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Preparation and Characterization of Azobenzene Liquid-Crystalline Elastomer Films with Homeotropic Alignment

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Azobenzene liquid-crystalline elastomer (LCE) films with homeotropic alignment were prepared by in-situ photopolymerization of mixtures of an LC monomer and a cross linker, both of which contain azobenzene chromophores. Thermodynamic and mesomorphic properties of the monomers and the LCE films were determined by differential scanning calorimetry and polarizing optical microscopy. X-ray diffraction patterns revealed that the LCE films show a smectic A phase. Polarized UV spectra and conoscopic observation with a polarizing optical microscope demonstrated that the azobenzene mesogens are aligned homeotropically in the films.

Keywords: homeotropic; liquid-crystalline elastomer; photopolymerization

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INTRODUCTION

LCEs are rubbers whose constituent molecules are orientationally ordered. Because of their unique optical and mechanical properties, LCEs have been intensively investigated over the last two decades [1–3]. One of the most characteristic properties of the LCEs was first suggested by de Gennes *et al.* [4]. They proposed that a slight drop in the temperature across the isotropic to nematic transition is able to cause a strong uniaxial deformation of LCEs at nearly constant volume, and thermomechanical effects are generated. After that, it was also observed that nematic LCEs exhibit a spontaneous contraction along the director axis when heated above the nematic to isotropic phase transition temperature [5].

Generally, the phase transition of LCEs from a nematic to an isotropic phase is induced by heating the samples to high temperatures. However, we have developed a concept of photochemically induced phase transition of LCs [6]. We found that some photochromic molecules such as azobenzene could isothermally trigger the phase transition of LCs through the photochemical reaction of the chromophores. The working principle of the photochemical phase transition can be interpreted in terms of the changes in geometrical structure of the chromophores: the *trans* azobenzene having a rod-like shape stabilizes the LC phase structure, whereas the bent *cis* acting as an impurity disrupts the orientational order. Recently, Finkelmann *et al.* achieved a large photocontraction by using azobenzene-containing LCEs ascribed to the photochemical phase transition [7]. Most lately, we have realized a bending mode of deformation in LCE films containing azobenzene moieties in response to light [8,9]. This phenomenon is assigned to the generation of a difference in volume between the film surface and the bulk by irradiation of light.

In the above works, all of the photoresponsive LCEs used were aligned homogeneously. It has been reported that the alignment direction of the azobenzene mesogens plays an important role for the photoinduced bending behavior [10,11]. Therefore, in this study, photoresponsive LCE films containing azobenzene moieties with homeotropic alignment were prepared, and their optical properties were investigated.

EXPERIMENTAL

Materials

The structures of a monofunctional LC monomer, 6-4-(4-hexyloxy-phenylazo)phenoxy]hexyl acrylate (**A6AB6**), and a difunctional

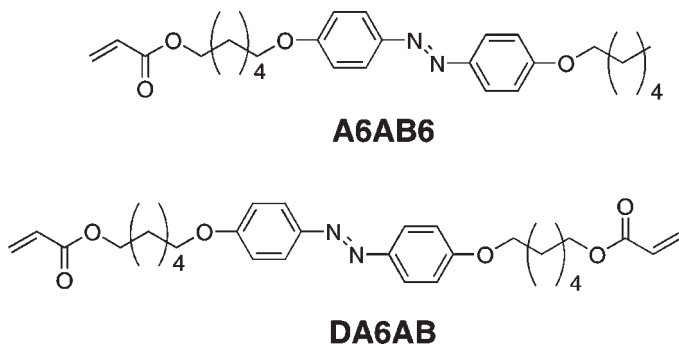


FIGURE 1 Structures and abbreviations of the LC monomer and the cross-linker used in this study.

monomer, 4,4'-bis[6-(acryloyloxy)hexyloxy]azobenzene (**DA6AB**), used in this study are shown in Figure 1. Both compounds were prepared according to the method reported previously [12].

