

# Photoresponsive Behavior of Liquid-Crystalline Networks

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## Abstract

*Freestanding azobenzene-containing liquid-crystalline network (LCN) films with macroscopic uniaxial molecular alignment were prepared by in-situ photopolymerization. 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 LCNs. Upon UV light irradiation to cause trans-cis photoisomerization of the azobenzene molecules, the LCN films underwent a significant and anisotropic bending toward the irradiation direction of UV light. When the bent LCN films were exposed to Vis light, unbending of the LCN films immediately took place and the initial flat LCN films were restored. This bending and unbending behavior of the LCN films could be repeated just by changing the wavelength of the irradiation light. It was suggested that the bending was induced by an absorption gradient which produced a volume difference between the front surface area and the bulk of the network films.*

## 1. Introduction

Polymer networks may deform in response to a variety of external stimuli such as temperature, pH, ionic strength, electric field and light [1-3]. In particular, light sensitive networks have attracted considerable interest because light could change the properties of networks effectively. Several successful examples have been reported on the light sensitive networks, especially on volume phase transitions in *N*-isopropylacrylamide (NIPA)-based networks induced by light [4-6]. Tanaka *et al.* observed that the incorporation of triphenylmethyl moieties into the NIPA-based network enabled the network to expand in water by irradiation. Furthermore, the NIPA-based

network containing a chlorophyllin derivative was found to collapse under illumination. However, the volume phase transition in those networks is due to the change in the osmotic pressure by the external stimuli, and the rate-determining step of the deformation is the diffusion process. Therefore, the response is too slow for various applications [7].

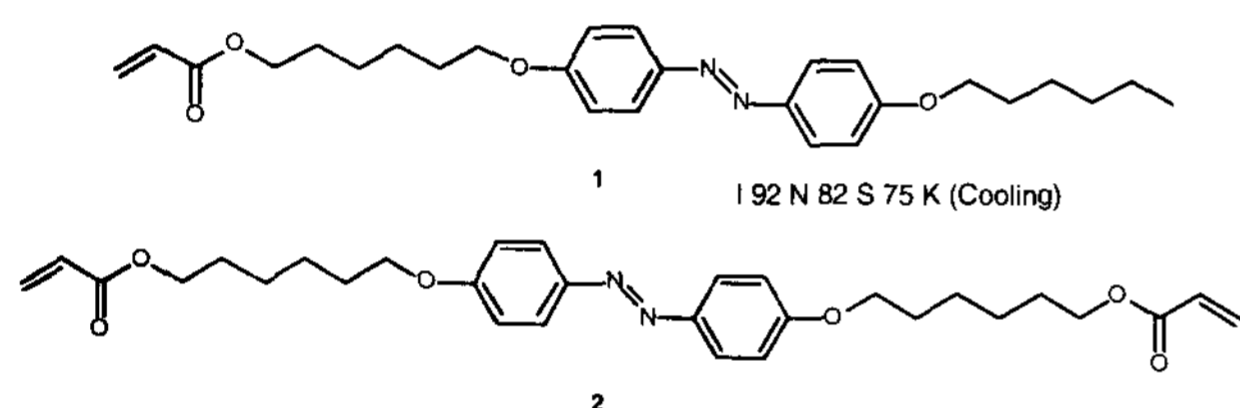
Azobenzene is a widely-used *trans-cis* photoisomerizable molecule [8]. It undergoes isomerization from the *trans* to the *cis* form under UV irradiation, while the *cis* form can return to the *trans* form either thermally or photochemically. During the isomerization, azobenzene undergoes a large structural change: the distance between 4 and 4' carbons decreases from 9.0 Å to 5.5 Å [9]. This photoinduced change of the azobenzenes could induce deformations, swelling and shrinking, of the azobenzene-containing networks. Agolini and Gay observed that an azobenzene-containing polyimide contracted upon UV irradiation. However, the observed contraction was very small (0.5 %) [10]. Eisenbach reported 0.15 ~ 0.25 % contraction of polymer films cross-linked with azobenzene under UV irradiation [11]. Although many systems showing photoinduced deformations have been reported previously, the deformations were very small [9].

