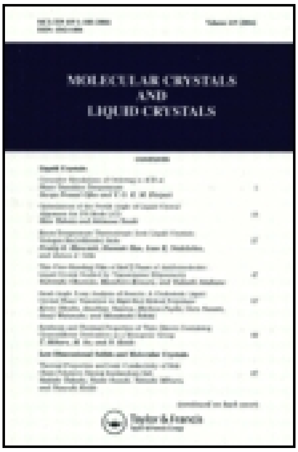

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Analysis of Photoinduced Change in Properties on Macroscopic Motion of Crosslinked Azobenzene Liquid-Crystalline Polymers

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Analysis of Photoinduced Change in Properties on Macroscopic Motion of Crosslinked Azobenzene Liquid-Crystalline Polymers

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Crosslinked azobenzene liquid-crystalline polymer films have been prepared by in-situ *photopolymerization, and their photoinduced changes in birefringence and stress on macroscopic motion were investigated. Upon exposure to UV light, the film bent toward an actinic light source along the rubbing direction, and the bent film also reverted to the initial flat state after exposure to visible light at room temperature. Moreover, the birefringence simultaneously decreased and the stress was generated upon UV irradiation. These results indicate that the molecular alignment in the film becomes disordered by* trans-cis *photoisomerization of the azobenzene moieties and the resultant contraction of the film generates the stress.*

Keywords photomobile material; crosslinked liquid-crystalline polymer; azobenzene; change in molecular alignment; generated stress

Introduction

Crosslinked liquid-crystalline (LC) polymers have attractive mechanical properties because mesogens are attached to the polymer backbones. When unidirectionally aligned, crosslinked LC polymers exhibit a large contraction along the molecular alignment of the mesogens by external stimuli such as heat, electricity, and magnetic field [1–3]. Finkelmann *et al.* achieved a photoinduced contraction of crosslinked LC polymer films containing azobenzene by 20%, which is caused by the *trans-cis* photoisomerization of the azobenzene moieties [4]. In addition to the contraction, various movements of crosslinked LC polymers have been reported. In our previous work, we first succeeded in reversible bending of crosslinked LC polymer films containing azobenzene moieties by photoirradiation [5, 6]. Furthermore, we could control bending directions of the crosslinked LC polymer films by irradiation with linearly polarized light [7]. Broer *et al.* have demonstrated a large photoinduecd bending behavior and a large amplitude coiling motion based on the twisted molecular alignment configuration [8]. Recently, the plastic films coated with the crosslinked LC polymer layer showed novel three-dimensional movements such as inchworm-walk, flexible robotic-arm, and rotary motions [9, 10]. In addition, we evaluated the photomechanical properties of the crosslinked LC polymer films with a different

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*Corresponding author. E-mail: tikeda@res.titech.ac.jp (Tomiki Ikeda); ashishid@res.titech.ac.jp (A. Shishido) content of an azobenzene moiety. It has been found that the stress generated in the films with an azobenzene content of 20 mol% is 2.6 MPa, about 10 times larger than that of human muscles [11]. However, relations among changes in molecular alignment, generated stress, and macroscopic motion have not been explored yet. Particularly, effect of the photoinduced changes in properties of the azobenzene moieties on the macroscopic motion could not be detected due to high absorbance of the films. The clarification of the details of the photoinduced macroscopic motion gives an important finding in the development of the photomobile materials.

In this study, we investigated photoresponsive behavior of the film with a low content of azobenzene moieties and evaluated relations among changes in molecular alignment of the mesogens, generated stress, and macroscopic motion by the simultaneous measurement of photoinduced changes in birefringence and stress upon UV irradiation.

Experimental

Materials

Chemical structures of the compounds used in this study are shown in Figure 1. These compounds were synthesized according to the procedures similar to the previous reports [12–14].

