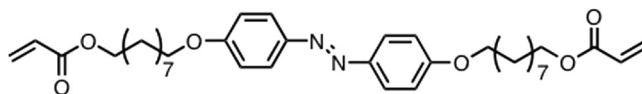
The LC monomers, 9-[4-(4-nonyloxyphenylazo)phenoxy]acrylate (molecule **1** shown in Fig. 1) and 4,4'-bis[9-(acryloyloxy)hexyloxy]azobenzene (molecule **2** shown in Fig. 1) were synthesized according to



Molecule 1

K 67 Sm 94 I (Heating)

K 60 Sm 92 I (Cooling)



Molecule 2

K 84 Sm 93 I (Heating)

K 74 Sm 91 I (Cooling)

**FIGURE 1** Chemical structures, properties and abbreviations of the LC monomer (molecule 1) and LC diacrylate (molecule 2) used in this study. I, isotropic; Sm, smectic; K, crystal. On cooling from 91°C, the mixture of molecule 1/molecule 2 (40/60 mol/mol) changes from an isotropic to a smectic phase, and at 61°C it becomes crystalline.

a procedure similar to the literature [14]. As a flexible plastic sheet, an unstretched low-density PE film with 50- $\mu\text{m}$  (Tohcello, T.U.X) was used because of its good flexibility and mechanical properties at room temperature. An adhesive mixture of an acid denaturation polyethylene emulsion (Unitika, ARROWBASE SB-1200) and a solution of waterborne polyurethane (Adeka, BONTIGHTER HUX380) was used to form the adhesion layer between a PE film and a CLCP layer.

## Photoirradiation and Observation Tools

Photoinduced motions of the films were observed by irradiation with UV light from a UV-LED irradiator (Keyence, UV-400, UV-50H) and visible light from a halogen lamp through a heat-absorbing filter (Shimadzu, FLH-50). A three-dimensional digital camera (Omron, VC-HRM20Z and VC1000) was used to record motion pictures.

## Mechanical Force Generated in the Films by Light Irradiation

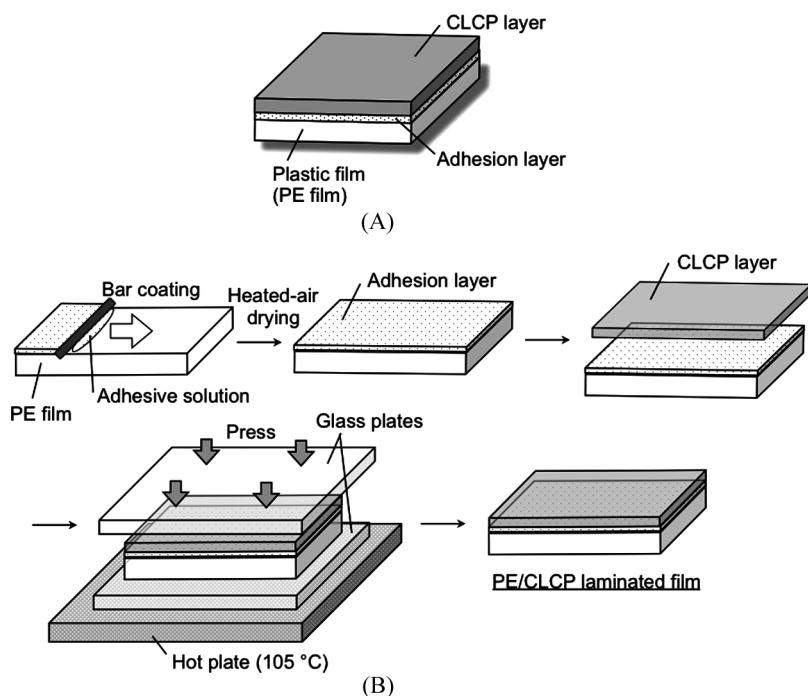
The mechanical force generated in the films upon photoirradiation was measured with a thermomechanical analyzer (Shimadzu, TMA-60) as follows: A film was fixed by clamping both ends and the initial

force was loaded on the film; then the film was irradiated with UV light at 30°C. As the length of the film was kept unchanged, the change of the stress in the film corresponds to the generation of mechanical stress by photoirradiation.

