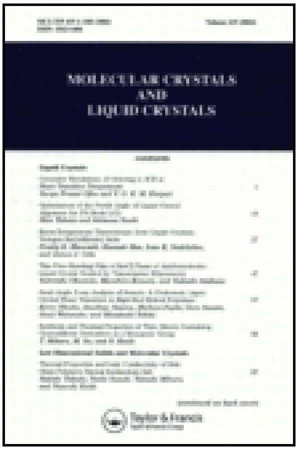

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Photoinduced Deformation Behavior of Crosslinked Azobenzene Liquid-Crystalline Polymer Films with Unimorph and Bimorph Structure

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The use of a crosslinked azobenzene liquid-crystalline polymer (CALP) system for micro-integrated actuators becomes especially attractive. CALPs can deform along the alignment direction of mesogens upon irradiation of UV/visible light owing to photochemical phase transition. In this study, to improve the bending speed, CALP films with a homogenous alignment on one surface and a homeotropic alignment on the opposite surface (hybrid alignment) were prepared and their bending behavior was investigated. The films showed photoinduced bending whose direction was determined by the surface alignment treatment, and the bending speed was greatly enhanced upon irradiation from both surfaces of the film at the same time.

Keywords: alignment; azobenzene; bending; bimorph; deformation; unimorph

INTRODUCTION

Light can be controlled remotely and rapidly as an external stimulus. This is suitable for controlling actuators [1] used in a special environment such as high vacuum and extreme microscopic areas. Polymers are much softer and lighter than inorganic materials with higher

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processibility. From these viewpoints, it is important to develop light-driven polymer actuators and many works have been reported to realize them using such materials as carbon nanotubes [2,3], spirobenzopyran gels [4], poly(vinylidene fluoride) [5], and cinnamic- or azobenzene-containing polymers [6–8]. Azobenzenes undergo *trans–cis* photoisomerization in response to light radiation. In the lower-energy *trans* state, azobenzenes are rod-like molecules, but when illuminated with UV light, the molecules switch to bent *cis* forms. It is known that uniaxially aligned crosslinked liquid-crystalline polymers (CLCPs) exhibit a spontaneous deformation along the alignment direction when changing their phase between LC and isotropic ones [9–13]. When azobenzene chromophores are incorporated into CLCPs, the resulting CLCPs can undergo a photoinduced deformation isothermally, which is larger than that of amorphous systems [14–16] thanks to the change in the nematic order. When CLCP films contain a high concentration of azobenzene moieties, the films have a large extinction coefficient; thus, upon irradiation of UV light, a localized deformation is generated in the irradiated surface, and a bending of the films is observed [17–23]. Tuning the initial alignment treatment can control the deformation behavior of the CLCP films. In the previous work, we have found that monodomain and polydomain CLCP films containing azobenzene chromophores alone (CALP) that are aligned planar (homogeneous) to the film surface showed different bending behavior: the bending of the former took place just along the alignment direction of mesogens, while in the latter the bending in any direction could be evoked [24]. We have also reported that the CALP films aligned normal (homeotropic) to the film surface bent away from the UV light source [25].

The CALP films, which bend upon photoirradiation, only utilize the deformation of one surface while the opposite surface just moves passively and disturbs the bending behavior like unimorph actuators. If we use this passive surface as a cooperative action layer, the bending speed would be expected to be improved. The simple method to realize this movement is to generate an expansion in one surface and a contraction in the opposite surface, like such bimorph actuators as dielectric polymer actuators and piezoelectric actuators. In the CLCPs, a hybrid alignment, a homogenous alignment on one surface and a homeotropic alignment on the opposite surface, is a suitable structure to realize it. Recently Broer *et al.* prepared thermally responsive CLCP films with the hybrid alignment and the films showed a spontaneous bending owing to a difference of the thermal expansion depending on the direction of the molecular alignment [26]. In this work, we incorporated this anisotropic structure into CALP films to improve bending speeds, and the bending behavior of these hybrid films was investigated.

