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Thiol-acrylate Catalyst Enabled Post-Synthesis Fabrication of Liquid Crystal Actuators

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Electronic Supplementary Information

Abstract Synthesizing orientated liquid crystal elastomers (LCEs) *via* the two-stage thiol-acrylate Michael addition and photopolymerization (TAMAP) reaction is extensively used. However, excess acrylates, initiators, and strong stimuli are inevitably involved in the second stage crosslinking. Herein, we simplify the strategy through taking advantage of a volatile alkaline (originally added to catalyze the thiol-acrylate addition in the first crosslinking stage). Without excess functional groups, the residual catalyst after annealing is still enough to trigger reactions of dynamic covalent bonds at a relatively mild temperature (80 °C) to program the alignment of LCEs. The reversible reaction switches off by itself after this process since the catalyst gradually but totally evaporates upon heating. The obtained soft actuators exhibit robust actuation during repeated deformation (over 1000 times). Many shape-morphing modes can be achieved by rationally designing orientation patterns. This strategy not only facilitates the practical synthesis of LCE actuators, but also balances the intrinsic conflict between stability and reprogrammability of exchangeable LCEs. Moreover, the method of applying volatile catalysts has the potential to be extended to other dynamic covalent bonds (DCBs) applied to crosslinked polymer systems.

Keywords Liquid crystal elastomer; Vitrimer; Covalent adaptable network; Soft actuator

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INTRODUCTION

Inspired by natural organisms, soft actuators have attracted much attention in recent years for their potential applications in soft robotics,[1,2] self-organizing origami,[3,4] wearable devices,[5,6] artificial muscles,[7,8] and biomimetic systems.[9,10] Their compliant structures and high degrees of freedom in deformation promise them improved versatility, safety in human-machine interaction, and adaptation to unpredictable environments over their rigid counterparts.[11–14] Liquid crystal elastomers (LCEs) are outstanding among stimuli-responsive soft matters for their large reversible deformation and high power density,[1,15] which have shown to be favorable actuating materials in building soft actuators.

Fabrication of monodomain LCEs, where the directors of liquid crystals are uniformly orientated, is indispensable for reversible actuation.[16,17] Otherwise, the unaligned polydomain LCEs cannot perform such deformation. Freestanding deformation of LCEs is induced from the phase transition of liquid crystals when the appropriate stimulus is on/off.[18,19] Several classical methods have been developed to achieve alignment, including surface anchoring, micro-patterned channels, electric and magnetic fields, photo alignment, and two-step crosslinking method.[20] However, these methods have several drawbacks, such as they are difficult to control the reaction or synthesize bulk samples. New chemistries emerge to provide a solution. Radical and Michael click reactions[21–23] as well as covalent adaptable networks[24–26] have attached much attention over the past few years since they can synthesize and tailor LCEs in a relatively easy way. Based on new chemistries, 4D printing also gained popularity in the LCE community since it can program delicate alignment patterns and fabricate complex 3D structures.[27–29] More recently, a digital photocuring method is reported to realize ultrafast template-free alignment of LCE, which is based on intrinsic light attenuation in the through-plane direction.[30] In addition, a solvent-assisted programming method is reported to align mesogens, where micropores acted as the physical crosslinking to memorize the aligned state.[31] To achieve post-synthesis regulation of the alignment, the crystalline

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melting transition temperature of a dual-phase LCE network is designed to be higher than its liquid crystalline transition temperature.[32] Among all reported methodologies to synthesize monodomain LCEs, the two-stage thiol-acrylate Michael addition and photopolymerization (TAMAP) reaction has been one of the most widely adopted techniques.[21,33] It was first reported by Bowman *et al*. in 2015.[21] Its polymerization is based on an orthogonal initiation mechanism—the first stage crosslinking keeps the polymer structure through the thiol-Michael addition between stoichiometrically excess diacrylate mesogens with thiols, while the second stage crosslinking retains orientation through independent photopolymerization reaction of excess acrylate. Due to the accessible procedure and commercially available starting monomers, the two-stage TAMAP method quickly gained increasing popularity in the LCE community.[1,7,8,34] As the use of UV light, this method is restricted to thin films if 3D printing is not used. Recently, thermally triggered crosslinking of acrylates has been developed in the second stage.[35,36] However, the addition of thermal initiators causes extra trouble during synthesis considering the potential of unwanted polymerization before aligning process. Despite great advances, this LCE system is always deemed to be a permanent network and incapable of further processing after synthesis.

