

Effect of Cross-linking Density on Photoinduced Bending Behavior of Oriented Liquid-Crystalline Network Films Containing Azobenzene

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Oriented liquid-crystalline network films with various cross-linking densities were prepared by polymerization of mixtures of mono- and diacrylates, both of which contain azobenzene chromophores. The optical anisotropy in the films was evaluated by polarizing optical microscopy and polarized IR spectroscopy. The dichroic ratios and the order parameters of the films were estimated from polarized UV absorbance. The free-standing films were found to show photoinduced bending and unbending behavior upon alternate exposure to unpolarized UV light at 366 nm and unpolarized visible light at >540 nm. It was observed that the films with different cross-linking densities exhibited different bending extents and speeds.

Introduction

Recently there has been a growing focus on the study and application of liquid-crystalline elastomers (LCEs) and networks (LCNs) due to their unique combination of the anisotropic aspects of LC phases and the rubber elasticity of polymer networks.^{1–7} Among their interesting and unusual properties, thermally induced deformation upon nematic (N)–isotropic (I) phase transition, which can be applied for actuators, sensors, and artificial muscles, has attracted significant interest.^{8–11} In the study of this thermomechanical effect, a theoretical analysis⁸ and experimental investigations^{9–11} of a substantial contraction in response to temperature, which is triggered by a subtle decrease in microscopic ordering upon N–I phase transition, have been reported. Accordingly, if the alignment order of LCEs/LCNs can be manipulated by light, a photoinduced large deformation should be generated. Light can be controlled remotely and rapidly as an external stimulus, so that it is of great importance to develop photomechanical effect in LCEs/LCNs.

Photochromic compounds, such as azobenzene, change their molecular structures by photochemical reactions.^{12,13} Incorporation of the chromophores into polymer systems, therefore, gives rise to conformation changes of the polymer chains and concomitant changes in physical and chemical properties of the polymer solutions and solids through photoisomerization, including photocontractility of rubbery networks and swollen gels.^{12–17} However, in the previous works on amorphous polymer systems, the contraction less than 10% limited this photomechanical effect for practical applications.

Recently, a new polymer system showing large photocontraction has been acquired by Finkelmann and other researchers by using azobenzene-containing LCEs.^{18–20} The driving force for the large shape changes is suggested to arise from the variation of alignment order caused by the well-known photochemical phase transition: upon UV light irradiation, the LC systems containing azobenzene chromophores experience a reduction in alignment order and even an LC–I phase transition due to the *trans*–*cis* photoisomerization of the azobenzene moieties, because the rodlike *trans*-azobenzene moieties stabilize the LC alignment, whereas the bent *cis* forms lower the LC order parameter.^{21,22}

However, in the other promising materials for the investigation of actuators, such as polymer gels and

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conducting polymers, besides contraction,^{23–26} a bending mode of deformation has been produced in response to external stimuli such as light,²⁷ electric field,^{28–31} temperature, and solvent composition.³² The bending mode should be advantageous for artificial “hands” and medical microrobots that are capable of completing particular manipulations.³⁰ The common concept for the induction of the bending in these systems, films, or bilayers, is 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 bending³³ and even succeeded in leading a single film to repeatedly and precisely bend along any chosen direction.³⁴ In our previous works, it was found that the oriented and polydomain LCN films showed different bending behavior: the bending of the oriented films took place just along the rubbing direction of the alignment layers, whereas multidirection bending could be evoked in the polydomain films. These results suggest that the orientation states of the azobenzene mesogens strongly affect the bending behavior. Moreover, it has been reported that the cross-linking strategy plays a very important role in the processing and the final orientation of the LCN films.^{35,36} In this work, therefore, we report the effect of cross-linking density on photoinduced bending behavior of the oriented LCN films containing azobenzene chromophores.

