## Programmable actuation of liquid crystal elastomer via “living” exchange reaction

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<td>Wang, Zhijian; University of California, San Diego, He, Qiguang; University of California, San Diego Wang, Yang; University of California, San Diego Cai, Shengqiang; UCSD, Department of Mechanical and Aerospace Engineering</td>
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Programmable actuation of liquid crystal elastomer via “living” exchange reaction

Zhijian Wang, Qiguang He, Yang Wang and Shengqiang Cai*

Liquid crystal elastomers (LCEs) have been recently intensively explored in various applications as soft actuating materials and opto-mechanical coupling materials. Since the orientation of mesogens in the elastomer largely determines its properties, various methods of programming the alignment of mesogens in LCEs have been recently developed. However, most of the methods either involve complex fabrication processes or have intrinsic limitations in their applicability. In this article, we synthesize an LCE with dynamic disulfide bonds and propose a facile room-temperature mechanical programming method via “living” exchange reaction without requiring additional stimuli and catalyst. We also, for the first time, reveal the “living” exchange reaction of disulfide bonds at room temperature in a bulk polymer. Such “living” exchange reaction relies on the significantly prolonged lifetime of free radicals generated during the breakage of disulfide bond, which is counterintuitive and in contrast to most previous understandings. Thanks to the disulfide bond, the patterned orientation of the mesogens in the LCE are erasable and reprogrammable. In addition, the synthesized LCE also exhibits shape memory effect, enabling the design of deployable soft actuating devices.

Introduction

Liquid crystal elastomer (LCE) is a combination of liquid crystal and polymer network, which exhibits excellent large and reversible actuation when subject to various stimuli. With the change of temperature, liquid crystal material can transit from isotropic phase to liquid crystal phase or vice versa, often accompanied by drastic shape change or the alteration of other properties such as light transparency or stiffness. The advent of LCE has greatly promoted the advancement of diverse fields including soft microactuators, reconfigurable structures, self-regulating systems, and soft robotics. Polydomain LCEs, in which liquid crystal molecules are aligned within individual tiny domains, are often obtained from the synthesis, if no special treatment is applied. However, in many applications including soft actuators and opto-mechanical devices, monodomain LCE, in which liquid crystal molecules are aligned macroscopically, is often needed. A milestone of the mesogens in the LCE are erasable and reprogrammable. In addition, the synthesized LCE also exhibits shape memory effect, enabling the design of deployable soft actuating devices.

LCE. Finally, a monodomain LCE was obtained and all the liquid crystal mesogens oriented toward the stretching direction. Later on, one crosslinking reaction with moderate rate has also been introduced into the fabrication of monodomain LCE, in which lightly-crosslinked sample can be successfully prepared before it is subject to mechanical stretch. This two-step crosslinking approach has been the most commonly adopted method in making monodomain LCEs due to its robustness and generality.

Certain drawbacks in the aforementioned two-step crosslinking method have been gradually recognized by the researchers. For instance, the first crosslinked polymer network increases the disorder in the final state of LCE; it is also challenging to use the method to make LCE structures with complex shapes. Consequently, several other methods of making LCEs with controlled mesogen alignment have been developed, including photoalignment, surface alignment, and the application of magnetic field. Very recently, exchangeable covalent bonds, which can undergo cleavage and formation in the presence of external stimuli, such as heating or UV irradiation, have been introduced into LCE to enable the programmability of the orientation of mesogens. The exchanging reaction of these covalent bonds can induce permanent rearrangement of polymer network experiencing deformation, and removal of the stimuli can stop the reaction and thus fix the alignment of liquid crystal mesogens in the network. The new approach to produce monodomain LCE through dynamic exchanging reaction has been shown to be robust and facile, which has also enabled the fabrication of LCE structures with complex shapes and programmed actuating behaviours.

* Department of Mechanical and Aerospace Engineering, University of California, San Diego, La Jolla, CA 92093, USA
b Materials Science and Engineering Program, University of California, San Diego, La Jolla, CA 92093, USA

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However, catalysts and external stimuli such as high temperature or UV light are often needed to trigger the bond exchange reaction. It often complicates the synthesize process and also limits the applicability of the method. For example, for high-temperature triggered exchange reaction, the reaction temperature ($T_d$) has to be higher than the isotropic transition temperature ($T_i$) of LCE. If not, exchange reactions can happen during the actuation of LCE, and consequently the shape and alignment of LCE cannot be preserved after several cycles of actuation. Therefore, compared to the two-step crosslinking method, to align the mesogens in the LCE at temperature higher than $T_d$ larger stress is needed (because the mesogens are in the isotropic state at high temperature), which may cause the rupture of the specimen. Processing of the LCE at high temperature may also bring additional complexity in real applications. Light-triggered exchange reaction is not very convenient in constructing complex three-dimensional structures because of the self-shadowing effect and the shallow light-penetration depth. The catalysts or initiators which are used to trigger the exchange reaction may lose its effectiveness after long storage or one-time processing.

