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Precisely Direction-Controllable Bending of Cross-Linked Liquid-Crystalline Polymer Films by Light

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Cross-linked liquid-crystalline polymer films were prepared by polymerization of mixtures containing azobenzene monomers and cross-linkers with azobenzene moieties. Two types of the cross-linked liquid-crystalline polymer films were prepared: monodomain films and polydomains films. Photoirradiation of the monodomain films with UV linearly polarized light (LPL) gave rise to bending of the films toward actinic light along the polarization direction, when the light polarization was parallel to the rubbing direction. When the two directions were perpendicular to each other, the bending was isotropic without a preferential direction. On the other hand, exposure of the polydomain films to UV LPL led to bending of the films always along the polarization direction of the actinic light. This means that one can induce bending of the film along any direction precisely by choosing the polarization direction of the actinic light.

Keywords: azobenzene; bending; cross-linking; liquid crystal; photomechanical effect

1. INTRODUCTION

A system capable of converting light energy to mechanical energy could serve as actuators in several applications. Photoreceptor chromophores,

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such as azobenzene, possess a special photoresponsive property that can transfer light energy into a conformational change of molecules (photoisomerization) [1,2]. When the chromophores are incorporated into polymer chains, the photoisomerization gives rise to conformation changes of the main and side chains, resulting in concomitant changes in physical and chemical properties of the polymer solutions and solids [1,2]. In particular, the photocontractility of rubbery networks and swollen gels, generating reversible photomechanical effect, is an area of great interest [3,4]. However, in the previous work, the deformation less than 10% limited this effect for a practical application.

To achieve large deformation, the change in the molecular structures of photochromic compounds should be magnified by an effective method. It has been found that an alignment change of mesogens could occur in the LC systems containing azobenzene arising from the photoisomerization, because the rod-like *trans*-form azobenzene stabilizes the LC alignment, whereas the bent *cis* form lowers the LC order parameter [5]. Recently, a large photocontraction (20%) has been reported in the LC networks (LCN) cross-linked with azobenzene chromophores, resulting from the change of nematic order parameter [6]. It provides a novel mechanism for photomechanical effect and is potential for application as microactuators [7,8].

However, in the other promising materials for the investigation of actuators, such as polymer gels [9–12] and conjugated polymers [13], besides contraction, a bending mode of deformation has been achieved in response to an infinitesimal change of external stimuli such as light, electric field, temperature, and solvent composition. The common concept for the induction of the bending in these systems, films or bilayers, can be summarized to create a difference in volume contraction between one surface/layer and the bulk/another layer by external stimuli.

Most recently, by inducing this inhomogeneity in the azobenzene-containing LCN films, we have achieved a photoinduced bending [14,15], and even succeeded in leading a single film to repeatedly and precisely bend along any chosen direction [16]. Here we report the different bending behavior of monodomain LCN (MLCN) films and polydomain LCN (PLCN) films upon irradiation of linearly polarized light (LPL).

2. EXPERIMENTAL

Materials and Characterization Methods

The structures of an LC monoacrylate, **A6AB2**, and a diacrylate cross-linker, **DA6AB**, used in this study are showed in Figure 1, both of

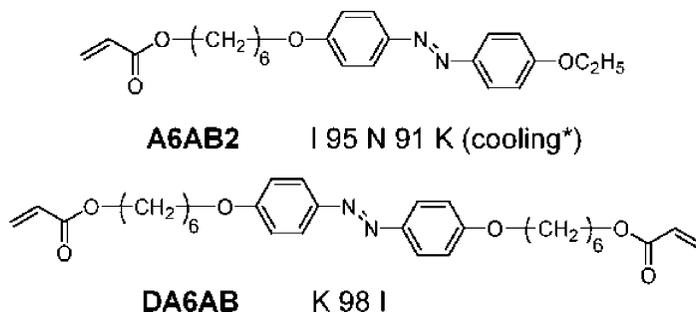


FIGURE 1 Structures, properties and abbreviations of the LC monomer and cross-linker used in this study. I: isotropic; N: nematic; K: crystal. ***A6AB2** shows a monotropic nematic phase when cooled from an isotropic phase.

which possess azobenzene moieties. The MLCN and PLCN films were both prepared by the copolymerization of **A6AB2** and **DA6AB** (mol/mol: 9/1) containing 2 mol% of a thermal initiator (1,1'-azobis (cyclohexane-1-carbonitrile), Wako Pure Chemical). The thermal polymerization was carried out in a glass cell coated with polyimide alignment layers that had been rubbed to align LC mesogens or not. The freestanding films were obtained by opening the cells and separating the films from the glass substrates. Mesomorphic properties of the LCN films were evaluated by polarized IR spectra measured with a FT/IR spectrometer and examined by a polarizing optical microscope (POM; Olympus, BH-2).

