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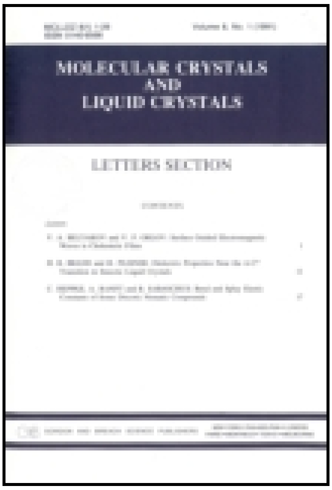

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
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Visible Light Induced Bending Behavior of Crosslinked Liquid Crystal Polymers Containing Azotolane with a Longer Spacer

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Published online: 06 Dec 2014.

To cite this article: Jianqiang Zhao & Yanlei Yu (2014) Visible Light Induced Bending Behavior of Crosslinked Liquid Crystal Polymers Containing Azotolane with a Longer Spacer, Molecular Crystals and Liquid Crystals, 601:1, 134-141, DOI: 10.1080/15421406.2014.940566

To link to this article: http://dx.doi.org/10.1080/15421406.2014.940566

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Mol. Cryst. Liq. Cryst., Vol. 601: pp. 134–141, 2014

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2014.940566

Visible Light Induced Bending Behavior of Crosslinked Liquid Crystal Polymers Containing Azotolane with a Longer Spacer

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One azotolane-containing acrylate monomer with a longer spacer and a non-azotolane crosslinker were synthesized. Crosslinked liquid crystal polymer (CLCP) films were obtained by thermal polymerization of the mixture of the monomer and the crosslinker with a molar ratio of 2:8. Thermodynamic and mesomorphic properties of the monomer, the crosslinker and the CLCP films were characterized by DSC and POM. The CLCP films showed a low glass transition temperature which ensured them to bend at room temperature upon visible light irradiation. Besides, the films have a faster bending speed compared with the previously-reported azotolane-containing CLCP films with a shorter spacer.

Keywords Azotolane; bending; deformation; alignment; Visible Light

1. Introduction

Recent years have witnessed a rapidly increasing interest in soft actuation materials which can experience macroscopic shape changes in response to physical or chemical stimuli, such as temperature [1], light [2], electric field [3], and pH variations [4]. Among various stimulating sources, light arises more interest because it can be manipulated conveniently, precisely, instantly and remotely. The most important is that it is a kind of clean energy. Crosslinked liquid crystal polymers (CLCPs) distinguish themselves from other polymers in possessing both the elasticity of polymer networks and the high order of mesogens inherited from liquid crystals (LCs) [5]. So it exhibits such unique properties as elasticity, anisotropy, stimuli resposiveness, and molecular cooperation effect. To perform a photomechanical effect, the CLCPs are necessary to incorporate photochromic moieties, whose photoisomeriazation triggers a large-scale photoinduced deformation of the CLCPs. Various kinds of deformation of the CLCPs have been achieved in response to UV light, including contraction, bending, and twisting [6]. Some novel three-dimensional movements driven by UV light have also been reported such as plastic motor [7], inchworm walk and flexible robotic arm motion [8], swimming [9], cilia motion [10], oscillators [11], cantilevers [12], micropumps [13], microvalves [14] and so on.

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The photoinduced deformations and various motions mentioned above are interesting, but the stimulating source is UV light, which is not environment-friendly and harmful to our health [15]. Our group has developed a new kind of the azotolane-containing CLCP films, whose deformation was induced by visible light due to an enlarged conjugation structure of the azotolane moieties [16]. We also prepared a visible-light-driven fully plastic microrobot based on the azotolane-containing CLCP films [17]. To extend the applications of this kind of the CLCPs in biological environment, our group further developed a novel composite CLCP material incorporated with lanthanide upconversion nanophosphors and succeeded in generating bending of the resulting composite film upon exposure to continuous-wave NIR light at 980 nm [18].

