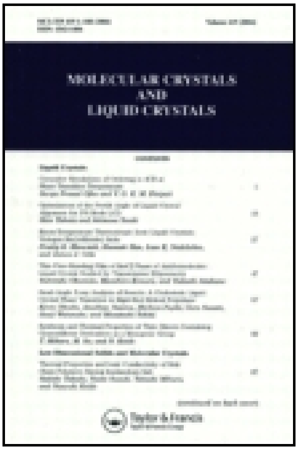

Molecular Crystals and Liquid Crystals

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Photoresponsive Behavior of Azobenzene Liquid-Crystalline Gels

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PHOTORESPONSIVE BEHAVIOR OF AZOBENZENE LIQUID-CRYSTALLINE GELS

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The azobenzene liquid-crystalline gel (LCG) films with macroscopic uniaxial alignment were prepared to investigate photoresponsive behavior. By polarizing microscopy, fiber-like structures aligned in one direction were observed. Furthermore, with a confocal laser scanning microscope (CLSM), it was confirmed that the fiber-like structures were formed even in the bulk of the LCGs. When the LCG films were irradiated with UV light below Tg, changes in the microscopic surface morphology were observed, while no appreciable macroscopic change was observed. On the other hand, when the LCGs were plasticized by suspending in solvents or heating above Tg, the LCG films showed macroscopic changes (e.g. bending) upon UV light irradiation. The bending and unbending could be repeated just by changing the wavelength of the irradiation light. It was suggested that the bending is induced by an absorption gradient which produces a volume difference between the front surface area and the bulk of the gel films.

Keywords: liquid crystals; polymer gels; azobenzene; isomerization

1. INTRODUCTION

Polymer gels are unique intelligent materials in the sense that no other class of materials can be made to respond to so many different stimuli. Many physical and chemical stimuli have been applied to induce various responses of gels such as temperature, electric fields, solvent composition, magnetic fields, pressure and light [1]. In recent years, these gels have become of major interest as novel intelligent or smart materials. Many kinds of such gels have been developed and studied with regard to the

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application to several industrial and medical fields: controlled drug delivery systems, muscle-like actuators and separation techniques [2–5].

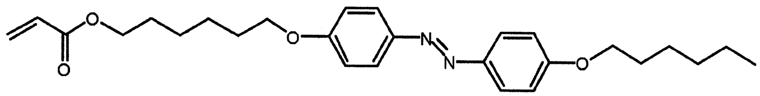
Since light can be imposed instantly and delivered in specific amount with high accuracy, it is of great importance to develop and study light-sensitive gels. Several successful examples have been known such as volume phase transitions in *N*-isopropylacrylamide (**NIPA**)-base gels induced by light. Tanaka *et al.* synthesized the UV-sensitive gels by introducing leuco derivatives into the polymer networks [6]. The photoinduced swelling of the gel is caused by an increase in osmotic pressure within the gel due to the appearance of cyanide ion formed by UV irradiation. Vis light-sensitive gels were prepared by introducing a light sensitive chromophore (e.g. trisodium salt of copper chlorophyllin) to **NIPA** gels [7,8]. When the gels are irradiated with Vis light at 488 nm, the chromophore absorbs light, the energy of which is then dissipated locally as heat by radiationless transitions, increasing the "local" temperature of the gels. The temperature increase alters the swelling behavior of **NIPA** gels, which are thermo-sensitive gels. In addition, when NIPA gels without any chromophores are irradiated by CO_2 laser, the volume change is also induced due to the high infrared light absorbency of water [9]. However, in those gels, the volume change is based on the change in the osmotic pressure by external stimuli, and the rate-determining step of the deformation is a diffusion process. Therefore, this process is too slow to be applied to various applications [10].

It is well known that azobenzenes, which can isomerize from the *trans* to the *cis* form under UV irradiation, undergo a large structural change: the distance between 4 and 4′ carbons decreases from 9.0 Å to 5.5 Å [11]. Since azobenzene-containing gels can expand and contract due to the photo-induced change in the molecular shape, volume changes of the gels can be induced without the diffusion process. However, so far the observed contraction of the azobenzene-containing gels was very small and isotropic [12–14]. To obtain materials that undergo large shape changes, we prepared azobenzene LCGs with macroscopic uniaxial molecular alignment. In those LCGs, the azobenzene moieties are highly aligned into one direction, so that the effect of the structural change of azobenzene moieties could be concentrated in one direction. As a result, a large and anisotropic deformation of the gel is expected to be induced by the structural change. Here, we report the large deformation of azobenzene-containing LCGs induced by light.

