Macromolecular Journals

Synthesis of a Photoresponsive Liquid-Crystalline Polymer Containing Azobenzene

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The synthesis of an oriented liquid-crystalline photoresponsive polymer, prepared by polymerization of mono- and di-acrylates, both of which contain azobenzene chromophores, is reported. The prepared free-standing polymer film shows strong reversible photoinduced deformation upon exposure to unpolarized UV light at 366 nm, as a result of an optically induced isomeric change of the azobenzene moieties in the polymer network. The synthesis process is relatively simple and more efficient compared to conventional ones, and can be used to synthesize other liquid-crystalline photoresponsive polymers. The use of this photoresponsive polymer film as an optical high-pass/low-pass switch under UV or natural light irradiation for a laser beam is demonstrated. This photoresponsive polymer may have applications in robotic systems, artificial muscles, and actuators in microelectromechanical systems (MEMS) and labs on chips.

Introduction

Light-driven soft actuators play an important role in many applications in a wide range of industrial and medical fields.[1–3] Recently, there has been much interest in the development of simple, efficient, and compact elastomeric polymer actuators that can be driven by light.[1–4] Liquid-crystalline elastomers (LCEs) are unique materials that combine the physical properties of both liquid crystals (LCs) and elastomers.[5,6] They exhibit a spontaneous contraction along the director axis when heated above their nematic/isotropic phase-transition temperatures because of the change in state of the orientational order. Therefore, LCEs could potentially serve as generic actuators and sensors with large amplitude and high sensitivity, e.g., as artificial muscles.[6–9] On the other hand, the change in shape of some photoisomerizable molecules or molecular chromophores inducible by light can effect powerful changes of a host material.[1,4] Therefore, it is conceivable that a photoresponsive polymer can be realized by incorporating photoisomerizable molecules or molecular chromophores into an LCE.

Azobenzene is one of the effective photoisomerizable molecules that switch its *trans*-structure to *cis*-structure when exposed to UV irradiation.[10,11] It is expected that azobenzene chromophores incorporated into various tailored LCE structures can transfer microscopic photochemical changes in the dimensions of azobenzenes to various macroscopic deformations, and these materials exhibit different deformations that have great potential for applications in robots, artificial muscles, actuators, and micromechanical devices. A new polymer system showing large photocontraction was recently demonstrated by

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using azobenzene-containing LCEs.[12–14] Upon UV light irradiation, a driving force for large shape changes of an LCE polymer that contains azobenzene chromophores is the *trans–cis* photoisomerization of the azobenzene chromophores, which induces a decrease in orientational order; the rod-like *trans*-azobenzene moieties stabilize the nematic alignment, whereas the formation of *cis*-azobezene lowers the orientational order of the LCE polymer.[15–18] Therefore, one of the strongest photoswitching effects for reversibility, speed, and simplicity of incorporation is photoresponsive liquid crystalline polymers that contain azobenzene chromophores.

One of the typical photoresponsive LCE polymers is based on crosslinked networks of acrylate or acrylate derivatives.[19–25] The constituent molecules of such liquid crystalline networks (LCNs) are orientationally ordered, owing to mesogenic groups being directed into or attached side-on to the flexible backbones. Based on this, the groups of Broer and Tabiryan developed photodeformable LCE polymers that contained azobenzene moieties.[26–31] Their salient feature is the strong coupling between the orientational order and the mechanical strain, which leads to large and reversible deformation upon photoinduction. Although photoresponsive LCN polymers based on acrylate or acrylate derivative crosslinked networks have been developed and researched, the synthetic processes are generally relatively complicated.[32–36]

In this work, we realize a new synthetic route to produce a photoresponsive LCN polymer based on crosslinked networks of monoacrylate and diacrylate that contain azobenzene moieties. We also demonstrate how to polymerize azobezene-based LCN polymers in a prealigned reaction chamber. The number of synthetic steps is reduced, which suggests that the synthesis is more suitable for a low cost and high throughput production process. The produced azobezene-based LCN polymer shows a strong photoresponse. Utilizing the action of reversible bending and restoration under alternate irradiations of UV and natural light, we demonstrate an optical switch, an important component for optical systems, for a laser beam with this photoresponsive polymer film. Experiments indicate that under UV or natural light, it effectively realizes high/low transmission of the laser beam.

Experimental Part

Materials

p-Phenetidine, 6-chlorohexan-1-ol, acryloyl chloride, tetrafluoroboric acid (HBF_4), sodium nitrite ($NaNO_2$), sodium bicarbonate ($NaHCO_3$), potassium iodide (KI), potassium carbonate (K_2CO_3), hydrochloric acid (HCl), magnesium sulfate ($MgSO_4$), ethyl acetate (EA), dimethylformamide (DMF), triethylamine, tetrahydrofuran (THF), hydroquinone, and methanol were purchased from Sigma–Aldrich Co. 4,4′-Dihydroxyazobenzene was purchased from BEAM Corp. 1,1′-Azobis(cyclohexane-1-carbonitrile) was purchased from Wako Pure Chemical.