In-situ Photopolymerization Method

The LCE films were prepared by in-situ photopolymerization of the mixture of **A6AB6** and **DA6AB** (mol/mol: 90/10), containing 1 mol% of a photoinitiator (Ciba Specialty, Irgacure 784). The melt of the mixture was put into a 10- μm -thick glass cell, which had been treated with n-octadecyltrimethoxysilane for homeotropic alignment. It was confirmed that the photoinitiator did not destabilize the LC phase at this concentration and no spontaneous thermal polymerization occurred during the injection of the polymerizable sample into the cell. After the sample was cooled down slowly (0.5°C/min) to a polymerization temperature (88°C, in the nematic phase), photoirradiation was performed at >540 nm (3 mW/cm², at 547 nm) with a 500-W high-pressure mercury lamp through glass filters (Toshiba, Y-52 + IRA-25) for 2 h. After polymerization, the LCE films were taken off from the cell.

Characterization Methods

The thermodynamic properties of the monomers and the LCE films were determined by differential scanning calorimetry (DSC, Seiko I&E, SSC-5200 and DSC220C) at heating and cooling rates of 2°C/min for the monomers and 10°C/min for the films. At least three scans were performed to check the reproducibility. The films were washed

with chloroform to completely remove unreacted monomers, and then dried under reduced pressure. The mesomorphic properties and phase transition behavior were examined with a polarizing optical microscope (POM, Olympus, BH-2) equipped with a hot stage (Mettler, FP-90 and FP-82). The X-ray diffraction measurement of the LCE films was performed by X-ray diffractometry (XRD, Rigaku, RINT 2000 Ultima + /PC; CuK α 1 radiation). The polarized UV spectra of the films were measured at room temperature with a UV-vis absorption spectrometer (Jasco, V-550).

RESULTS AND DISCUSSION

Mesomorphic Properties of Monomers

The mesomorphic properties of the monomers were studied by POM and DSC. For **A6AB6**, a typical schlieren texture of a nematic phase was observed at 86°C and then isotropization occurred at 92°C upon heating. When cooled from the isotropic phase, the nematic phase appeared at 92°C and then a monotropic smectic phase at 85°C. Crystallization started at 77°C. However, **DA6AB** did not show any mesomorphism. In addition, it was found that the polymerizable sample exhibited a nematic phase from 92°C to 86°C and a smectic phase from 85°C to 75°C. Thermodynamic properties of the monomers and the polymerizable sample are summarized in Table 1.

TABLE 1 Phase Transition Temperatures and Thermodynamic Parameters of Compounds Used in this Study

Compound	Phase transition temperature ^a (°C)	ΔH_{NI} (kJ/mol)	ΔS_{NI} (J/mol·K)	ΔH_{SI} (kJ/mol)	ΔS_{SI} (J/mol·K)	ΔH_{SN} (kJ/mol)	ΔS_{SN} (J/mol·K)
A6AB6	I 92 N (85 S) 77 K	1.1	3.1	—	—	1.3	3.7
DA6AB	I 92 K	—	—	—	—	—	—
Polymerizable sample	I 92 N 85 S 75 K	1.2	3.4	—	—	1.7	4.5
LCE film	I 147 SmA 60 G	—	—	3.3	9.9	—	—

^aI, isotropic; N, nematic; S, smectic; K, crystal; G, glass; ΔH_{NI} , change in enthalpy of N-I phase transition; ΔS_{SI} , change in entropy of N-I phase transition; ΔH_{SN} , change in enthalpy of S-N phase transition; ΔS_{SN} , change in entropy of S-N phase transition. ΔH_{SI} , change in enthalpy of S-I phase transition; ΔS_{SI} , change in entropy of S-I phase transition.

Mesomorphic Properties of LCE Films

The DSC thermograms of the LCE films are shown in Figure 2, and the results are gathered in Table 1. The glass transition temperature (T_g) of the LCE films appeared around 60°C , and the DSC curve also exhibited a broad endothermic peak around 147°C assigned to the LC to isotropic phase transition. By the study of POM equipped with the hot stage, light transmission with a film between crossed polarizers was observed up to temperatures as high as 200°C . It was found that some anisotropy remains in the film even at such a high temperature. In other words, the LC to isotropic phase transition is incomplete in the LCE films [13].