Photoinduced Bending and Unbending Behavior

The photoresponsive deformation of the MLCN and PLCN films was investigated by using a partially freestanding film put on a glass substrate and heated by the hot stage. The bending behavior of the film was observed upon irradiation of LPL at 366 nm from a 500 W high-pressure mercury lamp through glass filters (Toshiba, UV-D36A, UV-35 and IRA-25S) and a polarizer. After UV light irradiation, the bent film was exposed to visible light at >540 nm (Toshiba, Y-52 and IRA-25S).

3. RESULTS AND DISCUSSION

Mesomorphic Properties

The polarized IR spectra of the MLCN films were measured at room temperature and are shown in Figure 2A. The bands at 1601 and

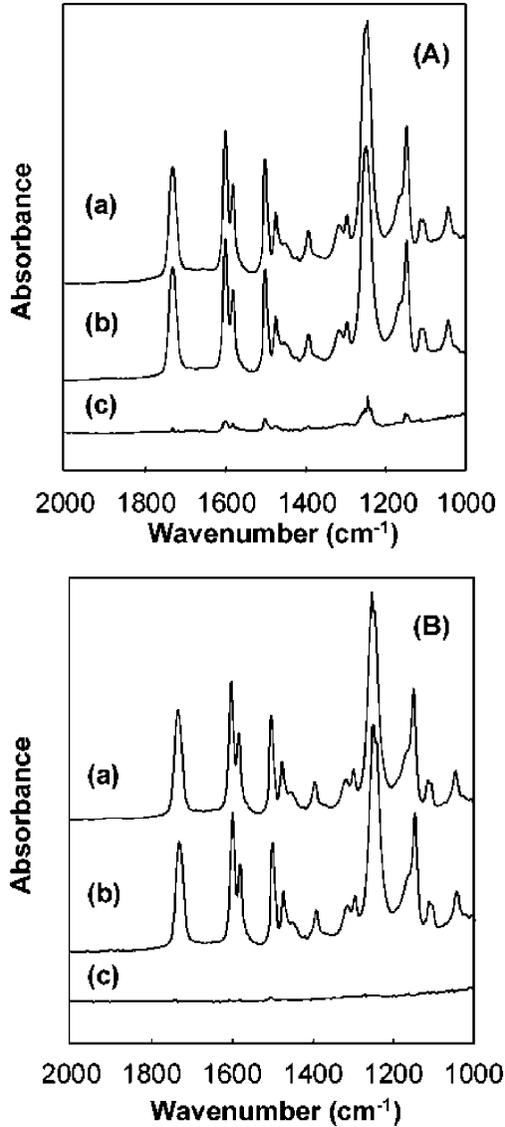


FIGURE 2 Polarized IR spectra of the MLCN films (A) and PLCN (B) films measured at room temperature. In (a) and (b), the polarization direction of the measurement IR beam was perpendicular to each other. (c) is the difference spectrum of (a) and (b).

1502 cm^{-1} , originating from the backbone stretching vibration of benzene rings, and the band at 1252 cm^{-1} , originating from the stretching vibration of ether groups, are characteristic of the mesogens. When the polarization direction of the IR beam was parallel to the rubbing direction, it was found that the absorbance of benzene and ether groups reached a maximum value (Fig. 2A(a)). On the other hand, when the two directions were perpendicular to each other, the absorbance of these groups showed a minimum value (Fig. 2A(b)). These results clearly demonstrate that the azobenzene moieties in the MLCN films are preferentially aligned along the rubbing direction of the alignment layers. In addition, the carbonyl groups at 1732 cm^{-1} , which are directly attached to the polymer main chains, exhibited no dichroism. This implies that the polymer main chains are essentially disordered without any preferential alignment direction.

Figure 2B shows the polarized IR spectra of the PLCN films. The polarization direction of the measurement IR beam in Figure 2B(a) and (b) was perpendicular to each other, and Figure 2B(c) is the difference spectrum of these two spectra. It is clear that there is no difference between Figure 2B(a) and (b), implying that the azobenzene mesogens have no preferential alignment direction in a whole film. As mentioned above, the chemical structure of the PLCN films is the same as that of the MLCN films. The only difference between them is that the

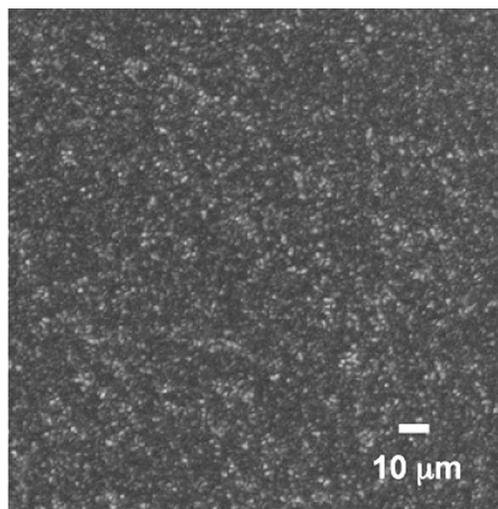


FIGURE 3 Polarizing optical micrograph of the PLCN films when the film was put between two crossed polarizers at room temperature.

