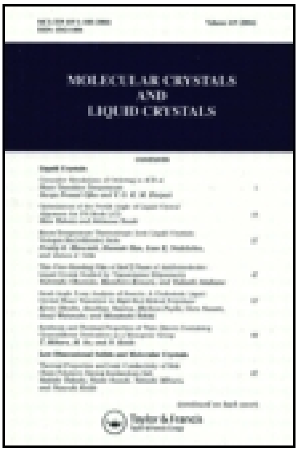

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Synthesis of Crosslinked Liquid-Crystalline Polymer Brushes on Flexible Polymer Films Toward Photomobile Materials

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Synthesis of Crosslinked Liquid-Crystalline Polymer Brushes on Flexible Polymer Films Toward Photomobile Materials

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We prepared crosslinked azobenzene liquid-crystalline polymer brushes on flexible polymer films by surface-initiated atom transfer radical polymerization and a subsequent crosslinking reaction. Reversible isomerization of azobenzene moieties was observed in the crosslinked films upon irradiation with UV and visible light. Upon exposure to linearly polarized UV light, the films bent slightly along the polarization direction of light toward an actinic light source. After turning off the UV light, the films maintained the bent shape, and then reverted to the initial form by irradiation with visible light. We have successfully developed a novel photomobile material with crosslinked azobenzene liquid-crystalline polymer brushes.

Keywords Azobenzene; liquid crystal; photomobile materials; polymer brush

1. Introduction

Azobenzene liquid-crystalline (LC) polymers have been investigated for the purpose of wide applications such as optical switching, image storage, and holographic recording [1–5]. Recently, photomechanical properties of crosslinked azobenzene LC polymers have been of great interest in the fields of polymer materials and photochromic molecules since large and anisotropic deformation can be generated by photoisomerization of azobenzene moieties [6–8]. A light-driven plastic motor, which can convert light energy directly into a continuous rotation, has been achieved in composite films containing a photoactive layer [9]. The composite films are prepared by attaching a crosslinked azobenzene polymer film on a polymer substrate with adhesive [9–11]. However, due to a weak bonding of the interface between the photoactive layer and the polymer substrate, the photoactive layer was peeled from the substrate by repeated expansion and contraction upon photoirradiation. If the photoactive layer is strongly bound to the substrate with chemical bonds, photomobile polymer materials with a good mechanical property, high processability and durability might be fabricated.

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Polymers prepared by surface-initiated polymerization are covalently bound to the substrate [12]. In particular, atom transfer radical polymerization (ATRP) has been widely employed for the formation of polymer brushes since it is applied to a wide variety of monomers. Moreover, polymers with a low poly-dispersiveness can be obtained under mild conditions compared with living anionic and cationic polymerizations. Previously, most of polymer brushes have been explored to tailor surface properties of solid substrates in various aspects such as colloidal stability [13,14], biocompatibility [15–17], and wetness [18,19]. Functional polymer brushes changing a physical property reversibly by an external stimulus have been reported. For instance, materials possessing a lower critical solution temperature (LCST) exhibit different wetting properties above and below the LCST temperature [19–21]. Polymer brushes with pH sensitivity tethered on a porous polymer membrane regulate the rate of water permeation through porous membranes by a change in pH condition [22,23]. Seki *et al.* demonstrated some interesting properties in polymer brushes with azobenzene mesogens prepared by ATRP; the azobenzene mesogens are in-plane aligned perpendicular to the direction of the polymer main chain [24]. In crosslinked LC polymer films, the initial alignment of azobenzene mesogens is important to control the bending directions upon UV light irradiation. In films with homogeneously aligned mesogens, the crosslinked azobenzene polymers have bent just along the alignment direction of the mesogens toward a light source by UV irradiation [25]. In polydomain films, in which the alignment direction of mesogens is uniform in each domain but macroscopically random, the direction of the bending can be selected by changes in the polarization direction of an incident light [26]. If azobenzene polymer brushes directly grow on a flexible polymer substrate by surface-initiated ATRP, we can develop novel photomobile polymer materials that are composed of covalently bound photoactive and substrate layers with no adhesive. In this study, we prepared flexible polymer films with crosslinked azobenzene LC polymer brushes by surface-initiated ATRP and a subsequent crosslinking reaction, and investigated their photoinduced bending behavior.