Experimental Section

Materials. The structures of an LC monoacrylate, **A6AB2**, and a diacrylate cross-linker, **DA6AB**, used in this study are shown in Figure 1, both of which possess azobenzene moieties. They were synthesized according to a procedure similar to that in the literature.³⁷ The LCN films were prepared by the copolymerization of **A6AB2** and **DA6AB** 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

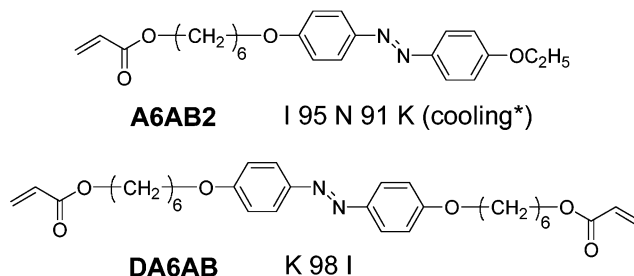


Figure 1. Structures, properties, and abbreviations of the LC monomer and cross-linker used in this study: I, isotropic; N, nematic; K, crystal. ***A6AB2** shows a monotropic nematic phase when cooled from an isotropic phase.

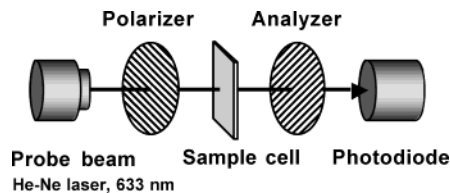


Figure 2. Schematic illustration of an experimental setup for the birefringence measurement.

had been rubbed to align LC mesogens. The free-standing films were obtained by opening the cells and separating the films from the glass substrates.

Characterization Methods. The thermodynamic properties of the monomers and the LCN films were determined by DSC (Seiko I&E, SSC-5200 and DSC220C) at heating and cooling rates of 1 °C/min for the monomers and 10 °C/min for the films. At least three scans were performed to check the reproducibility. The mesomorphic properties and phase transition behavior were examined by a polarizing optical microscope (POM; Olympus, BH-2) equipped with a Mettler hot stage (models FP-90 and FP-82). The polarized IR and UV spectra of the films were measured at room temperature with a UV-vis absorption spectrometer (Jasco, V-550) and an FT/IR spectrometer (Jasco, FT/IR-420), respectively. The setup for birefringence measurement is shown in Figure 2. The film with the rubbing direction vertical was placed between a pair of crossed polarizers (polarization directions at $\pm 45^\circ$ from the vertical). Intensity of the probe light at 633 nm from a He-Ne laser (NEC, GLC5370, 1 mW) transmitted through the crossed polarizers and the film, was measured with a photodiode.

Photoinduced Bending and Unbending Behavior of LCN Films. A partially free-standing film put on the glass substrate was placed on the Mettler hot stage. The bending behavior of the film was observed upon irradiation at 366 nm with a 500-W high-pressure mercury lamp through glass filters (Toshiba, UV-D36A, UV-35, and IRA-25S). After UV irradiation, the bent film was exposed to visible light at >540 nm (Toshiba, Y-52 and IRA-25S). The photographs of the bending and unbending behavior were taken by a digital camera (Sony, DSC-F505).

Results and Discussion

Thermal Polymerization. By the study of POM and DSC, it was found that **A6AB2** exhibited a monotropic nematic phase over a narrow temperature range from 95 to 91 °C when cooled from an isotropic phase, and **DA6AB** did not exhibit mesomorphism, as shown in Figure 1. The nomenclature for polymerizable mixtures and the polymerization conditions are summarized in Table 1. Because the polymerizable mixtures did not show mesomorphism, the polymerization was performed at a temperature 5 °C higher than the total-melt

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Table 1. Nomenclature and Composition of the Polymerizable Samples^a and the Polymerization Conditions

nomenclature	A6AB2 (mol %)	DA6AB (mol %)	polymerization conditions
A95D5	95	5	98 °C, 24 h
A90D10	90	10	98 °C, 24 h
A50D50	50	50	88 °C, 48 h

^a 2 mol % of the thermal initiator was added to the polymerizable samples.

