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Non-uniform Optical Inscription of Actuation Domains in Liquid Crystal Polymer of Uniaxial Orientation: An Approach to Complex and Programmable Shape Changes

Rong Yang[a,b] Yue Zhao*[a]

Abstract: Achieving complex shape change of liquid crystal polymer networks (LCNs) under stimulation generally requires spatial configuration of the orientation direction, i.e., patterned directors, of liquid crystal monomers prior to polymerization by means of treated surfaces. Herein we demonstrate a strategy that needs only the simple uniaxial orientation of mesogens (monodomain) induced by mechanical stretching of LCNs. Using a rationally designed liquid crystal polymer, photocrosslinking is utilized to pattern or spatially organize the actuating monodomains in order to generate a differential contractile and/or extensional force field required for targeted shape change. Moreover, the approach enables versatile actuation modes and allows multiple shape changes to be "programmed" on a single piece of the polymer. This important feature is demonstrated with a specimen cut to have eight strips that, upon thermal stimulation, display simultaneously eight types of shape morphing.

Future device applications in soft robotics, medicine, energy and aerospace require the use of advanced polymer actuators that can perform reversible, complex and programmable shape change under stimulation. Liquid crystal polymer networks including elastomers (LCNs) have been extensively studied and emerged as the material of choice.[1] Through the same actuation mechanism relying on the reversible LC–isotropic phase transition, there are two main preparation methods for LCN actuators. The first starts with a LCN film or sheet obtained from solution-casting or molding; after inducing the uniaxial orientation of mesogens (monodomain) by elongation, the specimen is chemically crosslinked.[2] Upon heating above and cooling below the clearing temperature, the actuator undergoes contraction and extension along the elongation direction, respectively. A recent study showed that by loading carbon nanotubes, light-triggered bending/unbending, resulting from photothermally induced superficial phase transition, could add up to the thermally activated contraction/extension and thus achieve versatile shape morphing.[3] The second approach enables more complex and precise shape changes, such as curling and helical formation, to be obtained from a flat LCN film.[4] It consists in polymerizing and crosslinking LC monomers (reactive mesogens) after spatially configuring their orientation state or patterning the directors of mesogens using generally treated surfaces. Moreover, using azobenzene derivatives as mesogenic moieties, LCN actuators prepared from both methods can be activated by light as a result of the trans-cis photoisomerization and related order-disorder phase transition.[5] In the present study, we demonstrate how to achieve complex shape morphing using only stretched LCN specimen with uniaxial LC orientation. We show that photocrosslinking can be applied to a monodomain LCN purposely in a non-uniform manner, i.e., only in spatially selected regions, to separate the actuation and non-actuation domains. Under thermal stimulation, a differential contraction and/or extension force field across the specimen can be generated, leading to targeted shape change. It should be emphasized that photocrosslinking monodomain of LCNs is well known,[2, 4] what is new in our study is the concept of spatially configuring or patterning the monodomain through photocrosslinking. As demonstrated below, this strategy makes complex shape morphing possible with easily processable, stretched LCNs.

Fig. 1 shows the characteristics of our designed LCN and its actuation behavior (synthesis details in Supporting Information). The polymer structure contains a biphenyl unit as mesogenic moiety, a pendent phenyl group for reducing phase transition temperatures and enhancing deformability,[6] and a cinnamyl group for crosslinking through photodimerization[7] (Fig. 1A). It has a low Tg near room temperature, a smectic and a nematic phase prior to the isotropic state (Fig. 1B). The efficient photodimerization of cinnamyl units in the polymer film exposed to UV light (320 nm) is visible from the decreasing absorption peak at 325 nm over irradiation time (Fig. 1C). This polymer has an appealing property that facilitates its preparation as LCN actuator. Compression-molded films (200 μm in thickness) can be readily stretched in the LC phases to induce the monodomain of uniaxial LC orientation without any pre-crosslinking; after removing external force the film relaxes only slightly and the monodomain retains without any load. The film can then be photocrosslinked to lock in the state of oriented mesogens for the reversible actuation. For a film exposed to UV light on both sides to have crosslinking throughout the sample, it contracts upon heating into the isotropic phase and extends after cooling to the LC phase (Fig. 1D), with a large actuation amplitude defined as the reversible actuation degree (RAD). The loss and recovery of the monodomain associated with the actuation can be noticed from the change in order parameter, S, calculated from X-ray diffraction (Figs. S4, S5). We further investigated the effect of film draw ratio λ (length after stretching over initial length) on the actuation performance. Fig. 1E summarizes the