As mentioned in new chemistry methods, introducing dynamic covalent bonds (DCBs) into LCEs is also a favorable solution for alignment fixation and repeated reprogramming. The topological structure of mechanically deformed LCEs can rearrange through the breaking and reforming of DCBs when subjected to external stimuli.[16,26] Moreover, DCBs also endow ordinary crosslinked LCEs with unprecedented properties including reshaping, remolding, self-healing, recycling, stress relaxation property, and assembling multiple building blocks, *etc*.[37,38] For the two-stage TAMAP method, several efforts have been put in to make the permanent network dynamic, such as using excess hydroxyls to promote transesterification,[39] or incorporating other additional reversible reactions activated by either light or heat.[40]

Herein, based on the extensively researched two-stage TAMAP LCE system, we present a method to fabricate soft actuators without the second stage crosslinking and extra efforts of adding DCBs, which has the potential to be a new protocol to obtain monodomain LCEs. This strategy is inspired by our previous finding that the thiol-acrylate LCE system became permanent monodomain state after fully crosslinked in the presence of residual amine (initially used as the catalyst for the thiol-acrylate reaction).[41] The materials are synthesized through the crosslinking of stoichiometrically equimolar thiols and acrylates. However, this previous work is inconvenient for practical fabrication since it takes too long time for orientation (nearly 7 days). Here, in our optimized new method, orientated LCEs can be obtained by simply heating the prestretched samples for 2 h at relatively mild temperatures (80 °C). Results showed that reversible reactions were involved in the alignment. The mechanism could be that reversible reactions are generated by residual amine existing in freshly dried samples to install orientation patterns, while terminated after the residual amine totally evaporates during heating to stabilize the actuation.

The methodology here keeps many advantageous characteristics of the classic two-stage TAMAP system. It not only avoids the complicated design and synthesis of new materials, but also further simplifies the starting materials and fabrication procedures. The whole process is free from strong stimuli such as high temperature and ultraviolet exposure. In addition, it provides a solution to solve the intrinsic contradiction between reprogrammability and actuation stability in thermally controlled exchangeable LCEs, enabling ultra-robust actuation for error-free working. On another aspect, more high-performance functional materials that contained dynamic covalent bonds can benefit from the strategy of using volatile catalysts, which has the potential to be a universal approach to design structure-durable covalent adaptable networks, as well as to bring about new possibilities in the application involving academic research, daily life, and industry.

EXPERIMENTAL

Materials

Commercially available starting materials were chosen to demonstrate the efficacy of the approach. The mesogen 1,4-bis-[4-(3-acryloyloxypropyloxy)benzoyloxy]-2-methylbenzene (RM257, 98%) was purchased from Shijiazhuang Sdynano Fine Chemicals. The flexible thiol spacer 3,6-dioxa-1,8-octanedithiol (EDDET, 97%), the crosslinker pentaerythritol tetrakis(3-mercaptopropionate) (PETMP, 95%) and the catalyst dipropylamine (DPA, 98%) were purchased from Energy Chemical. Dichloromethane (DCM, AR) was obtained from Beijing Tong Guang Fine Chemicals Company. All reagents were used as received without further purification.

Synthesis of Polydomain LCEs

The scheme of our strategy is presented in Fig. 1(a). To synthesize polydomain LCEs, diacrylate mesogens RM257 (0.61 g, 1.04 mmol), dithiol spacer EDDET (0.12 g, 0.63 mmol), and tetra-functional thiol crosslinker PETMP (0.11 g, 0.21 mmol) were dissolved into 5 mL dichloromethane DCM. Acrylate and thiol groups were equimolar to create well-defined LCE networks. Then 1 wt% volatile DPA was added into the solution to be the catalyst for the thiol-acrylate addition reaction and the subsequent transesterification. The mixture was poured into a 4 cm × 4 cm × 1 cm polytetrafluoroethylene (PTFE) mold, and then left at room temperature in open air for 12 h. The solvent in the crosslinked LCE samples was removed through vacuum drying at 30 °C for 24 h to obtain the freshly prepared polydomain LCEs.