The above-mentioned azotolane CLCP films bear a nonanyl spacer and an azotolane mesogenic group in each side chain, since both the monomer and the crosslinker contain an azotolane group [16]. However, the synthesis of the azotolane-containing crosslinker and the thermal polymerization to prepare these CLCP films are very difficult: (1) There are seven steps in the synthetic route of the azotolane-containing crosslinker and some synthetic steps require very stringent experimental conditions; (2) Polymerization shrinkage effects are easy to take place in the thermal polymerization, thus it is difficult to prepare the CLCP films without any holes. In additon, the cost of the chemical agent to supply the nonanyl spacer is very expensive. In this work, we prepared a new azotolane monomer with a longer undecyl spacer (A11ABT) and a non-azotolane crosslinker (C11A) (**Scheme 1**). The properties of the monomer and the crosslinker as well as the bending and unbending behavior of the resulting CLCP films have also been investigated.

2. Experimental

Materials

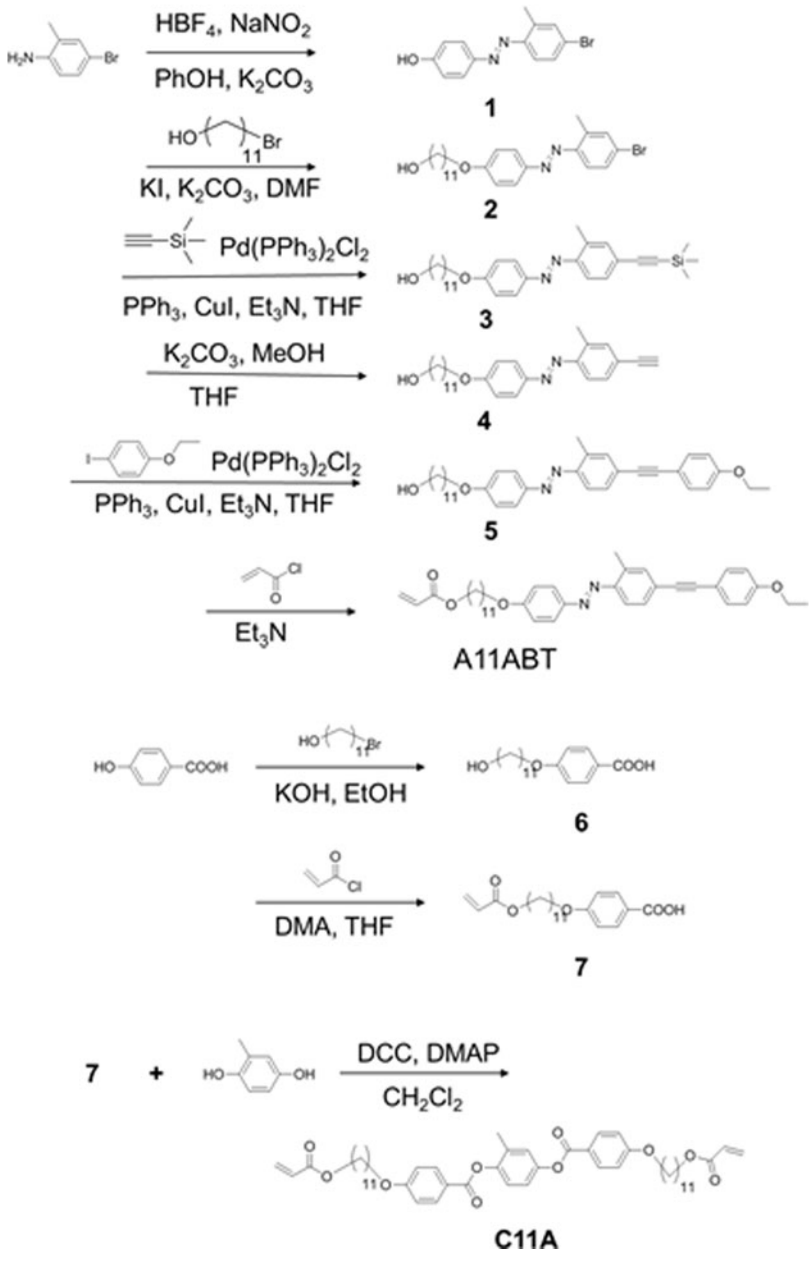
4-Bromo-2-methylaniline and 11-bromo-1-undecanol were purchased from Aldrich. Trimethyl silylacetylene, 4-iodophenetole, acrylate chloride, and 4-iodophenol were obtained from TCI. Tetrahydrofuran (THF) was purified by distilling. All the other reagents were used as received.

