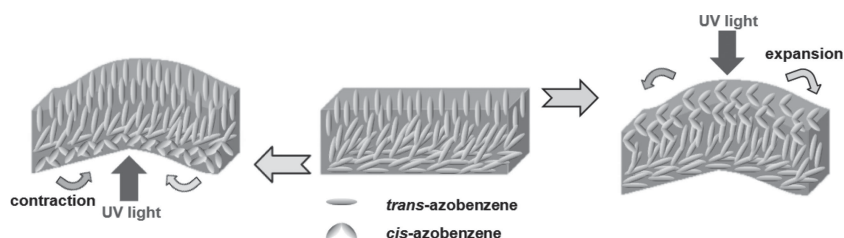


Photoinduced Bending Behavior of Cross-linked Azobenzene Liquid-Crystalline Polymer Films with a Poly(oxyethylene) Backbone

Jiu-an Lv, Weiru Wang, Jixiang Xu, Tomiki Ikeda, Yanlei Yu*

Cross-linked azobenzene liquid-crystalline polymer films with a poly(oxyethylene) backbone are synthesized by photoinitiated cationic copolymerization. Azobenzene moieties in the film surface toward the light source are simultaneously photoaligned during photopolymerization with unpolarized 436 nm light and thus form a splayed alignment in the whole film. The prepared films show reversible photoinduced bending behavior with opposite bending directions when different surfaces of one film face to ultraviolet light irradiation.



1. Introduction

Photodeformable cross-linked liquid-crystalline polymers (CLCPs) are most promising materials for applications such as artificial muscles and soft actuators.^[1] Since on the one hand, they are able to show large and reversible shape deformation due to the cooperation of the rubber elasticity of polymer networks and high order of liquid-crystalline (LC) mesogens. On the other hand, they can convert light energy directly into mechanical work and act by remote,

instant, and precise manipulation.^[2] In order to show photomechanical effect, the CLCPs need the incorporation of photochromic moieties such as coumarin, spiropyran, stilbene, and azobenzene.^[3] In particular, azobenzene is frequently used chromophore, because the CLCPs containing azobenzene chromophores can achieve a wide range of macroscopic deformations, for examples, contraction, expansion, and bending.^[4] Meanwhile, photochemical phase transition of the azobenzene-containing CLCPs can occur on a timescale of nanoseconds under optimized conditions.^[5] The azobenzene-containing CLCPs are thus of particular interest for applications in the field where various deformation and quick response are desirable, such as photomechanical cantilevers,^[6] light-driven plastic microrobots,^[7] artificial cilia,^[8] inchwormlike walker,^[9] and so on.

In the CLCPs, the LC phase behavior is known to depend upon several factors such as the structure of polymer backbone, mesogenic unit, as well as the nature and length of flexible spacer connecting the mesogenic group to the polymer backbone. Here, the flexibility of main chain in CLCPs not only affects the formation and

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thermostability of LC phase but also influences the orientation of polymer chains involving the changes in order parameter of mesogenic units, and finally respects to the macroscopic mechanical response to light irradiation in CLCPs. To date, the CLCPs with limited kinds of main chains have been investigated in the studies of photomechanical effects, in which polysiloxanes,^[1d] polyacrylates,^[10,1g] and polymethacrylates^[1e] are commonly used. However, to our knowledge, the CLCPs with poly(oxyethylene) backbone have rarely been reported up to now,^[11] and it is well known that epoxy-based polymers are widely used as engineering materials due to their excellent mechanical and thermal properties.

In order to synthesize the CLCPs with poly(oxyethylene) backbone, there are two strategies: thermal polymerization and photoinitiated polymerization. By contrast, photoinitiated polymerization is preferred to thermal polymerization since photoinitiated polymerization shows the advantage in oxygen insensitivity and LC epoxide monomers can be heated at any temperature for them to show LC phase during the photopolymerization without concern for polymerization occurring during the fabrication process. However, the employment of photopolymerization to prepare the azobenzene-containing CLCPs with poly(oxyethylene) backbone is infeasible due to the strong absorption of the azobenzene moieties to UV light and short-wavelength visible light. Fortunately, free-radical-promoted cationic polymerization can be used to overcome the problem of limited absorption wavelength range of commonly used cationic photoinitiators.^[11] Furthermore, the employment of the cationic photopolymerization can potentially yield thicker samples due to frontal photopolymerization, and the samples also tend to be more homogenous across the thickness as well, while acrylate-based systems can be heterogenous due to faster polymerization/consumption of monomer at the exposed surfaces.^[12]

In this work, we have synthesized the azobenzene CLCP films containing a poly(oxyethylene) backbone with long-wavelength-photoinitiated cationic polymerization promoted by free radical,^[13,14] and a splayed alignment of the azobenzene moieties formed simultaneously during the photopolymerization process. The as-prepared films showed reversible photoinduced bending independent from the direction of the incident light.