## RESULTS AND DISCUSSION

### Fabrication and Properties of the CLCP Laminated Films

The CLCP laminated films consist of a CLCP layer, a flexible plastic sheet (an unstretched low-density PE film) and an adhesion layer (Fig. 2(A)). The CLCP layers were prepared by photopolymerization of a mixture of an LC monomer (molecule **1**) and an LC diacrylate (molecule **2**) with a ratio of 40/60 mol/mol, containing 2 mol% of a photoinitiator (Ciba Specialty, Irgacure 784). First, the melt of the

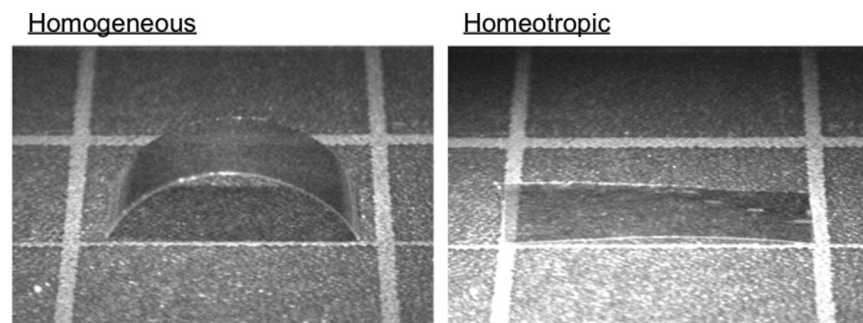


**FIGURE 2** Structure of the CLCP laminated films composed of a CLCP layer and a plastic film with an adhesion layer used in this study (A), and the fabrication method of the laminated films prepared by thermal compression bonding (B).

mixture was injected into a glass cell, which had been treated for homogeneous or homeotropic alignment, at 110°C. The homogeneous cell was coated with rubbed polyimide alignment layers, while the homeotropic one was treated with *n*-octadecyl trimethoxysilane. After the sample was cooled down slowly to a photopolymerization temperature at 87°C where it showed a smectic phase, photopolymerization was carried out at  $>540\text{ nm}$  ( $3\text{ mW cm}^{-2}$  at 545 nm) with a 500 W high-pressure mercury lamp through glass filters (Asahi Techno Glass, Y-52 and IRA-25S) for 2.5 h. The CLCP films were taken off from the cells after polymerization.

The CLCP laminated films were prepared by thermal compression bonding of a CLCP film and a PE film with an adhesion layer (Fig. 2(B)). First, the adhesive mixture was coated on a PE film with a bar coater and dried in an oven at 110°C for 60s, forming the adhesion layer on the PE film. Then a CLCP film and a coated PE film were laminated between two glass plates under pressure at 105°C for 60s. The CLCP laminated film was obtained by separating the film from the glass plates. The adhesion properties of the CLCP laminated films were good enough to prevent the films from being peeled off by deformation.

It was found that the shapes of the laminated films at room temperature differed between the homogeneous CLCP laminated film (homo-CLCP LF) and the homeotropic one (homeo-CLCP LF) (Fig. 3). The homo-CLCP LF was curled up to form an arch, while the homeo-CLCP was nearly flat.