Synthesis of 6-[4-(4-Ethoxyphenylazo)phenoxy]hexyl Acrylate (4)

As indicated in Scheme 1a, *p*-phenetidine (90 mmol) was first dissolved in a mixture of water (30 mL) and 42 wt.-% of HBF_4 (180 mmol). The solution was cooled to 0 °C. Under stirring, drops of an aqueous solution of $NaNO_2$ (90 mmol, water 45 mL) were added into the solution to generate the diazonium salt. After the resulting mixture was stirred for 20 min, 120 mL of an aqueous solution of phenol (110 mmol) and K_2CO_3 (110 mmol) was slowly added, and the mixture was stirred for 3 h at 0 °C. The pH of the resulting mixture was adjusted to 3 by adding HCl. The precipitate was collected by suction filtration, followed by extraction with ethyl acetate. The organic layer was dried with anhydrous $MgSO_4$. After evaporation of the solvent, the residue was purified by column chromatography (silica gel, eluent: ethyl acetate/*n*-hexane with a 1:1 volume ratio) to give 4-hydroxy-4′-ethoxyazobenzene (**2**) (yield ratio: 90%).

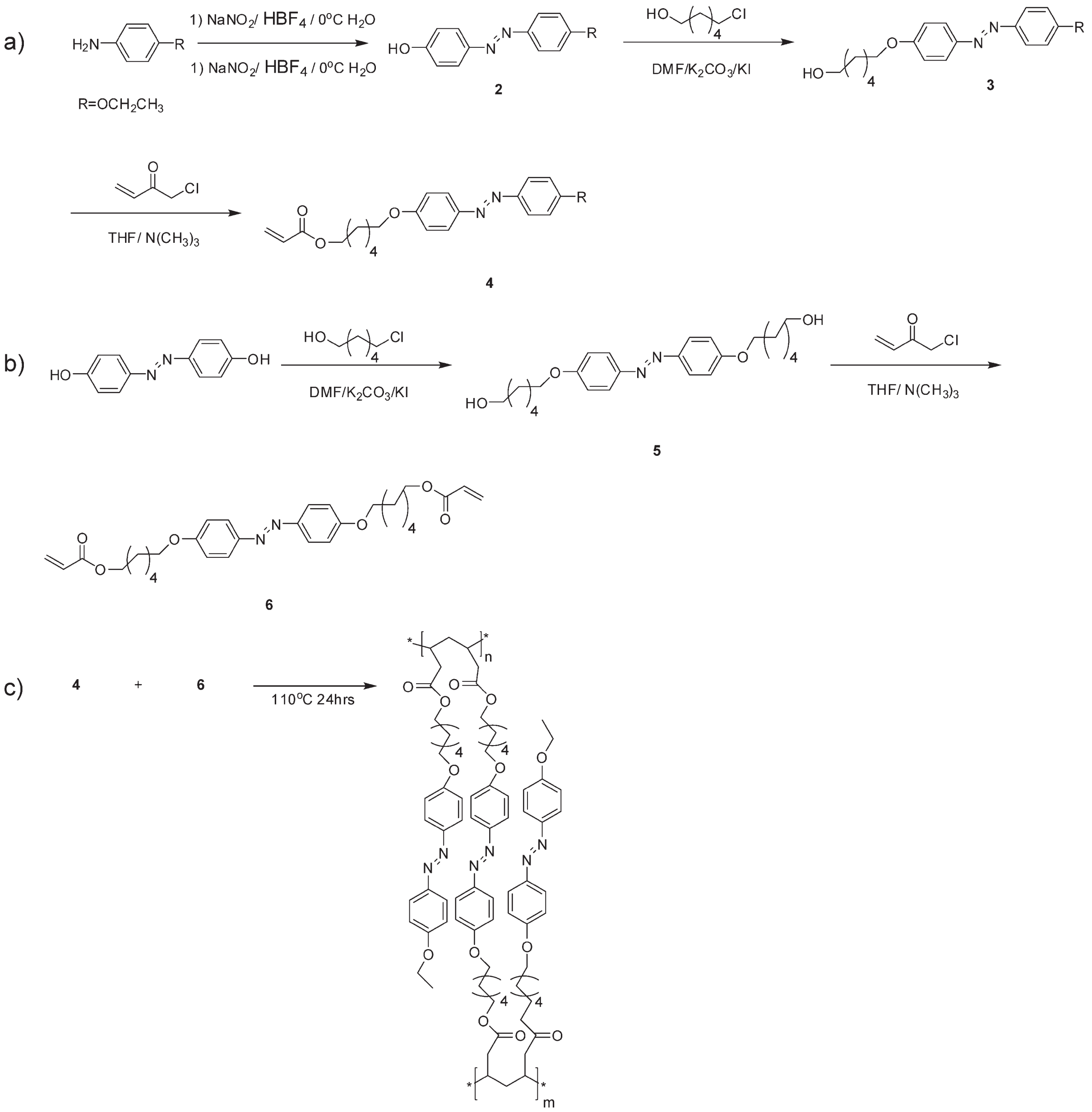
Compound **2** (100 mmol), 6-chlorohexan-1-ol (120 mmol) and K_2CO_3 (120 mmol) were dissolved in DMF (60 mL). A trace amount of KI was added, and the solution was heated with stirring at 120 °C for 6 h. The reaction mixture was poured into a large excess of water (1 000 mL) and the precipitated solid was collected and dried under vacuum. The crude product was extracted with ethyl acetate, and the organic layer was dried with anhydrous $MgSO_4$. After evaporation of the solvent, the resulting solid was recrystallized from ethanol to give 4-(6-hydroxyhexyloxy)-4′-ethoxyazobenzene (**3**) (yield ratio: 80%).

