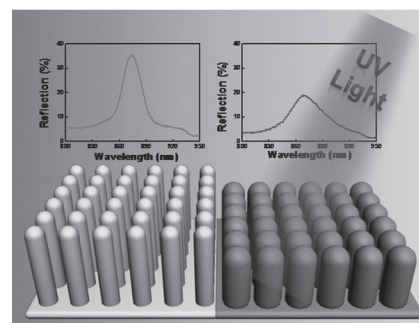


Light-Switchable Behavior of a Microarray of Azobenzene Liquid Crystal Polymer Induced by Photodeformation

Zeng Yan, Xinming Ji, Wei Wu, Jia Wei, Yanlei Yu*

A microarray with a period of about 1 μm was fabricated from a crosslinked liquid crystal polymer (CLCP) containing azobenzene groups by using the replica molding technique. In accordance with the photoinduced deformation of the CLCP induced by the photoisomerization of the azobenzene groups, on-off switch behavior on the reflection spectra of the microarray was observed by alternate irradiation with UV–Vis light. The reversible switch behavior indicates that the azobenzene CLCP microarray has potential applications in optical actuators.



1. Introduction

Crosslinked liquid crystal polymers (CLCPs) have recently attracted more and more attention because they exhibit such unique properties as elasticity, anisotropy, stimuli-responsiveness, and molecular cooperation effect.^[1] It has been reported that the CLCP films exhibited anisotropic contraction by heat because of the liquid crystal (LC)-isotropic thermal phase transition, accompanied by the cooperative effect of LC molecules and the strong correlation between the conformation of polymer chains and the alignment of mesogens.^[2] Furthermore, by incorporating azobenzene groups into the CLCPs, large deformations such as contraction and bending have been induced

by light due to the photoisomerization of the azobenzene chromophores.^[3–10]

Several thermoresponsive flexible microactuators have recently been fabricated from the CLCPs using such advanced techniques as soft lithography, microfluidic, and photomask technology.^[11–15] For example, Keller and co-workers^[12] used a soft lithography technique called replica molding to make the microarray of a main-chain LC elastomer and found each pillar showed ultralarge and reversible contraction during the phase transition from nematic to isotropic. Zentel and co-workers^[13] prepared monodisperse and monodomainic micrometer-sized LC elastomer beads by the use of a microfluidic setup, which exhibited a strong and rapid shape change of about 70% in length during the phase transition. Crawford and co-workers^[15a] used surface alignment and photopatterning techniques to fabricate a hexagonal array of 300 μm isotropic cylinders surrounded by a sea of chiral nematic LC, in which the maximum height difference between the chiral nematic and isotropic regions changed from 140 nm at room temperature to 300 nm upon heating to 200 °C. Elias et al.^[15b] fabricated thermally responsive patterned LC polymer films with the similar photopatterning method. Single-phase structures consisting of

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lines of cholesteric LC polymer as well as multiphase patterns with alternating domains of aligned and isotropic LCs were demonstrated to exhibit reversible thermomechanical behavior. However, there are few works about the fabrication of the light-driven microdevices from the azobenzene CLCPs.

Van Oosten et al.^[16] reported a pioneer work to use reactive LC inks and an inkjet printer to produce artificial microcilia, which consist of two different component CLCPs in one cantilever that are sensitive to two different wavelengths of light. In the previous work, we prepared a microarrayed CLCP film from an optimized azobenzene precursor and polydimethylsiloxane-soft-template-based secondary replication. Regulated by alternating irradiation of UV-Vis light (365/530 nm), the microarrayed film showed an ideal quick (<1 min) and reversible switch of superhydrophobic adhesion.^[17] In our work reported here, a two-dimensional (2D) microarray with a period of about 1 μm was first fabricated from an azobenzene CLCP by using the replica molding technique. It was found that the reflection spectra of the microarray showed the switchable behavior when irradiated with UV-Vis light alternately. This phenomenon is ascribed to the change in the order of the periodic structure of the microarray, resulted from the photoinduced deformation of the pillars made of azobenzene CLCP.