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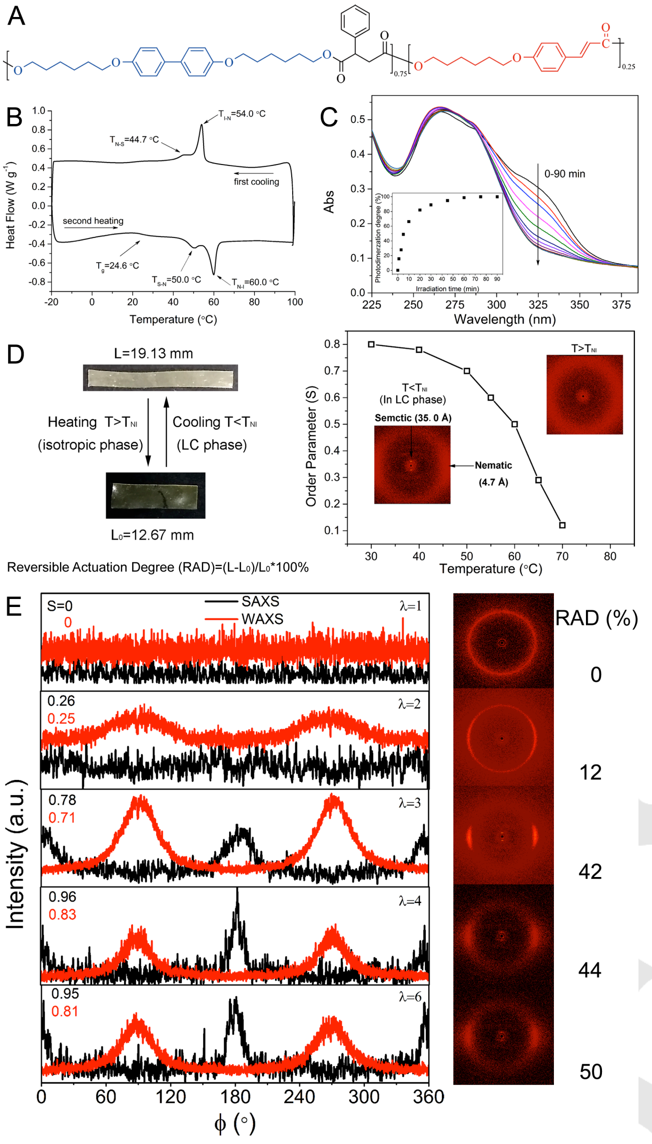


Figure 1. (A) Chemical structure of the liquid crystal polymer. (B) DSC heating and cooling curves of the polymer. (C) Absorption spectral change of a thin polymer film under UV irradiation (320 nm) for different times (from 0 to 90 min), the inset shows increase in photodimerization degree of cinnamyl groups calculated from decrease in absorbance at 325 nm. (D) Left side: photos showing the reversible contraction and extension along the stretching direction of a photocrosslinked polymer film upon heating to the isotropic state and cooling to the LC phase, respectively; right side: change in order parameter (S) of the mesogenic moieties upon heating to the isotropic phase, calculated from the 2D-XRD patterns. (E) 2D-XRD patterns, azimuthal diffraction profiles (black lines: 2θ=1.7-3.5° for smectic layers; red lines: 2θ=17.6-20.9° for nematic order), order parameters, and reversible actuation degrees for polymer films stretched to different draw rations (λ).

results by showing the 2D-XRD pattern, azimuthal diffraction profiles at the small-angle reflection of smectic order and wide-angle reflection of nematic order, calculated S for both mesogenic moieties and smectic layers as well as the resulting RAD. It is seen that both RAD and S increase with film elongation, but the increase of RAD is small beyond λ=3. In essence, the designed polymer is easy to deform and can be processed like a thermoplastic to generate the monodomain in free specimen that can then be photocrosslinked to give rise to LCN actuator with large reversible shape change. In what follows, the used LCN actuators were prepared using molded films with 300-400% elongation (60-80 μm-thick after stretching).