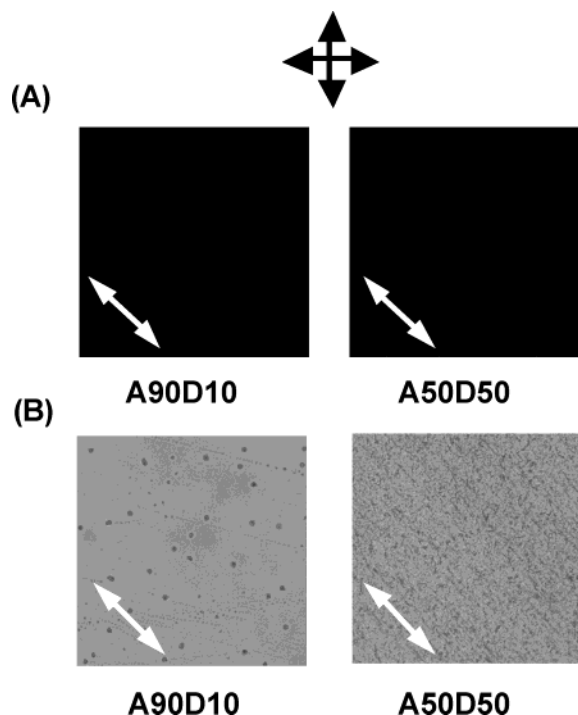


Figure 3. Polarizing optical micrographs of **A90D10** and **A50D50** before (A) and after (B) thermal polymerization. The black arrows indicate the direction of the optical axes of the polarizers, and the white arrows indicate the rubbing direction of the alignment layers. Thickness of the samples was 2 μm .

temperature of the mixtures, which was 98 °C for **A95D5** and **A90D10**, and 88 °C for **A50D50**.

The process of polymerization was observed by POM when the sample cell was placed between crossed polarizers and heated by the hot stage. Figure 3 shows the polarizing optical micrographs of **A90D10** and **A50D50** before and after thermal polymerization. Before polymerization, a homogeneous black view was observed (Figure 3A), meaning that the sample exhibits an isotropic phase. With the polymerization going on, a homogeneous bright view appeared, as the polarizing optical micrographs in Figure 3B show, which were taken after the polymerizations of **A90D10** and **A50D50** were carried out at 98 °C for 10 min and at 88 °C for 20 min, respectively. The light transmission indicates that an LC phase is formed during the polymerization process, although the polymerization was carried out in an isotropic phase of the polymerizable mixtures. Namely, a phase transition occurs during polymerization.

Mesomorphic Properties in LCN Films. The results of DSC measurement on the obtained LCN films are gathered in Table 2. The glass transition (T_g) of **PA95D5** and **PA90D10** in the DSC curves appeared in a similar range of temperatures around 50 °C, whereas

Table 2. Phase Transition Temperatures and Thermodynamic Parameters of the LCN Films Determined by DSC

LCN film	phase transition temperature (°C)	ΔH_{NI} (kJ/mol) ^a	ΔS_{NI} (J/mol·K) ^a
PA95D5	G 50 N 170 I ^a	1.6	3.6
PA90D10	G 50 N ^b		
PA50D50	G 55 N ^b		

^a G, glass; ΔH_{NI} , change in enthalpy of N–I phase transition; ΔS_{NI} , change in entropy of N–I phase transition. ^b Isotropization transition was not observed.

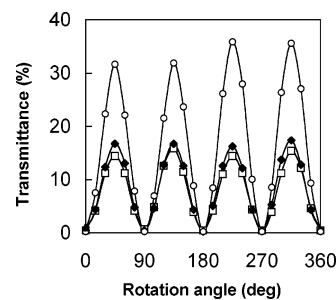


Figure 4. Angular-dependent transmittance of **PA95D5** (\square), **PA90D10** (\blacklozenge), and **PA50D50** (\circ) evaluated by polarizing optical microscopy at room temperature. The rotation angle indicates the direction of the polarizer with respect to the rubbing direction of the alignment layers. Thickness of the films was 2 μm .