2. Experimental Section

The monomers used to prepare the CLCP microarray include an azobenzene diacrylate LC monomer, 4,4'-bis[1,1'-(acryloyloxy)undecyloxy]azobenzene (DA11AB), and an azobenzene diacrylate LC monomer, 1,4-bis[4-(9-acryloyloxy-nonyloxy)benzoyloxy]-2-methylbenzene (C9A), which were synthesized according to the literature.^[18] The chemical structures of DA11AB and C9A are shown in Figure 1a and the synthesis routes are shown in Scheme S1 (Supporting Information). The ¹H NMR spectra of DA11AB and C9A are shown in Figure S1 and Figure S2, respectively (Supporting Information).

The fabrication process of the CLCP microarray is shown in Figure 1b. The microarray was prepared through in situ photopolymerization of the mixture of DA11AB and C9A (the mole ratio was 1:4) containing 2 mol% photoinitiator (Irgacure 784). To derive the 2D CLCP microarray, the melt of the mixture was injected into a cell with a space gap of about 30 μm at 95 $^{\circ}\text{C}$ and then cooled down slowly to the polymerization temperature at 85 $^{\circ}\text{C}$. The cell consisted of a glass plate and a silicon template, which

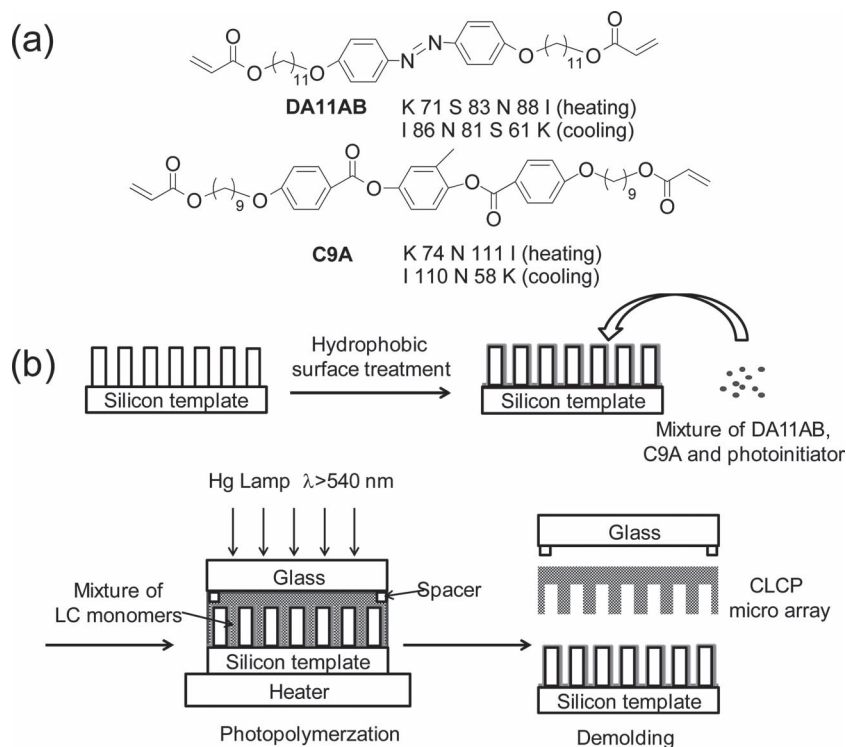


Figure 1. (a) The chemical structures and properties of the LC monomers DA11AB and C9A. K, crystal; S, smectic; N, nematic; I, isotropic. (b) The fabrication process of the 2D CLCP microarray.

had a periodically perforated hole array with a period of 1 μm and a diameter of about 800 nm. The silicon template was previously dealt with hydrophobic surface treatment using trichloro (1H, 1H, 2H, 2H-perfluorooctyl) silane to make the demolding process much easier. The photopolymerization was performed at the wavelengths longer than 540 nm (2.0 mW cm^{-2} at 540 nm) with a high pressure Hg lamp through glass filters (Toshiba, Y-52, and IRA-25S) for 3 h. After the photopolymerization, the azobenzene CLCP microarray was obtained by removing it from the cell.