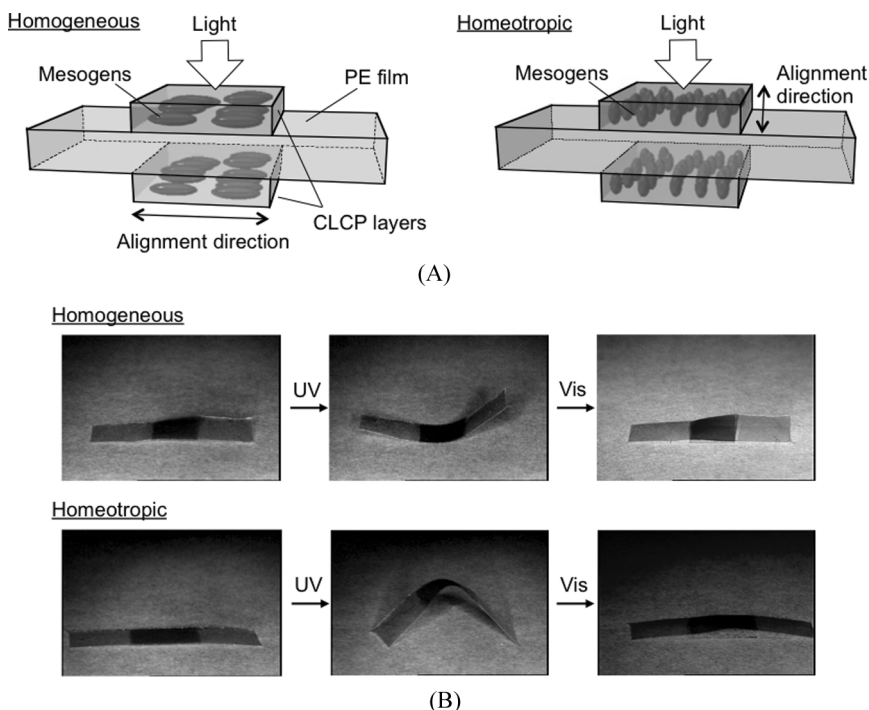


**FIGURE 3** Photographs of the homo- and homeo-CLCP LFs at room temperature. Size of the films: 10 mm  $\times$  5 mm. Thickness of the layers of the films: PE, 50  $\mu\text{m}$ ; CLCP, 16  $\mu\text{m}$ .

## Photoinduced Motions of the CLCP Laminated Films

We investigated the photoinduced motions of the homo- and homeo-CLCP LF's by irradiation with UV and visible light at room temperature. The PE films were partly laminated in their central parts (about one third of the area of the PE films) with the CLCP layers and coated on their both sides to make the laminated films flat (Fig. 4(A)). In the homo-CLCP LF, the azobenzene mesogens were aligned along the long axis of the film.

With the laminated films, we could induce large movements by light irradiation and make plastic films without photosensitive properties move flexibly by light irradiation, just by laminating the CLCP layers



**FIGURE 4** Schematic illustrations of the homo- and homeo-CLCP LF's (A), and series of photographs showing the photoinduced motions of the films by irradiation with UV (366 nm,  $120 \text{ mW cm}^{-2}$ ) and visible light ( $>540 \text{ nm}$ ,  $120 \text{ mW cm}^{-2}$ ) at room temperature (B). Size of the films:  $14 \text{ mm} \times 5 \text{ mm}$  (the laminated part:  $4 \text{ mm} \times 5 \text{ mm}$ ) (homogeneous),  $18 \text{ mm} \times 5 \text{ mm}$  (the laminated part:  $6 \text{ mm} \times 5 \text{ mm}$ ) (homeotropic). Thickness of the layers of the films: PE,  $50 \mu\text{m}$ ; CLCP,  $15 \mu\text{m}$  (homogeneous),  $16 \mu\text{m}$  (homeotropic).