Synthesis of Monodomain LCEs

To obtain uniaxially aligned monodomain LCEs, the freshly prepared polydomain LCEs were stretched to 30% strain under mechanical stress at first. After that, two ends of temporarily oriented films were fixed by PTFE tapes. Since the sample contained residual DPA, permanent orientation was fixed by heating at 80 °C for 2 h on a heating stage. For other actuation modes, such as bending, twisting, and reeling, it only needed to stretch and deform polydomain LCEs to desired shapes under mechanical stress and then repeat the above manipulation (Fig. 1b).

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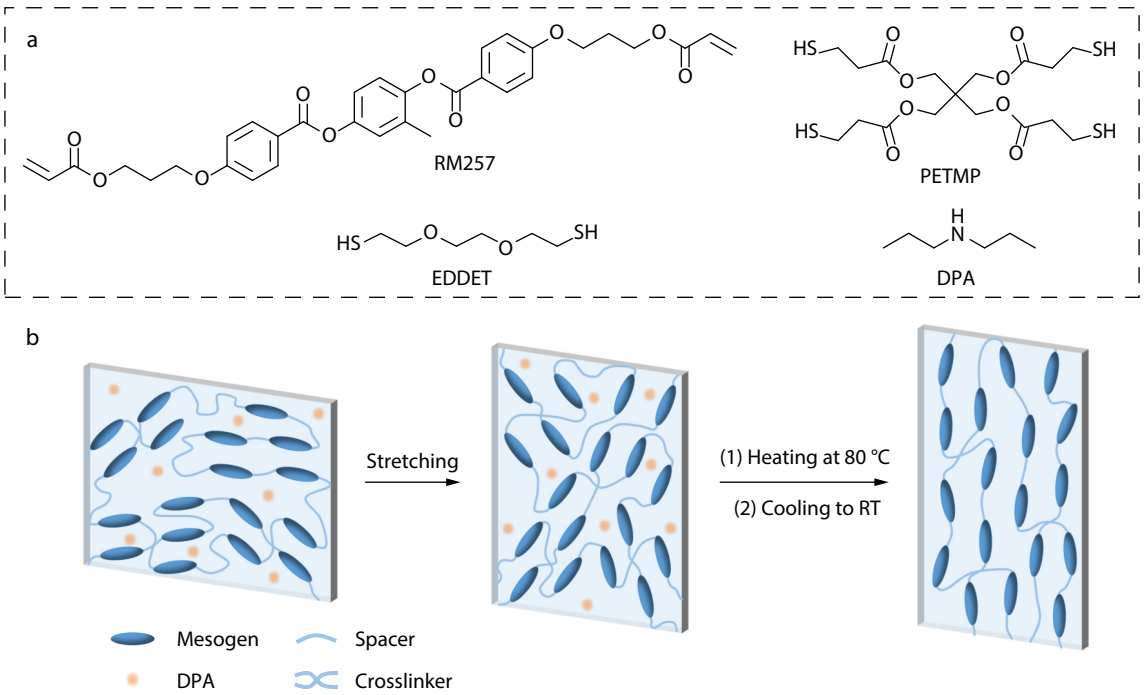

Fig. 1 Schematic of LCE soft actuators *via* post-synthesis strategy: (a) Chemical composition of the LCE. Diacrylate mesogen RM257, dithiol spacer EDDET, and tetra-functional thiol crosslinker PETMP were selected to form the system, where thiols and acrylates were stoichiometric. DPA was added as the catalyst for crosslinking and transesterification; (b) Fabrication process of monodomain LCEs. The obtained polydomain LCE contained DPA, and the mesogens were oriented temporarily under mechanical stress. Transesterification catalyzed by DPA accelerated the fixing of permanent alignment.

Synthesis of LCE Actuators with Different Actuation Modes

The reversible elongation actuation mode was obtained by stretching the LCE film uniaxially to 30% strain. The two ends of the film were fixed by PTFE tapes, with subsequent heating at 80 °C for 2 h to obtain monodomain actuators.