The thermodynamic properties of the LC monomers, the mixture, and the CLCPs film were characterized with differential scanning calorimetry (DSC, TA, Q2000) at the rate of 2 $^{\circ}\text{C min}^{-1}$ for the monomers and the mixture and 10 $^{\circ}\text{C min}^{-1}$ for the films. (Figure S3, Supporting Information). Three scans were performed to check the reproducibility. The morphology of the CLCP microarray was observed by SEM (XL30FEG*, PHILIPS). The alignment of the pillars was checked by polarizing optical microscope (POM, Leica DM4000M). The reflection spectra of the CLCP microarray were measured using a multichannel photo detector connected to a Y-type optical fiber. The light source was Deuterium-Halogen lamp (DH 2000, Micropack) and the range of the wavelength of detector (PG 2000, ideaoptics) was from 400 to 1000 nm. The absorption spectra of the CLCP microarray was measured with UV-Vis spectra instrument (HITACHI U-4100). A UV-LED irradiator (OMRON ZUV-C30H, $\lambda_0 = 365 \text{ nm}$) and a Vis-LED irradiator (CCS Inc. HLV-24GR-3W, $\lambda_0 = 530 \text{ nm}$) were used to induce the photoisomerization of azobenzene moieties.

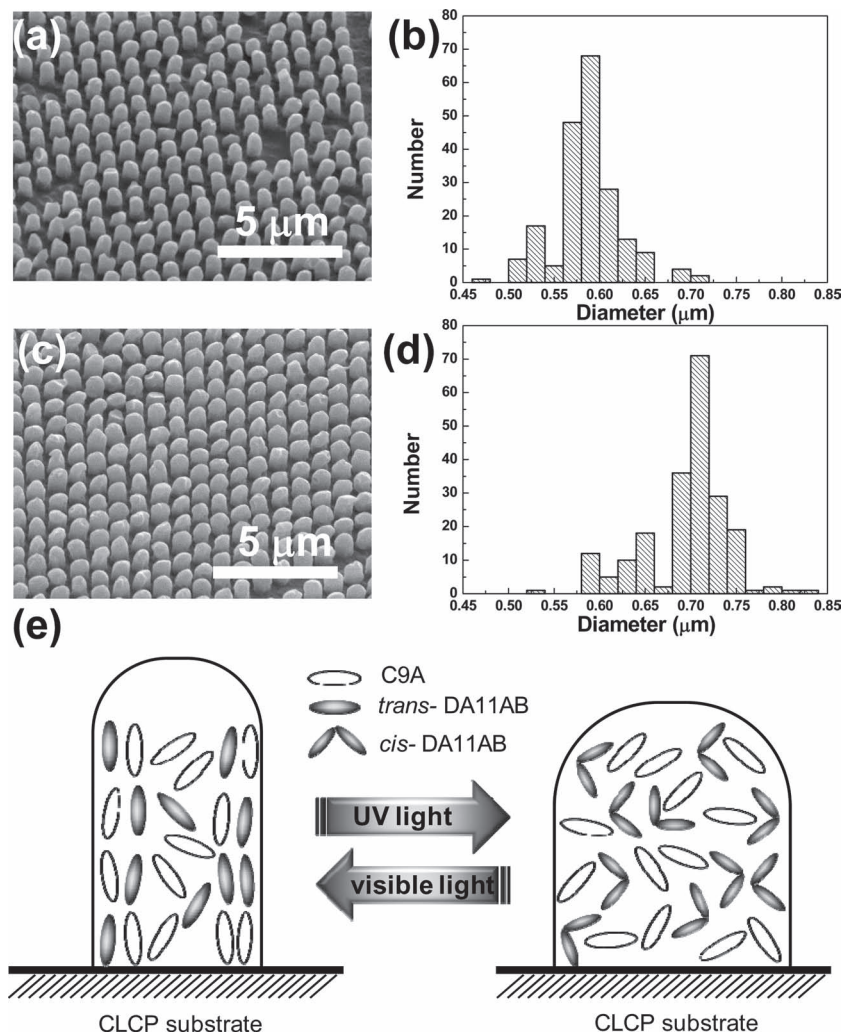


Figure 2. SEM images and size distribution of the azobenzene CLCP microarray before (a,b) and after (c,d) the irradiation of UV light, and schematic change in the geometry of the pillars of the azobenzene CLCP microarray (e).