2. Experimental Section

2.1. Long-Wavelength Photoinitiated Cationic Polymerization

Polymerizable mixtures were prepared by adding a photoinitiator mixture containing 4 mol% of a radical photoinitiator

camphorquinone (CQ) and 2 mol% of a cationic initiator diphenyliodonium hexafluorophosphate (DiPhIPF₆) to the mixture of E1AB2 and DE1AB (mol/mol: 50/50, Schemes S1–S3, Supporting Information). The melt of the mixture was injected into a sodium chloride (NaCl) cell coated with rubbing-treated polyimide (PI) layers (Semi-Automatic Rubbing Machine, CETC MCJ-12), and the cell gap was controlled by silica spacers with the diameter of 5 or 10 μm. The photopolymerization was performed upon unpolarized light irradiation at 436 nm (6.0 mW cm⁻²) from a 500 W high-pressure mercury lamp through glass filters (Toshiba, IRA-25S, V-40 and Y-44) at 160 °C for 10 h. After polymerization, the freestanding films were obtained after the NaCl substrates were dissolved in water. For the optimization of polymerization conditions, homopolymers of E1AB2 were prepared under different light intensities for different time (see PART S1, Supporting Information). Molecular weights of the linear polymers were measured by gel permeation chromatography (GPC; Japan Spectroscopy Co., model DG-980–50; column, Shodex GPC, models K802, K803, K804, and K805; eluent, chloroform) calibrated with standard polystyrenes and polymerization conversions were compared. The procedures of preparing the CLCP films are illustrated in Scheme S4 (Supporting Information).

2.2. Photoinduced Bending Behavior of Azobenzene CLCP Films

The photoinduced bending behavior of the CLCP films was studied as follows: a freestanding film put on a glass substrate was placed on the hot stage (heated to 120 °C) and exposed to unpolarized UV light at 366 nm and visible light at >545 nm from the 500 W high-pressure mercury lamp through glass filters. The glass filters of IRA-25S, UV-D36A, and UV-35 were used to obtain UV light, and the glass filters of IRA-25S and Y-52 were used to obtain visible light. The photographs of the photoresponsive behavior of the CLCP films were taken by a digital camera (Canon, IXY-Digital-500), and the bending time was measured through a CCD camera (OMRON, VC-HRM20Z).

2.3. Characterization Methods

The thermodynamic properties of the monomers, the monomer mixtures, and the CLCP films were determined by DSC (Seiko I&E, SSC-5200 and DSC220C) at a heating and cooling rate of 2 °C min⁻¹ for monomers and mixtures, and 10 °C min⁻¹ for CLCP films, respectively. At least three scans were performed to check the reproducibility. The mesomorphic properties and phase transition behavior of the monomers and the CLCP films, as well as the interference color of the CLCP films were evaluated with a polarizing optical microscope (POM, Olympus, BX50) equipped with a Mettler hot stage (Model FP-90 and FP-82). The polarized attenuated total reflectance (ATR) infrared spectra of the film were measured at room temperature with an FT/IR spectrometer (Jasco, FT/IR-420) 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.

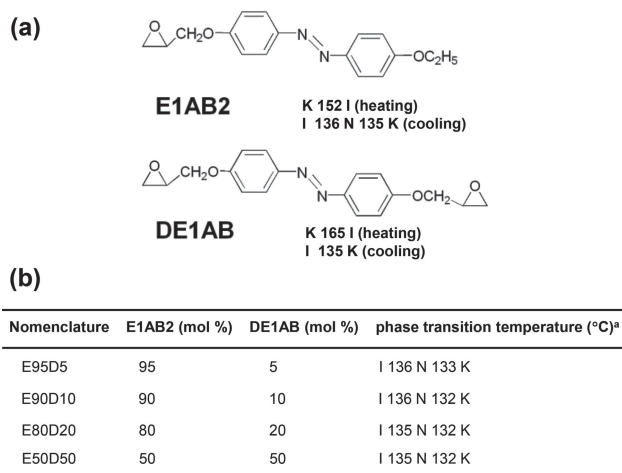


Figure 1. a) Structures and abbreviations of the LC monomer and cross-linker used in this study. K, crystal; N, nematic; I, isotropic. b) Nomenclature, composition, and phase transition temperatures of the polymerizable samples. 4 mol% of the radical photoinitiator and 2 mol% of the cationic initiator were added to the polymerizable samples. The phase transition temperatures were determined by DSC, and only the phase transition temperatures in the cooling process are listed.