Compound **3** (20 mmol), triethylamine (8.0 mL), and a trace amount of hydroquinone were dissolved in THF (60 mL). The resulting solution was cooled to 0 °C. Under stirring, drops of acryloyl chloride (60 mmol) were added to the solution under a nitrogen atmosphere, and the reaction mixture was stirred at room temperature for 26 h. After an aqueous solution of $NaHCO_3$ was added, the mixture was extracted with ethyl acetate, and the organic layer was dried with anhydrous $MgSO_4$. After evaporation of the solvent, the residue was purified by column chromatography (silica gel, eluent: chloroform). The resulting solid was recrystallized from ethanol to give 6-[4-(4-ethoxyphenylazo)phenoxy]hexyl acrylate (**4**) (yield ratio: 74.7%), ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.87$ (dd, 4H), 7.00 (dd, 4H), 6.42 (d, 1H), 6.14 (dd, 1H), 5.83 (dd, 1H), 4.20 (t, 2H), 4.13 (m, 2H), 4.05 (t, 2H), 1.83 (m, 2H), 1.76 (m, 2H), 1.5 (m, 2H), 1.48 (m, 2H), 1.44 (t, 3H).

MS (MALDI-TOF) *m/z* calcd. for $[M+H]^+$ 397.2, found 397.2.

Synthesis of 4,4′-Di(6-(acryloxy)hexyloxy)azobenzene (6)

As indicated in Scheme 1b, 4,4′-dihydroxyazobenzene (50 mmol), 6-chlorohexan-1-ol (130 mmol), and K_2CO_3 (130 mmol) were dissolved in DMF (50 mL). A catalytic amount of KI was added and the mixture was refluxed at 120 °C for 20 h. After the reaction mixture was cooled to room temperature, 800 mL of water was added. The precipitate was collected, dried, and then extracted with a mixed solvent of THF and chloroform (1:1 volume ratio).



Scheme 1. a) Synthetic route for 6-[4-(4-ethoxyphenylazo)phenoxy]hexyl acrylate (**4**). b) Synthetic route for 4,4′-di(6-(acryloxy)hexyloxy)azobenzene (**6**). c) The formation of an LCN through the polymerization of monomer and crosslinker.

The organic layer was dried with anhydrous $MgSO_4$. After evaporation of the solvent, the crude product was purified through recrystallization in a mixed solvent of THF and methanol (5:4 volume ratio) to give 4′-bis(6-hydroxyhexyloxy)azobenzene (**5**) (yield ratio: 79%).

A mixture of compound **5** (20 mmol), triethylamine (20 mmol), and a trace amount of hydroquinone were dissolved in dehydrated THF (500 ml), and the resulting solution was cooled to 0 °C. With stirring, 70 mmol of acryloyl chloride in dehydrated THF (60 ml) was added to the solution. The mixture was first stirred at 0 °C for 4 h, followed by stirring at room temperature for 24 h. The reaction mixture was quenched by pouring into water to remove unreacted acryloyl chloride. The target product was extracted from the solution with chloroform. The chloroform layer was dried with anhydrous $MgSO_4$. After the solvent was removed, the obtained yellow solid was purified by silica gel column chromatography (eluent: chloroform/ethyl acetate with a volume ratio of 1:1) and recrystallized from methanol to give 4,4′-di(6-(acryloxy)hexyloxy)-azobenzene (**6**) (yield ratio: 74%). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.86$ (dd, 4H), 6.98 (dd, 4H), 6.41 (d, 2H), 6.13 (dd, 2H), 5.82 (dd, 2H), 4.18 (t, 4H), 4.04 (t, 4H), 1.84 (m, 4H), 1.73 (m, 4H), 1.5 (m, 8H).