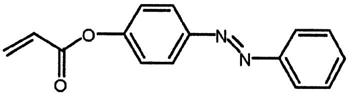
2. EXPERIMENTAL

Materials

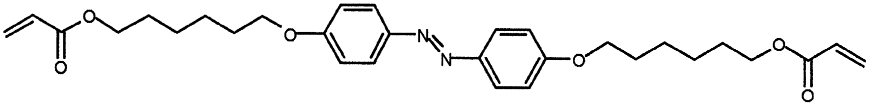
The structures of a monofunctional LC monomer, 6-[4-(4-hexyloxyphenylazo)phenoxy]hexyl acrylate (**A6AB6**), a monofunctional monomer,



A6AB6 I 92 N 82 S 75 K (Cooling)



A0AB



DA6AB

FIGURE 1 Structures of the azobenzene LC monomers used in this study and their abbreviations.

4-(phenylazo)phenyl acrylate (**A0AB**) and a difunctional monomer, 4,4′-bis[6-(acryloyloxy)hexyloxy]azobenzene (**DA6AB**), used in this study are shown in Figure 1. Both monomers were prepared according to the method reported [15].

The azobenzene LCG films were prepared by *in-situ* photopolymerization of the mixture of **A6AB6** and **DA6AB** at various ratios of **A6AB6/DA6AB** (mol/mol) (90/10 ~ 80/20). The mixture containing a photoinitiator (Ciba Specialty, Irgacure 784; 2 mol% concentration) was injected into a glass cell with polyimide alignment layers at 100°C (in an isotropic (I) phase). It was confirmed that the photoinitiator did not destabilize the LC phase at this concentration and no spontaneous thermal polymerization occurred during injection of the LC monomers into the cell. After the sample was cooled down slowly (0.5°C/min) to a polymerization temperature (85°C), photoirradiation at >540 nm (4 mW/cm^2) was performed with a 500-W high-pressure mercury lamp through glass filters (Toshiba, Y-52 + IRA-25) for 2 h. After polymerization, the LCG film was taken off from the cell and washed with chloroform completely to remove unreacted monomers and cross-linking agents. The LCG films were finally dried under reduced pressure. Polarized IR (JASCO FT/IR-420) spectra were recorded at room temperature.

Bending and Unbending Behavior of LCG Films

The LCG films were irradiated at 366 nm by a high-pressure mercury lamp through glass filters (Toshiba, UV-D36A + UV-35) or at 360 nm by a Xe lamp. The bent LCG films were exposed to Vis light at 436 nm from the high-pressure mercury lamp through glass filters (Toshiba, V-40 + Y-44) or at 450 nm from the Xe lamp. The bending and unbending behavior of the LCG films were observed by polarizing optical microscopy (Olympus BH-2).

Observation of Topology of LCG Films

The surface structure of the LCGs were investigated with an AFM (Shimadzu, SPM-9500 J2) and a confocal laser scanning microscope (CLSM; Leica, TCS-SL).

3. RESULTS AND DISCUSSION

Characterization of Samples

Figure 2 shows the polarized IR spectra of the LCG films. The absorption bands at 1601 cm^{-1} and at 1249 cm^{-1} are attributed to the backbone stretching vibration of benzene groups and the stretching vibration of ether groups, respectively. It was found that the absorbance of these groups changed with the polarization direction of the measurement IR beam. When the polarization direction of the measurement IR beam was parallel to the rubbing direction, the absorbance of benzene and ether groups reached a maximum value (a).

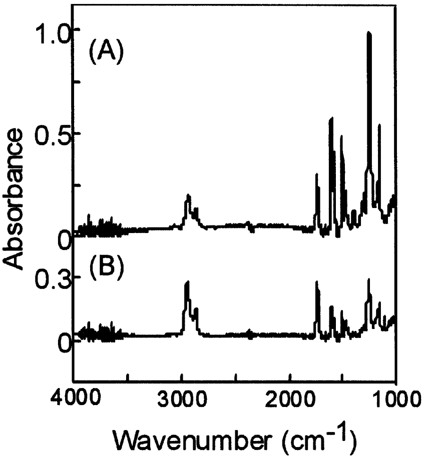


FIGURE 2 Polarized IR spectra of the LCG film. (A) Parallel to the rubbing direction; (B) perpendicular to the rubbing direction.

On the other hand, when the two directions were perpendicular to each other, the absorbance of these bands showed a minimum value (b). This result clearly indicates that the azobenzene moieties are preferentially aligned along the rubbing direction of the alignment layer of the cell used for the preparation of the LCG films.

