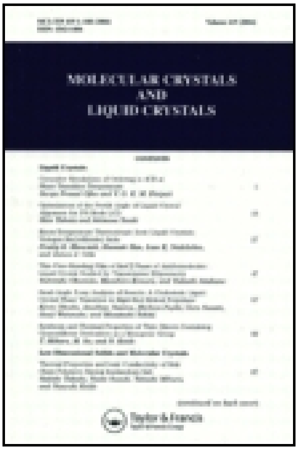

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# Preparation and Characterization of Crosslinked Liquid-Crystalline Polymer Films with a Long Spacer

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# Preparation and Characterization of Crosslinked Liquid-Crystalline Polymer Films with a Long Spacer

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*Three azobenzene acrylate monomers containing alkyl spacers of different length were synthesized. Thermodynamic and mesomorphic properties of the monomers were measured by differential scanning calorimetry and polarizing optical microscopy. A crosslinker with the undecyl spacer was also synthesized to prepare crosslinked liquid-crystalline polymer films by photopolymerization. Polarized UV spectra and polarizing optical micrographs demonstrated that the mesogens are aligned homogeneously in the films. Low glass transition temperature of the films enabled them to bend near room temperature upon UV irradiation. Besides, the films generally bent away from the light source before they at last bent towards the light irradiation.*

**Keywords:** crosslinked liquid-crystalline polymer film; long spacer; photoinduced bending

## 1. INTRODUCTION

Stimuli-responsive materials refer to those materials that exhibit abrupt property changes in response to small changes in external stimuli, such as pressure, stress, temperature, electric and magnetic

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field, pH, light and so on. These years researchers show more and more interest on smart deformable polymer materials, such as conducting polymers [1], shape memory polymers [2–4], polymer gels [5–8] and crosslinked liquid-crystalline polymers (CLCPs) [9–20], because polymers exhibit advantageous properties: high processabilty, softness, easy fabrication characteristics, high corrosion resistance and low manufacturing costs and their stimuli-responsive deformations qualify them for the applications in various actuators.

Among various deformable polymer materials, CLCPs, a kind of lightly-crosslinked polymer networks, attract increasing attention, because they exhibit elasticity similar to traditional rubbers combined with intrinsic high order of mesogens inherited from liquid crystals (LCs). It has been found that CLCP films contracted when heated above nematic-isotropic phase transition temperature ($T_{NI}$) and reverted to their original length when cooled down below $T_{NI}$ [9–11]. This is known as thermomechanical effect of CLCPs.

Recently it was discovered that CLCPs could also deform upon light irradiation (photomechanical effect) [12–20]. Compared to other stimuli, light has more advantages, for it can be controlled rapidly and remotely and allows actuate control. To show photomechanical behavior, CLCPs need the incorporation of such photochromic moieties as azobenzenes. For the azobenzene moieties, their rod-like *trans* form stabilizes the order of mesogens in CLCPs, while the bent *cis* form lowers the order parameter of the networks, and even leads to a transition from LC to isotropic phase in the whole system. The order changes may result in the deformations in CLCPs.

Finkelmann et al. introduced the azobenzene moieties into monodomain CLCP films with a siloxane main chain and obtained $\sim 20\%$ contraction when exposed to UV light at 360 nm [12]. Their work was followed by the discovery of the bending behavior of azobenzene-containing monodomain CLCP gels and solid films [14]. The polydomain CLCP films were controlled to bend along any direction precisely by changing the polarization direction of the actinic light [17]. It was also found that CLCP films with a homeotropic alignment showed a bending away from the actinic light [18]. Additionally, densely-crosslinked LCPs with a hybrid alignment were reported to be able to twist upon UV light irradiation [19].

From the above-mentioned results, we can see that the azobenzene moieties are incorporated into various tailored CLCP structures, which play an important role in transfering microscopic photochemical changes in dimensions of azobenzenes to various kinds of macroscopic deformations. These materials exhibiting different kinds of deformations are greatly potential for the applications in robots, artificial muscles, actuators and micromechanical devices.

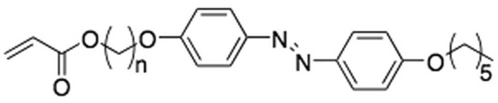
In our previous work, we prepared azobenzene-containing CLCP films with an acrylate main chain and a hexyl spacer and investigated their photoinduced bending behavior in good solvents or by heating them, for $T_g$s of the films are higher than room temperature [14–18]. It has been reported that the spacer length has much effect on the formation of LC phase [21]. On the other hand, the spacer links the main chain with the mesogen, thus influencing the rigidity of polymer chains and therefore $T_g$ of the polymers. In this study, we synthesized three kinds of azobenzene-containing acrylate monomers with octyl, decyl and undecyl as spacers to investigate the effect of the spacer length on the formation of LC phase. We also prepared the CLCP films with an undecyl spacer and observed the photoinduced bending behavior.