The crosslinked LC polymer film with the azobenzene content of 5 mol% and the crosslinker content of 60 mol% were prepared by *in-situ* photopolymerization of a mixture of the compounds (**DA9AB**:**A9BZ9**:**C9A** = 5:40:55) containing 2 mol% of a photoinitiator (Ciba Specialty, Irgacure 784). First, the melt of the mixture was injected into a 20-μm thick glass cell coated with rubbed polyimide (JSR, AL1254) at 110°C, and cooled down to an LC phase. The cooling rate of the sample was 0.5°C/min. Photoirradiation was carried out at $>$540 nm (2.0 mW/cm^2) with a 500-W high-pressure mercury lamp (USHIO, UI-501HQ) through glass filters (AGC techno glass, Y-52 and IRA-25S) for 2 h. The crosslinked LC polymer film was taken off from the glass cell, and rinsed in ethyl acetate after polymerization to remove unreacted monomers, and was dried over 1 night under reduced pressure.

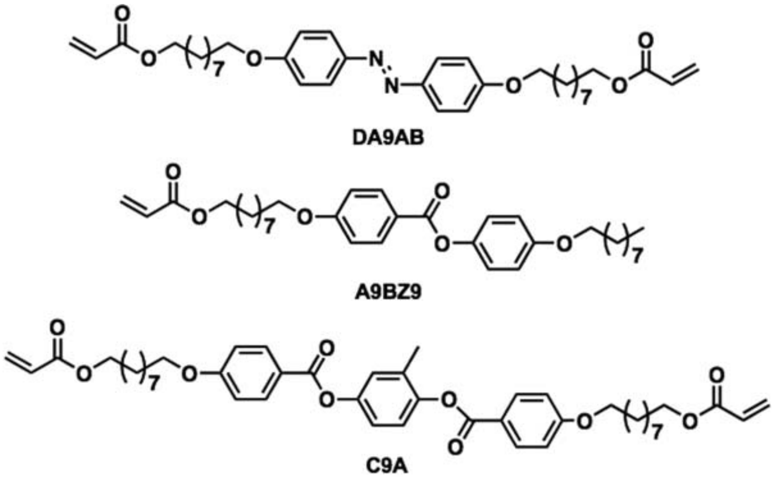

Figure 1. Chemical structures of compounds used in this study.

Characterization Methods

The thermodynamic properties of polymers were analyzed with a DSC (Seiko Instruments Inc., EXTRAR6000, DSC6220) at heating and cooling rates of 10°C/min. At least three scans were performed to check the reproducibility. The crosslinked LC polymer films were observed with a polarizing optical microscope (POM, Olympus, BH-2) at room temperature. Polarized absorption spectra of the films were measured at room temperature with a UV-Vis spectrophotometer (Jasco, V-650 with FLH-741). Photoinduced bending of the films was observed by irradiation with UV light at 365 nm (UV-LED, Keyence, UV-400) and visible light at 530 nm (CCS, PJ-1505–2CA with HLV-24GR-3W). The photographs of the photoinduced bending behavior were taken with a digital camera (Omron, VC-HRM20Z and VC1000). The experimental setup for the evaluation of the photoinduced changes in birefringence and stress in films is shown in Figure 2. The intensity of a probe beam at 633 nm from a He-Ne laser (MELLES GRIOT, 05-LHR-151) transmitted through a pair of crossed polarizers, with the film between them, was measured with a photodiode as a function of time and recorded on a computer. The photoinduced birefringence (Δn) was estimated from the change in transmittance by equation (1),

