

Photoresponsive Behavior of Photochromic Liquid-Crystalline Polymers

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Abstract

Photoresponsive behavior of photochromic liquid-crystalline polymer films is presented. Those polymers contain azobenzenes as a photochromic moiety and show liquid-crystalline behavior. Upon exposure to two coherent beams, holograms were formed in the polymer films, which are bright and in a high resolution. Crosslinked polymers exhibited completely different behavior, in which upon exposure to UV light the polymer films bent toward irradiation direction of the actinic light.

Introduction

Liquid crystals (LCs) are unique materials that show such characteristic properties as 1) a self-organizing nature, 2) fluidity with long-range order, 3) cooperative motion, 4) anisotropy in various physical properties (optical, electrical and magnetic), and 5) alignment change due to external fields at surfaces and interfaces. Due to these properties, modulation of alignment of LCs by external fields gives rise to a change in optical properties of LC cells, which forms the basis of LC displays.

Modulation of orientation of LCs also gives rise to an anomalous change in refractive index that is very difficult to achieve with amorphous materials.¹ This is an additional benefit of LC materials. Two types of photomodulation of orientation of LC molecules take place: 1) change in phases (phase transition, order–disorder change); 2) change in LC directors (order–order change). In both cases, a large change in properties can be induced by the cooperative effect. In this paper, we report photoresponsive behavior of various photochromic LC polymers. In linear azobenzene LC polymers, holographic gratings were formed by interference of two laser beams, which causes a periodic change in the photochemical phase transition and the change in molecular alignment. On the other hand, it was found that photoinduced bending is brought about in crosslinked azobenzene LC polymer films.

Linear Photochromic LC Polymers¹⁻⁶

Recently, holography has been of great interest as an optical data storage system with greater storage capacity and faster access to data than even blue-laser digital versatile discs (DVDs). The key component in the holographic devices is a holographic material that meets various requirements such as high diffraction efficiency, fast response, and stability. Several companies have already demonstrated prototypes of holographic systems, and plan to commercially launch write-once discs in the near future. However, rewritable holographic materials have never been developed yet due to their additional high

requirements: rewritability and reversibility. Since a large change in refractive index can be reversibly induced by light in photochromic LC polymers, one can expect that those polymers are suitable for holographic materials. In this paper, we fabricated rewritable holographic materials with high multiplicities by a simple formulation of photoresponsive, mesogenic, and transparent materials.

We synthesized a series of copolymers containing azobenzene moieties, cyanobiphenyl or tolane groups, and alkyl groups in the side chain by the similar procedure reported previously.^{2,3} The chemical structure and thermodynamic properties of the prepared polymers are shown in Figure 1. Here the azobenzene acts as a photoresponsive part to undergo photoisomerization. The cyanobiphenyl and tolane groups are involved in a change in refractive index triggered by the photoisomerization of the azobenzene, and the alkyl groups are to prevent light scattering. Almost all the obtained polymers showed no LC phase in spite of having common mesogenic moieties such as cyanobiphenyl or tolane groups. Incorporation of the alkyl groups responsible for transparency disturbed the appearance of an LC phase. The polymers were heated up to 180 °C on a hot stage, melted until air bubbles disappeared, and sandwiched between two plates of glass substrate with silica particles with diameter of 35-200 μm . Then the film was annealed at 150 °C for 2 h and cooled down to room temperature to yield optically transparent polymer thick films.

Two parallel linearly *s*-polarized beams at 488 nm from an argon ion laser were overlapped in the polymer film at an incident angle of 7 °, which forms the interference pattern with a grating period of $\sim 3 \mu\text{m}$ in the film. A linearly polarized beam at 633 nm from a He-Ne laser was incident to the film at 9.3 °, and the light intensity of a diffracted beam was detected with a photodetector. Diffraction efficiency was defined as the ratio of the light intensity of the diffracted beam (I_1) to that of the incident beam (I_0). All the measurements were carried out at room temperature.

Irradiation of the **AE5TL40M55** film with the writing beams caused an increase in the intensity of the diffracted beam (Figure 2). Upon further irradiation, the first-order diffraction efficiency reached 95 % that is nearly theoretical maximum (100 %). On the other hand, the intensity of the zeroth-order beam decreased in proportion to the increase in the intensity of the first-order diffracted beam. This clearly indicates that the intensity of the zeroth-order beam is transferred to that of the first-order diffraction with no optical loss due to the formation of the gratings. When the writing beams were turned off, the diffraction efficiency remained unchanged. When the recorded hologram was irradiated with a circularly polarized single beam, the diffraction efficiency decreased and the hologram was erased as shown in Figure 3. These cycles could be repeated.