The synthesis of A11ABT containing the azotolane moiety and C11A was carried out in a similar method which has been published [16, 19]. The synthetic routes of A11ABT and C11A are outlined in Scheme 1.

The azotolane CLCP films were prepared by copolymerization of the mixture of A11ABT and C11A with a molar ratio of 2:8 containing 4 mol% of a thermal initiator (2,2′-azobis(Ncyclohexyl-2-methylpropionamide), Wako Pure Chemical). The mixture and the initiator were injected into a glass cell at 104°C (in a nematic phase) and the glass substrates were coated with polyimide alignment layers that had been rubbed to align the LC mesogens. The thermal polymerization was carried out in a vacuum oven under argon at 104°C for 24 h. The free-standing monodomain CLCP film was obtained by opening the cell and separating the film from the glass substrates.

Measurements

The thermodynamic properties of the monomer, the crosslinker, their mixtures, and the azotolane CLCP films were determined by differential scanning calorimetry (DSC; TA, Q2000) at heating and cooling rates of 3°C min^{-1} for the monomers and 10°C min^{-1} for the films. Three scans were applied to check the reproducibility. The mesomorphic



Scheme 1. Synthetic routes for the monomer A11ABT and the crosslinker C11A used in this work

properties were studied using a polarizing optical microscope (POM; Leika, DM2500P) equipped with a Mettler hot stage (Mettler, models FP-90 and FP-82).

The photoinduced bending and unbending behavior of the CLCP films was examined as follows: a partially free-standing film was put on a glass substrate at room temperature. The bending behavior of the film was observed upon irradiation with short-wavelength visible light at 470 nm obtained from LED (CCS, PJ-1505–2CA, HLV-24GR-3W). The bent film was exposed to 530 nm visible light (CCS, PJ-1505–2CA, HLV-24BL-3W).

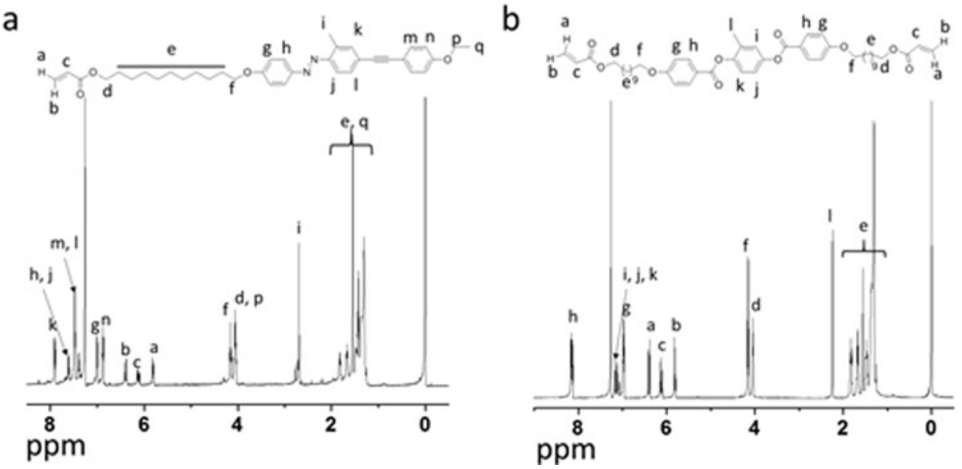


Figure 1. ^{1}H NMR spectra of A11ABT (a) and C11A (b) in $CDCl_3$.

The photographs of the bending and unbending behavior were taken by a digital camera (Olympus, SP-800UZ).