3. Results and Discussion

The SEM image shown in Figure 2a demonstrates the periodic array has a period of about 1 μm and the diameter distribution of pillars is shown in Figure 2b. After the irradiation of UV light, it is notable that the array experiences a photoinduced deformation; that is, the diameter of the pillars increases as Figure 2c and d show. It is found that after UV irradiation, the mean diameter of the pillars increases from 0.587 to 0.695 μm, showing about 18% diameter increase. Since the CLCP microarray was prepared by injecting the melt of the reactive LC mixture into the hole array of the silicon template, as Figure 2e shows, the LC molecules in the side surface region of the pillars should align parallel to the long axis of the pillars, resulting from the shearing force during the fabricating process. The alignment of the pillars was checked by polarizing optical

microscope (Figure S4, Supporting Information). When irradiated with UV light, the azobenzene groups undergo the *trans-cis* photoisomerization, leading to the shape change of the azobenzene CLCP.^[3–8] Because the rod-like *trans* isomers transform to the bent *cis* forms, resulting in the alignment change of the LC molecules especially in the side surface region of the pillars, the pillars contract along the long axis while they undergo an expansion along the short axis, thus leading to the increase in the diameter of the pillars.

The reflection spectra of the CLCP microarray were detected at different incident angles with a step change of 10° (Figure 3a). It was found that at normal incidence, no obvious reflection peak was detected and the diffused reflection was quite strong. And when the incident angle changes from 0° to 20°, no obvious reflection peak exists within 400 ~ 1000 nm wavelengths. Nevertheless, a reflection peak centered at about 600 nm appears when the incident angle is increased to 30°. It should be noted that the wavelengths of the reflection peak shift from 700 to more than 900 nm as the incident angle increases gradually from 40° to 80°. When the angle of incidence is up to 60°, a significant reflection peak arises at about 870 nm. Thus, the incident angle of 60° was chosen to characterize the photoresponsive properties of the CLCP microarray.

There is a possible explanation to the reflection peak shift as follows: when two parallel lights transport to the surface of the near two pillars with the incident angle θ , the reflection lights have an optical path difference $\Delta = d \sin \theta$ (Figure 3b). When $\Delta = N\lambda$ ($N = 0, \pm 1, \pm 2, \dots$), the reflection peak would be detected due to the enhancement effect of the two light interference. Here, d represents the period of the microarray and equals to 1 μm. As for $N = 1$, when the incident angle θ is given, the wavelength λ of the reflection peak could be calculated. In other words, different incident angle θ causes the wavelength λ of the reflection peak different. The calculated results and the experiment results are listed in Table S1 (Supporting Information). It is clear that they are consistent with each other. And for $N = 2$, when the incident angle changes from 60° to 80°, another reflection peak should be detected during the wavelength at 400 to