The reversible reeling actuation mode was obtained by stretching an LCE film to 50% strain and winding it on a Teflon tube (the following circle of the spiral was placed over the previous circle). The two ends of the film were fixed by PTFE tapes. The following procedures were the same as those in fabricating elongation actuators.

The reversible spiraling/contraction actuation mode was obtained by stretching an LCE film to 50% strain and winding it on a Teflon tube (the following circle of the spiral was placed next to the previous circle), with two ends of the film fixed. The following procedures were the same as those in fabricating elongation actuators.

A combination of bending and twisting deformation was obtained by processing half of the sample film to corresponding actuation modes simultaneously, with the middle part and two ends of the film fixed. After heating at 80 °C for 2 h, orientation was fixed. The bending part of the film was heated to 100 °C and pained black ink to obtain the actuator that combined two deformation modes.

RESULTS AND DISCUSSION

Experiment results showed that polydomain LCEs before aligning were fully crosslinked. Fourier transform infrared (FTIR) spectroscopy showed that acrylates and thiols were totally converted, where typical IR signals assigned to the acrylates (C=C stretching at 1637 cm^{-1}, =C−H stretching at 3054 cm^{-1}) and thiols (S−H stretching at 2686 cm^{-1}) disappeared (Figs. 2a–2c). In addition, Raman spectrum of the polydomain LCE sample at 25 °C shows no obvious band of thiol and acrylate alkene (Fig. S1, in the electronic supplementary information, ESI). The swelling experiment indicated that the sample had nearly 98% gel content, indicating the thiol-acrylate click reaction was accomplished (Fig. S2 in ESI). According to the differential scanning calorimetry (DSC) results, the glass transition temperature (T_g) and nematic-isotropic transition temperature (T_{ni}) of the sample are 3 and 88 °C respectively (Fig. 2d). Additional experimental results including the tensile tests (Fig. S3 in ESI), modulus-temperature curve (Fig. S4 in ESI), and thermogravimetric analysis (Fig. S5 in ESI) were conducted. The evaporation of DPA did not induce obvious porous structures in LCEs since its content is only 1 wt%, and scanning electron microscopy (SEM) image of the polydomain LCE sample also showed no pores (Fig. S6 in ESI).

The obtained monodomain LCE was an ultra-stable soft actuator. As Fig. 3(a) shows, if the freshly prepared polydomain LCE was uniaxially oriented, the corresponding soft actuator performed reversible elongation (at room temperature) and contraction (at 100 °C). Polarized optical microscope (POM) images of the samples showed a bright field at a certain position at room temperature while a dark field appeared when the sample was rotated for 45°, indicating the LCE was aligned (Fig. 3b). X-ray diffraction (XRD) pattern at room temperature also showed that the uniaxially aligned sample was

