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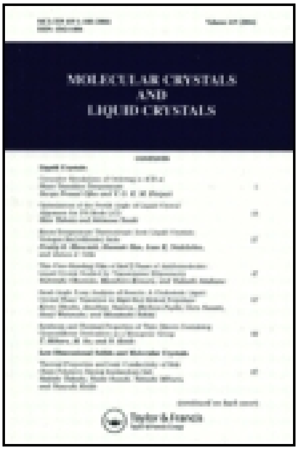

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Preparation and Photoresponsive Behavior of Plastic Films Coated with Azobenzene Liquid-Crystalline Polymer Layers

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Plastic films coated with crosslinked liquid-crystalline polymer (CLCP) layers containing azobenzene moieties (plastic/CLCP bilayer films) were prepared by thermal polymerization of mixtures of an azobenzene monomer and a crosslinker placed between a plastic film and a glass substrate. When the glass substrate was untreated, the obtained bilayer film bent slightly away from the UV light source when irradiated on the CLCP layer side. This bending direction was the same as that of a hybridly aligned CLCP film. When the glass substrate was coated with a rubbed polyimide to strengthen the homogeneous alignment of the azobenzene moieties of the CLCP surface layer, the obtained bilayer film bent toward the irradiation direction of the incident UV light. It was the same as a homogeneously aligned CLCP film and the degree of bending was larger than that of the untreated sample. This means that the photoinduced bending behavior of the plastic/CLCP bilayer films strongly depends on the alignment of the azobenzene moieties of the CLCP surface layer facing the incident light.

Keywords: azobenzene; bending; crosslinked liquid-crystalline polymer; photoresponsive function; plastic film

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INTRODUCTION

As a crosslinking of liquid-crystalline (LC) polymer chains makes a strong correlation among LC mesogens and polymers, CLCPs have two characteristic properties: anisotropic aspects of LC and rubber elasticity of polymer networks. Because of unique optical and other physical properties, CLCPs have been extensively investigated for the last several decades. First, de Gennes proposed theoretically that CLCPs would show a uniaxial contraction by the thermal LC-isotropic(I) phase transition [1]. Finkelmann *et al.* experimentally observed the anisotropic contraction resulting from the thermal LC-I phase transition of monodomain nematic CLCPs [2], and after that several groups observed the deformations of CLCPs by changing the alignment of LC mesogens by external stimuli such as electric fields and temperature [3,4].

Recently the photoinduced deformation was observed by incorporating some photochromic moieties such as azobenzene into polymer chains. The azobenzene moieties show *trans-cis* photoisomerization and exhibit a large change in the molecular length [5]. Finkelmann *et al.* achieved a large photoinduced contraction of CLCPs containing azobenzene moieties, resulting from the photochemical phase transition [6]. This provided a novel photofunctional mechanism of CLCPs and showed a possibility of applications as light-driven actuators, and a variety of actuation modes have been investigated.

Most recently, we have achieved a photoinduced bending in CLCP films showing a larger degree of deformation and a faster response by using CLCPs composed only of azobenzene moieties [7–10]. Additionally, we have succeeded in controlling the bending direction of the CLCP films precisely by irradiation with linearly polarized light [10]. The principle of these photoinduced bending behavior is the difference of volume contractions between the film surface and the bulk of the film. The photoisomerization occurs only in the surface region facing the incident light (within 1 μm), and in the bulk of the CLCP film the *trans*-azobenzene moieties remain unchanged [7–9].

In this study, plastic films having no photoresponsive properties coated with the CLCP layers containing azobenzene moieties were prepared and their photoresponsive behavior was investigated.

EXPERIMENTAL

Materials for CLCP Layers and Plastic Films

The structures of a monoacrylate LC monomer, 6-[4-(4-ethoxyphenylazo) phenoxy]hexyl acrylate (**A6AB2**) and a diacrylate crosslinker, 4,4′-bis [6-(acryloyloxy)hexyloxy]azobenzene (**DA6AB**) used in this study

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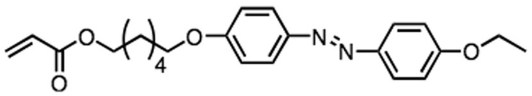
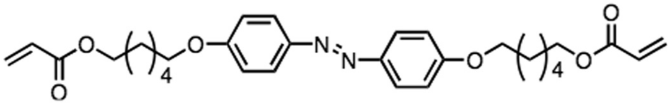


