# Soft Matter

## PAPER



Cite this: DOI: 10.1039/c7sm01291h

Received 30th June 2017, Accepted 24th July 2017

DOI: 10.1039/c7sm01291h

rsc.li/soft-matter-journal

### Introduction

Responding to a stimulus is a natural phenomenon as most of the biomolecules react to changes in their local environment,<sup>1</sup> such as opening of pine cones,<sup>2</sup> cracking of chiral seed pods,<sup>3</sup> and sunflowers. Taking inspiration from nature, scientists have been aiming to develop materials that respond to external stimuli such as pH,<sup>4</sup> temperature,<sup>5–9</sup> light<sup>10–13</sup> and electric field.<sup>14–16</sup> A liquid crystal polymeric system is a kind of excellent stimuliresponsive material because mesogens are sensitive to the environment and their alignments are easy to control. Early research focused on the two-dimensional (2D) expansion or contraction in liquid crystal elastomers induced by temperature.<sup>17–19</sup>



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Crosslinked liquid crystal polymers (CLCPs) containing azobenzene mesogens have been developed as stimuli-responsive materials, which can undergo photodeformation and thus convert light energy into mechanical force. The deformation behavior of CLCPs is strongly influenced by the alignment of the mesogens; however, a precise control of the alignment domain at micro-scale is still a challenge. Here we report complex molecular alignment in the CLCP film by using photoalignment technology. First, azo dye SD1 is aligned in-plane by UV light with a discrete alternating striped director profile. The SD1 molecules in adjacent strips are aligned orthogonal, and the widths of the strips are controlled in several hundred micrometers by a photomask with grating patterns. Then the liquid crystal molecules in the CLCP film are aligned by SD1 through the anchoring effect on one side (SD1 side), and aligned perpendicular by the polyimide (PI) alignment layer on the other side (PI side). With these alignments, two kinds of splayed structures are formed through the depth of the film. When irradiated by UV light, the film bends toward the SD1 side with the bending direction along the diagonal of the film, determined by the resultant direction of molecular alignment on the SD1 side. When irradiated by blue light and heat, the bending direction is along the edge of the film. This dual-responsive deformable film with complex alignment is anticipated to be used in shape-changing biomedical devices, multiple controllable switches, and microactuators.

After that, significant efforts have been devoted to create complex three-dimensional (3D) deformations through a programmable shape change from a soft, responsive 2D film.<sup>11,20–28</sup> Moreover, some CLCPs can show a dual-stimuli responsive behavior.<sup>29</sup> Recently, our group explored a humidity- and photo-responsive CLCP film, and this film realized not only a series of large and sophisticated contactless motions by utilizing moisture, including an inchworm walk, and tumbling locomotion, but also dual-mode actuation that can be applied in flexible electronics.<sup>30</sup>

Controlling the molecular alignment is an important method to dominate the deformation behavior of a CLCP film, which is generally parallel or perpendicular to the film surface induced by rubbing,<sup>31</sup> electric field, magnetic field<sup>32</sup> and so on. In recent studies, CLCPs with a twisted or splayed molecular alignment have also been investigated. Fletcher and Katsonis *et al.* reported a twisted aligned CLCP film to exhibit winding, unwinding and helix inversion, mimicking a coiled tendril of the wild cucumber plant.<sup>33</sup> Inspired by the motion of natural cilia, Broer *et al.* prepared a microactuator with a splayed structure to create flow and mixing in wet environments.<sup>34</sup> In order to realize a more complex and monolithic shape change, the spatial control of the LC director profile becomes essential.<sup>35–38</sup>



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<sup>†</sup> Electronic supplementary information (ESI) available: Synthetic routes of the monomer and the crosslinker, and phase behaviour investigations of the liquid crystal mixture. See DOI: 10.1039/c7sm01291h