rubbing-treated polyimide layers were used for the preparation of the MLCN films to align LC mesogens, whereas the polyimide layers had not been rubbed in the case of the PLCN films. Since the MLCN films show an anisotropic LC phase, the PLCN films hold a polydomain LC phase. In addition, the POM observation of the PLCN films was performed at room temperature when a film was put between two crossed polarizers. Figure 3 shows the polarizing optical micrograph of the PLCN films. The transmittance of the probe light through the crossed

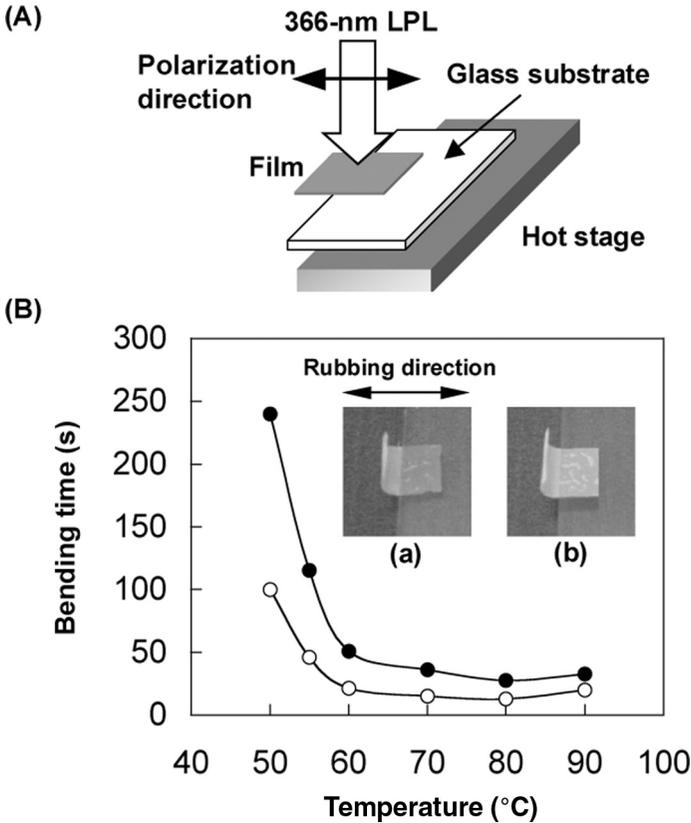


FIGURE 4 Schematic illustration of the experimental setup (A), and bending time of the MLCN film (○) and the PLCN film (●) when exposed to 366-nm LPL (1.5 mW/cm^2) at different temperatures. The polarization direction of 366-nm LPL was set perpendicular to one side of the glass substrate, which was parallel to the rubbing direction of the alignment layers in the case of the MLCN film. Inset figure shows the photographs of the MLCN film (b) and the PLCN film (a) curling up to the same extent. Size of the films: $3.5 \text{ mm} \times 3 \text{ mm} \times 7 \mu\text{m}$.

polarized was observed, arising from numerous bright-view domains with microscopic sizes ($1 \sim 2 \mu\text{m}$). This indicates that the PLCN films exhibit the anisotropy of an LC phase in micro-scale domains.

Photoinduced Bending Behavior of MLCN Films and PLCN Films upon Irradiation of LPL

In this study, an MLCN film and a PLCN film with the same size were put on the glass substrate and heated by the hot stage as illustrated in Figure 4A. The polarization direction of 366-nm LPL was set perpendicular to one side of the glass substrate, which was parallel to the rubbing direction of the alignment layers in the case of the MLCN film. It was observed that both of the MLCN film and the PLCN film bent toward the actinic light along the polarization direction (inset in Figure 4B). After visible light irradiation at $>540 \text{ nm}$, the bent films reverted to the initial flat state completely. Furthermore, the time for two films curling up to the same extent was measured. The results are shown in Figure 4B. It is clearly seen that at the same temperature, the bending time of the MLCN film was shorter than that of the PLCN film, especially in the low temperature region. This indicates that the bending behavior of the LCN films induced by LPL irradiation is deeply affected by the alignment states of the azobenzene mesogens.