PA50D50 exhibited a higher T_g at 55 °C. The DSC curve of **PA95D5** also exhibited a broad endothermic peak around 170 °C. The peak can be assigned to the N to I phase transition, as poly(**A6AB2**) has been reported to show an N phase.^{21a} However, when the fraction of **DA6AB** was ≥ 10 mol %, isotropization was not detectable by DSC. By the study of POM equipped with the hot stage, light transmission with the film between crossed polarizers was observed for **PA90D10** and **PA50D50** up to temperatures as high as 250 °C, indicating that some anisotropy remains in the film even at high temperatures. Additionally, the optical anisotropy in the LCN films was evaluated at room temperature by measuring the transmittance of the probe light through crossed polarizers as a function of the rotation angle (Figure 4). The rotation angle indicates the direction of the polarizer with respect to the rubbing direction of the alignment layers. When the rubbing direction was parallel or perpendicular to the direction of polarizer of the microscope, no or little transmitted light was observed, whereas the transmittance was highest when the angle between them was 45°. The regular maximum and minimum with 90° separations display that the azobenzene mesogens in the LCN films are preferentially aligned along the rubbing direction of the alignment layers.

The polarized IR spectra of the LCN films were measured at room temperature, and Figure 5 shows the spectra of **PA50D50**. The bands at 1601 and 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. On the other hand, when the two directions were perpendicular

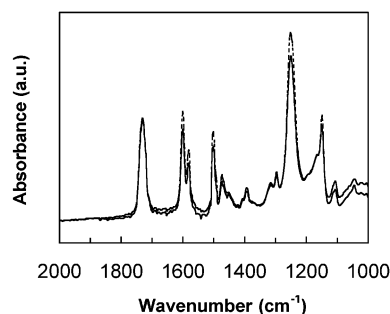


Figure 5. Polarized IR spectra of PA50D50 measured at room temperature with the IR beam polarized parallel (···) and perpendicular (—) to the rubbing direction.

Table 3. Birefringence (Δn) of the LCN Films at Room Temperature^a

LCN film	Δn
PA95D5	0.058
PA90D10	0.061
PA50D50	0.079

^a Calculated from eq 1, when the thickness of the films was 2 μm .

to each other, the absorbance of these groups showed a minimum value. These results clearly demonstrate that the azobenzene moieties are preferentially aligned along the rubbing direction of the alignment layers. This result is coincident with that of the POM observation mentioned above. 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.

The birefringence measurement in the LCN films was carried out at room temperature with the experimental setup represented in Figure 2. The intensity (I) of the probe light transmitted through crossed polarizers was measured. The relationship between I and birefringence (Δn) is given by the following equation:³⁸

$$I = I_0 \sin^2(\pi d \Delta n / \lambda) \quad (1)$$

where I_0 is the light intensity transmitted under parallel polarizers, d is the film thickness, and λ is the wavelength of the probe light. The calculated values of Δn of the LCN films are summarized in Table 3, revealing that the birefringence increases with the increment of the cross-linking density. It is suggested that the different alignment orders in the LCN films (see below) bring about this change of the birefringence in the films with the increment of the cross-linking density.

Order Parameters in LCN Films. To check the order parameters of the LCN films, the dichroism in the optical absorption spectra of the films was measured. The optical absorption spectra, detected with light polarized parallel and perpendicular to the rubbing direction of the alignment layers, are shown in Figure 6. The dichroic ratio is given by the following equation:³⁹