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Photoalignment<sup>39-42</sup> is one of the most effective and powerful methods to pattern LC alignments in 2D to program actuation.<sup>25,35,43</sup> It relies on the use of an ultrathin layer of photosensitive molecules, e.g., azobenzene, that can be aligned by the polarized light and orientate LC monomers (LCMs) placed on top of the layer. Indeed, azobenzenes can act as "master" molecules that control, through collaborative movements, the orientation of neighboring "slave" molecules. 44-47 Based on the photoalignment technology, Broer et al. fabricated CLCPs with azimuthal, spiral and radial alignments which exhibit trumpetlike or saddle-like deformation.43 In addition, CLCP films with a multiple patterned 3D nematic director profile were also reported, which can deform into an accordion shaped fold.<sup>37</sup> White et al. realized radial alignment within a local volume element as small as 0.0005 cubic millimetres. This actuator can transform 2D flat sheets into 3D objects through controlled bending and stretching and load becomes heavier tens of times larger than its own weight.35

Here we demonstrate a CLCP film with dual-responsive deformation induced by light and temperature. The film has a discrete alternating striped director profile in the plane of the photoalignment side aligned by SD1 (a sulfonic azo dye which can align perpendicular to the incident polarization,<sup>48</sup> the chemical structure is shown in Fig. 1a). The mesogens in adjacent strips are aligned orthogonal, and the widths of the strips are controlled in several hundred micrometers using a photomask with grating patterns. On the other side of the film, mesogens are aligned perpendicular by the PI alignment layer. With these alignments, two kinds of splayed structures are formed through the depth of the film (Fig. 2a and b). Upon irradiation of UV light, the film undergoes a reversible bending toward the in-plane aligned side with the bending director along the diagonal. Bending behavior of this film also can be triggered by 470 nm blue light. Different from UV light induced



**Fig. 1** (a) Chemical structure of the photoresponsive liquid crystal monomer, the crosslinker and the sulfonic azo dye molecule (SD1). (b) Schematic of the preparation of striped alignment patterns by an orienting SD1 layer. The yellow granules represent the SD1 molecules. First, polarized UV light was used to align SD1 along one direction. Then rotated the polarization direction of UV light by 90° and a photomask was used to realize a striped aligned SD1 layer.



**Fig. 2** (a) Schematic of mesogen alignment between the PI alignment layer and the SD1 alignment layer. (b) Side view of mesogen alignment between the PI alignment layer and the SD1 alignment layer. (c) Top view of the PI alignment layer of the film. (d) Top view of the SD1 alignment layer of the film.

deformation, it bends along one edge of the film and overrecovers after irradiation. Furthermore, the film can be reversibly curled like a cigarette upon heating, and the deformation occurs below clearing temperature.

### Experimental

#### Materials

The liquid crystal monomer A11AB6 and the crosslinker C3A were synthesized according to the methods reported in the literature.<sup>49</sup> The synthetic routes are described in the ESI† (Scheme S1 and S2). The photoinitiator Irgacure 784 was purchased from Ciba Specialty Chemicals. Dimethylformamide (DMF), acetone, methanol, and isopropanol were purchased from Sigma, which were of reagent grade or above. Deionized water (18.2 M $\Omega$ ) was filtered using a PureLab flex. The chemical structures of A11AB6, C3A and azo-dye SD1 are shown in Fig. 1a.

#### Preparation of liquid crystal cells

**Preparation of the PI alignment layer.** A solution of PI in pyridine (purchased from Nissan, Japan) was spin coated on glass slides at 200–300 rpm for 6 seconds and 1500–2000 rpm for 20 seconds, respectively. The obtained glass was heated at 80 °C immediately after spin coating for 10 min, then the temperature was increased to 250 °C and maintained for 1 h.

**Preparation of the SD1 alignment layer.** A solution of 0.3 wt% SD1 in DMF (purchased from Dainippon Ink and Chemicals Ltd, Tokyo, Japan) was spin coated on glass slides at 800 rpm for 9 seconds and 3000 rpm for 40 seconds, respectively. Then the glass was heated at 100  $^{\circ}$ C for 10 min and protected from light.

Preparation of the SD1 pattern with striped alignment<sup>50</sup>. The glass slides with the SD1 alignment layer were exposed under polarized blue light LED (wavelength:  $405 \pm 10$  nm, facula diameter: 50 mm, light power: 40 mW cm<sup>-2</sup>) for 10 min. Then the polarization direction of blue light was changed orthogonally,

and a photomask with grating patterns (the width of the transparent part is 300  $\mu$ m, transparent width : opaque width = 3 : 1) was used. The slides were irradiated with the same blue light for another 10 min to form a striped alignment pattern on the SD1 layer (Fig. 1b).