Photoinduced Bending and Unbending of LCGs

Polarizing optical micrographs of the LCG films are shown in Figure 3. Fiber-like structures aligned in the one direction were observed in the micrographs. The direction of the fiber was parallel to the rubbing direction of the alignment layer.

The AFM measurement was performed to observe those structures in detail as shown in Figure 4. The AFM observation of the surface of the film revealed that the size of the fiber-like structures was $5 \sim 10\,\mu\text{m}$ with a height $>1\,\mu\text{m}$.

To investigate the fiber-like structures in the bulk of the LCGs, the film was observed with CLSM. The cross-sections of the LCGs obtained from the refractive-mode observation with CLSM are shown in Figure 5. The cross-section of the LCGs revealed similar fiber-like structures as those observed with AFM. These results clearly indicate that the three-dimensional fiber-like structures are formed in the LCGs.

Figure 6 shows the effect of photoirradiation of the polymer films below Tg. Before UV irradiation, the fibers were observed by AFM (Fig. 6 (A)). After UV irradiation, a change in the microscopic surface morphology of the polymer fibers was observed: anisotropic grooves were observed in the direction perpendicular to the polymer fibers (Fig. 6 (B)). Upon UV irradiation, ***trans-cis*** photoisomerization of azobenzene moieties occurs and the volume change of the LCG film is induced. However, below Tg of the polymer, since the

FIGURE 3 (see COLOR PLATE I) Fiber-like structures observed in the LCG films.

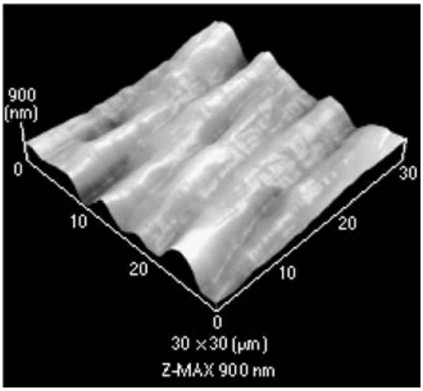


FIGURE 4 (see COLOR PLATE II) AFM image of the surface of the LCGs.

mobility of a polymer segment is restricted, the volume change does not lead to any appreciable macroscopic change of the LCGs (e.g. bending) but only to microscopic changes (e.g. the formation of grooves). As described above,

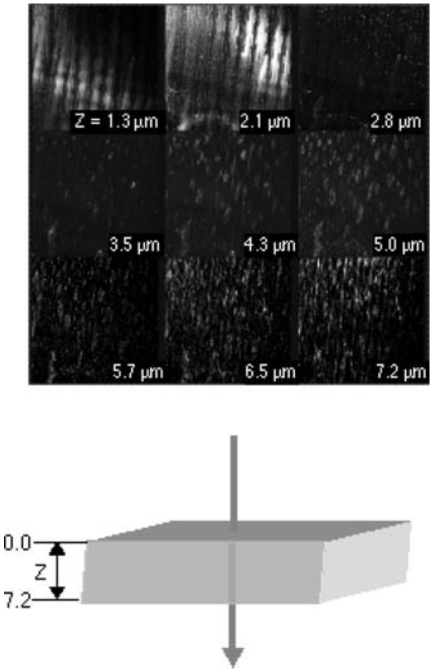


FIGURE 5 (see COLOR PLATE III) Images obtained with a confocal laser scanning microscope of the LCGs.

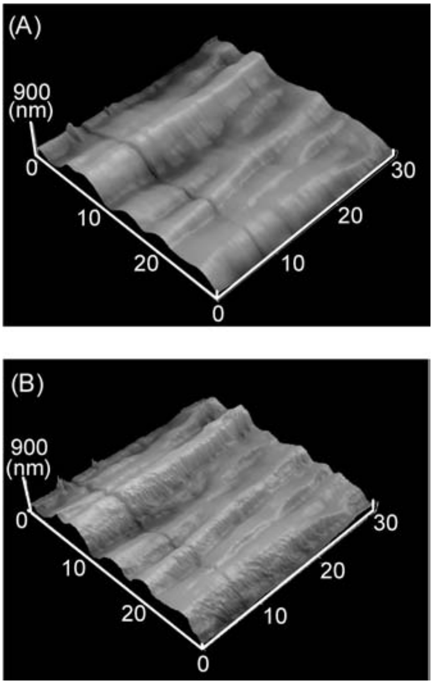


FIGURE 6 (see COLOR PLATE IV) AFM images of the fiber-like structure in LCG films. (A) Before UV irradiation; (B) after irradiation for 1 h.

since the azobenzene moieties are aligned along the direction of the polymer fiber, the contraction of the material is induced in the direction parallel to the polymer fiber, which leads to the formation of the anisotropic grooves in the direction perpendicular to the polymer fiber.