2. Experimental Methods

2.1. *Materials*

Polybutadiene (**PB**) ($M_w \sim 420{,}000$, *trans*-1,4-**PB** (55%); *cis*-1,4-**PB** (36%); vinyl (9%), Aldrich) was selected as a flexible substrate since it is easy to prepare thin films with a flat surface and contains unsaturated moieties which enable surface modification by a simple reaction. **PB** was purified by reprecipitation from tetrahydrofuran (THF) solutions in a large excess of methanol and hexane. Commercial reagents were used without further purification; they were formic acid (90%, Wako Pure Chemical Industries Ltd.), hydrogen peroxide (90%, Kanto Chemical Co., Inc.), 2-bromo-2-methylpropionic acid (Aldrich), 1,1,4,7,10,10-hexamethyltriethylenetetramine (**HMTETA**, Aldrich), formaldehyde aqueous solution (37%, Wako Pure Chemical Industries Ltd.), hydrochloric acid (35%, Kanto Chemical Co., Inc.). Copper (I) bromide (Cu(I)Br, Wako Pure Chemical Industries Ltd.) was purified as described in the literature [27]. Anisole was refluxed over sodium and then fractionated. An azobenzene monomer with a hydroxy group, 9-{4-[4′-(9-hydroxynonyloxy)phenylazo]phenoxy}nonyl acrylate, was synthesized according to the reported procedure similar to the literature (Fig. 1a) [28]. The azobenzene monomer exhibited

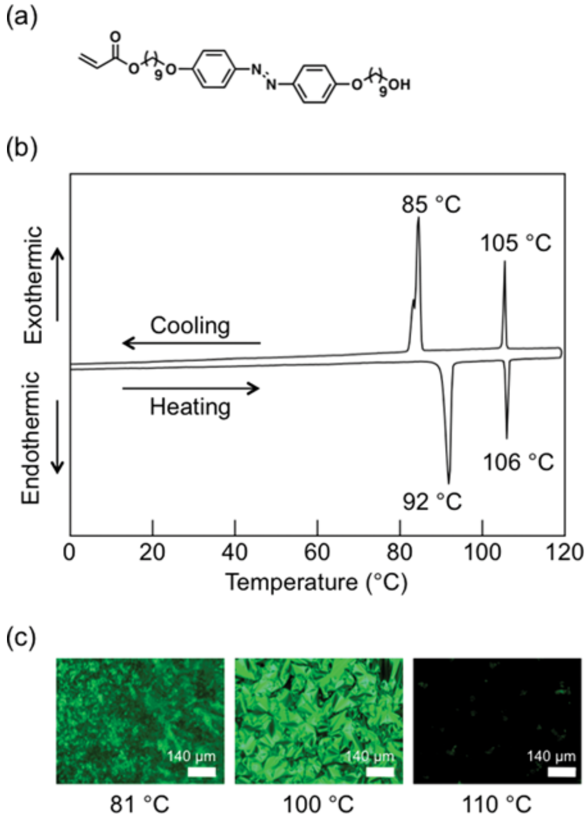

Figure 1. The chemical structure (a), a DSC thermogram (b), and polarizing optical micrographs (c) of an azobenzene monomer used in this study. (Figure appears in color online.)

an LC phase at 92–106°C and 105–85°C on heating and cooling at a scanning rate of 1°C/min, respectively (Fig. 1b and 1c).