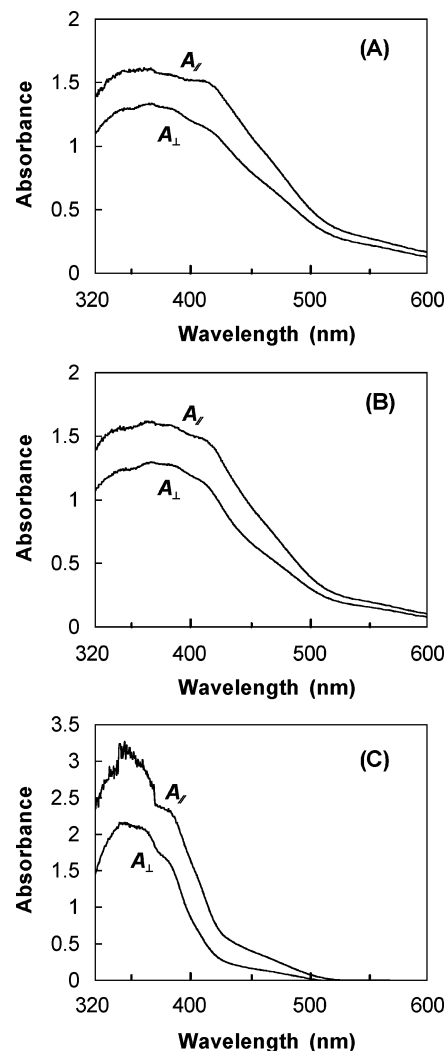


Figure 6. Polarized absorption spectra of PA95D5 (A), PA90D10 (B), and PA50D50 (C). $A_{||}$ and A_{\perp} are the absorbance measured with light polarized parallel and perpendicular to the rubbing direction of the alignment layers, respectively. Thickness of the films was 2 μm .

$$R = A_{||}/A_{\perp} \quad (2)$$

where $A_{||}$ and A_{\perp} are the absorbance measured with light polarized parallel and perpendicular to the rubbing direction of the alignment layers, respectively. The order parameter S is related to the dichroic ratio R by the following equation:³⁹

$$S = (R - 1)/(R + 2) \quad (3)$$

As Figure 6 shows, the absorption maximum in the optical absorption spectra of the LCN films is located at ≤ 365 nm due to a π - π^* transition of the azobenzene moieties. However, the absorption maximum of PA50D50 is too strong to be used for the calculation; the dichroic ratios and the order parameters of the LCN films are calculated from the polarized absorbance at 380 nm and shown in Table 4. It is clear that the order parameter increases with the increment of the cross-linking density. This is because the higher the cross-linking density, the more intense the constraints on the segmental motion, and the better the fixation of the molecular order. As stated above, this result is in agreement with that obtained from the birefringence measurement.

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Table 4. Dichroic Ratios and Order Parameters of the LCN Films^a

LCN film	<i>R</i>	<i>S</i>
PA95D5	1.20	0.062
PA90D10	1.24	0.074
PA50D50	1.41	0.120

^a Calculated from the polarized absorbance at 380 nm in Figure 6 according to eqs 2 and 3.

Photoinduced Bending and Unbending Behavior of LCN Films. As shown in Figure 7A, a partially free-standing LCN film was put on a glass substrate heated by the hot stage, and normal irradiation of unpolarized light was performed when the films with different cross-linking densities were heated to a temperature 20 °C higher than their T_g . Figure 7B shows the photographs of PA95D5 exhibiting bending and unbending behavior upon UV and visible light irradiation: Figure 7B(a) shows the film before photoirradiation. Figure 7B(b) and (c) show how the film bent after exposure to 366-nm light with the intensity of 1.5 mW/cm² for 1 and 2 min. It was found that the film bent toward the irradiation direction of the incident light along the rubbing direction. It was also observed that after the film was exposed to UV light for about 2 min, the bending extent reached maximum as shown in

Figure 7B(c), and had no increase upon further photoirradiation. Additionally, after visible light irradiation at >540 nm, the bent film reverted to the initial flat state completely as shown in Figure 7B(d). This photoinduced bending and unbending behavior could be repeated without apparent fatigue by alternate irradiation of UV and visible light. As Figure 7C and D show, the similar bending and unbending behavior could be induced by light in PA90D10 and PA50D50. As mentioned in the Introduction, the UV light irradiation brings out the *trans*–*cis* isomerization of the azobenzene moieties and even the LC–I phase transition; therefore, not only the size but also the alignment order of the azobenzene moieties is reduced and leads to a volume contraction. The volume contraction only at one surface of the films because of the strong absorption of light by the azobenzene moieties at about 360 nm is suggested to bring about the bending behavior.³³