A6AB2 I 93 N 88 K (cooling*)



DA6AB K 99 I

FIGURE 1 Structures, properties and abbreviations of the LC monomer and crosslinker used in this study. I, isotropic; N, nematic; K, crystal. ***A6AB2** shows a monotropic nematic phase when cooled from an isotropic phase.

are shown in Figure 1, both of which possess azobenzene moieties. Both compounds were prepared according to the method reported previously [11]. The CLCP layers were prepared by thermal copolymerization of **A6AB2** and **DA6AB** (mol/mol : 1/1), containing 2 mol% of a thermal initiator (1,1′-azobis(cyclohexane-1-carbonitrile). The plastic films used in this study are biaxially stretched polyethylene terephthalate (PET) film (thickness: 12 μm, glass transition temperature (T_g): 69°C) and silicone rubber sheet (thickness: 46 μm, T_g: -127°C). Neither of which shows photoresponsive behavior.

Photoinduced Bending Behavior

The photoinduced bending behavior of plastic/CLCP bilayer films was investigated as follows: a freestanding bilayer film was put on a hot stage (Mettler, FP-90 and FP-82) and heated. The bending behavior of the bilayer film was observed upon UV irradiation at 366 nm from a 500 W high-pressure mercury lamp through glass filters (Asahi Techno Glass, UV-36A, UV-35 and IRA-25S) and irradiation with visible light at $>$540 nm (Asahi Techno Glass, Y-52 and IRA-25S).

RESULTS AND DISCUSSION

Fabrication and Photoinduced Bending Behavior of Plastic/CLCP Bilayer Films

Figure 2 shows the fabrication process of the plastic/CLCP bilayer films. A plastic film coated with a rubbed polyimide was put on a glass

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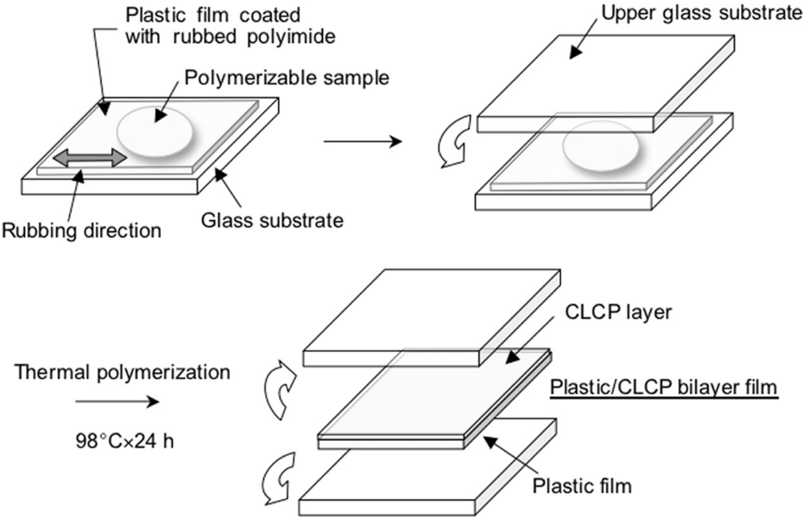

FIGURE 2 The fabrication process of plastic/CLCP bilayer films.

substrate and a mixture of an LC monomer, a crosslinker, and a thermal initiator was placed between the plastic film substrate and an upper glass substrate. Thermal polymerization of the mixture was carried out at 98°C for 24 h under vacuum. The freestanding plastic/CLCP bilayer film was obtained by taking it off from the glass substrates. In this way, two types of the plastic/CLCP bilayer films were prepared: one obtained with an untreated upper glass substrate and the other with an upper glass substrate coated with a rubbed polyimide to strengthen the homogeneous alignment of the azobenzene moieties of the CLCP surface layer, antiparallel to the rubbing direction of the rubbed polyimide.