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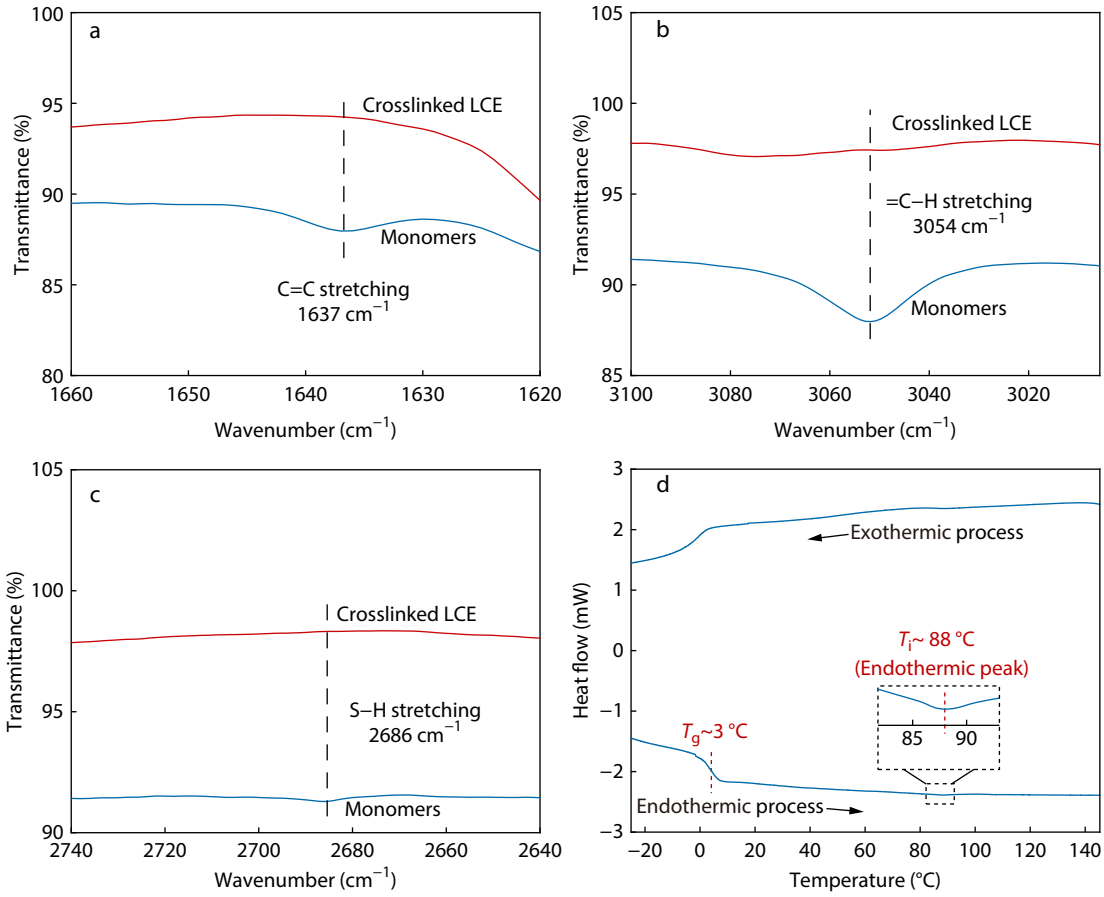

Fig. 2 Characterization of polydomain LCE. (a–c) FTIR spectra of monomers (mixture of diacrylate and thiol reactants) and crosslinked LCE; (d) Heating and cooling DSC curves of the polydomain LCE. Heating/cooling rate: 10 °C·min^{-1}.

uniformly oriented, and the order parameter was calculated to be 0.60 (Fig. 3c). In addition, the XRD pattern indicated that the LCE was in a nematic phase when the temperature was below T_{ni} since diffracting peak only appeared at wide angle region (Fig. S7 in ESI). Since residual DPA evaporated completely after heating at 80 °C for 2 h during processing monodomain, the dynamic reaction was nearly shut down to ensure the stability of the actuator. The monodomain sample exhibited stable actuation (about 50%) under repeated heating-cooling cycles between 30 and 100 °C over 1000 times (Fig. 3d).

Since IR spectrum, Raman spectrum and swelling experiment showed that acrylates and thiols were totally converted, the possibility of a small ratio of functional groups contributing to fixing orientation can be ruled out. Therefore, the alignment was fixed by reversible reactions of dynamic covalent bonds. One possibility is transesterification. It usually occurs at higher temperatures and often needs excess hydroxyls. However, some works reported that transesterification occurred in systems without specifically adding excess hydroxyls.[42–45] Xie's group proposed that bonded water molecules in the hygroscopic catalyst could give rise to hydroxyl groups in the network to promote transesterification.[42] Similarly, the LCE system here has the possibility to contain water since the evaporation of DCM can lead to the condensation of water vapor in air during the synthesis process. Our previous work (the LCE system was the same in this study) also found that transesterification catalyzed by DPA can even occur at room temperature according to stress-relaxation behavior, fluorescence experiments and the comparison of fixing alignment ability of samples with and without DPA.[41] Therefore, transesterification was probably involved in this system.