In this study, to obtain systems that undergo large shape changes, we prepared freestanding films of azobenzene liquid-crystalline networks (LCNs) with macroscopic uniaxial molecular alignment. With freestanding films, we can expect the network films free from the effect of interfaces at various substrates when network films are prepared on them and subjected to external stimuli. Furthermore, in the LCNs having azobenzene moieties the azobenzene moieties are highly aligned into one direction, so that a shortening of the distance between 4 and 4' carbons of the azobenzene could occur only in one direction. In such a system, the effect of the structural change of

the azobenzene moieties is concentrated in one direction. As a result, a large and anisotropic deformation of the network is expected to be induced by the structural change. Here, we report a large deformation of LCN films by light.

## 2. Experimental

The LCN films were prepared by *in-situ* photopolymerization of an LC monomer containing an azobenzene moiety (1) and a diacrylate with an azobenzene moiety (2) at various ratios of 1/2 (mol/mol) (95/5 ~ 80/20) (Figure 1). The mixture of 1 and 2 containing 2 mol% of a photoinitiator (Irgacure 784, Ciba Specialty) which has a sensitivity at >540 nm was placed in a cell with rubbed polyimide (PI) alignment layers. At the temperature where the LC mixture shows a nematic phase, the LC cell was irradiated at >540 nm to initiate polymerization. After polymerization, the LCN film was taken off from the cell and washed with chloroform completely to remove unreacted monomers and cross-linking agents.



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

The LCN film was finally dried under reduced pressure. The alignment of the azobenzene moieties in the LCN films was explored by polarized IR absorption spectroscopy. The surface structure of the LCNs was investigated with an AFM (Shimadzu, SPM-9500 J2) and a confocal laser scanning microscope (CLSM; Leica, TCS-SL).

## 3. Results and discussion

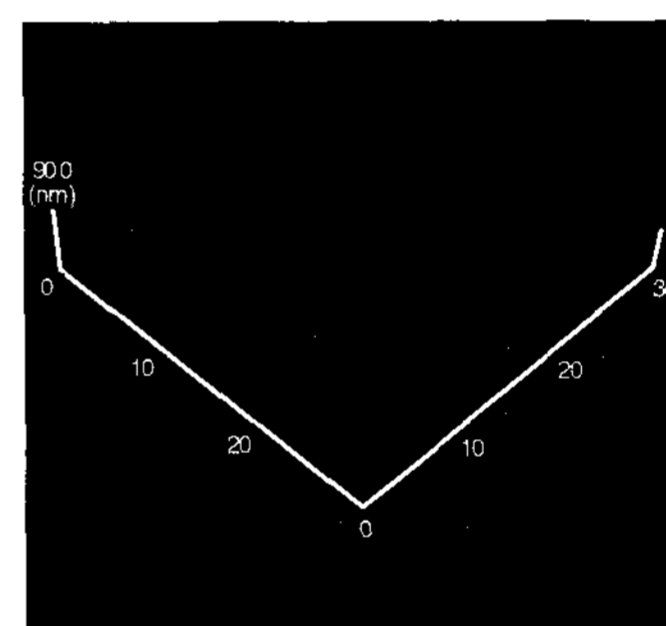
The alignment of the azobenzene moieties in the LCN films was explored by polarized IR absorption spectroscopy. It was revealed that the azobenzene moieties are preferentially aligned along the rubbing direction of the alignment layer in the cell used for the preparation of the LCN films. Polarizing optical micrographs of the LCN films are shown in Figure 2. 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.



**Figure 2 Fiber-like structures observed in the LCN films.**

The AFM measurement was performed to observe those structures in detail. The AFM observation of the surface of the film revealed that the size of the fiber-like structures was 5 ~ 10  $\mu\text{m}$  with a height of > 1  $\mu\text{m}$  as shown in Figure 3.



**Figure 3 AFM image of the surface of the LCNs.**

To investigate the fiber-like structures in the bulk of the LCNs, the film was observed with CLSM. The cross-sections of the LCNs obtained by the refractive-mode observation of CLSM are shown in Figure 4. The cross-section of the LCNs revealed similar fiber-like structures to those observed with AFM. These results clearly indicate that the three-dimensional fiber-like structures are formed in the LCNs.