^{1}H NMR ($CDCl_3$, δ, ppm): 1.23–1.84 (m, 34 H), 3.65 (t, $J=7$ Hz, 2H), 4.03 (t, $J=7$ Hz, 4H), 4.16 (t, $J=7$ Hz, 2H), 5.81 (dd, $J=10$, 2 Hz, 1H), 6.12 (dd, $J=17$, 10 Hz, 1H), 6.40 (dd, $J=17$, 2 Hz, 1H), 6.98 (m, 4H), 7.86 (m, 4H) Anal. Calcd. For $C_{28}H_{38}N_2O_3$: C, 74.63; H, 8.50; N, 6.22% Found: C, 74.35; H, 8.59; N, 6.23%.

2.2. *Preparation of Polymer Films with Initiators*

As shown in Figure 2, polymer substrates with initiators on the surface were prepared by two-step reactions: double bonds in **PB** were first substituted by epoxy groups, and then 2-bromoisobutyl groups as initiators were introduced on the surface of the epoxidized **PB** (**EPB**) film. We added stoichiometric amounts of formic acid and hydrogen peroxide to a **PB** solution in chloroform [29]. The **PB** solution was washed with water until its pH value became neutral, and dried over magnesium sulfate. The obtained **EPB** was dissolved in THF by stirring overnight. The **EPB** films were prepared onto naflon® tapes with a barcoater, and air-dried at room temperature. Next, 2-bromoisobutyl groups were connected on the surface of the **EPB** films by a gas-phase reaction of 2-bromo-2-methylpropionic acid, which is

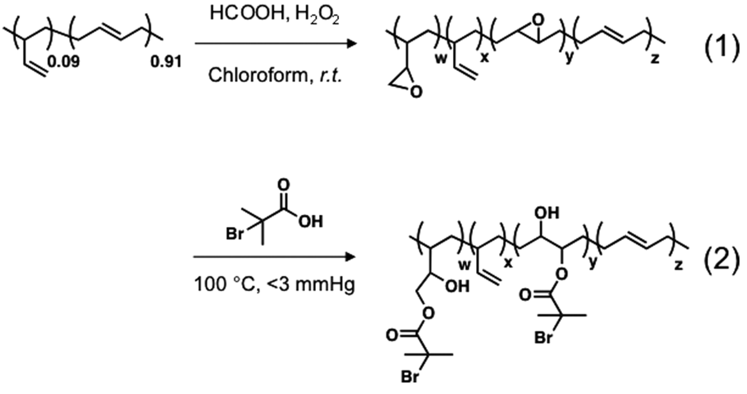

Figure 2. Synthetic routes of flexible polymer substrates with initiators on the film surface.

abbreviated as **EPB-Br** [30]. After the reaction, the **EPB-Br** films were washed thoroughly with 2-butanone and methanol.

2.3. *Synthesis of Azobenzene Polymer Brushes on Flexible Polymer Films*

Azobenzene polymer brushes were prepared on the **EPB-Br** films by surface-initiated ATRP. After an azobenzene monomer (0.26 g, 0.47 mmol), Cu(I)Br (4.7 mg, 0.033 mmol), **HMTETA** (8.6 µL, 0.032 mmol), anisole (4 mL) and **EPB-Br** films (size: 25 mm × 25 mm) were mixed in a flask under argon atmosphere, the mixture was degassed by a freeze-pump-thaw method and was sealed under vacuum. The reaction was carried out in a preheated oil bath at 80°C for 48 h. The obtained films were washed with THF and methanol.