MS (MALDI-TOF) *m/z* calcd. for $[M+H]^+$ 523.2, found 523.2.

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Preparation of LCN Films

The LCN films were prepared by the polymerization of 6-[4-(4-ethoxyphenylazo)phenoxy]hexyl acrylate (**4**) as the monomer and 4,4′-di(6-(acryloxy)hexyloxy)azobenzene (**6**) as the crosslinker, with a molar ratio of 85:15, containing 2 mol-% of a thermal initiator 1,1′-azobis(cyclohexane-1-carbonitrile). The thermal polymerization was carried out in a glass cell (as the reaction chamber) coated with polyimide layers that had been physically aligned by a rubbing machine to align the LC mesogens. The powdered mixture of monomer, crosslinker, and thermal initiator was heated to 90 °C to melt. The molten viscous liquid mixture was pushed to the entrance edge of the glass cell, and the molten liquid flowed into the cell by capillary force to completely fill the chamber. The polymerization process was carried out at a temperature of 110 °C and maintained for 24 h. As the polymerization completed, a free-standing film, 5 μm or 20 μm in thickness depending on the gap in the glass cell, was obtained by opening the cell and detaching the film from the glass substrates.

Photoinduced Reversible Shape-Change Behavior of LCN Films

A free-standing film on a glass substrate was placed on a hot stage. In order to reach an elasticity needed for sensitive deformation, the LCN film was heated to a temperature 10 °C above its glass transition temperature, T_g (about 56 °C, measured by differential scanning calorimetry, DSC N-650). The bending behavior of the film was induced by exposure to a UV light source (wavelength: 366 nm; power: 2.0 mW · cm^{-2}; Omnicure S2000 UV/Vis Spot curing system, EXFO Electro-Optical Engineering Inc). The restoring behavior was triggered by switching off the UV light. The bending and restoring behavior of the thin film was recorded by a digital camera (Sony, DSC-F505).

Laser Beam Switch

This experiment was carried out by using a Uniphase 1107P laser (wavelength: 633 nm, max power: 4.0 mW) as the source beam and a Coherent field max II laser power meter as detector. The LCN film was placed in the beam path as a switch. The temperature of the film and the UV light source were the same as described above.

Characterization Methods

UV-vis absorption spectra were taken with a U3010 spectrophotometer. For the measurement of UV-vis absorption spectra, the azo moieties were dissolved in chloroform and diluted to a concentration of 10^{-4} M. ^{1}H NMR spectra were recorded in $CDCl_3$ solutions with a Bruker Mercury300 spectrometer using tetramethylsilane (TMS) as the internal reference. Mass spectra (MS) were taken with a Bruker Daltonics Ultraflex III MALDI TOF/TOF Mass Spectrometer. The alignment of the LCE film was determined by measuring the transmission of a polarized laser with respect to the angle between the polarization direction and the rubbing direction. A film of 5 μm thickness was placed between a polarizer and the laser power meter (Coherent field max II. When the polarization angle was changed, the intensity of the light from the laser source (Uni-phase 1107P. 633 nm; 4 mW) transmitted through the polarizer and the film was measured with the laser power meter.

Results and Discussion

In this work, the synthesis of LC monomers of acrylate that contained azobenzene moieties, by using *p*-phenetidine as the starting compound, included three steps, as mentioned in the experimental section. The synthesis of this asymmetric acrylate monomer started with the preparation of diazonium salts through diazotization by adding HBF_4 in water with the aid of $NaNO_2$. The resultant diazonium salt was further oxidized with phenol to give 4-hydroxy-4′-ethoxyazobenzene (**2**). Using this prepared phenoxide, 4-(6-hydroxyhexyloxy)-4′-ethoxyazobenzene was obtained by Williamson synthesis by adding KI and K_2CO_3 to a DMF solution of **2**. The nucleophilic substitution of halides with phenoxides led to 4-(6-hydroxyhexyloxy)-4′-ethoxyazobenzene (**3**). Esterification of **3** was carried out by reacting with acryloyl chloride in a basic THF solution to give 6-[4-(4-ethoxyphenylazo)phenoxy]hexyl acrylate (**4**), the monomer.