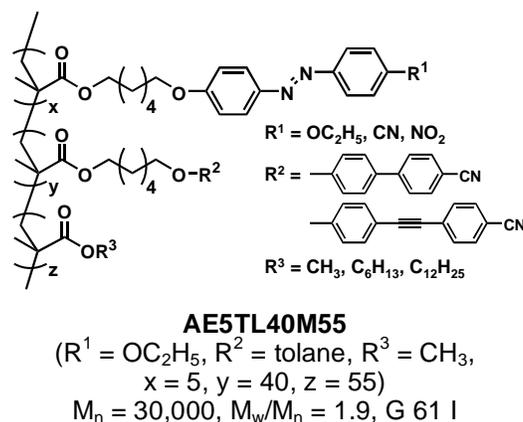


Figure 1. Chemical structure of azobenzene copolymers. Thermodynamic property and molecular weight are also shown.

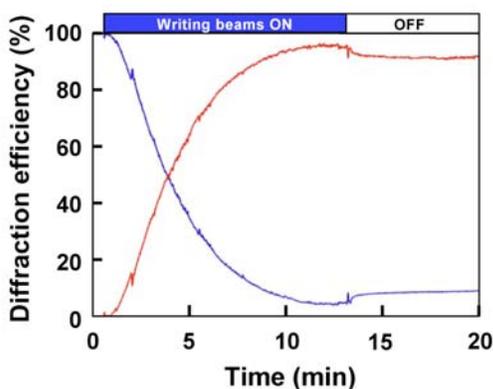


Figure 2. Diffraction efficiency as a function of time. Red and blue lines are the intensities of the first and zeroth order diffraction beams, respectively.

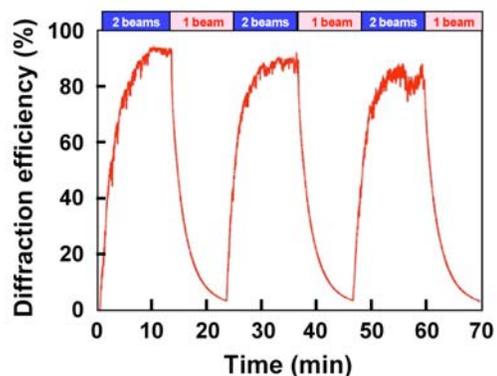


Figure 3. Recording and optical erasure cycles of the hologram.

Crosslinked Photochromic LC Polymers⁷⁻¹⁵

Recently, there has been a growing focus on the study and application of LC elastomers (LCEs) due to their unique combination of the anisotropic aspects of LC phases and the rubber elasticity of polymer networks.⁷⁻⁹ The LCEs can change dimensions under low stresses through phase transitions and retain network memory. If the deformation is caused by light, we can convert light energy into mechanical power directly (photomechanical effects). Recently, Finkelmann *et al.* have reported a pioneering work on a photoinduced large contraction in azobenzene-containing LCEs arising from the photochemical phase transition. They synthesized monodomain nematic LCEs containing polysiloxane main chain and azobenzene chromophores in cross-links.¹⁰ When exposed to UV light at 366 nm, the elastomers contracted about 20 %, caused by the decrease in order parameter due to the *trans-cis* photoisomerization of the azobenzene groups. Here, we focused our attention on a novel mode of the photomechanical effects, photoinduced bending, by using LCEs containing the azobenzenes.

The structures of an LC monoacrylate, **A6AB2**, and a diacrylate cross-linker, **DA6AB**, are shown in Figure 4. The monodomain LCE (MLCE) films, **P10**, were prepared by copolymerization of **A6AB2** and **DA6AB** (mol/mol: 9/1) containing 2 mol% of a thermal initiator (1,1'-azobis(cyclohexane-1-carbonitrile)). Thermal polymerization was carried out in a glass cell coated with polyimide alignment layers that had been rubbed to align LC mesogens. The polydomain LCE (PLCE) films were prepared in a similar manner in the glass cell with the polyimide layers that had not been rubbed. The free-standing films were obtained by opening the cells and separating the films from the glass substrates.