EXPERIMENTAL

Characterization Methods

The LC monomer and crosslinker (Fig. 1) were prepared according to a previously reported method [27]. The CALP films were prepared by in situ photopolymerization of a mixture of the LC monomer and crosslinker (80/20, mol/mol) containing 1 mol% of a photoinitiator (Ciba Specialty, Irgacure 784). Firstly, the melt of the mixture was injected into a glass cell, which had been treated for the hybrid alignment: the bottom glass plate was coated with a polyimide alignment layer that had been rubbed to align mesogens and induce a homogeneous alignment, while the top glass plate was treated with n-octadecyltrimethoxysilane that induced a homeotropic alignment. After the sample was cooled down slowly (0.5°C/min) to a polymerization temperature at 88°C (in the nematic phase), photoirradiation was performed at >540 nm (2.8 mW/cm^2 at 547 nm) with a 500-W high-pressure mercury lamp through glass filters (Asahi Techno Glass, Y-52 and IRA-25S) for 2 h. The CALP films were taken off from the cells after polymerization. Optical anisotropy of the films was observed with a polarizing optical microscope (POM; Olympus, BH-2) and a UV-vis absorption spectrometer (Jasco, V-550). Transmittance and attenuated total reflectance (ATR) infrared spectra were measured with an FT/IR spectrometer (Jasco, FT/IR-610) equipped with an ATR-300/H accessory, where a ZnSe crystal (refractive index: 2.4) and eight reflections at an incidence angle of 45° were used. The infrared beam was polarized perpendicular to the incidence plane, and the film was rotated to obtain polarized ATR spectra. Photoinduced bending and unbending behavior was observed upon irradiation of unpolarized UV light at 366 nm from the mercury lamp through glass filters (Asahi Techno Glass, UV-D36B, UV-35 and IRA-25S). The bent film was exposed to unpolarized visible light at >540 nm. Thermomechanical analysis was performed in a stretch mode under the external tension at a constant temperature using a thermomechanical analyzer (TMA; Simadzu, TMA-60).

RESULTS AND DISCUSSION

Optical anisotropy in the planar direction of the films was evaluated at room temperature by measuring the transmittance of the probe light

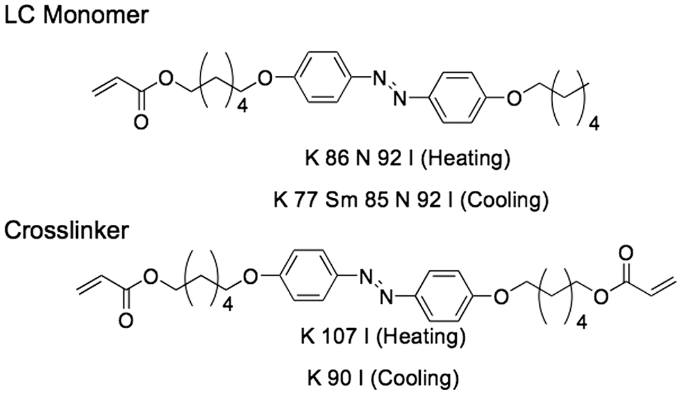


FIGURE 1 Chemical structures and properties of LC monomer and crosslinker used in this study.

through crossed polarizers with a sample film between them as a function of the rotation angle (Fig. 2). When the rubbing direction in the homogeneous surface was parallel or perpendicular to the direction of polarizer of the microscope, no or little transmitted light was observed, whereas the transmittance was highest when the angle between them was 45°. Regular maximum and minimum with 90° separations reveal that the azobenzene mesogens are preferentially aligned along the rubbing direction in the homogeneous surface.