The obtained bilayer film was put on a hot stage, heated to 70°C and irradiated with UV light on the CLCP layer side and the photoinduced bending behavior was observed as illustrated in Figure 3. Upon UV irradiation on the CLCP layer side, the PET/CLCP bilayer film obtained with an untreated upper glass substrate bent slightly away from the UV light source and reverted to the initial state when irradiated with visible light (Fig. 4A). The CLCP layer separated from the PET substrate bent away from the UV light source upon UV irradiation on the untreated surface side, whereas upon UV irradiation on the aligned PET surface side, it bent toward the UV irradiation direction (Fig. 4B). This bending behavior was the same

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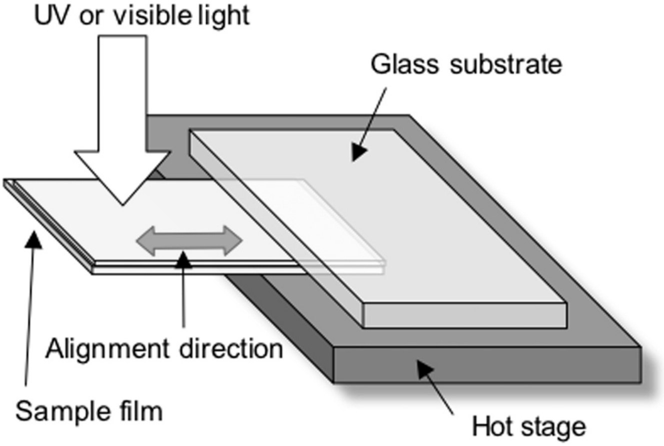

FIGURE 3 Schematic illustration of the experimental setup for investigation of the photoinduced bending behavior.

as that of a hybridly aligned CLCP film. It is suggested that the alignment of the PET/CLCP bilayer film obtained with an untreated upper glass substrate is hybrid as illustrated in Figure 4C.

With the PET/CLCP bilayer film obtained with an upper glass substrate coated with a rubbed polyimide, it bent toward the UV irradiation direction upon UV irradiation on the CLCP layer side and reverted to the initial state when irradiated with visible light (Fig. 5A). This bending behavior was the same as that of a homogeneously aligned CLCP film. The degree of bending was larger than that of the untreated glass substrate film. With silicone rubber as a plastic substrate, similar photoinduced bending behavior was observed (Fig. 5B). It is suggested that the alignment of the CLCP surface can be homogeneous as illustrated in Figure 5C.

It has been found that the photoinduced bending behavior of the plastic films coated with CLCP layers strongly depends on the alignment of the azobenzene moieties of the CLCP surface layer facing the incident light.

Effect of Plastic Film Substrate upon Photoinduced Bending Direction

To verify the effect of plastic film substrates upon photoinduced bending direction, the PET/CLCP bilayer film was prepared as the PET stretched direction and the alignment direction of the CLCP layer facing the PET

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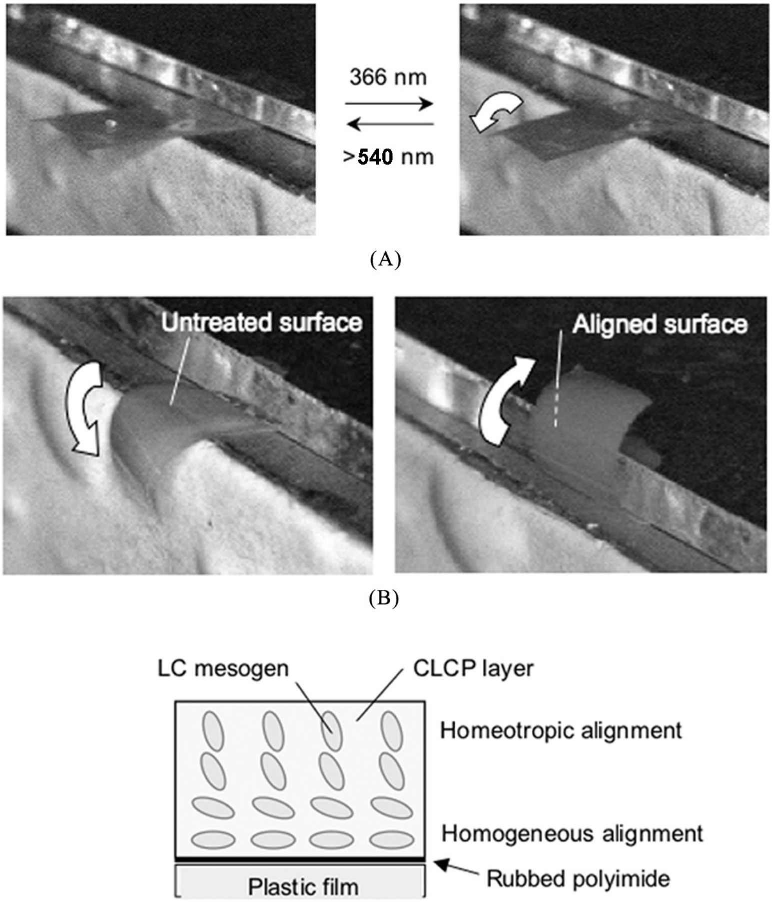