To investigate the LC phase in the LCE films, the X-ray diffraction measurement was performed, and the results are shown in Figure 3(A). A strong small-angle reflection was observed at $2\theta_1 = 2.86^\circ$, corresponding to a d-spacing of $d_1 = 3.08\text{ nm}$. A set of small-angle reflections from the second to the fourth order ($2\theta_2 = 5.68^\circ$, $2\theta_3 = 8.50^\circ$, $2\theta_4 = 11.32^\circ$, corresponding to $d_2 = 1.54\text{ nm}$, $d_3 = 1.04\text{ nm}$, $d_4 = 0.78\text{ nm}$, respectively) were also detected. The intramolecular reflection which was expected to be detected in a wide range was quite weak due to the homeotropic alignment of the LCE films. Figure 3(B) shows a molecular model of **A6AB6**, from which the molecular length (l) is calculated as $l = 3.22\text{ nm}$. Since the d-spacing of 3.08 nm is in agreement with the molecular length of 3.22 nm , a smectic A phase is

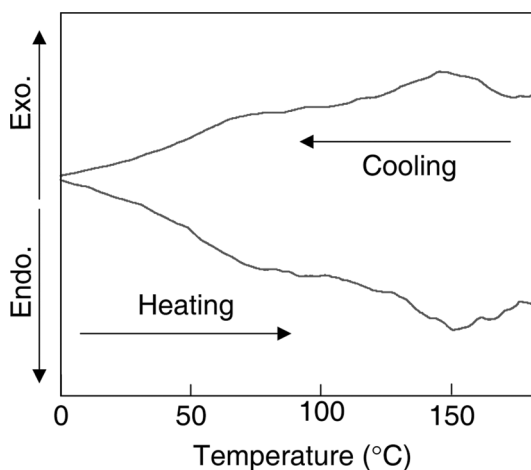


FIGURE 2 DSC thermograms of the LCE films. Scan was carried out at $10^\circ\text{C}/\text{min}$ for three times, and the result of the 3rd scan is shown.

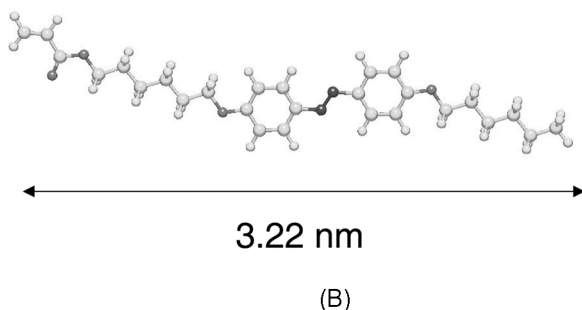
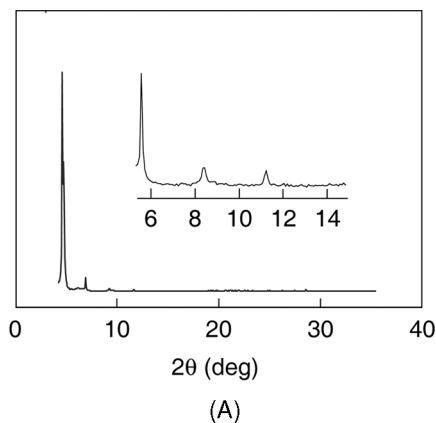


FIGURE 3 X-ray patterns of the LCE films (A) and a molecular model of the monomer **A6AB6** (B). Inset figure in (A) shows the magnified intensity profile in the regions of $2\theta = 5^\circ$ – 14° .

presumed [14]. This implies that a phase transition occurs during the photopolymerization, since the mixture of the monomers showing the nematic phase was used for the preparation of the LCE films.