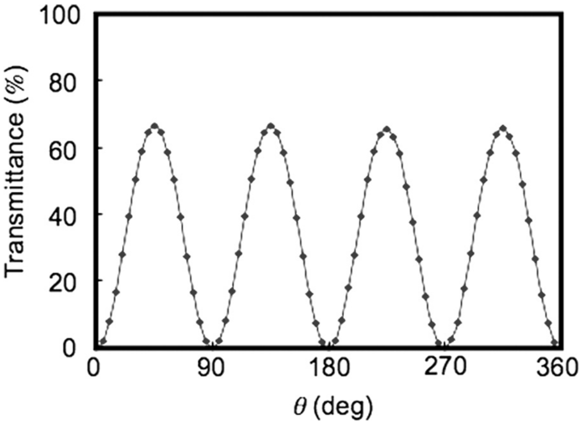
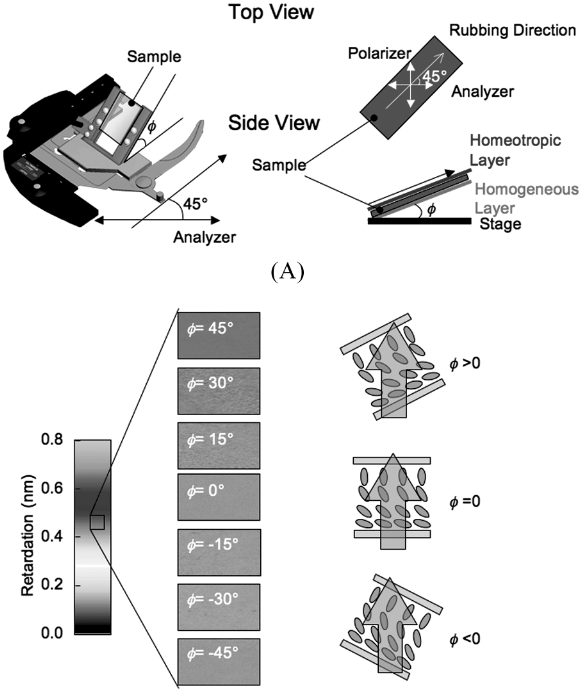


FIGURE 2 Angular dependent transmittance of the CALP film evaluated by polarizing optical microscopy at room temperature. The thickness of the film was 5 μm.

Additionally, the optical anisotropy in the films was evaluated by the polarized absorption spectra. It was found that the absorbance measured with light polarized parallel to the rubbing direction was higher than that with light polarized perpendicular to the rubbing direction. This result also indicates that a part of mesogens are aligned parallel to the rubbing direction in the homogeneous surface.

To check optical anisotropy in the normal direction of the films, we observed interference color of the film [28]. As shown in Figure 3(A), the film was fixed on the stage with the angle between the homogeneous alignment direction and the polarization direction of each polarizer being 45°, then the film was tilted from the horizontal state to the normal direction by changing the tilting angle (ϕ) from 0° to +45° and from 0° to −45°. It was observed that the image of the film colored red and the retardation of the film increased when the tilting angle ϕ was increased from 0° to +45° (Fig. 3(B)). On the other hand,



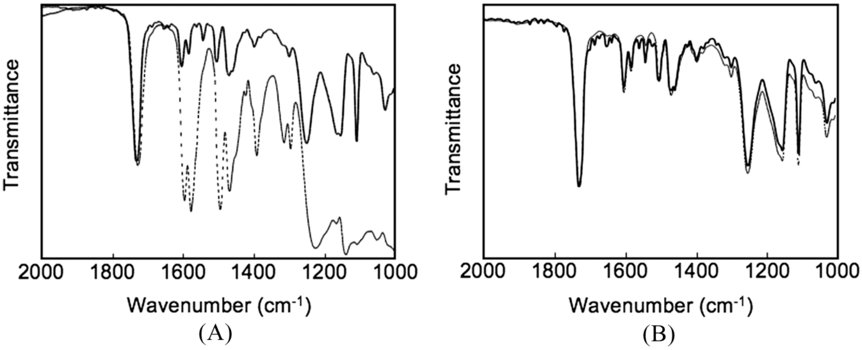
(A)

(B) (C)

FIGURE 3 Schematic illustration of the experimental setup (A) and the change in retardation of the probe light through the tilted hybrid film (B) with the corresponding side view (C). The thickness of the film was 5 μm.

the retardation decreased when ϕ was decreased from 0° to $-45°$, resulting in an unsymmetrical color change of the interference images (Fig. 3(B)). In the hybrid films, most of the mesogens locating next to the homogeneous surface tend to align along the rubbing direction with a small tilt angle to the film surface. As demonstrated in Figure 3(C), when ϕ was increased from 0° to $+45°$, more mesogens become perpendicular to the incident direction of the probe light and the total retardation increased. On the other hand, the retardation decreased when ϕ was decreased from 0° to $-45°$. Thus, the film showed an unsymmetrical change in retardation.