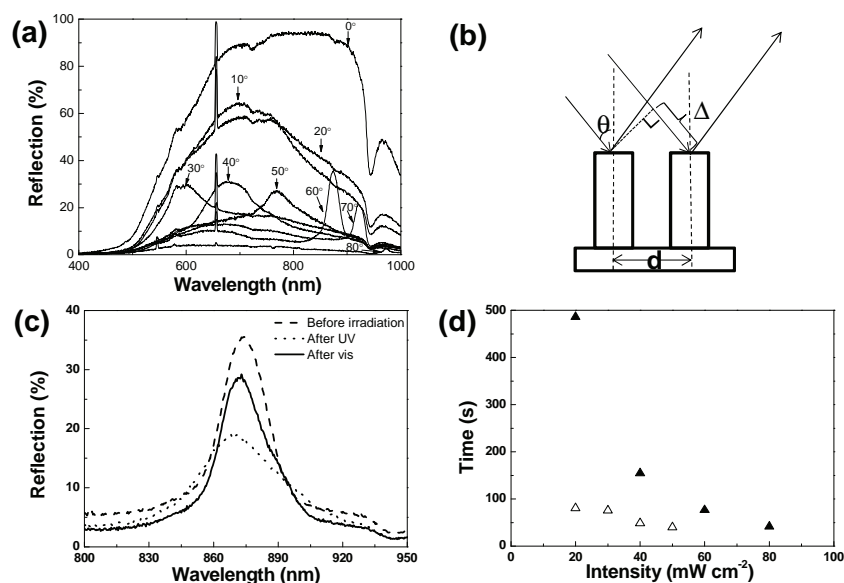


Figure 3. (a) Reflection spectra of the CLCP microarray measured at different incident angles. The reflection peak at about 550 and 650 nm are the peak of light resource. (b) Schematic drawing on the two parallel lights transporting to the surface of the two nearby pillars. (c) Reflection spectra of the azobenzene CLCP microarray under the UV light irradiation (365 nm, 20 mW cm^{-2} , 15 min) and the following visible light irradiation (530 nm, 20 mW cm^{-2} , 5 min) with the angle of incidence of 60° . (d) Change time of the CLCP microarray between the “on” state and the “off” state versus the intensity of the incident light.

1000 nm according to the calculation. However, it was not observed in the experiment. It is assumed that the intensity of the reflection peak is so weak that it could not be detected obviously.

The photoresponsiveness of the CLCP microarray was also characterized by the Y-type optical fiber to observe the change in the reflection spectra. We define the initial state is the “off” state, because large amount of light is reflected at the wavelength of 870 nm and cannot pass through the CLCP microarray. When the CLCP microarray were exposed to UV light with the incident angle of 60° (365 nm , 20 mW cm^{-2}), the intensity of the reflection peak at 870 nm decreased rapidly and the reflection peak becomes broader (Figure 3c), showing the “on” behavior of the microarray. During this process, the maximum intensity of the reflection peak changed from 34.3% to 18.9%. In other words, the maximum intensity contrast of more than 45% was realized between the “on” and “off” states under the excitation of UV light. Furthermore, with the visible light (530 nm , 20 mW cm^{-2}) replacing the UV light, the observed change in the reflection spectra reverted to the original state also as Figure 3c shows; that is, from the “on” state to the “off” one. The intensity of the reflection peak increased continuously until it reached the maximum value of 28% under the irradiation of visible light. Though there is a little difference with the original value prior to the UV light irradiation, it still demonstrates the

reversibility of the intensity of the reflection peak. This phenomenon suggests that the azobenzene CLCP pillars can be repeatedly deformed and reverted to their initial shape when exposed to UV and visible light alternately.

The dynamic switch mechanism of the CLCP microarray is based on the photo-induced deformation of the azobenzene CLCP pillars as mentioned above. Figure S5 (Supporting Information) shows the absorption spectra of the azobenzene groups in the CLCP microarray under the UV light irradiation and the following visible light irradiation. As shown in Figure S5a (Supporting Information), the absorbance around 380 nm ascribed to the $\pi-\pi^*$ transition of the *trans*-azobenzene groups decreases gradually with the increase of the irradiation time of UV light, whereas the absorbance around 450 nm mainly assignable to the $n-\pi^*$ transition of the *cis* isomers increases. This result indicates the *trans-cis* photoisomerization of the azobenzene groups takes place in the CLCP microarray and the deformation of the CLCP array occurs under the irradiation of UV light, which leads to the expansion of the pillars.