Another possibility of reversible reaction is retro thiol-Michael reaction as it can also occur at elevated temperature or pH stimulus.[37] We combined the results of our previous work[41] and also conducted some other experiments to investigate whether the alignment of LCEs is because of transesterification or dynamic thiol-Michael reactions. First, as shown in Fig. S1 (in ESI), Raman spectrum of the LCE sample at 25, 80 and 120 °C shows no obvious thiol (2569 cm^{-1}, highlighted in red) and alkene (1634 cm^{-1}, highlighted in blue) bands, indicating reversible thiol-Michael reaction undetected. Second, since retro thiol-Michael reaction can be activated just under thermal stimuli at around 90 °C,[46] LCE samples without DPA should be aligned if the reaction was a predominant factor. An LCE sample was swelled in DCM for 48 hours (solvent was refreshed every 12 h) with subsequent annealing at 100 °C for 48 h in vacuum to ensure DPA was totally removed. However, it failed to fix orientation at 80 °C for 2 h (Fig. S8 in ESI). Third, if dynamic thiol-Michael occurred, the viscosity of LCE may decrease obviously under high temperature since retro thiol-Michael reaction undergoes dissoci-

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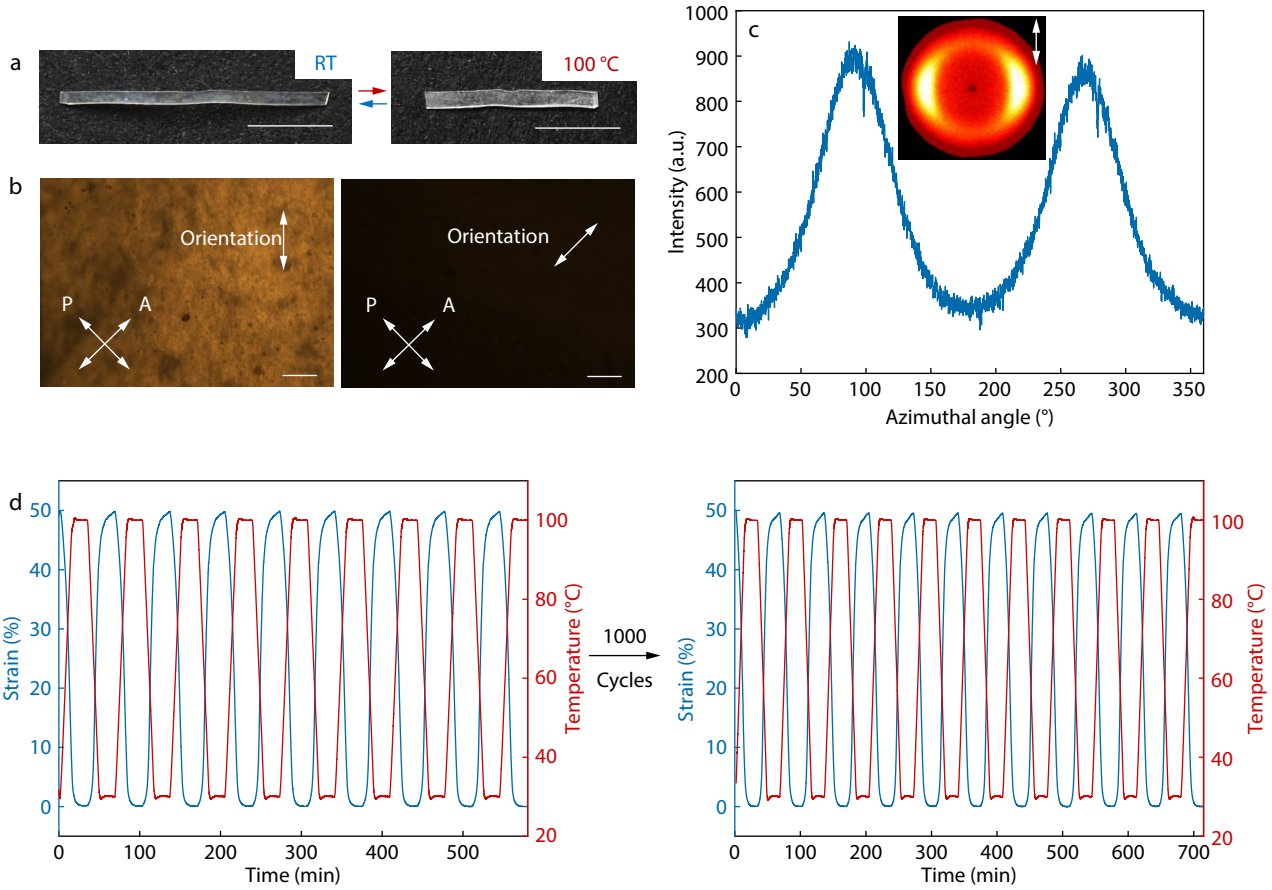