The hybrid films should have different optical properties in both surfaces, so we examined the optical anisotropy in the surface region of a film by polarized infrared ATR. It has been reported that ATR can be used for surface characterization [29], because only a part of the sample with a small thickness interacts with the evanescent wave occurring in the ATR experiment. By using the crystal with a high refractive index (ZnSe or germanium), it is possible to study the molecular orientation near the surface of the polymer films (the thickness probed was smaller than 0.5 μm). Polarized ATR spectra of each surface of the hybrid film are presented in Figure 4. Because the intensity of each spectrum was influenced by the measurement area, we dealt with the spectra measured with the IR beam polarized parallel and perpendicular to the homogeneous alignment direction, respectively, by regarding the intensity at $1729\,\mathrm{cm}^{-1}$ in each spectrum as the same. The band at $1729\,\mathrm{cm}^{-1}$ originates from the stretching vibration of carbonyl groups, which are directly attached to the polymer backbone



(A) (B)

FIGURE 4 Polarized ATR spectra in the hybrid film observed from homogeneous (A) and homeotropic surface (B) at room temperature. The IR beam was polarized parallel (⋯⋯) and perpendicular (——) to the homogeneous alignment direction. The thickness of the film was 20 μm.

and have been observed to show no anisotropy in polarized IR spectra [30]. The ATR spectra of the film clearly indicate that the homogeneous surface showed a high dichroism around 1600 cm^{-1}, originating from the stretching vibration of benzene rings, while the homeotropic surface did not show any dichroism and high transmittance around this band.

These optical properties are supported by the conoscopic observation of the film as shown in Figure 5. A dark cross image was

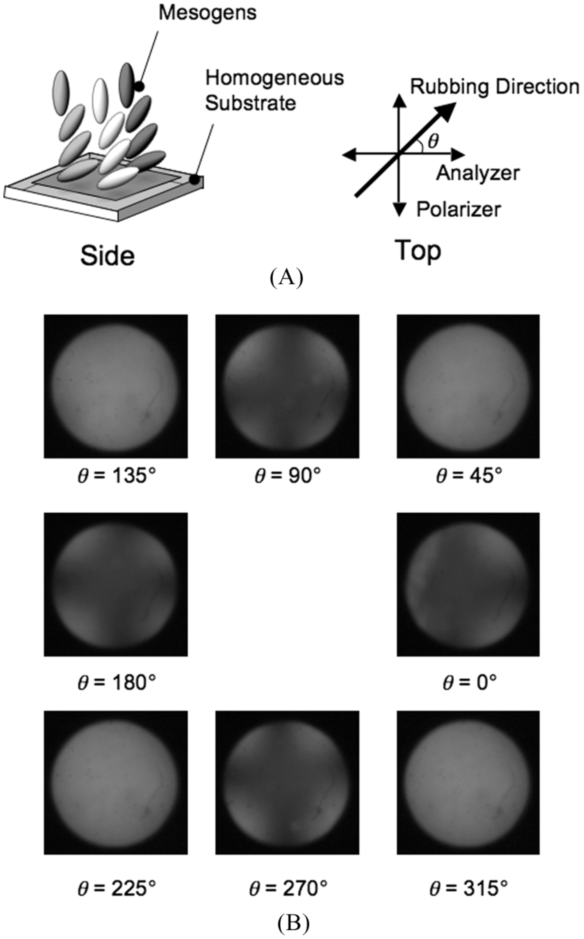
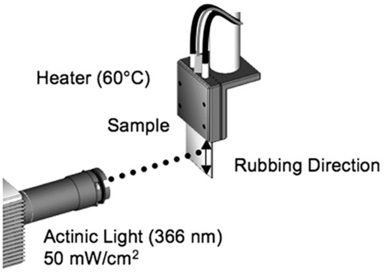


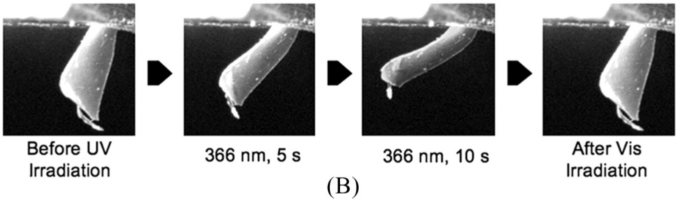
FIGURE 5 Schematic illustration of the experimental setup (A) and angular–dependent conoscopic images of the hybrid film (B). The rotation angle indicates the direction of the polarizer with respect to the homogeneous alignment direction. The thickness of the film was 20 μm.

observed when the alignment direction of the homogeneous surface was parallel or perpendicular to the polarization direction of the probe light. In these cases the mesogens aligned parallel to the homogeneous surface did not affect the transmittance of the polarized probe light. The cross-point that represents the optic axis of the LC phase [31] changed its position with reference to the rotation angle of the rubbing direction. Namely, the mesogens in the film are aligned homogeneously in the planar direction with a continuous change from a homogeneous to a homeotropic alignment in the normal direction. These results indicate that the azobenzene mesogens are aligned hybridly in the film.