2.4. *Characterization*

The thermodynamic properties of an azobenzene monomer were analyzed with a differential scanning calorimeter (DSC, SII NanoTechnology, EXSTAR6000, DSC6220) at a scanning rate of 1°C/min. At least three scans were performed to check the reproducibility. ^{1}H-NMR spectra were recorded with tetramethylsilane as an initial reference for a chemical shift in chloroform-d_3 using an FT-NMR spectrometer operating at 300 MHz (JEOL, Lambda-300) and 500 MHz (JEOL, JNM-LAMBDA WinLambda) for the monomer and polymers, respectively. FT-IR spectra were measured at room temperature with an FT-IR spectrometer (JASCO, FTIR-6100). The mesomorphic properties were examined with a polarizing optical microscope (POM, Olympus. BX50F4) equipped with a hot stage (Mettler, FP-90, FP-82) at a scanning rate of 1 or 10°C/min for a monomer and a polymer brush, respectively. The transmittance of the probe light through a pair of crossed polarizers with the film between them was observed. Isomerization of the azobenzene moieties was measured at room temperature in film by UV-Vis spectroscopy upon irradiation with UV and visible light from a 500 W high-pressure mercury lamp (USHIO) through glass filters (Asahi Techno Glass, UV light: $\lambda = 366$ nm, IRA-25S, UV-D36A, UV-35; visible light: $\lambda > 540$ nm, IRA-25S, Y-52). A digital camera (Omron, VCHRM20Z, VC1000) was used to record pictures upon irradiation with UV and visible light from UV-LED (Keyence, UV-400, UV-50H) and Vis-LED irradiators (CCS, PJ-1505-2CA), respectively.

3. Results and Discussion

Figure 3 shows the synthetic routes of crosslinked azobenzene LC polymer brushes on **PB** films. First, **PB** was epoxidized by addition of formic acid and hydrogen peroxide in a chloroform solution. By NMR spectroscopy, several peaks attributed to olefin moieties were observed at 4.9 and 5.4-5.6 ppm in ^{1}H NMR, and 114, 129-130 and 142 ppm in ^{13}C NMR, respectively. After the reaction, the peaks assigned to epoxy moieties appeared at 2.7 and 2.9 ppm in ^{1}H NMR, and 57 and 58 ppm in ^{13}C NMR, respectively [31]. The degree of epoxidation (DE) in **EPB** was estimated from the integration of the epoxy moieties (I_{epoxy}) to that of the olefin moieties (I_{olefin}) by the following equation.

$$\mathrm{DE}(\%) = \frac{I_{epoxy}}{I_{epoxy} + I_{olefin}} \times 100 \tag{1}$$

DEs calculated from ^{1}H- and ^{13}C-NMR spectra were 29 and 27%, respectively.

Next, initiators were linked on the **EPB** films deposited on naflon® tapes. Addition of 2-bromoisobutyl groups was ascertained by FT-IR measurements. The peaks corresponding to ester groups at 1735 cm^{-1} (C=O stretching) revealed the immobilization of the initiators on the **EPB** films (Fig. 4). A strong peak appeared at ~3400 cm^{-1}, indicating that hydroxy groups were simultaneously formed in **EPB-Br** films by the gas-phase reaction.

We grew azobenzene polymer brushes with hydroxy groups on **EPB-Br** films by surface-initiated ATRP. The **EPB-Br** films became yellow after polymerization. The IR spectrum clearly exhibited four peaks assigned to the in-plane vibration and the out-of-plane bending of the benzene rings as shown in Figure 4. For comparison,