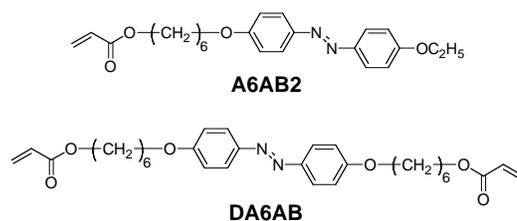


Figure 4. Chemical structures and abbreviations of the LC monomer and the crosslinker, respectively.

Photoinduced bending and unbending behavior^{11,12}

Normal irradiation of unpolarized light was performed on the film, when an LCE film was partially pasted on the glass substrate heated by a hot stage. Figure 5 shows the bending and unbending processes induced by irradiation of UV and Vis light, respectively, when the film was heated to 70 °C. It was observed that the LCE film bent toward the irradiation direction of the incident UV light along the rubbing direction, and the bent film reverted to the initial flat state after exposure to Vis light. This bending and unbending behavior was reversible just by changing the wavelength of the incident light. In addition, after the film was rotated by 90 °, the bending was again observed along the rubbing direction. These results demonstrate that the bending is anisotropically induced, only along the rubbing direction of the alignment layers.

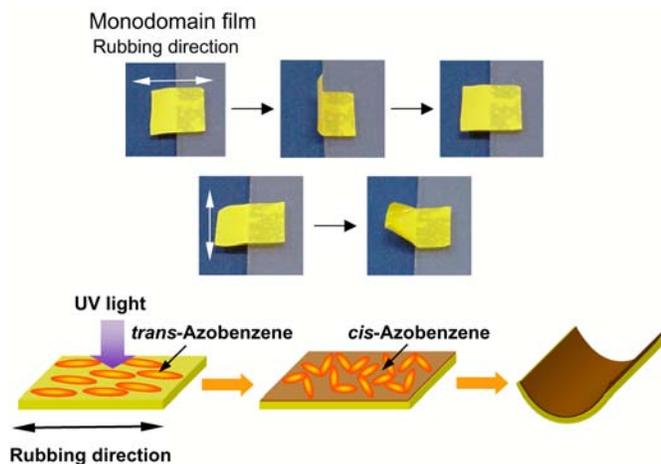


Figure 5. Anisotropic bending and unbending behavior of the monodomain LCE film and the schematic illustration of plausible mechanism of the anisotropic bending behavior.

Irradiation of UV light gives rise to the *trans-cis* isomerization of azobenzene moieties and even the LC-isotropic (I) phase transition of the LC systems; therefore, not only size but also alignment order of the azobenzene moieties is reduced, both of which can bring about a volume contraction of **P10**. However, the extinction coefficient of the azobenzene moieties at ~360 nm is large and more than 99 % of the incident photons are hence absorbed by the surface with a thickness less than 1 μm . Since the thickness of the films used was 20 μm , the change in alignment order of the azobenzene moieties occurs only in the surface region facing the incident light, but in the bulk of the film the *trans*-azobenzene moieties remain unchanged. As a result, the volume contraction is generated only in the surface region, causing the bending toward the irradiation direction of the incident light. Furthermore, the azobenzene moieties are preferentially aligned along the rubbing direction of the alignment layers, and the decrease in the alignment order of the azobenzene moieties is thus produced just along this direction, contributing to the anisotropic bending behavior. Additionally, the unbending behavior is ascribed to the recovery of the initial structure and alignment order of the azobenzene moieties due to *cis-trans* back isomerization induced by irradiation of Vis light.

Photoinduced direction-controllable bending of polydomain LCE films^{13,14}

In the MLCE film, the azobenzene mesogens were preferentially aligned along one direction, and the incident unpolarized light is a homogeneous external stimulus. In this case, the anisotropic bending is induced, whose direction is determined fully by the alignment direction of the azobenzene mesogens and cannot be controlled. Therefore, we used PLCE films and linearly polarized light (LPL).

The attractive bending and unbending behavior is shown in Figure 6. Figure 6(a) shows the film before light irradiation, and Figure 6(b) shows how the film curls up after exposure to 366-nm LPL. The film bent toward the irradiation direction of the incident light with bending occurring parallel to the direction of the light polarization. When the bent film was exposed to Vis light at > 540 nm, it completely reverted to its initial flat state.