Furthermore, it is interesting to note that the maximum bending extents were different among the LCN films with different cross-linking densities. As Figure 7B(c), 7C(c), and 7D(c) show, the maximum bending extent increased with the increment of the cross-linking density. Particularly, PA50D50 curled up to a column-like shape by conquering the effect of adhesion between

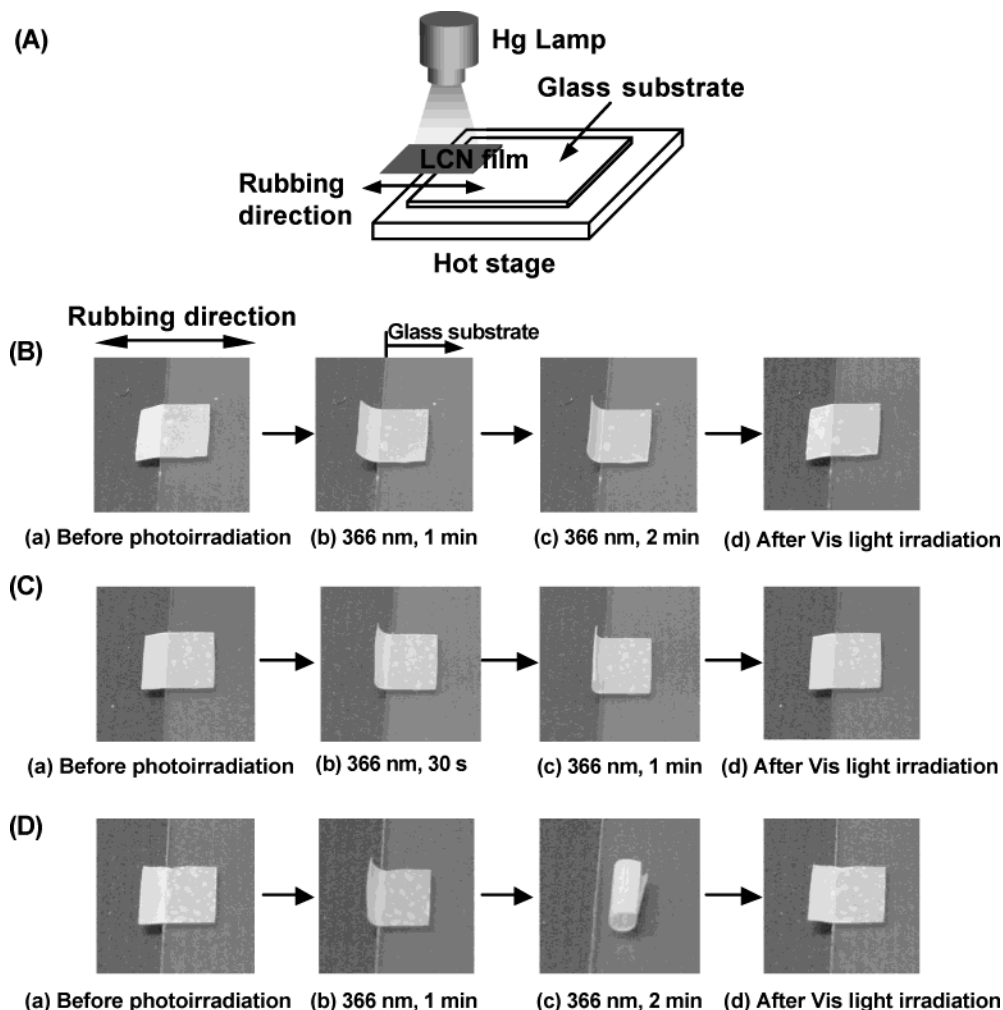


Figure 7. Schematic illustration of the experimental setup (A), and photographs of PA95D5 (B), PA90D10 (C), and PA50D50 (D) exhibiting photoinduced bending and unbending behavior. When heated to a temperature 20 °C higher than T_g , the flat films (a) bent toward the irradiation direction of the incident light after exposed to UV light at 366 nm (1.5 mW/cm²) (b, c), and the bent films were flattened again by irradiation of visible light at >540 nm (d). Size of the films: 5 mm × 5 mm × 17 μm.