**Preparation of liquid crystal cells.** The slides with the PI alignment layer and the SD1 striped alignment layer were spaced  $12 \mu m$  apart using a film spacer along the edges. The film spacer was fixed using an AB glue.

## Polymerization of the CLCP film with complex molecular alignment

The CLCP films were prepared by *in situ* photopolymerization of mixtures of A11AB6 and C3A (the molar ratio is 6:4) containing a 2 mol% photoinitiator. The melt of the mixtures was injected into the liquid crystal cell in the isotropic phase, then cooled down slowly (0.1 °C min<sup>-1</sup>) to the polymerization temperature at 2 °C below the clearing points of the mixtures (nematic phase). Photopolymerization was performed at >540 nm using a high pressure Hg lamp through glass filters (Toshiba, Y-52 and IRA-25S) for 3 h. After photopolymerization, the film was removed from the cell using a cutter.

## Characterization of the CLCP film with complex molecular alignment

The thermomechanical properties of the monomers and the films were determined by differential scanning calorimetry (DSC; TA, Q2000) at the rate of 5 °C min<sup>-1</sup> for the monomers and 10 °C min<sup>-1</sup> for the films. Three scans were performed to check the reproducibility. The film was washed with chloroform to remove the unreacted monomers completely and dried under vacuum before the DSC measurement. The liquid crystal properties and the phase transitions were observed using a polarizing optical microscope (POM; Leika, 2500P) equipped with a Mettler hot stage (models FP-90 and FP-82). The liquid crystal molecular alignment in the film was investigated using field-emission scanning electron microscope (FESEM, Zeiss, Ultra 55).

#### Photo- and thermal-induced bending behavior of the CLCP film

The bending behavior of the CLCP film was observed upon 365 nm UV light irradiation with the intensity ranging from 0 to 160 mW cm<sup>-2</sup> (OMRON, LED, ZUV-C30H) and 470 nm visible light irradiation with the intensity ranging from 0 to 150 mW cm<sup>-2</sup> (CCS, PJ-1505-2CA, HLV-24BL-3W), respectively. The thermal-induced bending behavior of the CLCP film was observed on the hot stage with temperature ranging from 20 °C to 300 °C. Photographs of the bending and unbending behavior were taken using a digital camera (Canon, EOS 70d).

### **Results and discussion**

## Design and fabrication of the CLCP film with complex molecular alignment

As described above, a CLCP film with unique splayed alignments was successfully fabricated. The liquid crystal monomer

and the crosslinker used here have been previously investigated.<sup>20</sup> The phase behavior of the mixture of the liquid crystal monomer A11AB6 and the crosslinker (the molar ratio is 6:4) is similar to that of A11AB6 itself. From DSC data, the clearing temperatures of the mixture are 93 °C in the heating process and 92 °C in the cooling process, respectively (Table S1, ESI†). The POM pictures also show a variety of textures in the smectic phase and the nematic phase, respectively (Fig. S1, ESI†). These results demonstrate that polymerization of the liquid crystal mixture occurs in a nematic phase.

The liquid crystal mixture is polymerized in a liquid crystal cell. On one side of the cell the PI alignment layer is present (Fig. 2c), and on the other side the SD1 alignment layer (Fig. 2d). Mesogens are oriented perpendicular by the PI alignment layer on the PI side of the film, and oriented in plane with a discrete alternating striped director profile by the SD1 alignment layer on the SD1 side of the film (Fig. 2b). The alignment directors of the adjacent strips on the SD1 side are orthogonal, and the widths of the adjacent strips are 300  $\mu$ m and 100  $\mu$ m, respectively (named as wide strips and narrow strips as shown in Fig. 2b). As a result, two kinds of splayed structures are formed through the depth of the film (Fig. 2a).