## 2. EXPERIMENTAL

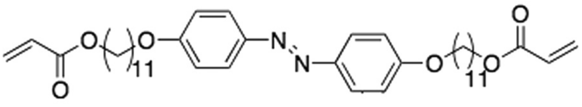
### 2.1. Materials

The structure of the monomers, **AnAB6** ($n = 8, 10, 11$), and a crosslinker, **DA11AB**, involved in this study are shown in Figure 1. These compounds were synthesized according to the method reported in literature [22].

The CLCP films were prepared by in-situ photopolymerization of a mixture of **A11AB6** and **DA11AB** (mol/mol = 9/1) containing 1 mol% photoinitiator (Ciba Specialty, Irgarcure 784). The melt of the mixture was injected into a cell with 20-μm-thick gap at 95°C, then cooled down slowly (0.5°C/min) to the polymerization temperature at 78°C (in a nematic phase). The inner surfaces of the cell had been coated with



**AnAB6 (n = 8, 10, 11)**



**DA11AB**

**FIGURE 1** Structures and abbreviations of the monomers and the crosslinker used in this study.

a rubbed polyimide layer (JSR, AL1254) to obtain a homogeneous alignment of the mesogens. The photopolymerization was performed at >540 nm (2.1 mW/cm$^2$ at 547 nm) with a high pressure Hg lamp through glass filters (Toshiba, Y-52 and IRA-25S) for 3 hours. After photopolymerization, the film was removed from the cell with a cutter.

### Characterization Method

The thermodynamic properties of the monomers and films were determined by differential scanning calorimetry (DSC; Seiko I&E, SSC5200 and DSC220C) at the rate of 2°C/min for the monomers and 10°C/min for the films, and three scans were performed to check the reproducibility. The films were washed in chloroform to remove the unreacted monomers completely and dried in vacuum before the DSC measurement. The mesomorphic properties and phase transitions were observed with a polarizing optical microscope (POM; Olympus, BX50) equipped with a Mettler hot stage (models FP-90 and FP-82). The polarized UV spectra of the films were measured at room temperature with a UV-Vis absorbance spectrometer (Jasco, V-550).

## 3. RESULTS AND DISCUSSION

### 3.1. Mesomorphic Properties of Monomers and Crosslinker

The mesomorphic properties of the monomers were investigated by DSC and POM, and the results are listed in Table 1. It was found that **A8AB6** melted at 100°C upon heating, and crystallized at 93°C upon cooling, exhibiting no mesomorphism. **A10AB6** did not show LC phase, just with a melting point at 95°C during the heating process

**TABLE 1** Phase Transition Temperatures of Compounds in This Study

| Compound | Phase transition temperature (°C) |
|---|---|
| **A8AB6** | Heating: K 100 I<br>Cooling: K 93 I |
| **A10AB6** | Heating: K 95 I<br>Cooling: K 78 I |
| **A11AB6** | Heating: $K_1$ 69 $K_2$ 84 N 89 I<br>Cooling: K 56 S 67 N 87 I[a] |
| **DA11AB** | Heating: K 71 S 83 N 88 I<br>Cooling: K 61 S 81 N 87 I |
| **A11AB6**/**DA11AB** (mol/mol = 9/1) | Cooling: K 50 S 66 N 86 I |

[a] K, crystal; S, smectic; N, nematic; I, isotropic.

and a crystallization temperature at 78°C during the cooling process. For **A11AB6**, a recrystallization was observed at 69°C, and a nematic phase from 84°C to 89°C upon heating. When cooled down from the isotropic phase, **A11AB6** entered a nemectic phase at 87°C and a smectic phase at 67°C, followed by a crystallization at 56°C.

To prepare the CLCP films, we synthesized the crosslinker **DA11AB** that has the same spacer length as **A11AB6**. **DA11AB** was observed to exhibit enantiotropic smectic and nematic phases (Table 1). The mesomorphic properties of the mixture of **A11AB6** and **DA11AB** (mol/mol = 9/1) was also measured by DSC and POM. It was found that a nematic phase appeared between 86°C and 66°C, and a smectic phase between 66°C and 50°C during the cooling process (Table 1).