3. Results and Discussion

The thermal phase transition of the LC monomer and cross-linker used in this study was examined by differential scanning calorimetry (DSC) and polarizing optical microscope (POM) (Figure S1, Supporting Information). It was found that 4-ethoxy-4'-(2,3-epoxypropoxy) azobenzene (E1AB2) exhibited a monotropic nematic (N) phase on cooling over a narrow temperature range from 136 to 135 °C, while 4,4'-di(2,3-epoxypropoxy) azobenzene (DE1AB) did not exhibit mesomorphism (Figure 1a). Four compositions comprised of E1AB2 and DE1AB were prepared as Figure 1b shows. All of the mixtures showed a monotropic N phase whose temperature range was broader than that of E1AB2 due to the good compatibility between E1AB2 and DE1AB. The nomenclature and the phase transition temperatures of the polymerizable mixtures are summarized in Figure 1b.

Because of the strong absorption of the azobenzene moieties to UV light irradiation around 360 nm (Figure S2, Supporting Information), the visible radical photoinitiator **CQ** that shows a strong absorption at 436 nm, and the cationic initiator **DiPhIPF₆** were used as the photoinitiator mixture. In the free-radical-promoted cationic polymerization, photochemically formed radicals from the radical photoinitiator can be oxidized by onium salts, and the generated cations act as initiating species for the cationic polymerization of epoxide compounds.^[11]

The photopolymerization conditions, including polymerization time, light intensity, and polymerization

temperature, were determined after optimization. For the optimization, the molecular weights of the homopolymers of E1AB2 prepared under different conditions were measured by means of GPC, and the polymerization conversions were calculated and compared (see PART S1, Supporting Information). Accordingly, the polymerizable mixtures containing E1AB2 and DE1AB with different ratios were polymerized under the optimum conditions. The photopolymerization was performed at 160 °C in an isotropic phase of the polymerizable mixtures, since a higher conversion was obtained at this temperature than that in the nematic phase temperature region. Here, the copolymer of the mixture of E50D50, PE50D50, was found to exhibit good film formability after polymerization; as a result, we mainly studied the physical properties and the photoinduced bending behavior of PE50D50. In the DSC thermogram, the glass transition (T_g) of the copolymer PE50D50 appeared around 117 °C, while isotropization was not detectable by DSC measurement. The T_g of PE50D50 is around 117 °C, which is higher than T_g s of previously reported acrylic systems, since the latter usually contain a longer spacer group.^[1g,11]

By the study of POM equipped with the hot stage, light transmittance through a PE50D50 film between two crossed polarizers was observed at temperatures up to 180 °C, indicating that anisotropy remains in the film even at high temperatures due to the cross-linking in the polymer networks. Although a poly(acrylate)-containing azobenzene similar to E1AB2 has been reported to show an N phase and a smectic A phase in the cooling process,^[15] the mixture of E50D50 only exhibited a nematic phase, and the photopolymerization was performed in the isotropic phase temperature region of the polymerizable mixture, suggesting that PE50D50 holds an N phase.

The in-plane optical anisotropy in the PE50D50 films was evaluated at room temperature by observing the light transmittance of the probe light through two crossed polarizers with a sample film placed between them. Figure 2a shows the polarizing optical images of the film with a thickness of 10 μm. When the rubbing direction of the NaCl cell used in the preparation of the PE50D50 film was parallel or perpendicular to the direction of optical axis of the polarizers, the transmitted light was weakest, while the transmittance was highest when the angle between them was 45°. Consequently, periodic transition of dark and bright images was observed by rotating the film. These results indicate that there are some azobenzene moieties in the film preferring the anisotropic alignment along the rubbing direction.