Exposure of the LCG film in toluene to UV light at 360 nm brought about bending of the LCG film as shown in Figure 7(A). When the bent LCG films were exposed to Vis light at 450 nm, unbending of the LCG films immediately took place and the initial flat LCG films were restored. This bending and unbending of the LCG films could be induced by changing the wavelength of the irradiation light. It must be mentioned here that the bending of the LCG films occurs only in the direction parallel to the rubbing direction of the polyimide alignment layer of the cell.

The optical properties of the LCG films during the bending and unbending processes were also examined by polarizing optical microscopy. It was clearly observed that the LCG films showed optical anisotropy at any stage of the bending and unbending processes (Fig. 7(B)). This means that the bending and unbending occur in the anisotropic phases.

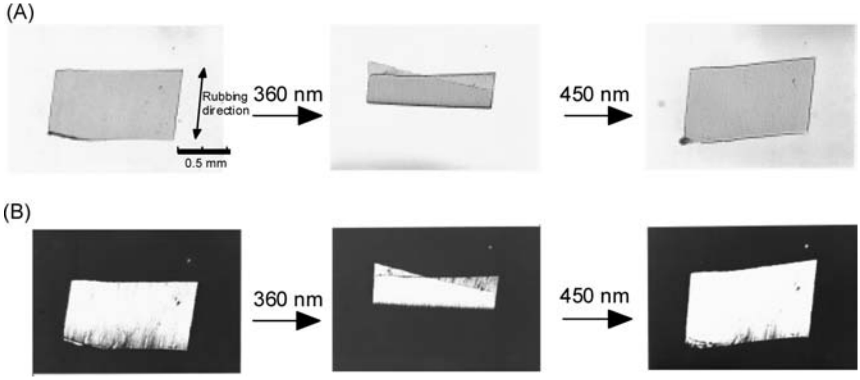


FIGURE 7 (see COLOR PLATE V) Bending and unbending behavior of the LCG films in toluene. (A) Photographs taken during bending and unbending processes; (B) polarizing micrographs observed during the bending and unbending processes.

We examined the photoresponsive behavior of isotropic gels made of **A0AB** (80 mol%) and **DA6AB** (20 mol%), and found that bending and unbending of the isotropic gel took place to some extent in toluene, but no preferential direction in bending was observed in those films.

In addition, the LCG film underwent the bending even without solvents, when the LCG film was heated above Tg. This finding seems to rule out the possibility that the bending of the LCG film is caused by the shrinkage of the films with *cis*-azobenzene moieties due to exclusion of solvent molecules, arising from the increased polarity of the azobenzene. To induce the bending, the LCG films need to be plasticized. By swelling in solvents or heating above Tg, the LCG could fulfill the requirement of the bending.

Mechanism of Bending

The mechanism of the photoinduced bending is assumed as follows. The thickness of the LCG film is typically 10 μm. The absorption coefficient of the azobenzene moieties at 360 nm is large (2.6×10^{-4} l/Mcm) and 99% of the incident photons are absorbed by the surface within a thickness <1 μm. This means that upon photoirradiation at 360 nm the *trans-cis* photoisomerization occurs only in the surface region, and in the bulk of the film the *trans* forms of the azobenzene remain unchanged. In other words, the volume contraction is induced only in the surface region of the LCG film upon irradiation, and the volume in the surface region becomes different from that of the bulk in the gels. Therefore, the bending is induced toward the incident direction of light. Furthermore, since azobenzene moieties are aligned into one direction in the LCG films, the films could contract only in one direction on *trans-cis* photoisomerization. Thus, the LCG films undergo an anisotropic bending.

CONCLUSION

To obtain materials that undergo large shape changes, we prepared the azobenzene LCGs with macroscopic uniaxial molecular alignment. Fiber-like structures aligned in the one direction were observed in the micrographs. The observation of the fiber-like structures with CLSM clearly indicates that the three-dimensional fiber-like structures are formed even in the bulk of the LCGs. Below Tg, changes in microscopic surface morphology of the LCGs films were observed upon UV irradiation, while any appreciable macroscopic changes were not induced. On the other hand, when the LCGs were plasticized by suspending in solvent or heating above Tg, the LCG films showed the anisotropic bending and unbending upon light irradiation. This bending and unbending of the LCG films could be induced by changing the wavelength of the irradiation light. The origin of the bending is an unbalanced contraction between the surface area and the bulk of the gel. The anisotropic bending of the LCG films enables the gel to be applied to various applications such as photoresponsive valves and actuators.

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