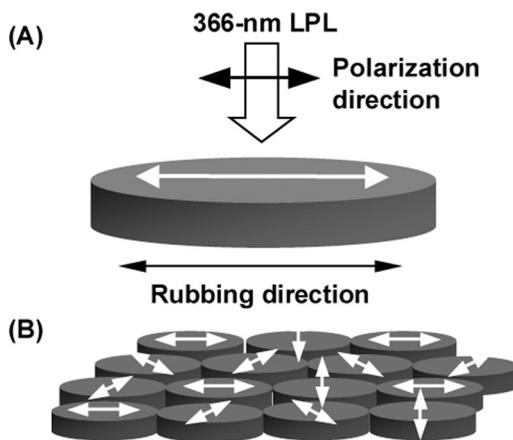


FIGURE 5 Schematic illustration for the mechanism of the different bending behavior in the MLCN film (A) and the PLCN film (B), when the polarization direction of 366-nm LPL is parallel to the rubbing direction of the MLCN film. White arrows indicate the alignment directions of the azobenzene mesogens.

In the MLCN film, the azobenzene mesogens are preferentially aligned along the rubbing direction of the alignment layers, which is here parallel to the polarization direction of 366-nm LPL (Fig. 5A). On the other hand, the PLCN film consists of a large number of micro-size domains of the azobenzene mesogens, in which the mesogens are aligned in one direction in each domain but macroscopically the direction of alignment is random (Fig. 5B). Thus, for a unit film area, the number of the azobenzene mesogens aligned along the polarization direction in the MLCN film is larger than that in the PLCN film.

It is well known that upon irradiation of LPL, the photoisomerization is activated only when the transition dipole moment axis of chromophores has a component parallel to the light polarization [5].

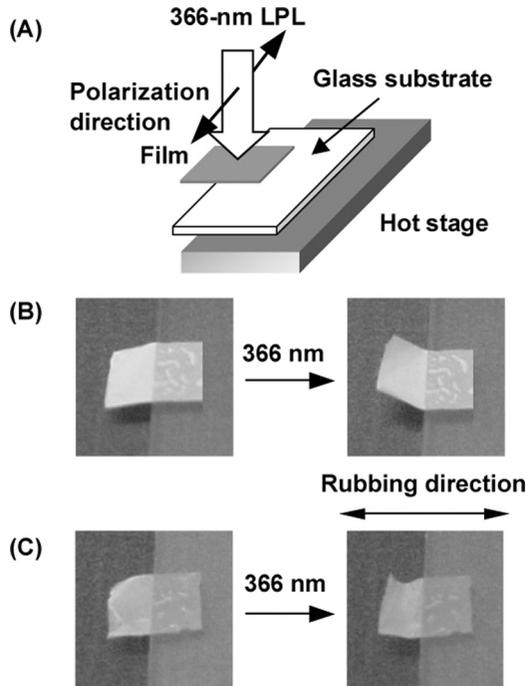


FIGURE 6 Schematic illustration of the experimental setup (A), and photographs of the bending behavior of the PLCN film (B) and the MLCN film (C) induced by irradiation of 366-nm LPL. The polarization direction of 366-nm LPL was set parallel to one side of the glass substrate, which was perpendicular to the rubbing direction of the alignment layers in the case of the MLCN film. Size of the films: $3.5 \text{ mm} \times 3 \text{ mm} \times 7 \mu\text{m}$.

Therefore, with the same irradiation energy, the selective absorption of light along the polarization direction results in that more azobenzene mesogens undergo the *tran-cis* isomerization in the MLCN film than in the PLCN film. The resultant reduction in size and alignment order of these more azobenzene moieties gives rise to a larger volume contraction, contributing to faster bending of the MLCN film than the PLCN film.

Additionally, the polarization direction of 366-nm LPL was changed by 90° in such a way that it became parallel to one side of the glass substrate (Fig. 6A) and perpendicular to the rubbing direction of the alignment layers in the case of the MLCN film. Figure 6B shows the states of the PLCN film before and after irradiation of 366-nm LPL. It is clear that the bending direction of the PLCN film was still along the polarization direction, which is caused by the direction-selective volume contraction due to the selective absorption of LPL. On the other hand, it was observed that the bending of the MLCN film was incomplete and isotropic without a preferential direction as shown in Figure 6C. In the MLCN film, the azobenzene mesogens are preferentially aligned along the rubbing direction, but not totally. Some azobenzene mesogens not aligned along the rubbing direction have weak absorption of LPL. Since the alignment directions of these mesogens are random, the volume contraction arising from their photochemical changes has no direction-selectivity, bringing about the isotropic bending.

CONCLUSION

The bending behavior of the MLCN film and the PLCN film was compared upon irradiation of 366-nm LPL. When the polarization direction of LPL was parallel to the rubbing direction of the alignment layers in the MLCN film, it was observed that the bending direction of the MLCN film and the PLCN film was both along the polarization direction, and the former bent faster than the latter. When the polarization direction of LPL was changed by 90°, the bending direction of the PLCN film was still along the polarization direction, whereas the bending of the MLCN film was isotropic without a preferential direction.

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