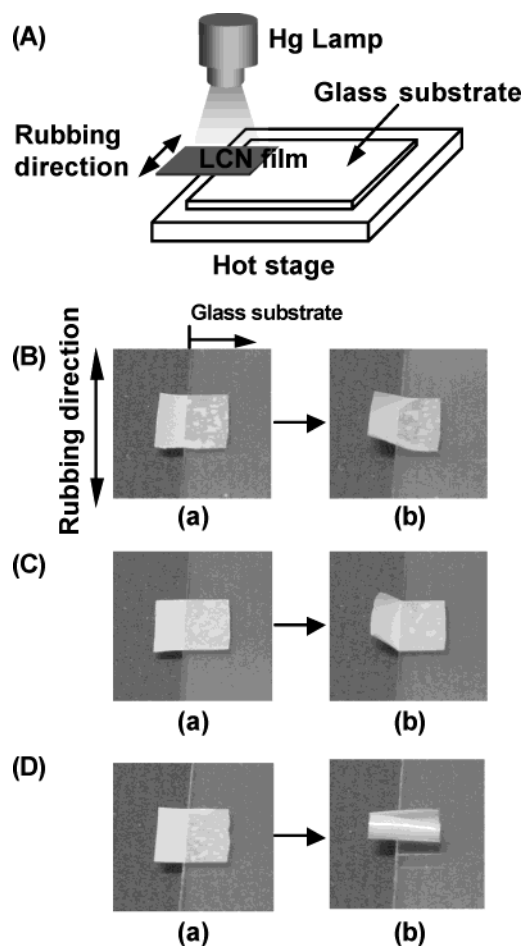


Figure 8. Schematic illustration of the experimental setup (A), and photographs of PA95D5 (B), PA90D10 (C), and PA50D50 (D) before (a) and after (b) irradiation of unpolarized light at 366 nm, when the rubbing direction was parallel to one side of the glass substrate.

the substrate and the film. Because the LCN film with higher cross-linking density holds higher order parameter, meaning that more azobenzene moieties are aligned along the rubbing direction, the reduction in size and alignment order of these more azobenzene moieties gives rise to larger volume contraction along the rubbing direction, contributing to larger bending extent of the film along this direction.

In addition, the bending speeds were also different among the LCN films with different cross-linking densities. As Figure 7B and C show, it took about 2 min for PA95D5 to bend maximally, whereas it took just about 1 min for PA90D10—namely, the bending of PA90D10 was faster than that of PA95D5. This result is ascribed to larger volume contraction in PA90D10 than PA95D5. However, the bending of PA50D50 was slower than that of PA90D10, although larger volume contraction is produced in PA50D50 than PA90D10. This is because, for the occurrence of the photoinduced bending, a relaxation of polymer segments is necessary to transfer the change in structure and alignment of the azobenzene moieties at the film surface to the transformation of the conformation in the entire polymer network. From the DSC measurement, it has been clarified that PA50D50 exhibits higher T_g than PA90D10, demonstrating that the mobility of the polymer segments in