Similar to most of the exchanging reactions, the disulfide bonds have been known to be exchangeable upon heating or UV light through the radical intermediate mechanism and the reaction would stop after removing external stimuli. The disulfide bond has been previously introduced to make LCEs reprogrammable under UV light or high temperature. In this article, we surprisingly find that, in contrast to the previous understanding, the disulfide exchange reaction could continue for hours after the removal of external stimuli. Based on the discovery, we develop a new kind of LCE with disulfide bonds, which can be easily processed and programmed at room temperature without requiring any additional external stimuli. In the disulfide LCE, the disulfide bonds can be cleaved into thyl radicals at high temperature (above $T_c$). Then, the generated thyl radicals initiate the chain transfer between disulfide bonds, enabling the rearrangement of polymer network. Decreasing the temperature below $T_c$ discontinues the generation of thyl radicals and the concentration of thyl radicals drops to a low level. However, unlike most other conventional exchange reactions, the disulfide exchange reaction does not completely stop due to the decrease of temperature. The survived thyl radical reacts with disulfide bond to form a new disulfide bond and a new thyl radical, resulting in the chain transfer of active free radicals. This chain transfer process suppresses the irreversible bimolecular termination and can significantly prolong the lifetime of thyl radicals, which means that the disulfide exchange reaction can continue even at room temperature. The concentration of survived free radicals would decay slowly through the irreversible bimolecular termination, and finally the LCE polymer network is stabilized. We use the term of “living” exchange reaction to refer to the exchange reactions in which the irreversible terminations can be sufficiently suppressed, in line with the terminology of living polymerizations. The unique property of “living” exchange reaction makes it possible to process the LCE from polydomain into monodomain at room temperature even after removing external stimuli. According to our knowledge, it is also the first time to observe and confirm the happening of such “living” exchange reaction process of disulfide bonds in bulk polymer, possibly because of the lack of detection methods in polymer of solid state. Reversible actuation of an LCE, which is initially in polydomain state, can provide direct evidence of the rearrangement of polymer networks at room temperature, which can be only achieved by the “living” exchange reaction in the system as described below.

Results and discussion
We synthesized three entries of disulfide LCE (LCE-Mn) with different crosslinking densities (Figure S1 and Table S1). The detailed synthesis steps can be found in S1. Here, n is denoted as the average number of liquid crystal mesogens between two crosslinking points. The mechanical properties of the obtained LCEs are measured by uniaxial tensile tests (Figure S2 and Table S2). The isotropic phase transition \( T_i \) of the LCEs is around 85 °C, measured by differential scanning calorimetry (DSC) (Figure S3).

To confirm the validity of our design principle, we first try to program these disulfide LCEs from polydomain to monodomain state at room temperature following the steps in Figure 1c. We first heat the LCE film (stage (i)) to 180 °C, which is above the disulfide cleavage temperature \( (T_{cl})^{22-23} \) and much higher than \( T_i \) of LCE (stage (ii)). The LCEs are in isotropic state and disulfide bonds are cleaved into free radicals through homolytic cleavage. Then, we cool down the sample to room temperature (stage (iii)). The generation of thiyl radicals discontinues and the equilibrium between the active thiyl radicals and dormant disulfide bonds is shifted. The concentration of thiyl radicals drops to a low level, which, however, is still sufficient to trigger exchange reaction as well as the rearrangement of polymer network.

After the sample is cooled down to room temperature, we stretch the LCE film immediately from initial length \( L_0 \) to \( L_p \) (prestretch \( \lambda_p = L_p / L_0 \) (stage (iv)) and maintain the stretch for 24 h. Because of the stretch, the rearrangement of polymer network through “living” exchange reaction leads to the transition of the LCE from polydomain state to monodomain state. During the process, the free radicals are consumed gradually because of the irreversible bimolecular termination. After long enough time, the concentration of free radicals is too low to induce effective rearrangement of polymer network. As a result, the topology of the polymer network is permanently fixed and acts just like a thermoset (stage (v)). After we release the prestretch of all the samples during the processing are in monodomain states with rearranged topology of the polymer network. Polarized optical microscope (POM) images shown in Figure S5 also confirm the alignment of mesogens in LCE-M2 and LCE-M4. While the initially polydomain LCE-M4 cannot be fixed into monodomain state with stretch in the presence of radical scavenger (Figure S6), indicating that the long-lived free radicals are essential in the programming process of LCEs. The room-temperature programmability of the disulfide LCE clearly demonstrates the happening of the “living” exchange reaction of disulfide covalent bonds in bulk LCE sample, as proposed previously.

