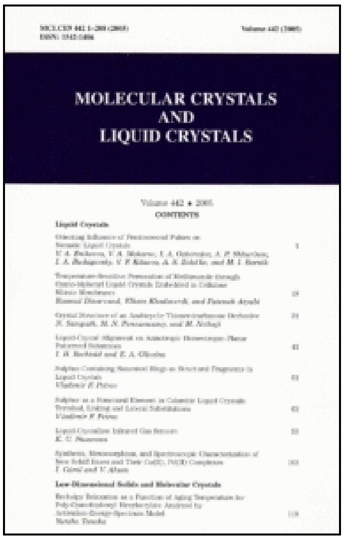

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713644168

Photoresponsive Behavior of Crosslinked Liquid-Crystalline Polymer Films with a Different Content of an Azobenzene Moiety

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To cite this Article Shimamura, Aki , Hiraoka, Tomohiro , Kondo, Mizuho , Kubo, Shoichi , Mamiya, Jun-ichi , Shishido, Atsushi and Ikeda, Tomiki(2010) 'Photoresponsive Behavior of Crosslinked Liquid-Crystalline Polymer Films with a Different Content of an Azobenzene Moiety', Molecular Crystals and Liquid Crystals, 529: 1, 53 — 59

To link to this Article: DOI: 10.1080/15421406.2010.495676

URL: http://dx.doi.org/10.1080/15421406.2010.495676

Mol. Cryst. Liq. Cryst., Vol. 529: pp. 53–59, 2010

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2010.495676

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Photoresponsive Behavior of Crosslinked Liquid-Crystalline Polymer Films with a Different Content of an Azobenzene Moiety

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Crosslinked liquid-crystalline polymer films with a different content of an azobenzene moiety were prepared by in-situ *photopolymerization, and their photoresponsive behavior was investigated. Observation of the films by polarized absorption spectroscopy and polarizing optical microscopy has revealed that the azobenzene moieties are aligned along the rubbing direction in the films. Upon irradiation with UV light, a film with 5 mol% of the azobenzene bent toward an actinic light source along the rubbing direction. The bent film reverted completely to the initial state upon irradiation with visible light. On the other hand, films with 3 and 1 mol% of the azobenzene showed no obvious bending by continuous irradiation with UV light. The bent film also reverted to the flat state upon continuous irradiation with UV light.*

Keywords Azobenzene; crosslinked liquid-crystalline polymer; *in-situ* photopolymerization; photoinduced bending

Introduction

Azobenzene, which is one of the most widely used photochromic molecules, isomerizes from a *trans* form to a *cis* form upon UV irradiation, and the produced *cis* form goes back to the *trans* form by exposure to visible light or heating. The *trans* form of the azobenzene has a rodlike shape, which stabilizes the phase structure of liquid crystals (LCs), whereas its *cis* form with a bent shape tends to destabilize the phase structure of LCs. When a small amount of the azobenzene is incorporated into LCs, a photoinduced change in alignment of mesogens from an ordered state to a disordered state can be induced isothermally by the *trans*-*cis* photoisomerization [1]. Crosslinked LC polymers have the properties of both LCs and elastomers [2].

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Finkelmann *et al.* achieved a large photoinduced contraction by using crosslinked LC polymers containing the azobenzene [3].

In our previous work, crosslinked LC polymer films containing azobenzene moieties showed reversible bending by photoirradiation [4]. Furthermore, we revealed that the photoinduced bending was strongly affected by crosslinking density [5], the order of mesogens [6], and alignment direction of mesogens [7,8] in the crosslinked LC polymer films. Recently, we have reported three-dimensional movements such as an inchworm walk and rotation with laminated films [9,10].

We assume that the bending of the crosslinked LC polymer films is based on the *trans*-*cis* photoisomerization of azobenzene moieties, followed by the change in molecular alignment, and the resultant contraction at the surface of films [4]. However, detailed bending processes have not been explored. Particularly, the change in molecular alignment of the azobenzene could not be detected due to high absorbance of the film.

In this work, we focused on the effect of the azobenzene content on the photoinduced bending behavior. Crosslinked LC polymer films with a low content of an azobenzene moiety were prepared, and their photoresponsive behavior was investigated.

Experimental

Materials

Chemical structures of compounds used in this study are shown in Figure 1. These compounds were synthesized according to the procedures similar to the previous reports [11–13].