In previous works, the synthesis of crosslinkers of azobenzene-containing diacrylates have been complicated,[32–36] and generally involved more than five steps, thus leading to longer time, more complex reaction conditions, and lower yield. In this work, the preparation of a symmetrical crosslinker started by reacting 4,4′-dihydroxyazobenzene, which is commercially available, with an excess amount of 6-chlorohexan-1-ol by a Williamson reaction to give 4,4′-bis(6-hydroxyhexyloxy)azobenzene (**5**). Esterification of **5** with acryloyl chloride gave 4,4′-di(6-(acryloxy)hexyloxy)azobenzene (**6**). According to our synthesis route, only two steps are needed. Therefore, the synthesis process is greatly simplified, the time is reduced, and the production efficiency is increased.

From ^{1}H NMR spectra (Figure 1) and MS measurement, the structures and molecular weights of the synthesized monomer and crosslinker are consistent with those of 6-[4-(4-ethoxyphenylazo)phenoxy]hexyl acrylate (**4**) and 4,4′-di(6-(acryloxy)hexyloxy)azobenzene (**6**), respectively.

The free radical polymerization reaction process is shown in Scheme 1c. The olefinic bonds of acrylate groups were opened by the initiation of a thermal initiator, and then polymerized through chain addition to form long molecular chains. The crosslinker has two olefinic groups, which serve as connections between polymer chains, crosslinked networks were thus formed during the polymerization. The incorporated mesogenic groups were attached side-on to the flexible backbone as side groups. The mesogens have to

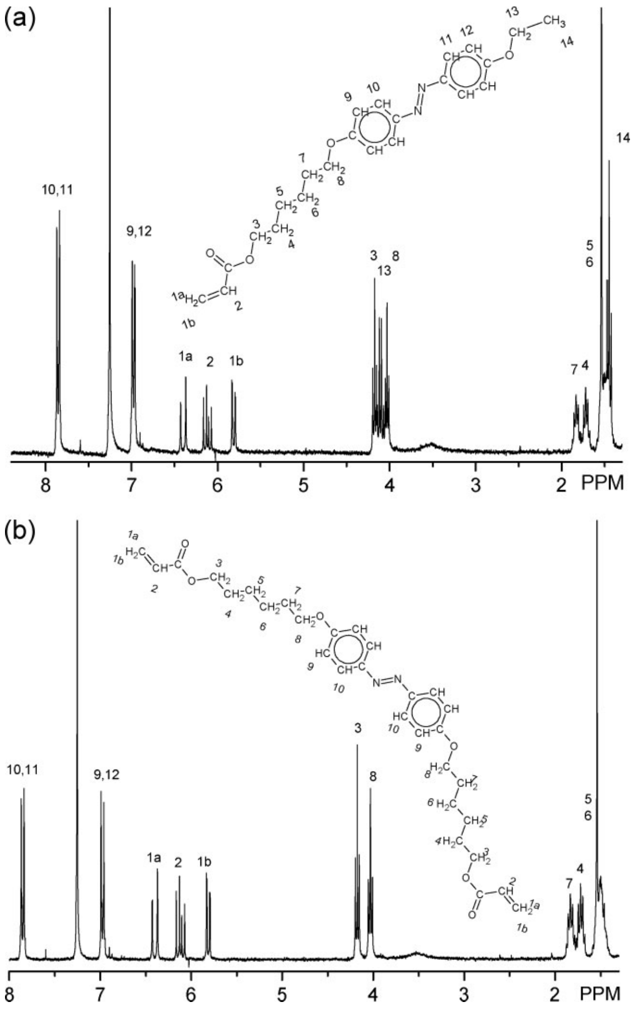

Figure 1. a) ^{1}H NMR spectrum of monomer 6-[4-(4-ethoxyphenylazo)phenoxy]hexyl acrylate (**4**). b) ^{1}H NMR spectrum of crosslinker 4,4′-di(6-(acryloxy)hexyloxy)azobenzene (**6**).