## 3.2. Mesomorphic Properties of CLCP Films

The DSC thermogram of the CLCP films is shown in Figure 2. $T_g$ of the CLCP films appeared around 19°C. Another endothermal peak appeared around 71°C, whose ascription is not clear and still under investigation. By the study of POM equipped with the hot stage, we found that light transmission with a film set between two crossed polarizers was observable even when the temperature was raised up to 200°C. This indicates that some anisotropy remains in the films even at such a high temperature and the transition from LC to isotropic phase is incomplete in the CLCP films.

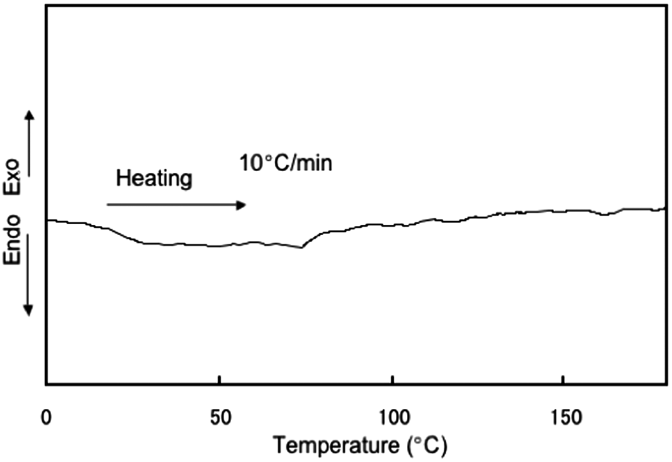


**FIGURE 2** DSC curve of the CLCP films. Three scans were carried out at 10°C/min, and the result of the 3rd scan is shown.

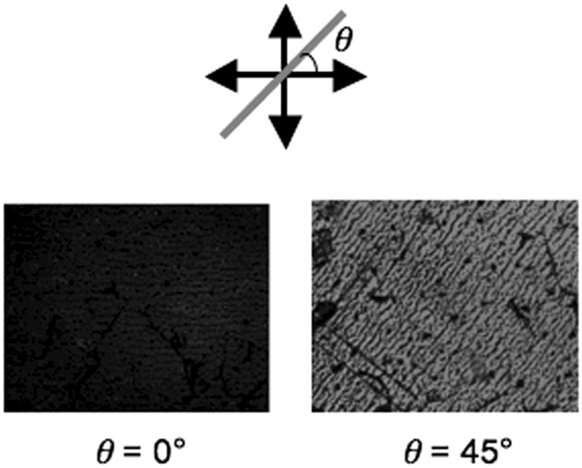


**FIGURE 3** Polarizing optical micrographs of the films. The black arrows indicate the direction of optical axes of the polarizers, while the grey line shows the rubbing direction of the alignment layers. Thickness of the films was 2 μm.

### 3.3. Optical Properties of CLCP Films

The anisotropic alignment of the mesogens in the CLCP films was evaluated at room temperature by measuring the transmittance of probe light through two crossed polarizers with a film between them. The polarizing optical micrographs of the film are shown in Figure 3. The highest transmittance appeared when the angle between the rubbing direction and the polarization direction of either polarizer was 45°, and the lowest appeared when the rubbing direction was parallel with the polarization direction. Consequently, periodic changes of dark and bright images were observed by rotating the film with an interval of 45°. These results reveal that mesogens are preferentially aligned along the rubbing direction of the cell used in the preparation of the film.

In order to further check the alignment of azobenzene moieties in the CLCP films, the polarized absorption spectra were detected and shown in Figure 4. It is known that *trans* azobenzenes show angular-dependent absorption of linearly polarized light: *trans* azobenzenes with their transition moments parallel to the polarization direction of linearly polarized light are activated very effectively to their excited states, followed by *trans-cis* isomerization, while *trans* azobenzenes with their transition moments perpendicular to the polarization

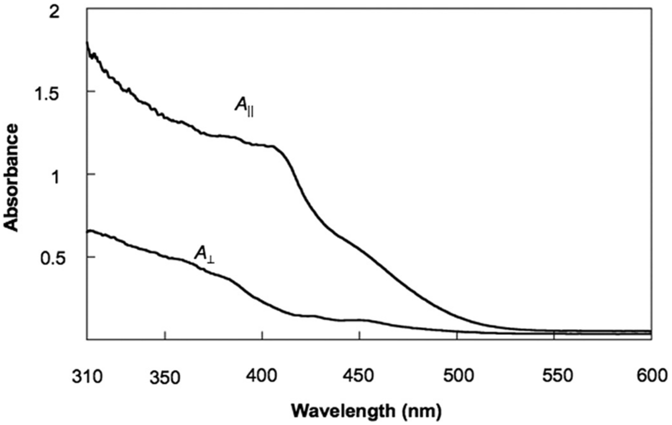


**FIGURE 4** Polarized absorption spectra of the CLCP films. $A_{\parallel}$ and $A_{\perp}$ are the absorption measured with the light polarized parallel and perpendicular to the rubbing direction of the alignment layers, respectively. Thickness of the films was 2 μm.