The crosslinked LC polymer films were prepared by *in-situ* photopolymerization of a mixture of the compounds containing 2 mol% of a photoinitiator (Ciba Specialty, Irgacure 784). First, the melt of the mixture was injected into a 10-μm thick glass cell coated with rubbed polyimides (JSR, AL1254) at 110°C, and cooled down to an LC phase. The cooling rate of the sample was 0.1°C min^{-1}. Photoirradiation was carried out at >540 nm (1.0 mW cm^{-2}) with a 500-W high-pressure mercury

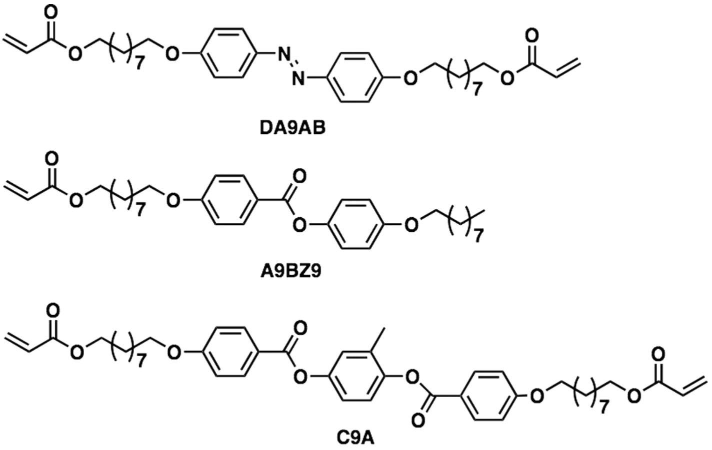

Figure 1. Chemical structures of compounds used in this study.

Table 1. Nomenclature and feed ratio of compounds

Sample	**DA9AB** (mol %)	**A9BZ9** (mol %)	**C9A** (mol %)
P5	5	95	0
P3	3	95	2
P1	1	95	4

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 cells in ethyl acetate after polymerization, and dried over 1 night under reduced pressure. To investigate the effect of the concentration of the azobenzene moiety, 1, 3, and 5 mol% of the azobenzene crosslinker were used with a non-photoresponsive crosslinker to adjust the concentration of the total crosslinking density at 5 mol%. Abbreviations and feed ratio of the samples are shown in Table 1.

Characterization Methods

The films were observed with a polarizing optical microscope (POM, Olympus, BH-2). Polarized absorption spectra of the films were measured at room temperature with an absorption spectrometer (Jasco, V-650 with FLH-741). Photoinduced bending of the crosslinked LC polymer films was observed by irradiation with UV light at 365 nm (UV-LED, Keyence, UV-400) and visible light at 530 nm (CCS, PJ-1505-2-CA with HLV-24GR-3 W). The photographs of the photoinduced bending behavior were taken with a digital camera (Omron, VC-HRM20Z and VC1000).

Results and Discussion

Molecular Alignment of the Crosslinked LC Polymer Films

A molecular alignment of the crosslinked LC polymer films was evaluated with polarizing optical micrographs and polarized absorption spectra. Polarizing optical micrographs of the crosslinked LC polymer films are shown in Figure 2. By rotating the crosslinked LC polymer films, a bright image was observed at ±45° with respect to the analyzer. Figure 3 shows polarized absorption spectra of the crosslinked LC polymer films. It was found that all the films showed a dichroism. Order parameter (S) of the films was evaluated by the following equation:

$$S = \frac{(A_{\parallel} - A_{\perp})}{(A_{\parallel} + 2A_{\perp})} \tag{1}$$

where $A_{\parallel}$ and $A_{\perp}$ are the absorbance measured with light polarized parallel and perpendicular to the rubbing direction of the alignment layers, respectively. As shown in Figure 3, the absorption maximum in the polarized absorption spectra of the crosslinked LC polymer films is located at around 370 nm due to a π-π^* transition of the azobenzene moieties. However, the absorbances of **P5** and **P3** at maximum were so large to be used for calculation that the order parameters of the films were calculated

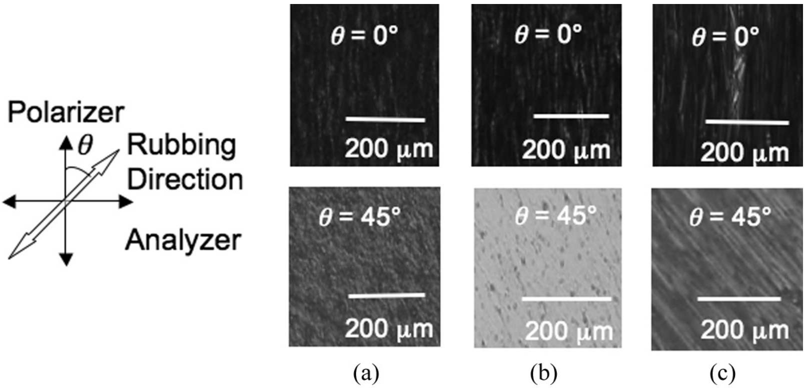

Figure 2. Polarizing optical micrographs of the crosslinked LC polymer films. **P5** (a), **P3** (b), and **P1** (c).

from the averaged absorbance at 390–410 nm and the values thus obtained are listed in Table 2. These results indicate that the azobenzene moieties are efficiently aligned along the rubbing direction in all the films.