3. Results and Discussion

Characterization of Monomer, Crosslinker and Polymerizable Mixtures

The ^{1}H NMR spectra of A11ABT and C11A are shown in Fig. 1. In Fig. 1a, the methyl peak (i) of the azotolane group of A11ABT is located at 2.7 ppm and the vinyl peaks a, b, and c of the acrylate group are at 5.8, 6.4, and 6.1 ppm, respectively. In Fig. 1b, the methyl peak (l) of the phenyl group of C11A is around 2.2 ppm and the vinyl peaks a, b, and c of the acrylate group are at 5.8, 6.4, and 6.1 ppm, respectively. In addition, other chemical shifts and peak integrations of the protons in A11ABT and C11A are in excellent agreement with their expected structures, therefore we can infer the compounds have been successfully synthesized.

The mesomorphic properties and phase transitions of the monomer, the crosslinker, and their mixture were characterized by DSC and POM. The results are listed in Table 1. A11ABT shows an LC phase over a wide temperature range due to the rigid structure

Table 1. Phase transition temperatures of monomer, crosslinker, and polymerizable mixture

Compound	Phase transition temperature (°C)
A11ABT	Heating: K 89 N 142 I Cooling: K 62 N 141 I
C11A	Heating: K 82 N 101 I Cooling: K 66 N 100 I
A11ABT/C11A (mol/mol = 2/8)	Heating: K 78 N 107 I Cooling: K 37 N 106 I

[a] K, crystal; N, nematic; I, isotropic

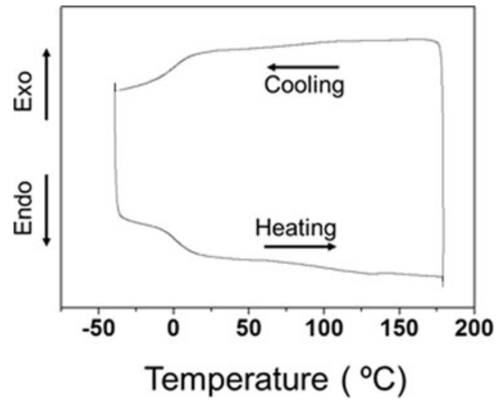


Figure 2. DSC curves of the CLCP films. Three scans were carried out at 10° C/min, and the result of the 3rd scan is shown.

of three benzene rings, which is able to stabilize the LC system. It was observed that a nematic phase exits from 89°C to 142°C upon heating. When cooled down from the isotropic phase, A11ABT entered a nematic phase at 141°C, followed by crystallization at 62°C. A11ABT has a lower clearing point compared with our previous azotolane-contaning monomer bearing a nonanyl spacer (171°C) [16], because A11ABT has a longer spacer. C11A was observed to exhibit a nematic phase from 82°C to 101°C upon heating and from 66°C to 100°C upon cooling, which also has a lower clearing point compared with our previous azotolane-contaning crosslinker (131°C) [16]. The mesomorphic properties of the mixture of A11ABT and C11A (mol/mol = 2/8) were found that a nematic phase appeared between 78°C and 107°C upon heating and between 37°C and 106°C upon cooling. The clearing point of this mixture is 37°C lower than that of our previous azotolane-contaning mixture [16].

Mesomorphic Properties of Azotolane CLCP Films

The results of DSC measurement on the obtained CLCP films are shown in Fig. 2. T_g of the CLCP films appeared around 0°C, much lower than that of our previously-reported azotolane CLCP films (about 23°C) [16], which is good for the deformation of CLCP film. The azotolane CLCP films exhibited a stable LC phase, even when the temperature was higher than 180°C.

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 a film are shown in Fig. 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.

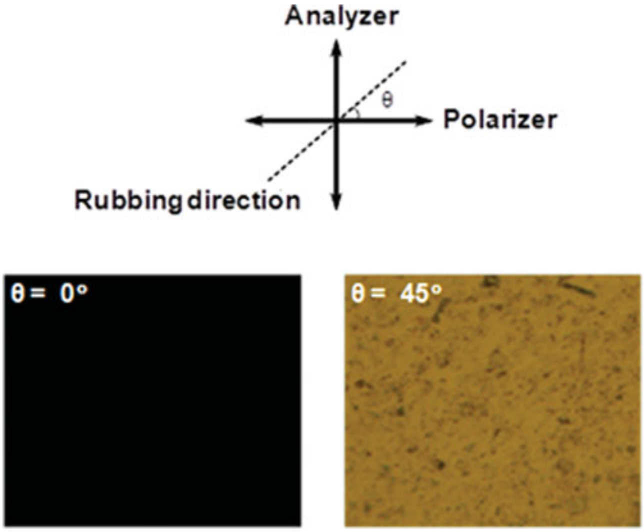


Figure 3. Polarizing optical micrographs of the films. The black arrows indicate the direction of optical axes of the polarizers, while the dashed line shows the rubbing direction of the alignment layers. Thickness of the film was 2 μm.