The presence of cynnamyl units in the polymer structure is for optically crosslinking a monodomain specimen only in spatially selected regions. Because only crosslinked monodoamin regions can permanently "memorize" the shape change associated with the LC-isotropic phase transition, they are the actuation domains, while uncrosslinked or crosslinked polydomain regions are non-actuation domains. It is easy to picture that varying the separation and organization of the actuation and non-actuation domains can change the differential contraction/extension force field that acts across the specimen and dictates its shape evolution upon actuation. Before showing the achievable complex shape changes, it is worth highlighting an interesting feature of our polymer due to the easy processability: a specimen with the same optically inscribed actuation domains can be processed to exhibit the same shape change from a flat state either by cooling (isotropic-LC) or heating (LC-isotropic). In the illustration in Fig. 2A, only the central area close to the side exposed to UV light is crosslinked and thus can act as actuation domain, while the remainder of the sample is non-actuation domain. The actuator film can then be treated in two ways. In one (left side of Fig. 2A), it is allowed to contract for stress release in the isotropic phase while being kept flat; on subsequent cooling into the LC phase, the actuation domain undergoes a superficial extension to result in a "bump" in the center of the film. Taking the second way, the film under strain is heated in the isotropic phase for stress release, then by cooling to the LC phase, the monodomain is recovered in the actuation domain while the film remains flat after removing the external force. When this film is heated to the isotropic phase, the actuation domain leads to a spatially localized contraction that also results in a "bump". Either way, the treatment of the LCN in the isotropic phase to release stress in non-actuation domains is important for the actuation to be repeated over numerous cycles. After this step, non-actuation domains (polydomain in the LC phases) can also be crosslinked by "flood" exposure of the specimen to UV light, which may adjust the rigidity of the entire actuator but have no effect on the actuation domains.

Given the spatiotemporal control of photocrosslinking that can be done in many ways, it is easy to imagine that actuation domains can be inscribed in a 3D and on-demand manner to give many possibilities of shape morphing as a result of an imbalanced contraction and/or extension force field, which is determined by the size, location and distribution of actuation domains within the LCN actuator. Fig. 2B shows examples of shape change, each of which can be achieved from a flat film either by heating or cooling. By increasing the proportion of actuation domain on one side of the film, i.e., deepening the photocrosslinked region along the thickness direction, actuation can lead to simple bending, buckling and rolling into multiple rings, respectively. The bending curvature increases with increasing the photocrosslinking time on one side (Fig. S6). If the one-side actuation domain is confined in a diamond-shape-region, the film deforms into a "dumpling" upon actuation.