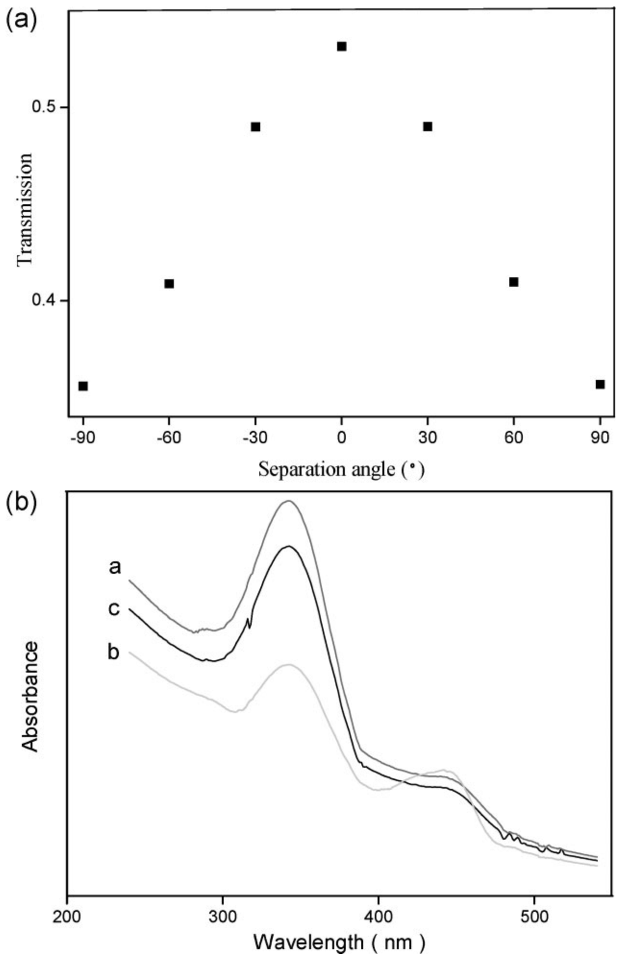

Figure 2. a) Transmission of a polarized laser through an LCN film with various angles between the polarization direction and the rubbing direction. Intensity of the polarized laser was 3.6 mW. b) UV-Vis absorption spectra of the azo moieties dissolved in chloroform (curve a), after UV light irradiation (curve b), and then after vis light irradiation (curve c).

be aligned in order to exhibit the properties of LCN polymers. The polymerization was carried out in a chamber that was precoated with rubbed polyimide alignment layers. The alignment layer assisted to align the mesogens when the monomer and crosslinker were melted under heating so that they could be polymerized in an aligned state.

To determine the alignment of the LCN films, the transmission of a polarized laser through the film with different polarization angles was measured, as shown in Figure 2a. The transmission varied with different polarization angle. The transmission reached a maximum when the polarization was parallel to the rubbing direction, and a minimum when the polarization was perpendicular to the rubbing direction, which indicates notable alignment character. The change in the UV-vis absorption spectra of the synthesized azobenzene-containing LC polymer dissolved in chloroform upon UV and natural light irradiation is shown in Figure 2b. The azobenzene chromophores exhibited an absorption maxima at about 343 nm and a weak band at about 440 nm, which were related to π–π^* and n–π^* transition bands of the *trans*-azobenzene and *cis*-azobenzene, respectively (curve a).[37,38] Upon UV light irradiation, the intensity of the π–π^* transition band at 343 nm decreased and that of the n–π^* transition band at 440 nm increased (curve b), which indicates that the *trans* was isomerized to the *cis*. After natural light irradiation, the *cis* recovered to the *trans* isomer (curve c). The structure change between the *trans* and *cis* isomer of the azobenzene chromophores upon UV and natural light irradiation is shown in Figure 3a.

Figure 3b shows the observed photoinduced bending behavior of an LCE film using the experimental setup shown in Figure 3c. The LCE film exhibits bending and restoration behavior upon alternate irradiations of UV light and natural