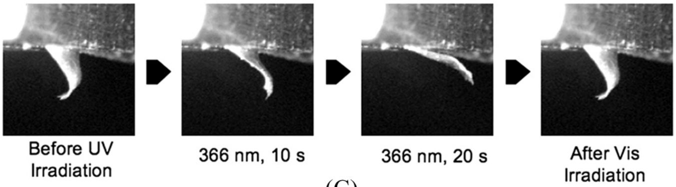
We observed the photoinduced bending and unbending behavior of the CALP films as shown in Figure 6(A). A part of a freestanding film



(A)



(B)



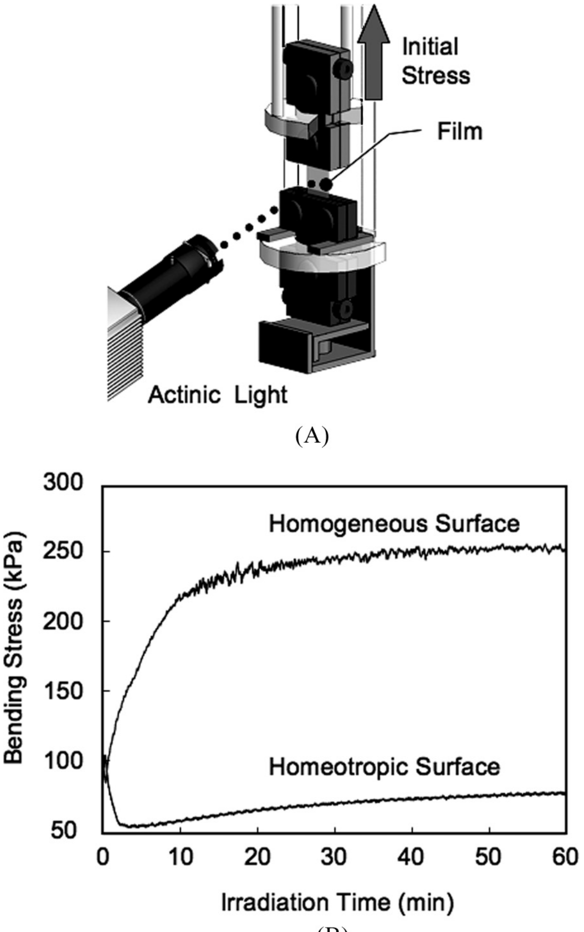
(C)

FIGURE 6 Schematic illustration of the experimental setup (A) and photographs of the hybrid film that exhibits photoinduced bending and unbending behavior when the homogeneous surface (B) and homeotropic surface (C) were irradiated respectively.

was pasted to an aluminum block attached with a heater and irradiated with unpolarized light. The film was heated to 60°C, a little higher than the glass transition temperature of the film ($T_g \approx 60°C$) to eliminate thermally induced bending [24]. Upon irradiation of UV light on the homogeneous surface, the film bent toward the irradiation direction of the actinic light along the alignment direction (Fig. 6(B)), while the film bent away from the actinic light source when the homeotropic surface was irradiated (Fig. 6(C)). This demonstrates that the bending direction is determined by the surface alignment treatment. The bent film reverted to the initial flat state upon irradiation of visible light.

We also measured the mechanical force generated upon photoirradiation by thermomechanical analysis. As shown in Figure 7(A), a hybrid film was fixed by clamping both ends of the film and then heated to 60°C. An external force was loaded on the film to keep the length of the film unchanged. Upon irradiation of UV light on the homogeneous surface, the bending stress increased, while it decreased at first upon irradiation on the homeotropic surface. In the homogeneous surface, as the azobenzene mesogens are aligned parallel to the rubbing direction, an anisotropic contraction is generated along this alignment direction upon UV-light irradiation. On the other hand, the alignment direction of the azobenzene mesogens in the homeotropic surface is perpendicular to the film surface; thus, exposure to UV light induces an isotropic expansion [25]. However, in the hybrid films, the bending stress on the homeotropic surface increased after 10-min irradiation of UV light. This is because the homeotropic surface has a low extinction coefficient, when irradiated for a long time, the inner mesogens of the film align parallel to the rubbing direction isomerize from *trans* to *cis* forms and subsequently a contraction occurs in the hybrid film.