$$T = \sin^2\left(\frac{\pi d \Delta n}{\lambda}\right) \tag{1}$$

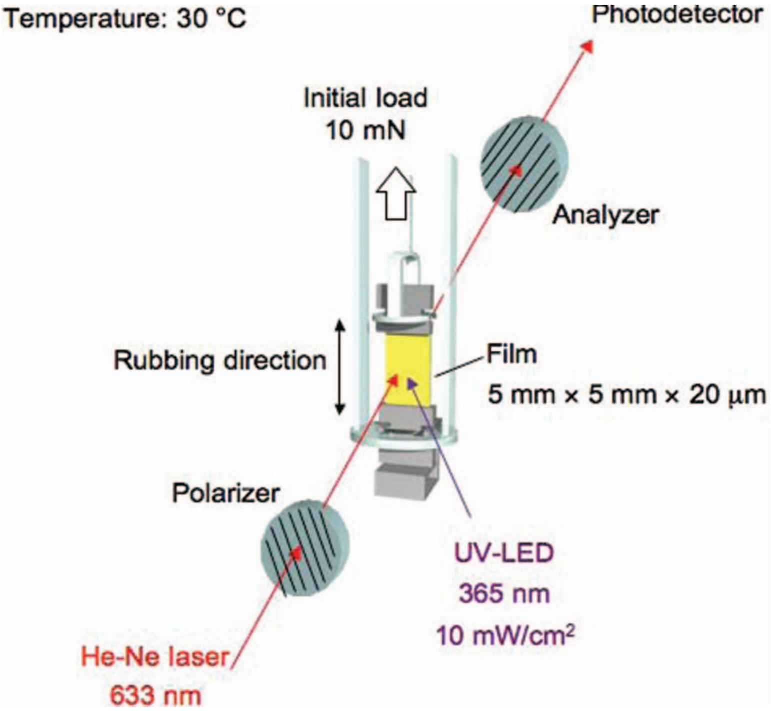

Figure 2. Schematic illustration of the experimental setup to evaluate the photoinduced change in molecular alignment and contraction of the crosslinked LC polymer film.

where d is the film thickness and λ is the wavelength of the probe beam, respectively. The generated stress of the films was measured with a thermomechanical analyzer (TMA, Shimadzu, TMA-60). A film was fixed by clamping both ends and 10 mN was added as an initial load on the film at 30°C. The direction of the initial load was parallel to the alignment direction.

Results and Discussion

Characterization of the Crosslinked LC Polymer Films

The DSC thermograms of the crosslinked LC polymer film are shown in Figure 3. It was found that the shift of the base line due to glass transition of the film appeared around room temperature.

We also evaluated a molecular alignment of the crosslinked LC polymer film with polarizing optical micrographs and polarized absorption spectra. Polarizing optical micrographs of the crosslinked LC polymer film at room temperature are shown in Figure 4. By rotating the film, a bright image was observed at ±45° with respect to the analyzer. Figure 5 shows polarized absorption spectra of the crosslinked LC polymer film at room temperature. It was found that the film showed a dichroism. Order parameter (*S*) of the film was evaluated by the following equation (2),

$$S = \frac{A_{//} - A_{\perp}}{A_{//} + 2A_{\perp}} \tag{2}$$

where $A_{//}$ and $A_{\perp}$ are the absorbance measured with light polarized parallel and perpendicular to the rubbing direction of the alignment layers, respectively. The order parameter of the film was calculated from the averaged absorbance at 400–450 nm and the value was

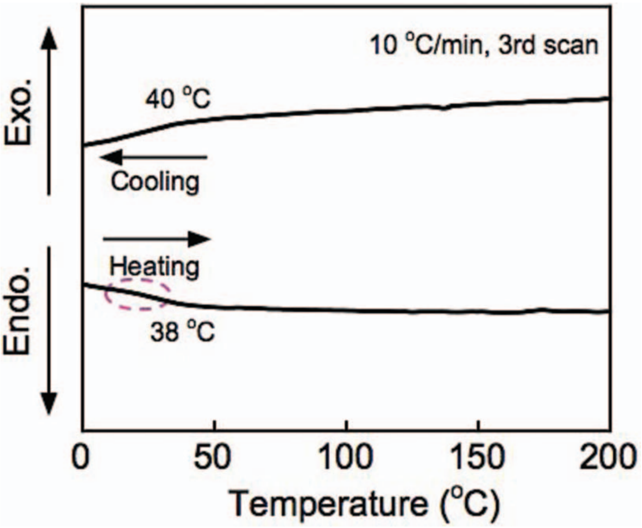

Figure 3. DSC thermograms of the crosslinked LC polymer film on the third scan at a rate of 10 °C/min.