However, because the LC molecules are not highly aligned in the CLCP microarray, the expansion ratios of different pillars are different. Thus the order of the structures is disturbed, which in turn leads to the decrease of the maximum intensity of the reflection peak of the microarray (Figure 3c). When exposed to visible light, the azobenzene groups transform to their original *cis* state (Figure S5b, Supporting Information), resulting in the recovery of the absorption spectra and the periodical structure.

Figure 3d shows that the change time between the “on” state and the “off” state decreases drastically with the increase in the intensity of the incident light due to the acceleration of the photoisomerization of the azobenzene groups. The off-to-on time decreased from 486 to 42 s as the intensity of the UV light increasing from 20 to 80 mW cm^{-2} . When the intensity of the visible light was increased from 20 to 50 mW cm^{-2} , the change time from “on” to “off” was reduced from 80 to 27 s. The results indicate the on-off switch of the azobenzene CLCP microarray would be speed up if we use high-intensity light such as laser to trigger the photoisomerization of the azobenzene groups. The CLCP microarrays are potential to be applied as attenuators simply by adjusting the wavelength of the light, whose transforming time can be manipulated by the light intensity.

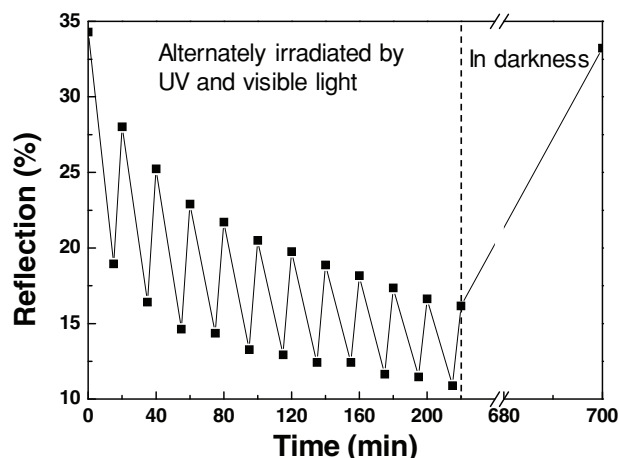


Figure 4. The intensity of the reflection peak ($\lambda = 870$ nm) of the azobenzene CLCP microarray under the alternate irradiation of UV light (365 nm, 20 mW cm $^{-2}$) for 15 min and visible light (530 nm, 20 mW cm $^{-2}$) for 5 min (left) and kept in darkness for 8 h (right).

The change in the maximum intensity of the reflection peak of the CLCP microarray at 870 nm under the alternate irradiation of UV–Vis light are shown in Figure 4. The results indicate that the change of the maximum intensity of the reflection peak could be repeatedly induced by alternate irradiation of UV and visible light, though the reversibility is not ideally complete. The assumed explanation for this phenomenon is existence of a delay between the deformation of pillars and the photoisomerization of the azobenzene under irradiation. As a result, the deformation does not recover to the state of the previous wholly in a short time and that leads to the decrease of the intensity of the reflection peak. However, after the sample was put into the dark environment for 8 h, the intensity of the reflection peak returned to the original one before the light irradiation (33.2%).

4. Conclusion

The photoresponsive 2D microarray with a period of about 1 μm was made from the azobenzene CLCP by using the replica technique. In accordance with the deformation of the CLCP pillars induced by the photoisomerization of the azobenzene groups, the CLCP microarray showed switchable behavior on the reflection spectra by alternate irradiation of UV–Vis light mainly caused by the change in the order of the microarray. It is the first time to use the CLCPs to fabricate the microarray with a period of about 1 μm and manipulate switchable behavior on the reflection spectra of the CLCP microarray by light. The on-off change time could be tuned by the intensity of the incident light and the reflection peak of the microarray showed an acceptable reversibility, indicating that the on-off behavior was

reversible. Since a small amount of light cannot transmit at the “on” state, there is some limitation for the azobenzene CLCP microarray to be used as transmitters and for-bidders; thus more work of the CLCP microarray is being under research, such as inducing the tunable behavior in the highly aligned CLCP microarray containing the azobenzene groups.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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