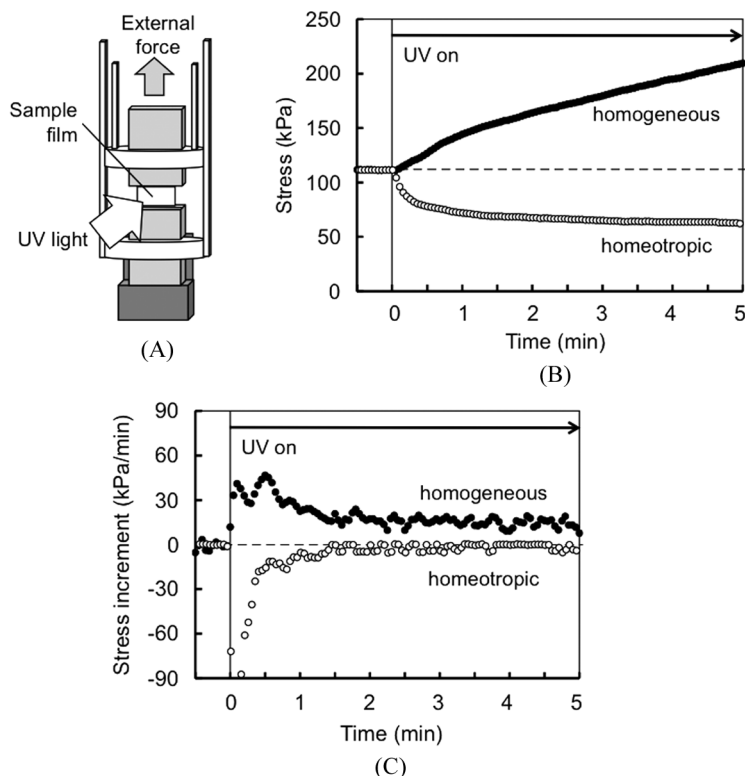


partly. Additionally, low glass-transition temperature of the CLCP layer appearing around room temperature and high flexibility of the PE film allow the laminated films to change their shapes drastically at room temperature. As shown in Figure 4(B), the photoinduced movement direction of the laminated films was completely dependent on the initial alignment of the azobenzene mesogens of the CLCP layers, which is similar to that of the CLCP monolayer films [15]. When the homo-CLCP LF was exposed to UV light, the whole film bent from both ends and reverted to the initial shape by irradiation with visible light. On the other hand, when the homeo-CLCP LF was exposed to the actinic light, the whole film bent up from the center of the film toward the light source and reverted to the initial shape when irradiated with visible light. It is worth mentioning here that the CLCP laminated films are so readily fabricated that one can design the laminated films so as to deform at any position in a direction of choice by choosing and combining the homogeneous and homeotropic CLCP layers.

### Mechanical Force Generated in the CLCP Laminated Films Upon Photoirradiation

The generated mechanical force in the CLCP laminated films by light irradiation was measured with a thermomechanical analyzer (Fig. 5(A)). As the length of the film was kept unchanged, the increase and the decrease of the stress indicate the generated contraction and expansion stress by photoirradiation, respectively.

Figure 5(B) shows the change in the stress on the homo- and homeo-CLCP LFs upon irradiation. The stress of the homo-CLCP LF increased from approximately 110 kPa to 210 kPa after irradiation with UV light (366 nm,  $40 \text{ mW cm}^{-2}$ ) for 5 min, indicating that a contraction stress of 100 kPa was induced on the whole film. If we assume that only the CLCP layer generates the force by photoirradiation, the generated contraction stress is calculated to be 500 kPa by taking into account the cross-sectional area of the CLCP layer ( $5 \text{ mm} \times 15 \mu\text{m}$ ) alone, which is larger than the contraction force of human muscles (around 300 kPa). On the contrary, the stress of the homeo-CLCP LF decreased from approximately 110 kPa to 60 kPa after irradiation with UV light for 5 min, indicating that an expansion stress of 50 kPa (CLCP layer: 250 kPa) is induced. The absolute value of the generated stress in the homo-CLCP LF was larger than that of the homeo-CLCP LF, probably because the contraction in the former is induced only along the alignment direction parallel to the long axis of the film,



**FIGURE 5** Schematic illustration of the experimental setup to determine the generated mechanical force in the films by light irradiation (A), and the change in the generated stress (B) and the stress increment (C) on the CLCP laminated films by irradiation with UV light ( $366\text{ nm}$ ,  $40\text{ mW cm}^{-2}$ ) at  $30^\circ\text{C}$ . Size of the films:  $2.5\text{ mm} \times 5\text{ mm}$ . Thickness of the layers of the films: PE,  $50\text{ }\mu\text{m}$ ; CLCP,  $15\text{ }\mu\text{m}$  (homogeneous),  $16\text{ }\mu\text{m}$  (homeotropic).

while the expansion in the latter is dispersed in a plane vertical to the alignment direction.

Figure 5(C) shows the change in the stress increment on the films by irradiation with UV light calculated from the results shown in Figure 5(B). With the homo-CLCP LF, the stress was not saturated after irradiation with UV light for 5 min, whereas it reached a maximum within 2 min in the homeo-CLCP LF. This is presumably because the homo-CLCP LF shows higher UV absorption than the homeo-CLCP LF, requiring longer time to make UV light penetrate deeply and to change the alignment of mesogens in the CLCP layer.

## CONCLUSIONS

In the laminated films composed of an azobenzene CLCP layer and a PE film, large three-dimensional motions can be induced by light irradiation at room temperature. The photoinduced motions of the CLCP laminated films were completely dependent on the alignment direction of the azobenzene mesogens in the CLCP layers: the homo-CLCP LF bent from both ends by irradiation with UV light, while the homeo-CLCP LF bent up from the center of the film toward the light source. Moreover, the maximum stress generated in the films and the stress increment also differed between the homo- and homeo-CLCP LFs. As the CLCP laminated films are readily fabricated, one can easily design the laminated films so as to deform at any position in a direction of choice by choosing and combining the homogeneous and homeotropic CLCP layers.

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