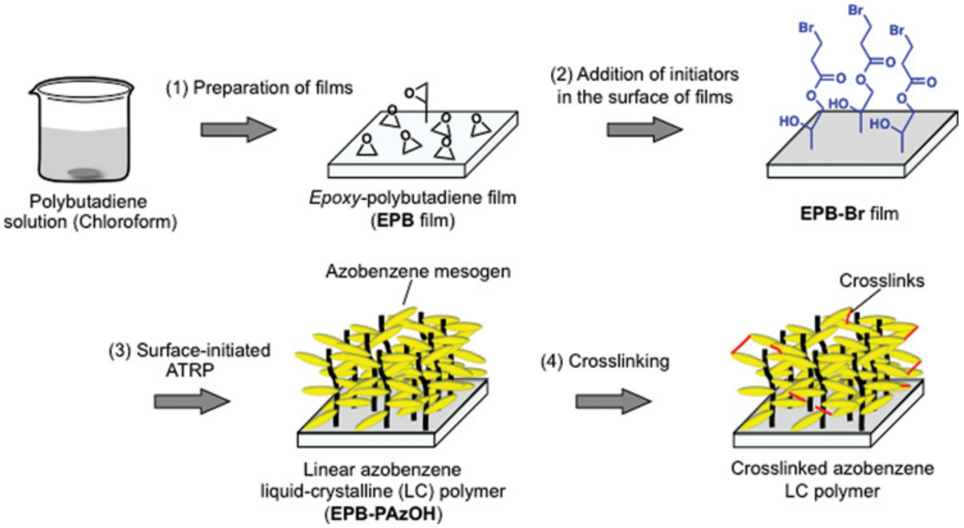

Figure 3. Synthesis of crosslinked azobenzene liquid-crystalline (LC) polymer brushes on a flexible polymer film by surface-initiated atom transfer radical polymerization (ATRP) and a subsequent crosslinking reaction. (Figure appears in color online.)

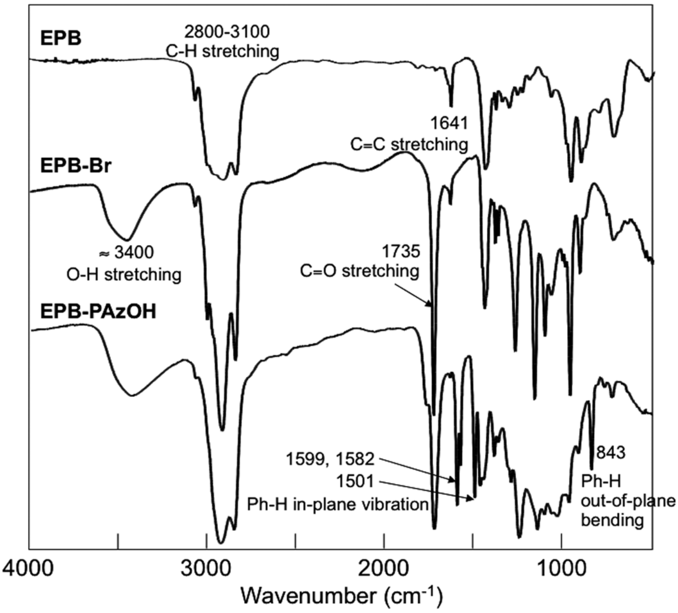

Figure 4. The IR spectra of epoxidized polybutadiene (**EPB**) films, **EPB** films with initiator (**EPB-Br**) and the films with azobenzene polymer brushes (**EPB-PAzOH**).

the **EPB** films without initiators were placed in the same reaction system. The color of the **EPB** films remained unchanged after polymerization. Therefore, the azobenzene polymer brushes were found to be prepared from the sites of the initiator on the surface of the **EPB-Br** film. The obtained films containing the azobenzene polymer brushes are abbreviated as **EPB-PAzOH**.

The LC properties were examined with a POM on heating at a rate of 10°C/min. The texture according to an LC phase was observed in the temperature range of 70~100°C (Fig. 5). The texture gradually disappeared by heating above 100°C, suggesting an LC-isotropic phase transition. However, the POM image did not become dark completely even when the sample was heated above 170°C. It is assumed that the in-plane alignment of azobenzene mesogens is stable in the polymer brushes because the main chain is covalently bound to the substrate films, and the LC-isotropic phase transition is suppressed [24,32].

Crosslinking of azobenzene polymer brushes was carried out by a formalization reaction. The reaction could link two hydroxy groups in the polymers at room temperature [33–35]. In a capped bottle, the **EPB-PAzOH** films were suspended with two small beakers containing 37% formaldehyde aqueous solution ($HCHO_{aq.}$, 10 ml) and 35% hydrochloric acid aqueous solution ($HCl_{aq.}$, 10 ml), respectively. The reaction was performed by exposure to mixed vapor of $HCHO_{aq.}$ and $HCl_{aq.}$ for 48 h at 40°C. After the reaction, the films were washed with sodium hydrogen carbonate solution and water and dried under vacuum for over a day at room temperature. While ester groups were expected to form after the exposure, the IR spectrum of the film remained unchanged. To confirm the formation of crosslinks in the films with azobenzene polymer brushes, a model reaction was performed. A small amount of the azobenzene monomers with a hydroxy group was put in a capped bottle under