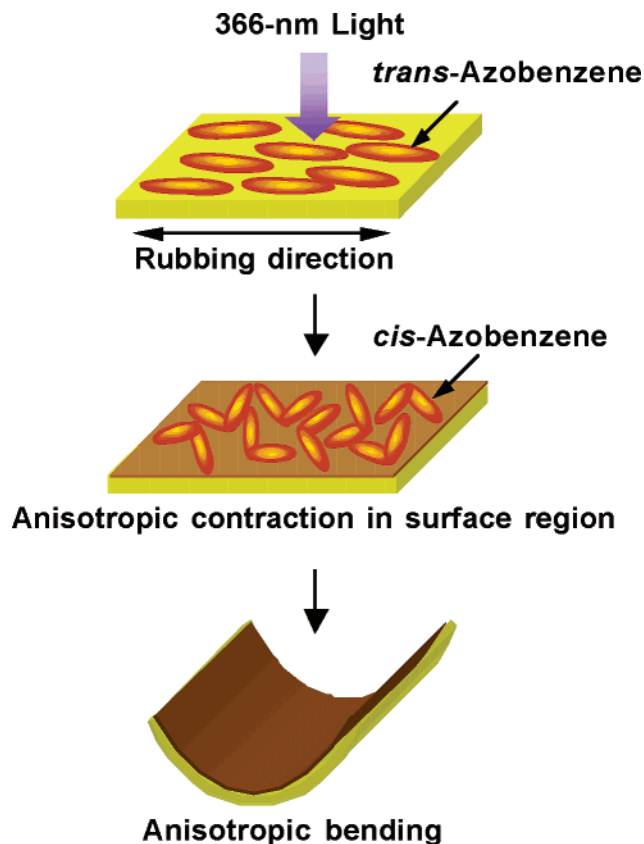


Figure 9. Schematic illustration of plausible mechanism of the anisotropic bending behavior.

PA50D50 is less than that in PA90D10; therefore, PA50D50 bent more slowly than PA90D10.

The LCN films have been demonstrated to possess anisotropy in the alignment of the azobenzene moieties; therefore, anisotropic behavior was expected in their response to external stimuli. As Figure 8A shows, the films used in Figure 7 were rotated by 90° in such a way that the rubbing direction became parallel to one side of the glass substrate. The photographs of the films before and after irradiation of unpolarized light at 366 nm are shown in Figure 8B–D. It was observed that the films still bent along the rubbing direction, indicating that the bendings of the films are anisotropically induced, only along the rubbing direction of the alignment layers. It is because the azobenzene moieties are preferentially aligned along the rubbing direction of the alignment layers, that the decrease in size and alignment order of azobenzene moieties is produced just along this direction. The resultant anisotropic volume contraction in the surface region contributes to the anisotropic bending behavior only along the rubbing direction (Figure 9).

Conclusion

It was shown that the mixtures of an LC monoacrylate and a diacrylate can be used in preparation of anisotropic networks with various cross-linking densities by thermal polymerization carried out in an isotropic phase of the polymerizable mixtures. The optical anisotropy in the films evaluated by POM and polarized IR spectroscopy demonstrates that the azobenzene moieties are preferentially aligned along the rubbing

direction of the alignment layers, whereas the polymer main chains are essentially disordered without any preferential alignment direction. The order parameters of the films were determined from the polarized UV absorbance, and it was found that the order parameter increased with increasing the cross-linking density. The birefringence of the films measured at room temperature was also found to increase with the increment of the cross-linking density due to the effect of the different order parameters in the films.

The free-standing films were found to show photoinduced bending and unbending behavior: upon exposure to unpolarized UV light at 366 nm, the films bent toward the irradiation direction of the incident light, and the bent films reverted to the initial flat state completely upon exposure to unpolarized visible light at >540 nm. It is suggested that the volume contraction

only at the film surface induced by the photochemical changes in size and alignment order of the azobenzene moieties leads to the bending behavior. It was observed that the maximum bending extent increased with increasing the cross-linking density, because higher order parameter in the film with a higher cross-linking density results in a larger volume contraction at the film surface. Moreover, the bending speeds, affected not only by the volume contraction at the film surface but also by the mobility of the polymer segments, were different for the films with different cross-linking densities. In addition, the bendings in the films were anisotropically induced, only along the rubbing direction of the alignment layers.

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