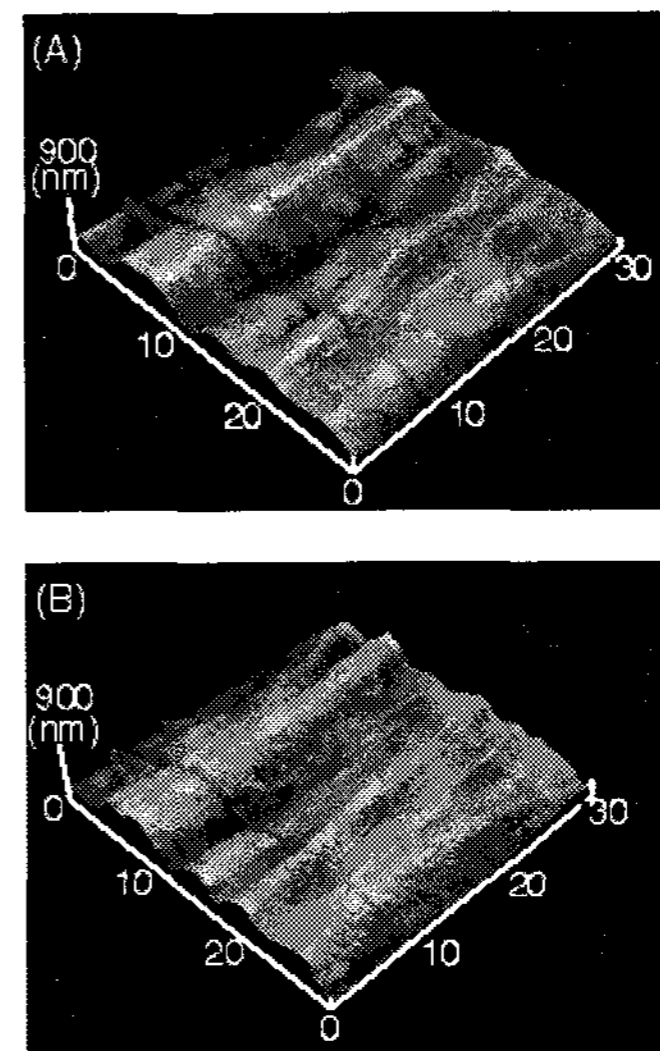
Figure 5 shows the effect of photoirradiation of the polymer films below  $T_g$ . Before UV irradiation, the fibers were observed by AFM (Figure 5 (A)). After UV irradiation, a change in the microscopic surface morphology of the polymer fibers was observed: anisotropic grooves were observed in the direction perpendicular to the polymer fibers (Figure 5 (B)).