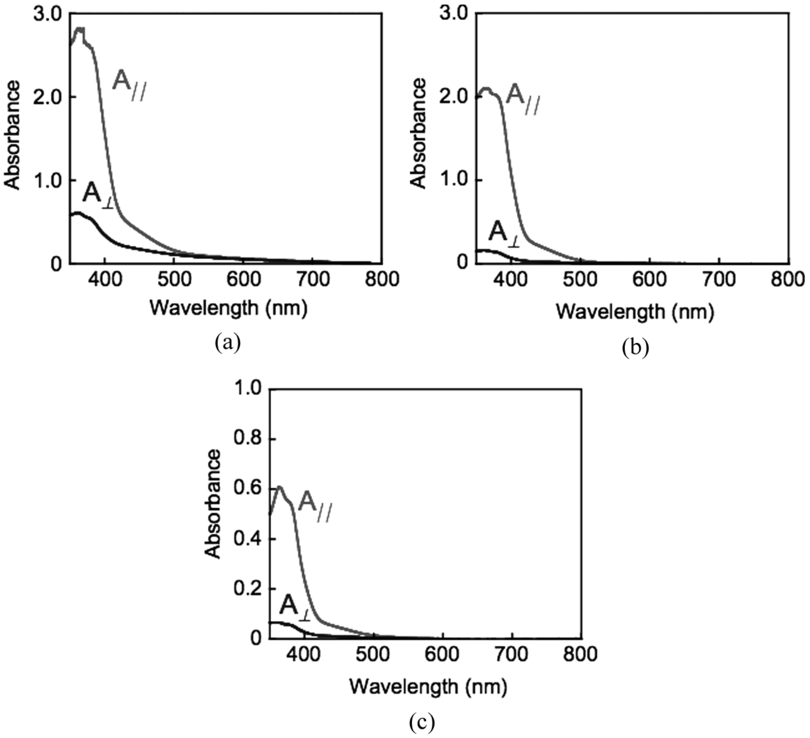

Figure 3. Polarized absorption spectra of the crosslinked LC polymer films. **P5** (a), **P3** (b), and **P1** (c). $A_{\|}$ and $A_{\perp}$ are the absorbance measured with light polarized parallel and perpendicular to the rubbing direction of the alignment layers, respectively.

Table 2. Order parameter (S) of the crosslinked LC polymer films

Sample	S
P5	0.54
P3	0.83
P1	0.72

Photoresponsive Behavior of the Crosslinked LC Polymer Films

Next, we investigated the photoresponsive behavior of the crosslinked LC polymer films. As shown in Figure 4(a), part of the freestanding crosslinked LC polymer films was clamped with two glass substrates, and normal irradiation with UV light at 365 nm was performed at room temperature. Figure 4(b) shows the photographs of the crosslinked LC polymer films exhibiting photoinduced deformation upon UV and visible light irradiation. Upon irradiation with UV light at 10 mW cm^{-2}, **P5** bent toward an actinic light source along the rubbing direction. The bent film also reverted completely to the initial state upon irradiation with visible light at 20 mW cm^{-2}. On the other hand, **P3** and **P1** with 3 and 1 mol% of the azobenzene did not show obvious bending by continuous irradiation with UV light. We observed *trans*-*cis* photoisomerization and contraction in all the films upon irradiation with