DSC and POM were used firstly to investigate the molecular alignment in the CLCP film, as shown in Fig. 3. The obtained film shows the glass transition temperature  $(T_g)$  about 40 °C, which is slightly above room temperature. Even the temperature is as high as 140 °C, this film can maintain a liquid crystal phase attributed to its crosslinking network, which makes sure that this film doesn't change to an isotropic phase in the thermal-induced deformation process. The anisotropic orientation of mesogens was evaluated by tracing the transmittance of the CLCP film in POM, which was sandwiched between two crossed polarizers at room temperature. Typical polarized optical micrographs are shown in Fig. 3b. The highest transmittance occurred at an angle of 45° between the polarization direction of either the polarizer and the alignment direction on the SD1 side (Fig. 3b, down), whereas the lowest transmittance appeared when the polarization direction was parallel/perpendicular to the long edge of the film (Fig. 3b, up). Therefore, a periodic change of dark and bright images was observed by rotating the composite film with an interval of 45°. Furthermore, the boundaries of the adjacent strips show higher transmittance,



**Fig. 3** (a) DSC curve of the CLCP film. The heating and cooling rate is 10 °C min<sup>-1</sup>. (b) POM pictures of the CLCP film with  $\theta$  is 0° (up) and 45° (down), where  $\theta$  is the angle between polarizer and the mesogen director in wide strips.



**Fig. 4** FESEM images of different splayed structures in the cross-section of the film in Fig. 2b. (a) Mesogens in a wide strip show a distinct splayed alignment. (b) Mesogens in a narrow strip show a perpendicular alignment. The white dotted lines indicate the boundaries of this film.

which is attributed to that the molecular alignments in the transitional section change their directors continuously from wide strips to narrow strips, and maintain splayed structures through the depth of the film.<sup>51</sup> This result indicates an excellent alignment of mesogens in the CLCP film.

There are two different morphologies in the cross-section of the film investigated by FESEM. The wide strip shows a splayed oriented morphology (Fig. 4a), and the narrow strip shows a straight oriented morphology (Fig. 4b), which is consistent with the schematic in Fig. 2b. These morphologies demonstrate different orienting directors of the two splayed structures. Combining the results of POM and FESEM, we can confirm that a CLCP film with complex molecular alignment is fabricated successfully.

#### UV-induced deformation of the CLCP film

When the PI side of this CLCP film was irradiated with UV light, the film bent away from the light source. The bending reached maximum value in 5 seconds and recovered in 15 seconds after turning off the light (Fig. 5a). The mechanism of bending behavior by UV irradiation is shown in Fig. 5c. When UV light is on, the perpendicularly oriented azobenzene mesogens on the PI side of the CLCP film change from *trans* conformation to *cis* conformation, resulting in the expansion of the PI side and bending of the film. When UV light is off, the high internal stress in the film causes automatic recovery.

When the SD1 side of this CLCP film was exposed to UV light, the film bent toward the light source in 4 seconds and recovered in 10 seconds after turning off the light (Fig. 5b and Movie S1, ESI<sup>†</sup>). *trans* to *cis* transition of azobenzene mesogens aligned in-plane leads to contraction of the SD1 side and bending of the film (Fig. 5c). By changing the director orientation through the depth of this film, significantly larger deformation can be achieved compared with a uniaxially aligned film.<sup>45</sup> It is remarkable that whichever side UV light irradiates on, the film bends toward the SD1 side, and the bending direction is coincident with the resultant direction of molecular alignment on the SD1 side. Different from uniaxially aligned films with a splayed structure, the bending direction under UV irradiation is along the diagonal of a rectangular film, influenced by the resultant direction of molecular alignment on the SD1 side. It is expected that the bending direction under UV irradiation could be controlled by changing the width ratio of wide strips and narrow strips.

#### Visible light-induced deformation of the CLCP film

Upon the irradiation of 470 nm unpolarized blue light, the azobenzene mesogens are reoriented along the propagation direction of light, known as the "Weigert effect". Light around this wavelength regime is absorbed nearly equivalently by both



**Fig. 5** (a) Photo-induced deformation of the CLCP film with UV irradiation toward the PI side. (b) Photo-induced deformation of the CLCP film with UV irradiation toward the SD1 side. (c) Schematic of the photo-induced deformation mechanism of a complex aligned CLCP film under UV irradiation. The left shows UV irradiating on the PI side, and the right shows UV irradiating on the SD1 side.



**Fig. 6** (a) Photo deformation of the CLCP film with 470 nm blue light irradiation toward the SD1 side. (b) Schematic of the photodeformation mechanism of the complex aligned CLCP film irradiated by 470 nm blue light.