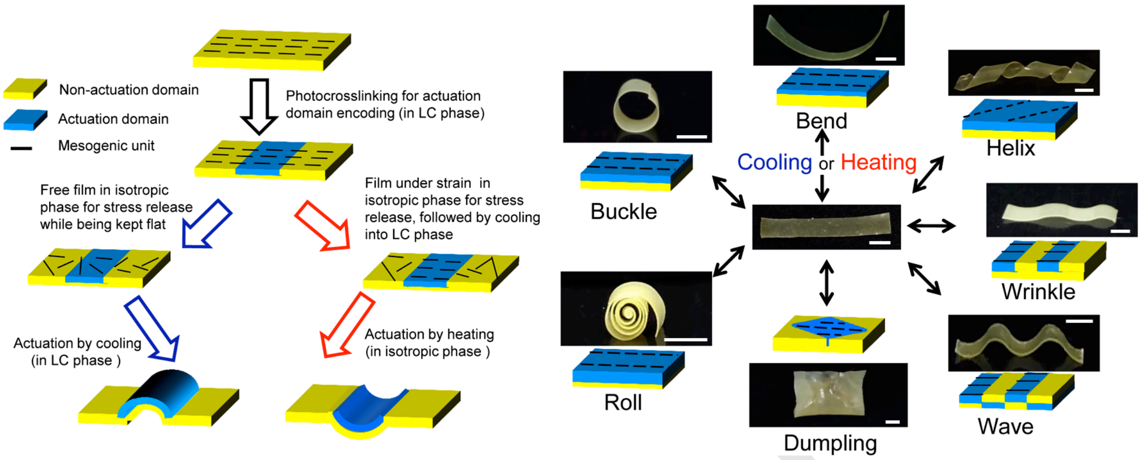


Figure 2. (A) Schematic showing how to inscribe an actuation domain in a monodomain-specimen through photocrosslinking and how the polymer actuator can be processed to exhibit a given shape change either by heating (LC-isotropic) or cooling (isotropic-LC). (B) Photos and corresponding schematics showing examples of the complex and versatile shape morphing of the polymer actuator through spatially controlled inscription of actuation domains in a flat monodomain-specimen. Scale bars: 2 mm. (Movies S1-S4)

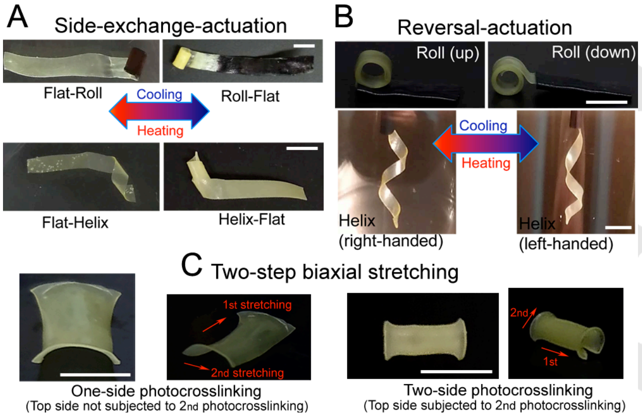
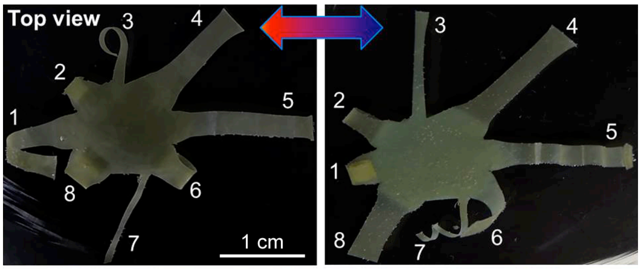


Figure 3. Photos showing peculiar actuation modes and sophisticated shapes: (A) side-exchange-actuation (the two sides exchange their respective shape), (B) reversal-actuation (the actuator switches between two opposite configurations), and (C) hyperbolic paraboloid shapes obtained by two-step biaxial stretching and phosocrosslinking. Scale bars: 3 mm. (Movies S5-S7).

By inscribing the actuation domain on one side of a film whose orientation of mesogens makes an angle with the long axis of the strip, actuation results in formation of a helix. While parallel-patterning of actuation domains on one side of the film produces wrinkling upon actuation, patterning on both sides in a shifted fashion for alternating actuation and non-actuation domains accentuates the periodic deformation and gives rise to “deep waves”. While the targeted shape change can easily be programmed, the actuation speed is largely governed by the heating or cooling rate (Movies S1-S4).