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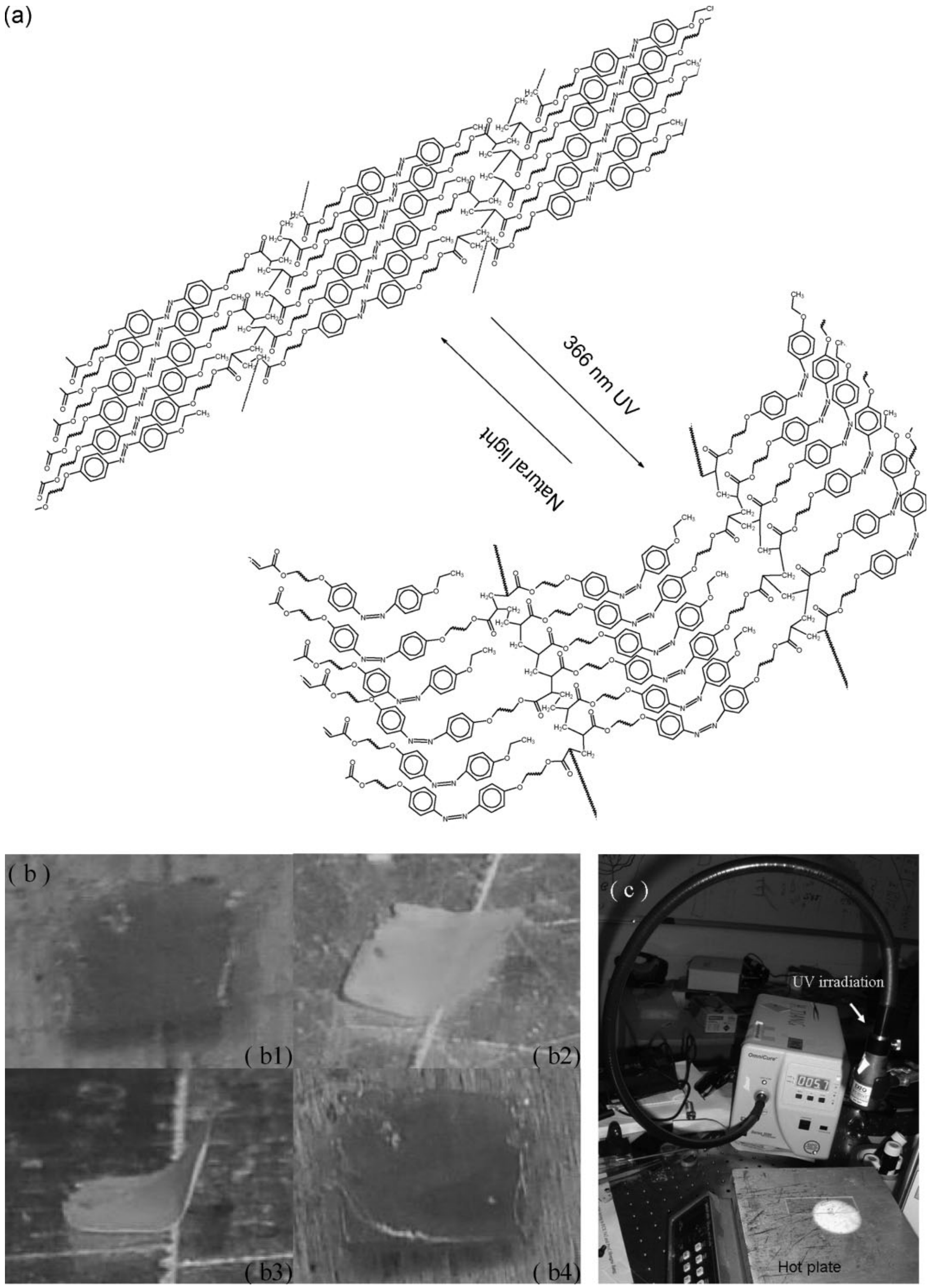

Figure 3. a) Schematic illustration of the shape deformation of an LC polymer film caused by a *trans* to *cis* change of azobenzene chromophores. b) Photographs that exhibit the photoinduced bending and unbending behavior of the film. The flat film (b1) bent toward the irradiation direction of the incident UV light after exposure (366 nm; 2.0 mW · cm^{-2}) (b2, b3), and flattened again upon irradiation of natural light (b4). Size of the film: 10 mm × 10 mm × 20 μm. The rubbing direction was parallel to the surface of the glass slide and perpendicular to the edge of the glass slide. c) The experimental setup for observing the photoinduced behavior of the film.

light. Figure 3b1 shows the film before photoirradiation. Figure 3b2 and Figure 3b3 show how the film bent after exposure to 366 nm light with the intensity of 2.0 mW · cm^{-2} for 10 and 35 s. It was found that the film bent toward the irradiation direction of the incident light along the rubbing direction. It was also observed that after the film was exposed to UV light for about 35 to 50 s, the bending reached a maximum, as shown in Figure 3b3; no further bending was observed upon further photoirradiation. After natural light irradiation, the bent film completely reverted to its initial flat state as shown in Figure 3b4. The maximum bending was near 85°. This photoinduced bending and unbending behavior could be repeated without apparent fatigue by alternate irradiations of UV and natural light.

The synthesized LCE is a crosslinked network of polymer chains that incorporate mesogenic groups as side groups attached to the flexible backbone; it has orientationally ordered constituent molecules, as shown in Scheme 1c. Its salient feature is strong coupling between the orientational order and the mechanical strain. Changing the orientational order gives rise to internal stress, which leads to strains and changes the shape of the sample. UV light irradiation induces the *trans*–*cis* isomerization of the azobenzene moieties: the alignment order and the size of the azobenzene moieties are reduced, which leads to the contraction of the polymer network, as shown in Figure 3a. Because the azobenzene moieties can strongly absorb the light at around 360 nm, and UV light has limited penetration depth into the polymer matrix,[1] the majority of the UV light was absorbed by the azobenzene moieties near the surface. Thus the contraction occurs only at the surface of the film, while in the bulk of the film the *trans*-azobenzene moieties basically remain unchanged. This causes the bending toward the incident light. The azobenzene moieties are preferentially aligned along the rubbing direction of the alignment layers, so that the decrease in size and alignment order of the azobenzene moieties leads to surface contraction just along this direction. Therefore, the bending of the film is anisotropically induced, only along the rubbing direction of the alignment layers. After the irradiation of natural light, the azobenzene moieties isomerize from *cis* to *trans*, and the LC polymer molecules revert to their initial states. Thus the bent film reverts to the initial flat shape.