We next systematically study the effects of the stretch holding time and sample storage time on the programmability of the disulfide LCE, which can be important for the applications of LCE and also provide more detailed insights into the “living” exchange reaction of disulfide bonds in a bulk polymer. Stretch holding time is defined as the time of maintaining the LCE sample in a stretched state at room temperature as shown in stage (iv) in Figure 1c. The sample storage time is defined as the duration between the moment that LCE sample is cooled to room temperature and the moment that the sample subject to a mechanical stretch for programming. The stretch holding time of all the samples is 2. The actuation stretch decreases when the sample storage time exceeds 4 h. (d) The relationship between the maximum actuation stretch \( \lambda_m \) and the prestretch \( \lambda_p \) of LCE-Mn. All the samples are stretched immediately after being cooled down to room temperature and the prestretch is kept for 24 h.

Figure 2. Reversible actuation of the disulfide LCE through room-temperature processing. (a) Temperature-dependent contraction of the processed LCEs of different crosslinking densities. The prestretch of all the samples during the processing is 2. (b) The relationship between the maximal actuation stretch and the prestretch holding time of the as-prepared LCEs. Stretch holding time is defined as the time of maintaining the LCE sample in a stretched state at room temperature as shown in stage (iv) in Figure 1c. The samples are prestretched immediately after being cooled down to room temperature (i.e. the storage time is 0). The prestretch of all the samples is 2. After about 6 h of holding the prestretch, the actuating stretch of the LCEs reaches maximal value, and further increase of the stretch holding time does not increase the actuating stretch of the LCEs. (c) The relationship between the maximal actuation stretch and the sample storage time of as-prepared LCE at room temperature. The sample storage time is defined as the duration between the moment that LCE sample is cooled to room temperature and the moment that the sample subject to a mechanical stretch for programming. The stretch holding time of all the samples is 24 h. The prestretch of all the samples is 2. The actuation stretch decreases when the sample storage time exceeds 4 h. (d) The relationship between the maximal actuation stretch \( \lambda_m \) and the prestretch \( \lambda_p \) of LCE-Mn. All the samples are stretched immediately after being cooled down to room temperature and the prestretch is kept for 24 h.
the disulfide bonds, or more explicitly the termination of thiyl radicals almost completes after 6 h. The quantitative conclusion above can be also confirmed by the relationship between the methods. (b) Reversible actuation of the processed LCE film with ‘UCSD’ letters. The scale bar is 5 mm. (c) Demonstration of the reprogrammability of the disulfide LCE. The scale bar is 5 mm. (i) The patterns of nine pyramids is first introduced into the LCE film through the room-temperature embossing method. (ii) When the sample is heated above 100 °C, the pyramid pattern disappears, and the pattern can reappear after the sample is cooled down to room temperature. (iii) Further heating up the sample to 180 °C can permanently erase the pyramid pattern. The pattern of nine pyramids does not appear after the sample is cooled down to room temperature. Instead, a new pattern of five pyramids can be introduced into the LCE film through room-temperature embossing method as shown in (iv). (v) The new pattern also shows reversible actuating behavior.

The samples are stretched immediately after they are cooled down to room temperature without any storage. The results shown in Figure 2b indicate that the “living” exchange reaction of the disulfide bonds, or more explicitly the termination of thyl radicals almost completes after 6 h. The quantitative conclusion above can be also confirmed by the relationship between the maximal actuation stretch λm and storage time as shown in Figure 2c. We find that λm keeps as a constant in short storage time and decreases in an exponential fashion when the storage time is longer than 4 h for both LCE-M2 and LCE-M4, implying that after 4 h, the concentration of thyl radicals decays to a level which is not sufficient to initiate effective rearrangement of polymer network to fix LCE into monodomain state. The lifetime of thyl radicals estimated from both the results of Figure 2b and c is around several hours, which is consistent with the report of lifetime of active free radicals in RAFT living polymerization. It is noted again such long lifetime of free radicals in RAFT polymerization and disulfide exchanging reaction results from the suppression of irreversible bimolecular termination, providing us a great opportunity to program the alignment of mesogens in the LCE and the shape of the LCE at room temperature only using mechanical deformation.