**Figure 4 Images obtained with a confocal laser scanning microscope of the LCNs.**

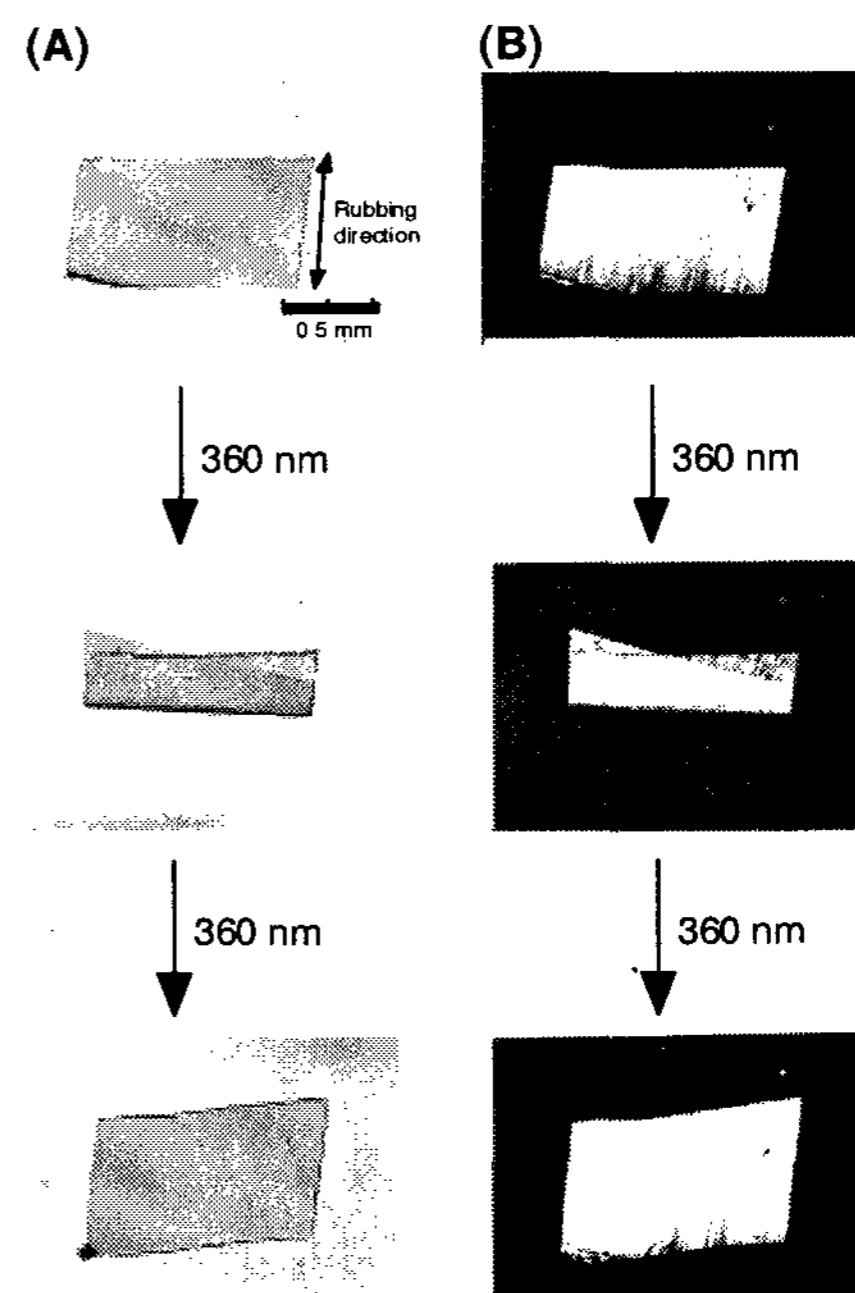
Upon UV irradiation, *trans-cis* photoisomerization of azobenzene moieties occurs and the volume change of the LCN film is induced. However, below  $T_g$  of the polymer, since the mobility of polymer segments is restricted, the volume change does not lead to any appreciable macroscopic changes of the LCNs (e.g. bending) but to microscopic changes (e.g. the formation of grooves). As described above, 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 LCN film in toluene to UV light at 360 nm brought about bending of the LCN film as shown in Figure 6(A). When the bent LCN films were exposed to Vis light at 450 nm, unbending of the LCN films immediately took place and the initial flat LCN films were restored. This bending and unbending of the LCN films could be induced by changing the wavelength of the irradiation light. It must be mentioned here that the bending of the LCN films occurs only in the direction parallel to the rubbing direction of the polyimide alignment layer of the cell.

The optical properties of the LCN films during the bending and unbending processes were also examined



**Figure 5 AFM images of the fiber-like structure in LCN films. (A) Before UV irradiation; (B) after irradiation for 1 h.**



**Figure 6 Bending and unbending behavior of the LCN films in toluene. (A) Photographs taken during bending and unbending processes; (B) polarizing micrographs observed during the bending and unbending processes.**

by polarizing optical microscopy. It was clearly observed that the LCN films showed optical anisotropy at any stage of the bending and unbending processes (Figure 6(B)). This means that the bending and unbending occur in the anisotropic phases.

The mechanism of the photoinduced bending is assumed as follows. The thickness of the LCN film is typically 10  $\mu\text{m}$ . The absorption coefficient of the azobenzene moieties at 360 nm is large ( $2.6 \times 10^4$  l/Mcm) and 99 % of the incident photons are absorbed by the surface within a thickness of  $<1 \mu\text{m}$ . 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 LCN film upon irradiation, and the volume in the surface region becomes different from that of the bulk in the networks. Therefore, the bending is induced toward the incident direction of light. Furthermore, since azobenzene moieties are aligned into one direction in the LCN films, the films could contract only in one direction upon *trans-cis* photoisomerization. Thus, the LCN films undergo an anisotropic bending.

#### 4. Conclusion

To obtain materials that undergo large shape changes, we prepared the azobenzene LCNs 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 LCNs. Below  $T_g$ , although some changes in microscopic surface morphology of the LCNs films were observed upon UV irradiation, no

appreciable macroscopic changes were induced. On the other hand, when the LCNs were plasticized by suspending them in solvent or heating above  $T_g$ , the LCN films showed the anisotropic bending and unbending upon light irradiation. This bending and unbending of the LCN 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 network. The anisotropic bending of the LCN films enables the network to be applied to various applications such as photoresponsive valves and actuators.

#### 5. References

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