In order to further investigate the alignment of the azobenzene moieties in the irradiated surface (surface A) and the opposite surface (surface B) of the PE50D50 films, we measured both surfaces by polarized attenuated total reflection infrared spectroscopy (ATR-IR). Figure 2b shows

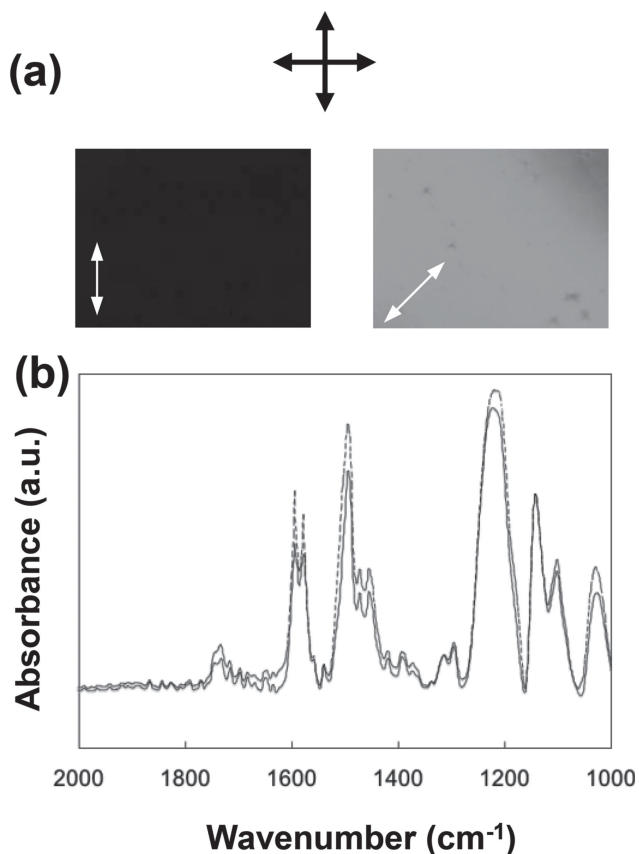


Figure 2. a) Polarizing optical images of the PE50D50 film. The black arrows indicate the direction of the optical axes of the crossed polarizers, and the white arrows indicate the rubbing direction of the NaCl cell used in the preparation of the film. The thickness of the film was 10 μm . b) Polarized ATR-IR spectra of surface A (—) and surface B (---) in the PE50D50 film measured at room temperature. The polarization direction of the IR beam was parallel to the rubbing direction.

the absorption spectra of surface A and surface B, respectively. The bands at 1597 and 1497 cm^{-1} , originating from the stretching vibration of benzene rings, and the bands at 1223 cm^{-1} , originating from the stretching vibration of phenyl ether groups in the side chains, are characteristic of the azobenzene moieties. In the measurement, when the polarization of IR beam was parallel to the rubbing direction, it was found that the absorbance of benzene and phenyl ether groups in surface A was less than that in surface B. It is well known that the absorbance of mesogens can reach a maximum value once the polarization direction of the IR beam is parallel to the alignment of mesogens, but a minimum value when the two directions are perpendicular to each other. The results demonstrate that the number of the azobenzene moieties aligned along the rubbing direction in surface A is less than that in surface B. This difference suggests that the reorientation of azobenzene moieties take place in surface A, since

the light source used in the photopolymerization of the PE50D50 films was 436 nm, which is easy to promote the *trans-cis-trans* photoisomerization cycles and the reorientation of azobenzene moieties to be perpendicular to the light polarization. The unpolarized 436-nm light used in this work owns only one direction (propagation direction) perpendicular to the electric vector of the light, the azobenzene moieties in surface A thus reorient to be parallel with the light propagation direction, namely a homeotropic alignment. In addition, taking account of the polarizing optical images described above, there are some other azobenzene moieties in the bulk and surface B of the PE50D50 films preferring the anisotropic alignment along the rubbing direction.

This splayed alignment was further evaluated with POM by the observation of the interference color of the transmitted light through the PE50D50 film placed between two crossed polarizers and the experimental setup is represented in Figure 3a. The film was fixed on the stage with the angle between the rubbing 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°. The thickness of the film was 5 μm , and the probe light was white light. Surface A of the film was kept upward in the whole observation process. The polarizing optical images of the film in Figure 3b show that the interference color changed from light yellow to red gradually when the angle of φ was altered from -45° to 45°, indicating that the retardation increases with the change of φ from -45° to 45°.