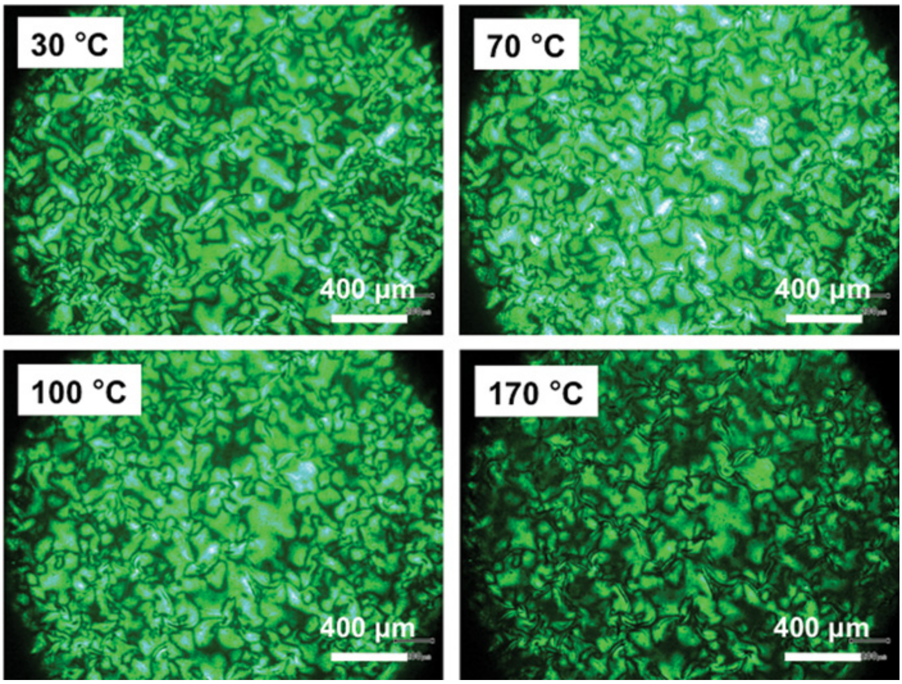

Figure 5. Polarizing optical micrographs of **EPB-PAzOH** films at various temperatures. (Figure appears in color online.)

the same condition as that of the azobenzene polymer brush. The new peaks at 3.5 and 4.6 ppm appeared in the ^{1}H-NMR spectrum after the reaction, indicating the formation of a dimer. Thus, we consider that crosslinks are formed in the azobenzene polymer brushes as well as the monomers.

Optical properties were explored in the films with crosslinked LC azobenzene polymer brushes by UV-Vis spectroscopy. It was found that reversible *trans*-*cis* isomerization of azobenzene mesogens was induced in the films with the

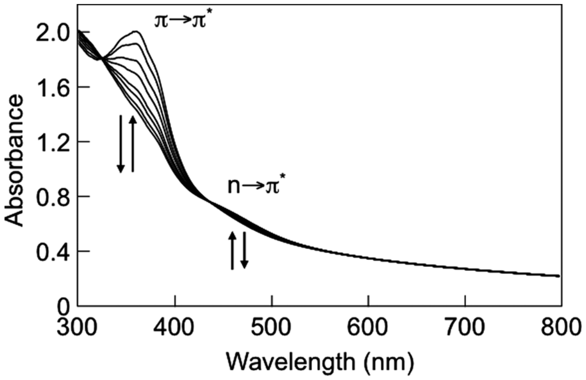

Figure 6. A change in UV-Vis absorption spectra of the crosslinked azobenzene polymer brushes by irradiation with UV (366 nm, 2 mW/cm^2) and visible (>540 nm, 4 mW/cm^2) light.

crosslinked polymer brushes upon irradiation with UV and visible light as shown in Figure 6. To investigate the photoinduced motion of the film with crosslinked azobenzene polymer brushes, a piece of the film (size: 4 mm × 4 mm) was placed on the tip of an aluminum rod (length: 3 mm), in which was fixed on a hot stage heated at 70°C (Fig. 7). Exposure to unpolarized UV light induced no bending motion of the films. On the other hand, it was found that the films slightly bent along the polarization direction of an incident light toward an actinic light source upon exposure to polarized UV light. The bent films were restored to the initial form by irradiation with visible light. The photomobile behavior was first observed in the polymer films with crosslinked LC polymer brushes. Distinct bending can be expected by further optimization in thickness and crosslinking density of the photoactive layer.