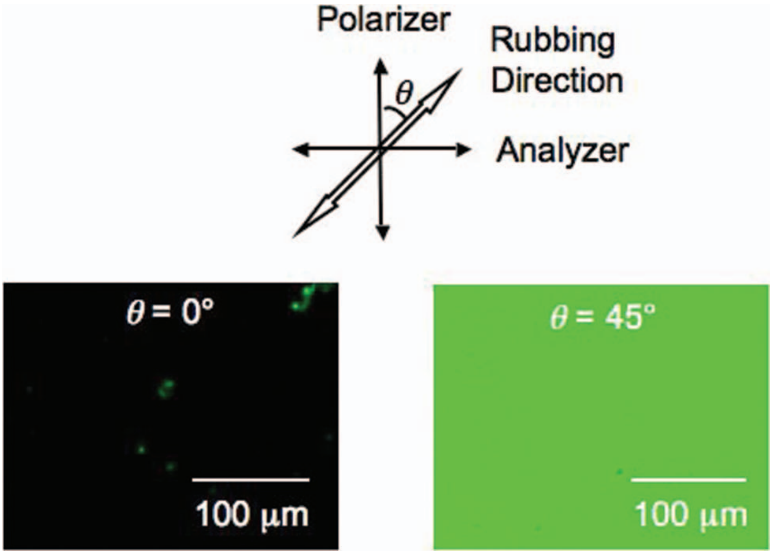

Figure 4. Polarizing optical micrographs of the crosslinked LC polymer film observed at room temperature.

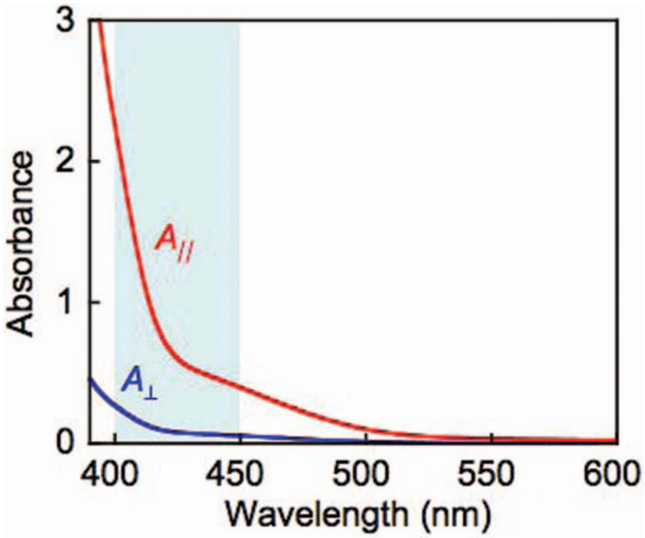

Figure 5. Polarized absorption spectra of the crosslinked LC polymer film at room temperature. $A_{//}$ and $A_{\perp}$ are the absorbance measured with light polarized parallel and perpendicular to the rubbing direction of the alignment layers, respectively.

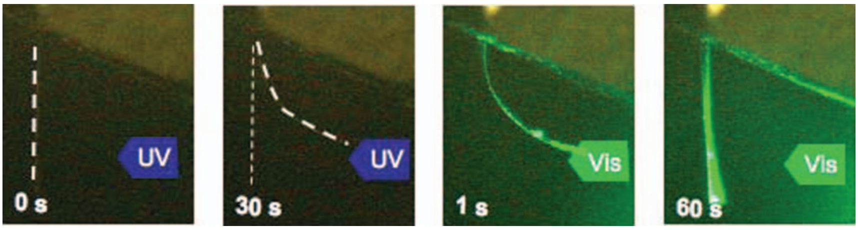

Figure 6. Photographs of the crosslinked LC polymer film exhibiting photoinduced bending upon UV and visible irradiation at 30°C. The white dashed lines show the edges of the films. Size of the films: 5 mm × 5 mm × 20 μm.

0.69. These results indicate that the azobenzene moieties are efficiently aligned along the rubbing direction in the film.

Photoinduced Changes in Birefringence and Stress on Macroscopic Motion of the Crosslinked LC Polymer Films

We observed photoinduced bending of a crosslinked LC polymer film at 30°C (Figure 6). Upon irradiation with UV light at the light intensity of 10 mW/cm^2, the film bent toward an actinic light source along the rubbing direction. The bent film also reverted to the initial state upon irradiation with visible light (25 mW/cm^2). Figure 7 shows the photographs of the film exhibiting bending and unbending behavior upon continuous irradiation with UV light. It was found that the bent film also reverted to the flat state upon continuous irradiation with UV light [11].