direction of actinic light are inactive towards isomerization. From Figure 4 we can see that the absorption measured with light polarized parallel to the rubbing direction of the alignment layers ($A_{\parallel}$) is larger than that measured with the two directions perpendicular to each other ($A_{\perp}$). This result indicates that the azobenzene mesogens are preferentially aligned along the rubbing direction of the alignment layers.

In order to calculate order parameter of the CLCP films, the dichroic ratio $R$ is given by the following equation:

$$R = A_{\parallel}/A_{\perp}$$

and the order parameter $S$ is related to the dichroism by the following equation:

$$S = (R - 1)/(R + 2)$$

For the CLCP films, the order parameter $S$ is calculated to be 0.39.

### 3.4. Bending and Unbending Behavior

The bending and unbending behavior of a CLCP film was investigated with the setup shown in Figure 5A. In lower temperature region (30°C–80°C), when the film was irradiated with UV light at 366 nm, it bent away from the light source at first and then toward the actinic

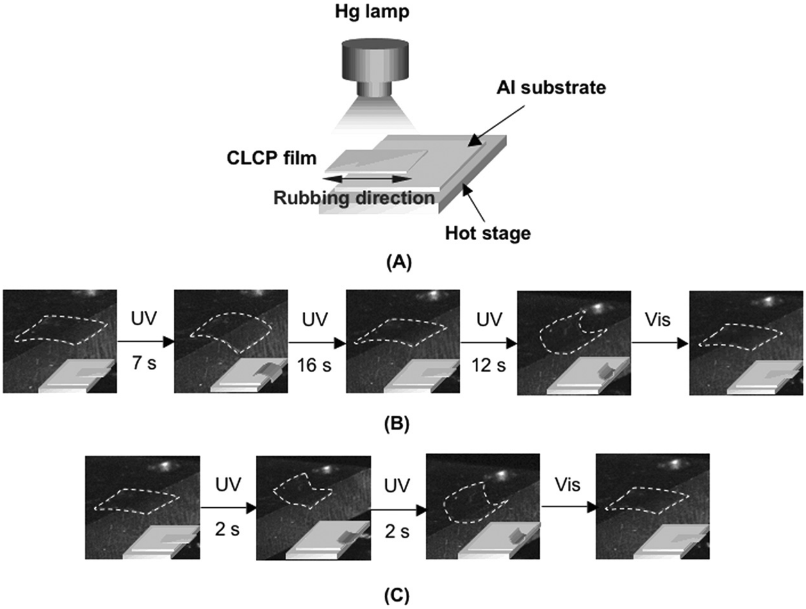


**FIGURE 5** Schematic illustration of the experimental setup (A), and photographs of the film exhibiting photoinduced bending and unbending behavior upon UV and visible light irradiation at 70℃ (B) and 100℃ (C). Intensity of UV light at 366 nm was 18 mW/cm$^2$. Size of the film was 4 mm × 4 mm × 20 μm.

light. Figure 5B shows the bending and unbending behavior of the CLCP film at 70℃ upon UV and visible light irradiation. However, as the temperature was raised, the bending away from the light source became less and less obvious, and even disappeared near 100℃. That is to say that the film bent towards the light resource directly at high temperatures, as illustrated in Figure 5thinsp;C. The bent film reverted to its original flat state when it was exposed to visible light at $>$545 nm.

## 4. CONCLUSIONS

Three azobenzene-containing acrylate monomers with different alkyl spacers were synthesized, and the CLCP films were prepared through in-situ polymerization of the mixture of **A11AB6** and **DA11AB**, both of which contain the undecyl spacer and exhibited LC property. The optical anisotropy of the films was evaluated by POM and the order parameter of the films was calculated according to the polarized absorption spectra. Due to the relatively long spacers, the films exhibited a low $T_g$, and could undergo bending and unbending behavior near room temperature. Upon UV light irradiation, the films always bent towards the light resource, but at lower temperatures the bending away from the actinic light was observed at beginning. This bending mode is quite different from that discovered in other azobenzene CLCP films we reported previously [14–17], and the bending mechanism is still under investigation.

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