To confirm whether the bending property can be improved, we irradiated both surfaces of the film with UV light at the same time as demonstrated in Figure 8(A). Upon irradiation of UV light, the hybrid film bent toward the right side, and the bending speed was greatly enhanced, because the homeotropically aligned surface on the left side generated an expansion, while a contraction took place in the opposite homogeneously aligned surface on the right side (Fig. 8(B)). For comparison, we also prepared a uniaxially aligned homogeneous film by the previously reported method [25] and observed its photoinduced bending behavior. It was found that the homogeneous film a ways bent toward the irradiation direction of the actinic light with a higher intensity, and the bending speed was not improved compared with irradiation with one UV light source (Fig. 8(C)). Under the high



(A)

(B)

FIGURE 7 Schematic illustration of the experimental setup (A) and the force generated upon 366-nm light irradiation (3.7 mW/cm^2) at 60°C (B). Size of the film was 5.5 mm × 5 mm × 20 μm and initial stress was 100 kPa.

intensity, trans- and cis-azobenzene moieties reach quickly to a photostationary state, and the relaxation process of polymer segments becomes a rate-determining step for the bending rather than the changes in structure and alignment of azobenzene moieties. Because the relaxation of polymer segments has no relation to the light intensity, the bending time is insensitive to the increment of the light intensity when the intensity is high [19].

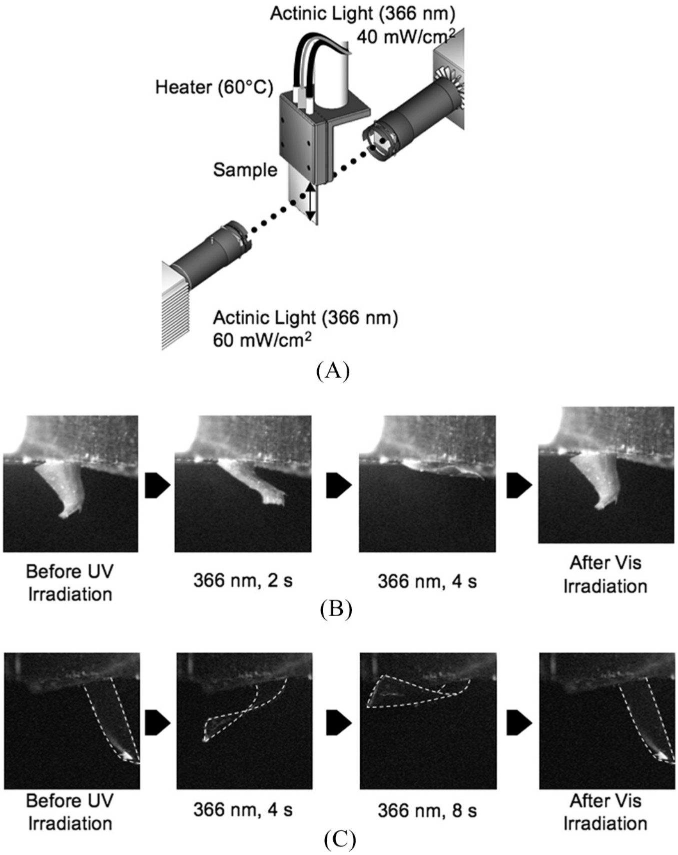


FIGURE 8 Schematic illustration of the experimental setup (A) and photographs of the hybrid film (B) and uniaxially aligned homogeneous film (C) that exhibit photoinduced bending and unbending behavior, when both surfaces were irradiated at the same time. The homogeneous surface of the hybrid film in (B) was on the right side. The white dash lines in (C) show the edges of the film.

CONCLUSIONS

In summary, we prepared novel CALP films with the hybrid alignment. The films showed photoinduced bending behavior upon irradiation of UV light and the bending direction was determined by the surface alignment treatment. The films always bent to the homogeneous side and the bending speed was enhanced upon irradiation of UV light on both surfaces of the film. This is a good method to control the bending direction of the CALP films and to improve the bending speed. In the meantime, we proceed to make further investigation on the stability of the bending behavior and the practical applications of the films.

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