Fig. 3 Characterization of monodomain LCE. (a) The reversible elongation/contraction deformation of monodomain LCE under cooling/heating. Scale bars: 5 mm. (b) POM images of the oriented LCE under crossed polarizers and analyzers. Scale bars: 200 μm. (c) XRD image and the intensity of azimuthal angle of uniaxially oriented monodomain LCE. The white arrow shows the aligning direction. (d) Actuation stability test of the obtained actuator between 30 and 100 °C.

ative mechanism. However, the LCE sample remains structural integrity at as high as 180 °C. Moreover, when swelled in *N*,*N*-dimethylformamide (DMF) and heated at 100 °C for 12 h, the sample was undamaged (Fig. S9 in ESI). Nevertheless, the possibility of this dynamic reaction cannot be totally excluded from the alignment of LCEs.

This strategy facilitates the fabrication of various deformation modes and 3D structures. Basic deformation modes including reeling, spiraling, bending and twisting were easily realized (Figs. 4a–4c). The manipulation was convenient and conducted at a relatively mild temperature, where the freshly prepared polydomain LCE was subjected to mechanical stress and heated at a mild temperature for 2 h. The targeted actuation modes could be tailored rationally. In addition, stepwise control and precise local control of different deformation patterns in a monolithic construction were realized when multi-responsiveness was combined with the soft actuator. As shown in Fig. 4(c), the LCE sample was divided into two regions. Its left part was black and performed bending deformation, while its right part was transparent and performed twisting deformation. When the sample was exposed to infrared (IR) light (the wavelength was 808 nm), the black part contracted since the photothermal effect heated up the region, while the transparent part was unchanged at this stage. Sub-

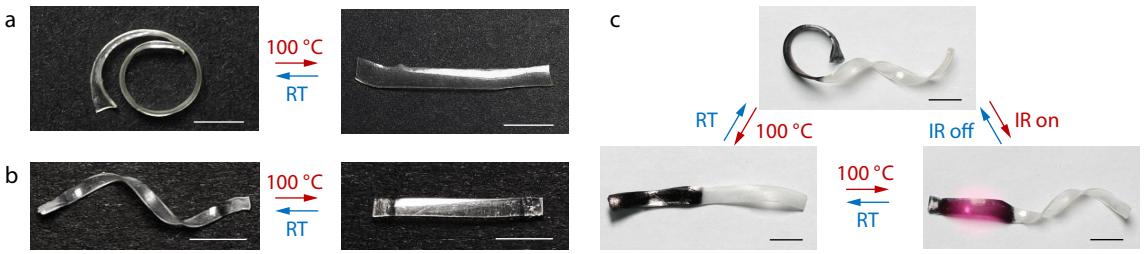

Fig. 4 Demonstration of varied actuation modes. (a) Illustration of reeling/contraction deformation mode; (b) Illustration of spiraling/contraction deformation mode; (c) Combination of bending and twisting deformation in an actuator which exhibited multi-responsiveness. Scale bars: 5 mm.

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sequently, the right twisting part also shrank when heated to 100 °C. If the IR light was off, the sample recovered to the original state (bending at left and twisting at right) again.

CONCLUSIONS

In summary, based on the widely used method of TAMAP reaction, a more convenient strategy to synthesize LCE actuators is proposed. This strategy needs no excess functional groups, no second crosslinking, and no introduction of new dynamic covalent bonds. Volatile DPA is used to catalyze reversible reactions and almost totally evaporates under heating, which enables stable actuation of LCEs. Diverse deformation modes can be rationally designed by applying external force. Additionally, multi-responsiveness and stepwise control can be easily realized by modifying the LCE samples, such as adding photothermal conversion layers, doping nanoparticles, and introducing specific monomers into the network structure. The demonstrations exhibited here are basic deformation modes, which can be combined and precisely controlled to bring about complex functionality for practical applications. In addition, for other covalent adaptable networks, the strategy of using a volatile catalyst has the potential to be a new way to realize reprogrammability while ensuring structural stability.

Conflict of Interests

The authors declare no interest conflict.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at http://doi.org/10.1007/s10118-023-3031-2.

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