Next, to study the photoinduced change in molecular alignment and contraction of the crosslinked LC polymer film, we carried out simultaneous measurement of photoinduced changes in birefringence and stress. Figure 8 shows the photoinduced changes in birefringence and stress by UV irradiation (10 mW/cm^2). When the film was exposed to UV light, the birefringence decreased and the stress was generated. These results indicate that the molecular alignment in the film becomes disordered by *trans-cis* photoisomerization of the azobenzene moieties and the resultant contraction of the film generates the stress. Upon irradiation with UV light, the stress of the film reached over 1 MPa after 30 s. Previously, we have reported that the stress of the film with the azobenzene content of 100 mol% reached over 1 MPa after irradiation with UV light (25 mW/cm^2) for 5 min [15]. In such

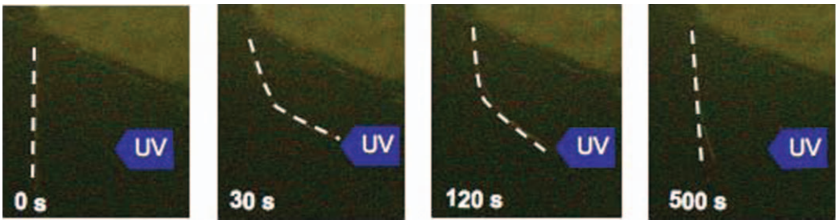

Figure 7. Photographs of the crosslinked LC polymer film exhibiting photoinduced bending and unbending behavior upon continuous irradiation with UV light. Size of the films: 5 mm × 5 mm × 20 μm.

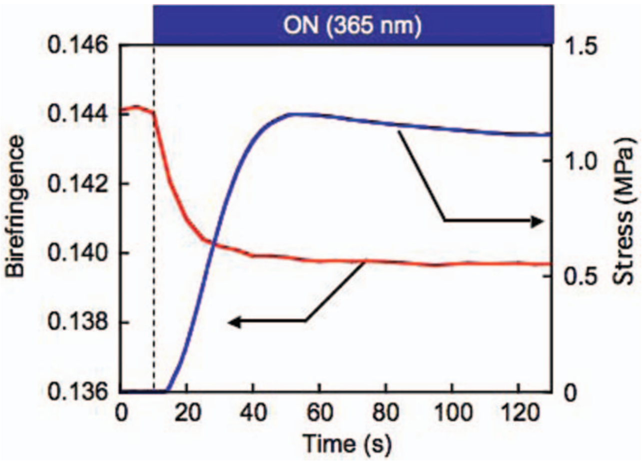

Figure 8. Photoinduced changes in birefringence and stress of the crosslinked LC polymer film by UV irradiation at 30°C.

a film, UV light is absorbed at the surface due to the high absorbance, and only the surface area contributes to the generation of the stress. It has been considered that the fast and strong mechanical response in the film with a low content of azobenzene moieties is due to the efficient change in molecular alignment of mesogens in the film at any depth. We successfully developed the photomobile materials with the fast and strong mechanical response.

Finally, we discuss the relations among photoinduced changes in molecular alignment, generated stress, and macroscopic motion of the crosslinked LC polymer film. After UV irradiation, the birefringence decreased, the stress was generated, and the film bent toward an actinic light source along the molecular alignment direction simultaneously (Figure 9). Table 1 shows the values of photoinduced changes in birefringence, generated stress, and bending angle of the crosslinked LC polymer film by UV irradiation as a function of time at 30°C. As shown in Table 1, degree of the bending and generated stress do not reach the maximum value, while the photoinduced change in birefringence is in the stationary state by photoirradiation for 20 s. It has been revealed that photoinduced bending and generation of the stress are caused by the change in molecular alignment of the mesogens. Upon irradiation with UV light, we observed the largest degree of bending in the film after 30 s when the photoinduced changes in birefringence and stress are in the stationary states. These

Table 1. The values of photoinduced changes in birefringence, generated stress, and bending angle of the crosslinked LC polymer film by UV irradiation as a function of time at 30°C.