The retardation is defined by the follow equation:^[16,17]

$$R = d(n_e - n_o) = d\Delta n \quad (1)$$

where R is the retardation of the film, and n_e and n_o are the refraction index of extraordinary ray and ordinary ray, respectively. Δn means the birefringence of the film, and d is the film thickness. Usually, light incident along the direction of molecular axis of the azobenzene moieties shows a maximum refraction index, while the refraction index of light incident along any direction in the plane perpendicular to the molecular axis is minimum. As a result, when the probe light is incident along the alignment direction of azobenzene moieties, no birefringence exhibits. The birefringence and the retardation increase with an increase in the angle between the incident direction of the probe light and the alignment of azobenzene moieties. Finally, the birefringence and the retardation reach the maximum value when the two directions are perpendicular to each other. In the PE50D50 film, the increase in retardation as shown in Figure 3b reveals that in the process of changing φ from -45° to 45°, the average alignment of the azobenzene moieties in the film changes

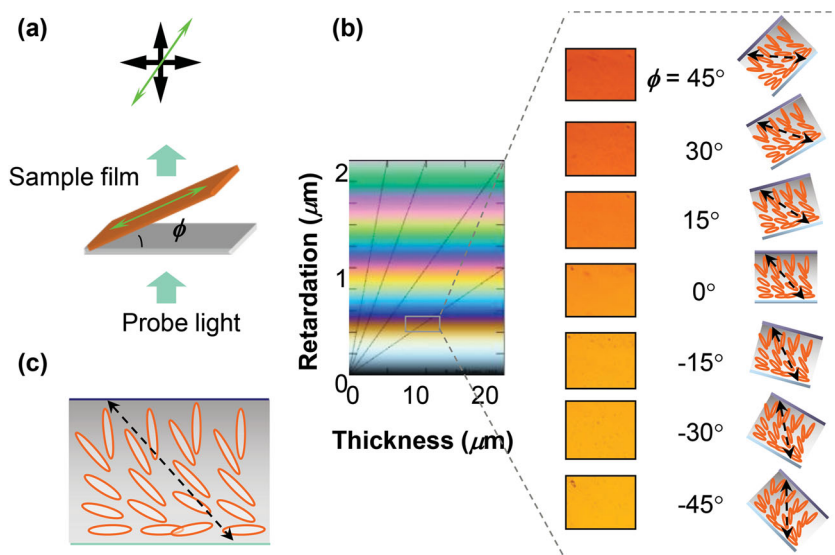


Figure 3. a) Schematic illustration of the experiment setup, b) polarizing optical images of the change in interference color of the transmitted light through the PE50D50 film (thickness of $5\ \mu\text{m}$) between two crossed polarizers, and c) schematic illustration of the splay alignment of azobenzene moieties in the film. The black arrows and green arrows indicate the direction of optical axes of the crossed polarizers and the rubbing direction, respectively. The black-dashed arrows indicate the average alignment of azobenzene moieties in the film. ϕ is the angle between horizontal and the film surface.

from the direction parallel to the incident direction of the probe light to the perpendicular direction. In other words, the average alignment of azobenzene moieties in the film is parallel to the incident direction of the probe light when ϕ is -45° , while perpendicular to it when ϕ is 45° . It is consistent with the splayed alignment illustrated in Figure 3c, and further confirms the photoinduced reorientation of the azobenzene moieties in surface A.

Photoinduced bending behavior of the PE50D50 film is showed in Figure 4b,c, when the film was heated to a temperature above its T_g . The *trans-cis* photoisomerization of azobenzene moieties upon UV light irradiation can induce the LC to isotropic phase transition, accompanying with the reduction of the molecular size and anisotropic alignment ordering of azobenzene moieties, which provides the driving force for the photoinduced contraction or expansion in the CLCP films. Furthermore, since the strong absorption of azobenzene moieties to 366-nm light leads the occurrence of the phase transition only in the irradiated surface, and the asymmetric contraction or expansion of the films results in the photoinduced bending upon UV light irradiation.^[18] The splayed alignment, namely, the homeotropic alignment in surface A together with the homogeneous alignment along the rubbing direction in surface B leads to the different photoinduced bending directions, as illustrated in Figure 4d. When surface A faced to the UV light irradiation, an expansion in the surface region is generated due to the homeotropic alignment of the azobenzene moieties normal to the surface,

giving rise to the bending along the light irradiation direction. On the other hand, in the case of the homogeneous surface (surface B) acting as the irradiated surface, UV-light-induced contraction in the surface region led to the bending toward the light source (Figure 4d). This photoinduced deformation behavior is similar with the acrylate-based hybrid films prepared by a cell with a homeotropic-anchoring layer on the one side and a planar-anchoring layer on the other side.^[19] In addition, the temperature of the films in the observation of the photoinduced bending behavior was high enough to induce the *cis-trans* back isomerization, as a result the film reverted to the flat state without visible light irradiation although correspondingly slowly.