We also demonstrated an optical high-pass/low-pass switch for a laser beam by using an LCE film as the switch, as illustrated in Figure 4a. An LCE film was placed in the laser beam path and the actuating UV light was irradiated perpendicular to the laser beam. The LCE film was initially set flat and the beam path was open so that the optical output reached its maximum. As the film was exposed to UV light, the LCE film bent towards the light source, blocked the laser beam, and decreased the optical output. By alternating between the actuating UV light and natural light, we were able to control the optical output, as shown in Figure 4b. The ratio between the high-pass and low-pass transmission was about 20:1. The switch showed good repeatability after several tens of cycles.

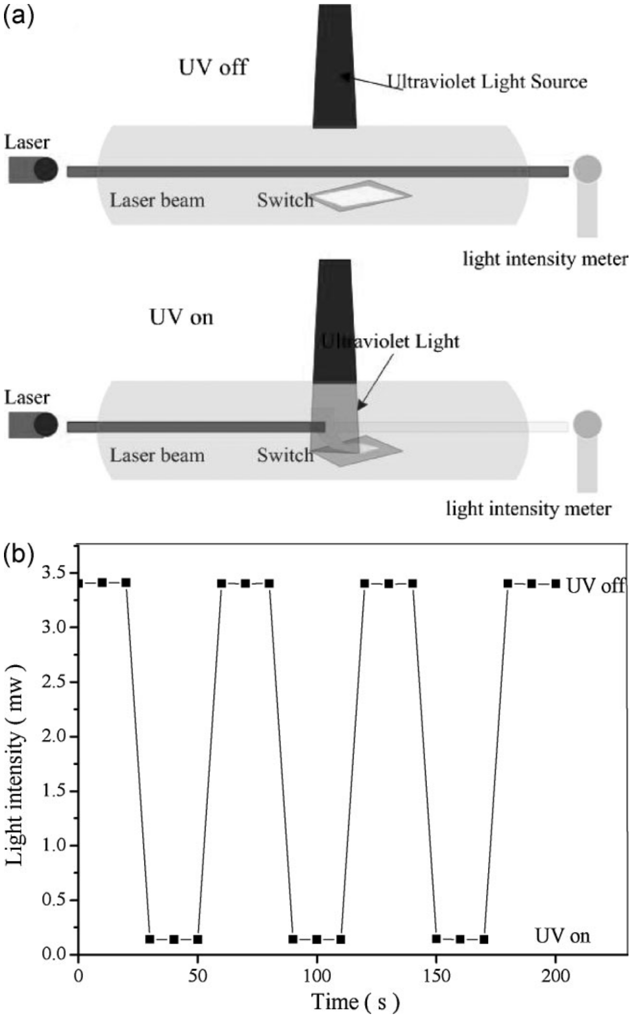

Figure 4. a) Schematic illustration of a light-driven high-pass/low-pass optical switch of a laser beam. b) Power output when the optical switch was on and off alternately. The transmitted light was recorded every 10 s.

Conclusion

We report the synthesis of an LCE that contains azobenzene moieties. The synthesized LC monoacrylate and diacrylate were used to prepare anisotropic networks through cross-linking polymerization. The prepared LCE films showed photoinduced bending and unbending behavior, and the bending in the films was anisotropically induced. Compared to previous works, the synthesis was relatively simple, the consumed time was much shortened, the process conditions were simplified, the production efficiency was increased, and the cost could be lowered. The method reported here can be used to synthesize other derivatives or homologues of azobenzene-containing acrylate monomers and crosslinkers with different side-chain groups or spacer lengths, which can influence the material

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characteristics such as the formation of an LC phase, rigidity of the polymer chains, and the T_g of the polymers.[39]

The azobenzene chromophore is a unique molecular switch that exhibits a clear and reversible photo-isomerization that induces a reversible change in geometry of azo-materials. Azo-materials can convert light energy directly into mechanical work without the aid of batteries, electric wires, or gears. Utilizing the LCE films, we demonstrated a light-driven optical switch for a laser beam. It effectively realized high/low transmission of the laser beam under the actuation of UV or natural light. Azo-materials can offer a promising potential as photomechanical materials in artificial muscles, micro-robots, micro-actuators in micro-electromechanical systems (MEMS), and labs on chips.

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