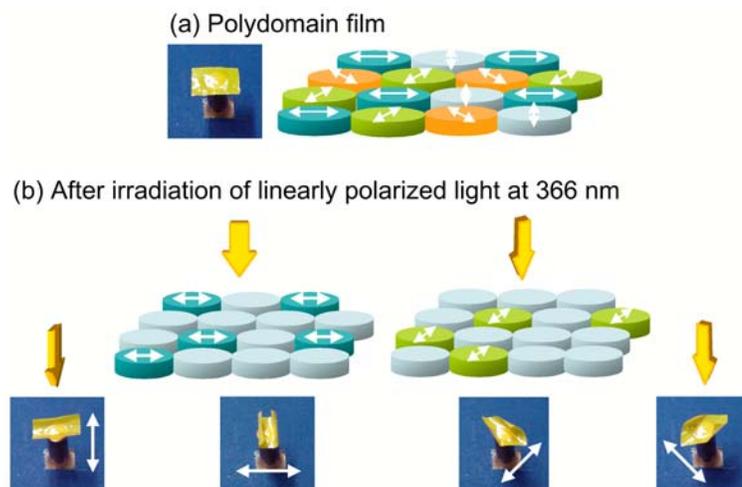


Figure 6. Bending and unbending behavior of the polydomain LCE film and the schematic illustration of plausible mechanism of the direction-controllable bending behavior.

It is known that light absorption to give excited states of molecules meets exclusive requirements including the coincidence of the electric field vector of light with the direction of a transition moment of the molecules (photoselection), thereby *trans*-azobenzene molecules with π - π^* transition moments approximately parallel to the molecular long axis show angular-dependence absorption of LPL: the *trans*-azobenzene molecules with their transition moments parallel to the polarization direction of LPL are activated very effectively to their excited states. By utilizing the selective absorption of LPL in the PLCE films, we successfully achieved the photoinduced direction-controllable bending in which a single LPL film can be bent repeatedly and precisely along any chosen direction.

Effect of LC alignment on photoinduced bending behavior¹⁵

Alignment state of the azobenzene mesogens in the LCE films is the most important factor, which affects the photoinduced bending behavior. Homogeneous LC alignment is conventionally achieved by mechanically rubbing a polymer alignment layer coated on glass substrates. The LC alignment is controlled by surface modification of the glass substrates. Therefore, the homeotropic LC alignment films were obtained by hydrophobic treatment of the glass substrate, and the bending behavior of the homeotropic LCE films upon UV light irradiation was investigated (Figure 7). It was found that the homeotropic LCE films bent along

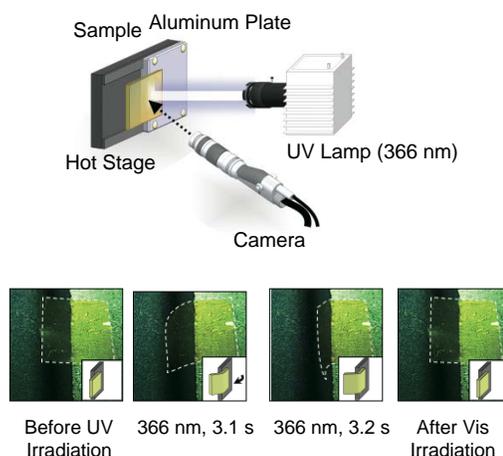


Figure 7. Schematic illustration of the experimental setup and photographs of the photoinduced bending behavior of the homeotropic LCE film.

the irradiation direction of the incident light upon exposure to UV light in contrary to the results obtained in the homogeneous films.

Conclusions

In this paper, we prepared linear and crosslinked polymer films containing photochromic mesogens, and investigated their photoresponsive behavior. In the linear azobenzene copolymer films, highly efficient holographic gratings with 100-% diffraction efficiency were formed due to the periodic change in molecular alignment induced by photoisomerization cycles of the azobenzene moiety. On the other hand, the photoinduced bending was observed when the crosslinked azobenzene LC films were irradiated with unpolarized and polarized UV light. Even if the observed phenomena are completely different between the linear and crosslinked polymers, cooperative molecular motions of mesogens triggered by the azobenzene moieties play a key role in the unique photoresponsive behavior.

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