Optical Properties of LCE Films

The optical anisotropy in the LCE films was evaluated at room temperature by measuring the transmittance of the probe light through crossed polarizers, when a film was set between the polarizers and rotated (Fig. 4(A)). In order to avoid any angular-dependent absorption of the azobenzene moieties, light with a wavelength longer than 540 nm, which is far from the absorption band of the azobenzene moieties, was used as the probe light [15]. As shown in Figure 4(A),

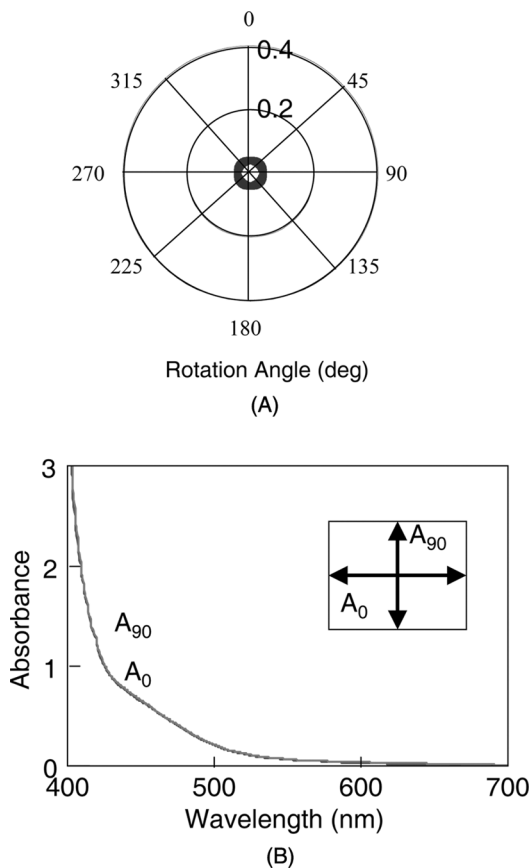


FIGURE 4 Angular-dependent transmittance of the LCE films evaluated by POM at room temperature (A) and polarized absorption spectra of the LCE films (B).

the intensity of transmittance of the probe right was quite low ($< 3\%$), and showed no change when the film was rotated. These results indicate that there is no in-plane anisotropy in the films.

To verify whether the azobenzene mesogens in the LCE films have in-plane anisotropy or not, the polarized absorption spectra were measured and shown in Figure 4(B). The polarization directions of the measurement beam for A_0 and A_{90} were perpendicular to each other. It is clear that there is no difference between these two spectra, demonstrating that the azobenzene mesogens have no in-plane alignment direction in the films.

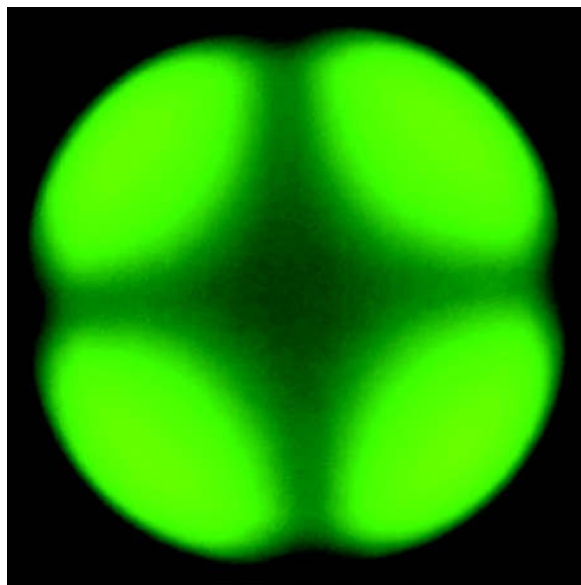


FIGURE 5 Conoscopic image of the LCE films observed with POM.

In addition, the conoscopic observation of the films by POM exhibited a dark cross image as shown in Figure 5. The cross point represents the optic axis of the LC phase; it is clear that the azobenzene mesogens are aligned homeotropically in the films.

CONCLUSIONS

The azobenzene LCE films with homeotropic alignment were obtained by *in-situ* photopolymerization. With the X-ray diffraction measurement, it was found that the LCE films show a smectic A phase. By the POM observation, no in-plane anisotropy was found in the LCE films. Furthermore, the conoscopic observation of POM exhibited that the azobenzene mesogens are aligned homeotropically in the films. Using the homeotropic LCE films, we think that different photoinduced bending behavior may be obtained compared with that of the homogeneous LCE films previously reported. This is now under investigation.

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