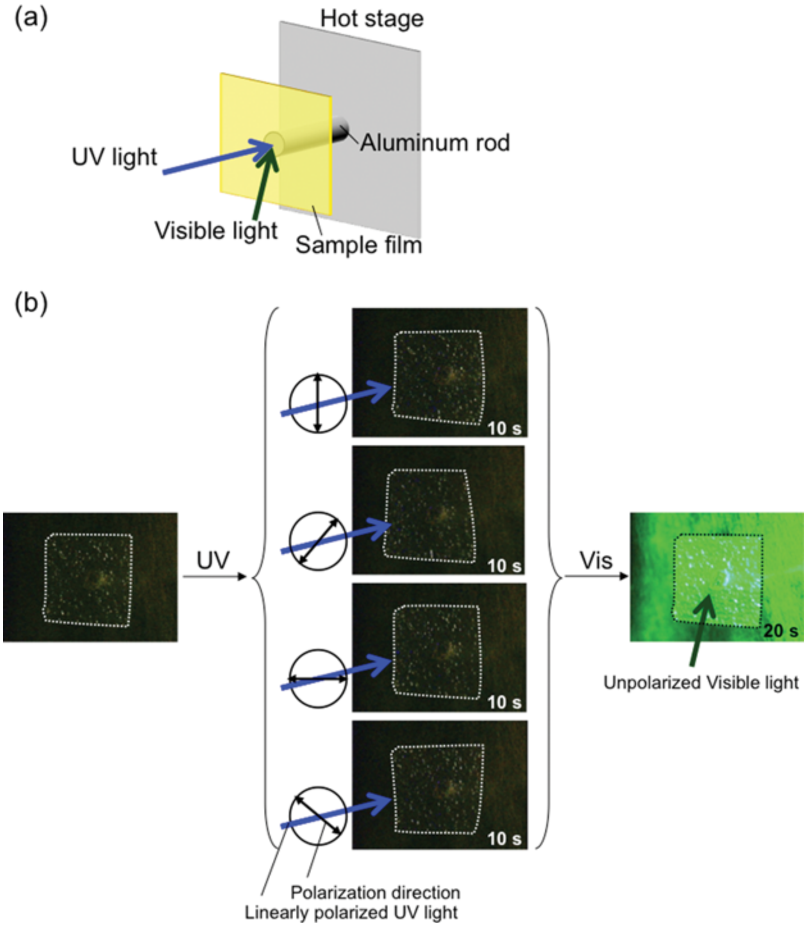

Figure 7. Schematic illustration of the experimental setup (a) and photoresponsive behavior of the films with the crosslinked azobenzene polymer brushes upon irradiation with UV (365 nm, 14 mW/cm^2) and visible (530 nm, 12 mW/cm^2) light on a hot stage at 70°C (b). (Figure appears in color online.)

4. Conclusions

The azobenzene polymer brushes with hydroxy groups were prepared on a flexible polymer film by surface-initiated ATRP and were crosslinked by exposure to mixed vapor of formaldehyde and hydrogen chloride. The azobenzene polymer brushes on the polymer films exhibited an LC phase. In the crosslinked films, reversible isomerization of azobenzene moieties was observed upon irradiation with UV and visible light. Upon exposure to polarized UV light, the films bent slightly along the polarization direction of light toward an actinic light source. After turning off the UV light, the films maintained the bent shape, and then reverted to the initial form by irradiation with visible light.

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