Irradiation time (s)	Photoinduced change in birefringence ($\times 10^{-3}$)	Generated stress (MPa)	Bending angle (°)
10	3	0.2	25
20	4	0.7	35
30	4	1.1	45

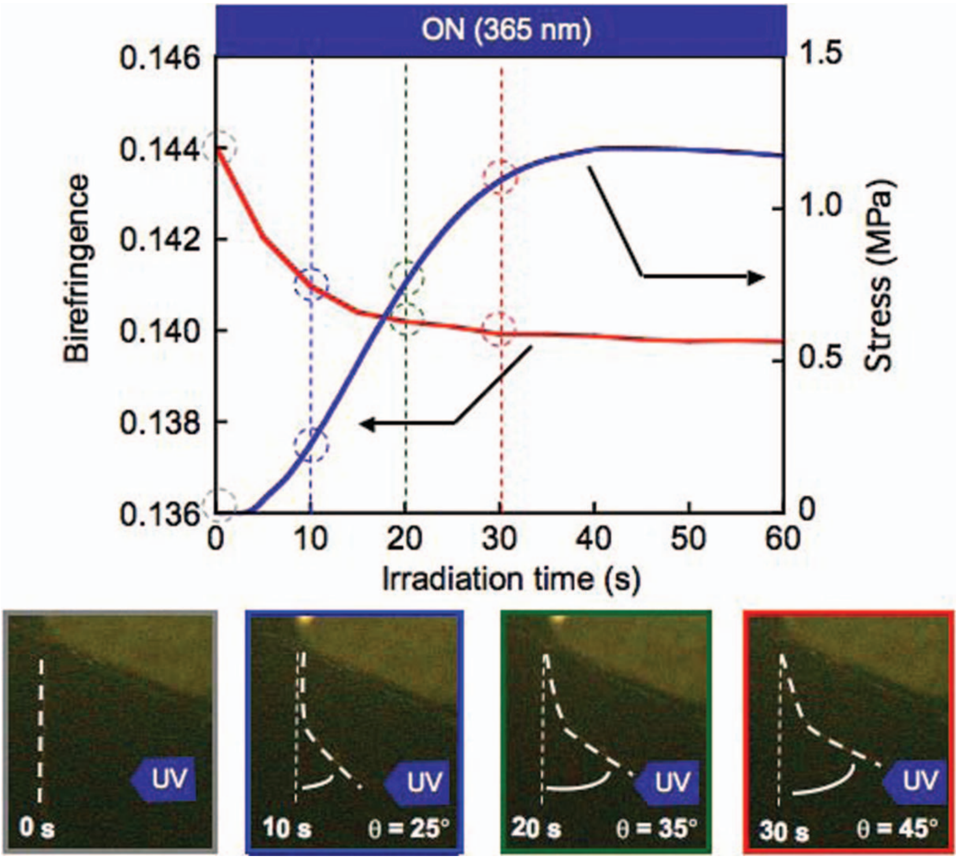

Figure 9. Photoinduced changes in birefringence, generated stress, and macroscopic motion of the crosslinked LC polymer film by UV irradiation at 30°C.

results are consistent with the photomobile processes, in which photoinduced macroscopic motion of the crosslinked LC polymer films is based on the *trans-cis* photoisomerization of azobenzene moieties, followed by the change in molecular alignment of the mesogens, and the resultant contraction of the films.

Conclusions

We prepared crosslinked LC polymer films with a low content of azobenzene moieties, and investigated their photoinduced changes in properties on the macroscopic motion. Upon irradiation with UV light, the film bent toward an actinic light source along the rubbing direction. The bent film also reverted to the initial state upon irradiation with visible light. We also evaluated the photoinduced changes in molecular alignment of the mesogens and generated stress upon UV irradiation. Simultaneous measurement of the photoinduced changes in birefringence and stress revealed that the birefringence decreased and the stress was generated, which means that the photoisomerization of the azobenzene moieties induces a change in molecular alignment and the resultant contraction of the film causes the generation of the stress.

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