(A)

(B)

(C)

FIGURE 4 Photographs of the photoinduced bending behavior of the PET/CLCP bilayer film obtained with an untreated upper glass substrate (A), the separated CLCP layer upon UV irradiation (B), and schematic illustration of the LC mesogens alignment (C). Thickness of the bilayer film: 22 μm (PET: 12 μm, CLCP layer: 10 μm).

film substrate being shifted by 45° and its photoinduced bending direction was investigated. Upon UV irradiation on the CLCP layer side, the film bent slightly along the alignment direction of the CLCP layer, not along the PET stretched direction. This indicates that there is little or no relationship between the photoinduced bending direction and the stretched direction of the plastic film.

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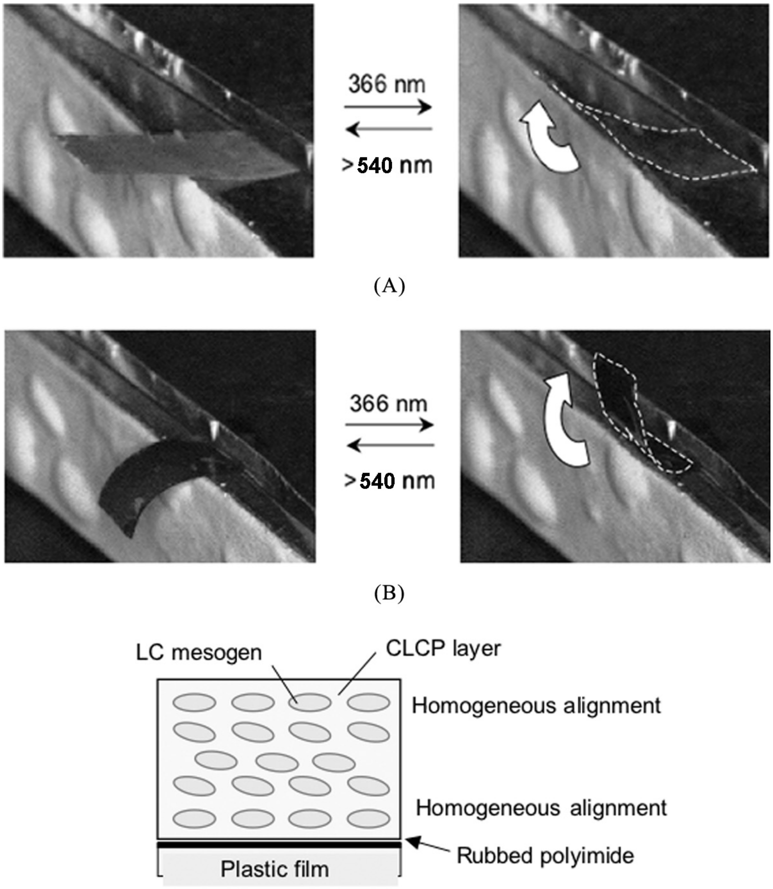

(A)

(B)

(C)

FIGURE 5 Photographs of the photoinduced bending behavior of the PET/CLCP bilayer film obtained with an upper glass substrate coated with a rubbed polyimide (A), the silicone rubber/CLCP bilayer film obtained with an upper glass substrate coated with a rubbed polyimide (B), and schematic illustration of the LC mesogens alignment (C). Thickness of the PET bilayer film: 19 μm (PET: 12 μm, CLCP layer: 7 μm) and the silicone rubber bilayer film: 63 μm (silicone rubber: 46 μm, CLCP layer: 17 μm).

CONCLUSIONS

The plastic films coated with the CLCP layers containing azobenzene moieties were obtained by thermal polymerization of CLCPs on the plastic films. It has been found that the plastic/CLCP bilayer films show the photoinduced bending behavior and the bending behavior strongly depends on the alignment of the azobenzene moieties of the CLCP surface layer facing the incident light. By controlling the alignment of the film surface, we can provide various kinds of plastic films with photoresponsive functions.

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