It is further found that maximal actuating stretch λm is very close to the prestretch λp if λp is less than 1.7 for LCE-M2 and 2 for LCE-M4, respectively (Figure 2d). The maximal actuation stretch keeps constant with λm=1.7 for LCE-M2 and λm=2 for LCE-M4 with the further increase of applied prestretch (λp>1.7 for LCE-M2 and for λp>2 LCE-M4). This means that the pre-deformation used to program the LCE is fully reversible, which enables us to precisely control the geometries of the LCE in both actuated and unactuated states. Thus, we are able to fabricate the LCE into complex active 3D structures with high precision through simple room-temperature embossing method. It is noted that all the 3D structures demonstrated in the followings are made of LCE-M4. The male and female molds are prepared through 3D printing technique (Objet350 Connex3, Stratasys) using VeroClear as printing material. The as-prepared LCE-M4 film is compressed between male and female molds for 24 h, after it is heated up to 180 °C and cooled down to room temperature subsequently (Figure 3a). LCE film with designed 3D structures can be obtained. As shown in Figure 3b, we prepare an LCE film with “UCSD” letters underside. When heated to 100 °C, the 3D pattern totally disappears, and the film becomes transparent, implying the isotropic state. The LCE film recovers to the original 3D shape after cooling and shows excellent reversible actuation performance upon cyclic heating and cooling (Movie S1). The LCE can also be processed into reconfigurable twisted stripes through torsion in addition to stretching or compression. Heating the twisted LCE stripe to 100 °C enables it to recover to its original flat shape with high transparency. When cooling it down, the LCE stripe twists gradually with the decrease of temperature and goes back to the twisted shape (Figure S7).

Due to the reversibility of exchange reaction of disulfide bonds, the programmed 3D shapes of the LCE can be easily erased and new patterns can be reprogrammed in the LCE by simply heating the LCE film above Tc to generate thyl radicals and initiate the rearrangement of polymer network. As illustrated in Figure 3c, we first make an LCE film with 3×3 pyramid structure through room-temperature embossing method. The film shows reversible actuation behavior upon heating and cooling. When we heat up the LCE film at 180 °C for 1 h, it transits into isotropic state and undertakes the rearrangement of polymer network. When the LCE film is cooled down to room temperature, the pyramid patterns are completely erased. After it is cooled down, we can rewrite a different shape with 5 pyramids on side at room temperature through “living” exchange reaction. After 24 h, the newly programmed shape shows similar reversible actuation behavior upon cyclic heating and cooling (Movie S2).

In addition to the (re)programmable actuation, the synthesized LCE also shows additional shape-memory effect due to the crystallization of alkyl chain of the chain extender. Such shape memory effect in the LCE enables us to make deployable LCE actuators. The DSC measurements show multiple endothermic peaks around 50 °C in the first heating scan of LCE-M4 (Figure S8), corresponding to the melting temperature (Tm) of the crystallization phase. Uniaxial tensile tests demonstrate that it takes around two days for the crystallization of the LCE-M4 (Figure S9), which is much longer than the active time of “living” exchange reaction. The difference of time scales of the two processes allows us to program the reversible actuation and shape memory effect into an LCE through two subsequent steps at room temperature. As demonstrated in Figure 4b, we first compress an as-prepared LCE film for 1 day to program its actuation through “living” exchange reaction. After one day, the polymer network is fixed.
The crystallization of the polymer chain, similar to shape memory polymers. When the folded LCE film is heated up to 100 °C, the LCE film recovers to the unfolded geometry, which can exhibit the programmed reversible actuation as shown in Figure 4c. Our experiment shows that the programming of both reversible actuation and non-reversible shape memory effect can be simply achieved by two subsequent mechanical deformation steps at room temperature. Such combination enables us to easily fabricate deployable soft actuators, which may find wide applications in biomedical engineering and aerospace exploration.

Conclusions

In conclusion, we have developed a simple and facile method to fabricate a disulfide LCE, whose shape and reversible actuation are programmable at room temperature through “living” exchange reaction without requiring any catalyst and additional external stimuli. The programmed shape and actuation of the LCE can be easily erased at high temperature, and reprogrammed and reprocessed again at room temperature. In addition, our studies have generated important insights into the exchanging reaction of dynamic disulfide bond in bulk polymer. Our experiments have shown clear evidence of significantly prolonged life time of free radicals in a bulk polymer at room temperature and the proceeding of effective exchange reaction of disulfide bond in the polymer even several hours after the generation of new free radicals stops, which is completely counterintuitive and in contrast to previous understandings. Because time scales for exchange reaction and crystallization of the polymer chains are different, we also demonstrate the programming of both actuation and shape memory effect in the LCE film. The shape memory effects of the disulfide LCE developed in this article will enable us to make various deployable soft actuators, which may find their applications in biomedical engineering and space explorations.

Conflicts of interest

There are no conflicts to declare.

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Notes and references

2. T. J. White, D. J. Broer, Nat. Mater. 2015, 14, 1087-1098.
We report a facile room-temperature mechanical programming method of liquid crystal elastomers via “living” exchange reaction of disulfide bonds.