4. Conclusions

We have demonstrated that the azobenzene CLCP films with the poly(oxyethylene) backbone can be prepared by in situ long-wavelength photoinitiated cationic polymerization, in which the radical photoinitiator together with the cationic initiator initiates the free-radical-promoted cationic polymerization. Simultaneously with the photopolymerization, the photoinduced reorientation of the azobenzene moieties in the irradiated surface was achieved upon exposure to unpolarized light at 436 nm, leading to the splayed alignment in the CLCP films. The splayed alignment, including the homeotropic alignment in the irradiated surface formed during the photopolymerization and the anisotropic homogeneous alignment along the rubbing direction in the other surface, was confirmed by the POM observation, polarized ATR-IR spectroscopy, and the change in interference color.

The photoinduced bending behavior with opposite bending directions of the splayed films was observed: when the homeotropic surface faced to the unpolarized UV light irradiation at 366 nm, the film bent along the irradiation direction of the incident light, while the homogeneous surface acted as the irradiated surface, the film bent toward the light source. The bent film reverted to its initial flat state upon heating with or without exposure to unpolarized visible light at $>545\ \text{nm}$. It is suggested that the expansion in the homeotropic surface and the contraction in the homogeneous surface, resulting from the photochemical changes in both of molecular size and alignment order of azobenzene moieties lead to the photoinduced bending along the irradiation direction and

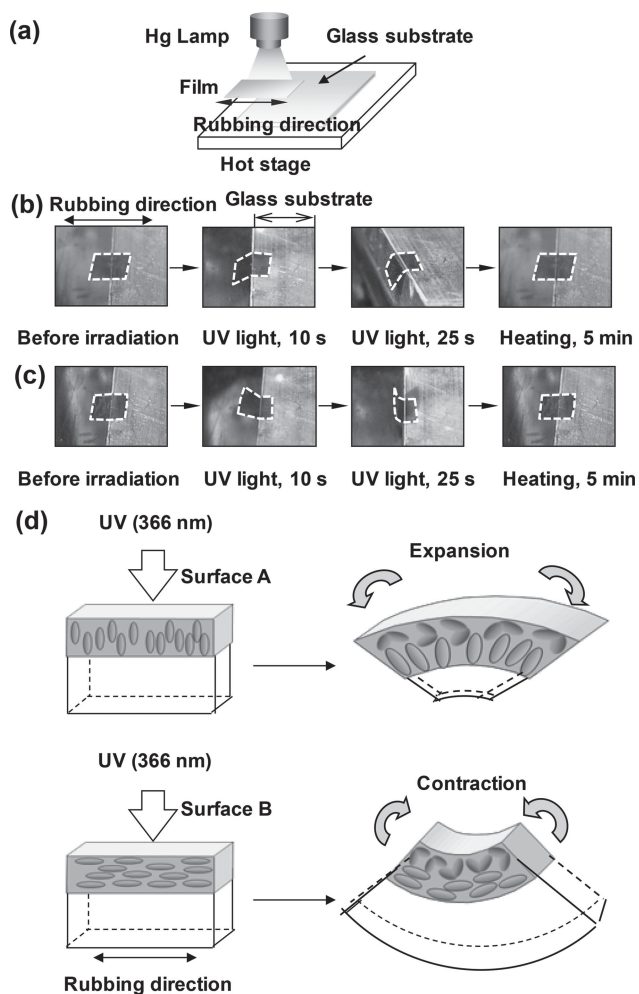


Figure 4. a) Schematic illustration of the experimental setup, and photographs of the photoinduced bending behavior of the PE50D50 film with b) surface A and c) surface B facing to the UV light irradiation. When heated to 120 °C, the initial flat film bent along and toward the irradiation direction of the incident light, respectively, after exposure to UV light at 366 nm (24 mW cm⁻²), and the bent film reverted to the initial state by heated at the same temperature for 5 min. Size of the film: 3 mm × 3 mm × 10 μm. The dotted line shows the shape of the PE50D50 film, which indicates the deformation of the film. d) Schematic illustration of plausible mechanism of the photoinduced bending behavior of the CLCP film with surface A and surface B facing to the UV light irradiation.

toward the light source, respectively. The azobenzene CLCP films with various alignment modes leading to diversified photoinduced bending behavior are promising materials for the applications of optics, photonics, programmable structures, force actuators, and artificial muscles.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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