More complex actuation modes or shapes are accessible due to the combined ease of processing and ability of inducing the same shape change by either heating or cooling a flat film. Examples are given in Fig. 3. The first is the side-exchange-actuation where the two sides of a specimen exchange their respective shape upon actuation (Fig. 3A). This can easily be obtained by programming the two sides to exhibit the same shape change upon heating and cooling, respectively. In one example, the rolled side flattens and the flat side rolls (right side painted black for better viewing); while in the other case, the helical side unwinds and the flat side coils (Movie S5). Another unique actuation mode is the reversal-actuation where the specimen can switch between reversed configurations while carrying out the same type of shape change (Fig. 3B). In one example, the downward rolling switches to upward rolling on heating and vice versa on cooling (film glued to a black tape for better viewing) (Movie S6). In the other case, a left-handed helix turns to right-handed helix on heating and the opposite switching occurs on cooling (Movie S7). The reversed rolling is used to explain the underlying mechanism. By inscribing the actuation domain deep on one side of the film (Fig. 2B), it should roll in the isotropic phase and straighten on cooling to the LC phase. When the rolling in the isotropic phase reaches about halfway, the film is intentionally flattened and kept for stress release. On cooling to the LC phase, the extension of the actuation domain in the flat film leads to downward rolling, while on subsequent heating into the isotropic phase, after the contraction in the actuation domain flattens the film, the halted contraction during the initial isotropic phase actuation resumes and leads to upward rolling. Basically, actuators displaying reversed shape-morphing is obtained by halting the initially programmed shape change at halfway in the isotropic phase, followed by cooling to the LC phase. Fig. 3C illustrates the possibility to obtain sophisticated shapes through the photocrosslinking-enabled configurability of the actuator. Here, the specimen was subjected to a two-step biaxial stretching and photocrosslinking. More specifically, a strip was stretched in the nematic phase to induce the monodomain and photocrosslinked on one side. After stress release in the isotropic phase, the strip was stretched a second time in the nematic phase but in the perpendicular direction, and under strain it was photocrosslinked again either on the same side or on the opposite side. On cooling from the isotropic phase to room temperature, hyperbolic paraboloid plane and tube were formed. Both geometries are manifestation of two extension directions, normal to each other, arising from the inscribed actuation domains with perpendicular LC orientation. While the extension of the lower side subjected to the first photocrosslinking bends the strip upward, the extension of the upper side due to the second photocrosslinking acts to curl the strip downward. With the second photocrosslinking directly on the upper side, the perpendicular extension appears more prominent, rolling the strip into a tube.



1 bend ↔ roll, 2 roll ↔ bend, 3 buckle ↔ flat, 4 contraction ↔ expansion, 5 flat ↔ wave, 6 bend (down) ↔ bend (up), 7 flat ↔ helix, 8 roll ↔ flat

Figure 4. Photos of an "octopus-like" actuator made with a single piece of polymer, with the eight arms processed to carry out eight types of shape change upon immersion in cold or warm water for the isotropic-LC or LC-isotropic phase transition, respectively. (Movies S8 and S9)

Soft robots are an inspiring future application for polymer actuators.[8] Soft actuators capable of controlled and continuous curvature change, like the arms of an octopus, may be a key component. Thanks to the easy processing of thr polymer, multiple shape changes can readily be "programmed" into a single piece of specimen. To illustrate this important feature, a single film was cut to have eight strips emanating from the center, each of them was then stretched, photocrosslinked and processed to display a given but different shape change (Fig. S3). By immersing the multi-arm actuator in water and changing the water temperature for LC-isotropic phase transition, the eight strips could execute eight different shape changes and related motions simultaneously (Fig. 4, Movie S8 and Movie S9).

In conclusion, we have demonstrated a new concept that allows the use of simply stretched liquid crystal polymers with only uniaxial orientation of mesogens to achieve complex and programmable shape changes upon thermally induced LC-isotropic phase transition. Using a rationally designed polymer, we used photocrosslinking to spatially configure or pattern the actuation monodomains to generate differential contraction/extension force fields required for complex shape morphing. Making use of the easy polymer processing, a variety of interesting actuation features and modes, including a given shape change by either heating or cooling, side-exchange-actuation, reversal-actuation, hyperbolic paraboloid shapes and, more importantly, the possibility to program various shape changes using a single piece of the polymer. Given the ease of processing and the many light technologies for spatially-resolved photocrosslinking, the approach of non-uniform inscription of actuation domains in LCNs simplifies the fabrication of actuators capable of complex and controlled shape change, which is a significant step forward towards applications.

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Keywords: liquid crystals • polymers • actuators • photocrosslinking

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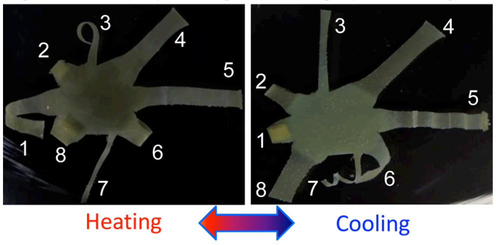
COMMUNICATION

An easily processable liquid crystal polymer with only uniaxial orientation of mesogens can be "programmed" to display multiple, complex shape morphing on a single piece of the material. The approach consists in using photocrosslinking to spatially configure and organize the actuation domains in mechanically stretched specimen.

Eight different shape changes on a single piece of polymer



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