*trans* and *cis* isomers, so that the dichroism of the azobenzene material dictates the reorientation of the chromophore parallel to the propagation direction of the light source.<sup>52</sup> When blue light irradiates on the SD1 side, the alignment of azobenzene mesogens changes from in-plane to vertical. This variety of alignment induces volume contraction on the SD1 side of the film, and causes film bending toward the light source (Fig. 6b). The film reaches the maximum bending value in 2 s, and recovers to the original state in 3 s after turning off the light (Fig. 6a and Movie S2, ESI<sup>+</sup>).

It is worth noting that the film can over-recover after removing the light source for the first time. When the film is laid up for more than 3 s after turning off the light, the film bends toward the other side. The bending behavior of the overrecovered film can be repeated when irradiated with 470 nm blue light again. Of critical importance to the phenomenon is the generation of a photoelastic response (*e.g.* surface contractile strain only generated in the presence of the actinic light).<sup>52</sup>

#### Thermal-induced deformation of the CLCP film

Not only induced by light, the CLCP film with complex molecular alignment also exhibits bending behaviour by heat. Upon heating the film on a hot stage set at 60 °C, it bends toward the SD1 side with a large bending curvature that the film curled to be a cylinder. As investigated previously, the deformation caused by splayed alignment is larger than that caused by uniaxial alignment in a CLCP film upon heating.<sup>53</sup> After the heat source is removed at the first heating-cooling cycle, the film over-recovers to bend toward the PI side (Fig. 7a and Movie S3, ESI<sup>†</sup>). POM pictures also show a change of transmittance in heating and cooling processes. At room temperature, the film exhibits low transmittance. Upon increasing the temperature to 60 °C, the film turns to high transmittance, demonstrating the activation of mesogens and the alignment directional change. Upon cooling the film to room temperature again, the film turns back to high transmittance, illustrating the recovery of the mesogen alignments (Fig. 7b).

The mechanism of thermal-induced bending is presented as follows. When the temperature is higher than  $T_g$ , mesogens in the film become more active than that at room temperature. So the mesogens on the PI side change from perpendicular alignment to tilt alignment with an angle to the plane owing to the cooperative effect of liquid crystals, which causes the expansion of the PI side. At the same time, mesogens on the SD1 side also change from in-plane alignment to tilt alignment with an angle



Fig. 7 (a) Deformation of CLCP film by heating and cooling. (b) POM pictures of CLCP film at different temperatures. (c) Schematic of the deformation mechanism of the complex aligned CLCP film by heating and cooling.

to the plane by the cooperative effect, causing the contraction of the SD1 side. As a result, the bending deformation of the film with increasing temperature proceeds smoothly and with large amplitude. When the temperature is cooled below  $T_{\rm g}$ , internal stress is released. As shown in Fig. 7c, the mesogens arranged in-plane on the SD1 side are packed more closely than arranged perpendicularly on the PI side. The reduction of free volume on the SD1 side is thus less than that on the PI side, which causes the over-recovery of the film.

## Conclusions

A CLCP film with complex molecular alignment is fabricated by the photoalignment technology. First, azo dye SD1 is aligned in-plane with a discrete alternating striped director profile. The molecules in adjacent strips are aligned orthogonal, and the widths of the strips are controlled in several hundred micrometers by a photomask with grating patterns. The width ratio of the adjacent strips is 3:1. Then the mesogens are aligned by SD1 through the anchoring effect on one side of the film (SD1 side), and aligned perpendicular to the PI alignment layer on the other side of the film (PI side). With these alignments, two kinds of splayed structures are formed through the depth of the film. The bending deformation of the film is triggered by UV, blue light and heat. Different from uniaxial aligned films with a splayed structure, the bending direction under UV irradiation is along the diagonal of the film, influenced by the resultant direction of molecular alignment on the SD1 side. It is expected that the bending direction under UV irradiation could be controlled by changing the ratio of the different strips on the SD1 side. Over-recovery occurs followed by blue lightand heat-induced bending at the first time, which is explained by the release of internal stress in this film. Overall, this dual-responsive film has potential applications in shapechanging biomedical devices, multiple controllable switches, and microactuators.

## Acknowledgements

This work was supported financially by the National Key R&D Program of China (No. 2016YFA0202902), Shanghai Outstanding Academic Leader Program (No. 15XD1500600), and Natural Science Foundation of Shanghai (No. 17ZR1440100).

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