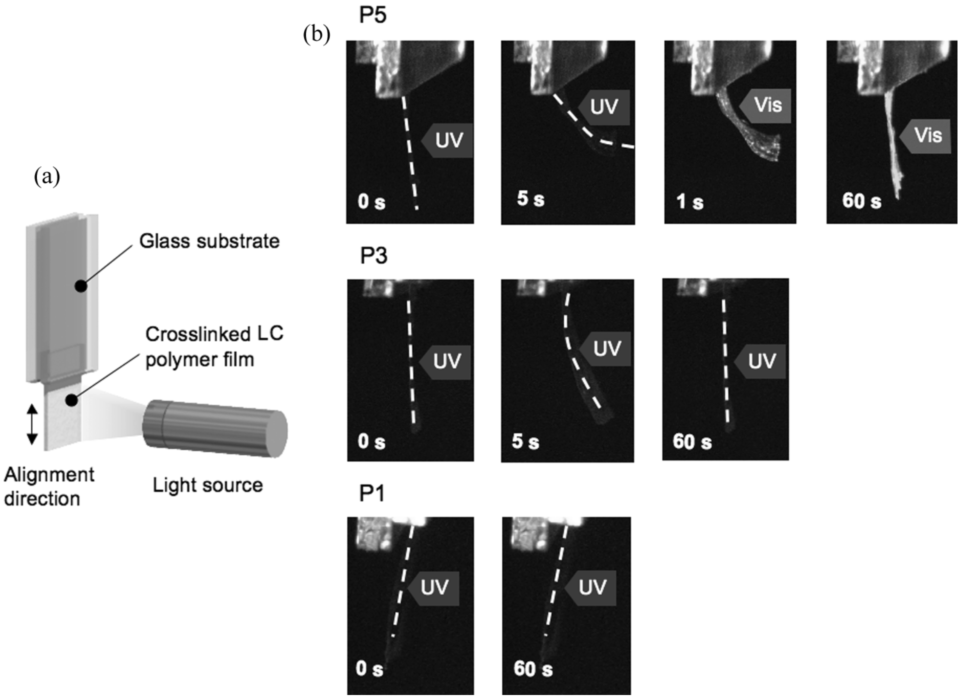

Figure 4. Schematic illustration of experimental setup (a) and photographs of the crosslinked LC polymer films exhibiting photoinduced deformation upon UV and visible light irradiation. The white dashed lines show the edges of the films. Size of the films: 5 mm × 7 mm × 10 μm (b).

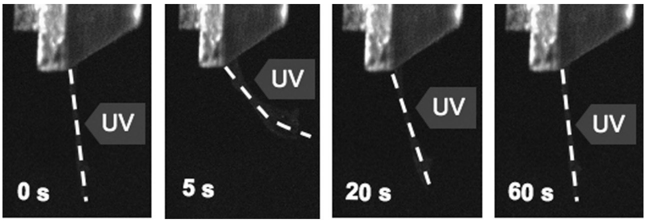

Figure 5. Photographs of **P5** exhibiting photoinduced bending and unbending behavior upon continuous irradiation with UV light. Size of the films: 5 mm × 7 mm × 10 μm.

UV light by absorption spectroscopy and thermomechanical analysis, respectively (not shown). In the previous work, Broer *et al.* have reported that the bending response depended on the concentration of azobenzene in crosslinked LC polymer films [14]. Thus, we consider that **P3** and **P1** did not show obvious bending and exhibited contraction because the gradient of the concentration of the *cis*-azobenzene is low. However, the change in molecular alignment is not clear. Investigation of the change in molecular alignment of crosslinked LC polymer films with a low content of an azobenzene moiety is now in progress. In addition, we will optimize the condition of the concentration of azobenzene and crosslinking density in bending behavior.

Figure 5 shows the photographs of **P5** 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.

Figure 6 shows the schematic illustration of the bending and unbending mechanism upon continuous irradiation with UV light. Upon UV irradiation, the *trans*-*cis* photoisomerization and the change in molecular alignment induce a contraction at the surface, leading to the bending [4]. By continuous irradiation, the contraction occurs even in the deep part, which causes the reversion of the bent film to the flat state.

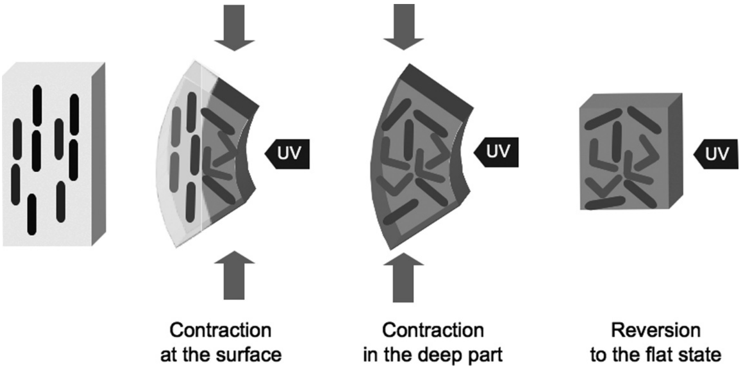

Figure 6. Schematic illustration of the bending and unbending mechanism upon continuous irradiation with UV light.

Conclusions

We prepared crosslinked LC polymer films with a different content of an azobenzene moiety and investigated their photoresponsive behavior. By polarizing optical micrography and polarized absorption spectroscopy, it was found that the azobenzene moieties in the crosslinked LC polymer films are aligned along the rubbing direction. Upon exposure to UV light, the film with 5 mol% of the azobenzene bent toward an actinic light source, and the bent film reverted to the initial state completely upon exposure to visible light. On the other hand, films with 3 and 1 mol% of the azobenzene showed no obvious bending by continuous irradiation with UV light. The bent film also reverted to the flat state upon continuous irradiation with UV light.

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