Photoinduced Bending and Unbending Behavior

Figure 4 shows photoinduced bending and unbending behavior of the obtained CLCP films when alternately exposed to visible light with two different wavelengths. A partially free-standing film was put on a glass substrate and the light irradiation was performed from

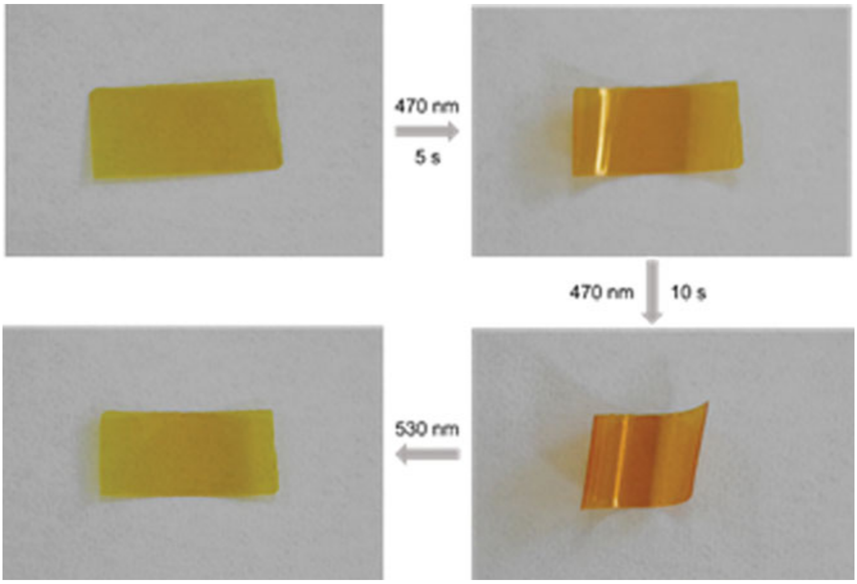


Figure 4. Photographs of the film exhibiting photoinduced bending and unbending behavior upon irradiation with 470 nm light (20 mW cm^{-2}), and then reverting back to the initial flate state after irradiation with visible light at 530 nm. Size of the films: 5 mm × 10 mm × 20 μm.

above. We can see that the CLCP film exhibits bending and unbending behavior at room temperature. When the film was irradiated with visible light at 470 nm, it bent toward the light source. Due to the lower azotolane content, the CLCP film reaches its maximum bending in 10 s and has a faster bending speed compared with our previously-reported azotolane CLCP films which need 60 s to reach the maximum bending [16]. It is because the lower azotolane concentrations, the deeper the incident light penetrates into the CLCP film, and thus the thicker the photoinduced contraction region generated, which causes the faster bending. The bent film reverted to its original flat state when it was exposed to visible light at 530 nm.

4. Conclusions

In conclusion, one azotolane-containing acrylate monomer with the undecyl spacer and a non-azotolane crosslinker were synthesized, both of which exhibited LC property. The CLCP films were prepared through in-situ polymerization of the mixture of A11ABT and C11A. Due to the longer spacer, the CLCP films have a low T_g around 0°C, which is rather lower than room temperature; therefore, the films can bend and unbend at room temperature induced by visibile light at 470 nm and 530 nm, respectively. Their bending speed is higher than our previously-reported azotolane CLCP films when irradiated with the same light intensity.

Funding

Financial supports from National Natural Science Foundation of China (Nos 51225304, 21134003, 21273048, and 51203023), and Shanghai Natural Science Foundation (No. 12ZR1401600) are greatly acknowledged.

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