

Supporting Information for

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

Zhijian Wang,[†] Qiguang He,[†] Yang Wang,[‡] and Shengqiang Cai^{*,†,‡}

[†] Department of Mechanical and Aerospace Engineering, University of California, San Diego, La Jolla, CA 92093, USA

[‡] Materials Science and Engineering Program, University of California, San Diego, La Jolla, CA 92093, USA

* Corresponding author

E-mail: shqcai@ucsd.edu (Shengqiang Cai)

KEYWORDS: Liquid crystal elastomers, disulfide metathesis reactions, living exchange reactions, dynamic covalent chemistry, shape memory effect

1. Materials and methods.

(1,4-bis-[4-(3-acryloyloxypropoxy) benzoyloxy]-2-methylbenzene) (RM257) (Wilshire company, 95%), 1,6-hexanedithiol (HDT, Alfa-Aesar, 97%), pentaerythritol tetrakis (3-mercaptopropionate) (PETMP, Sigma-Aldrich, 95%), dipropylamine (DPA, Sigma-Aldrich, 98%), 30% hydrogen peroxide solution (Fisher Chemical), sodium iodide (Sigma-Aldrich, 99%), sodium thiosulfate pentahydrate (Fisher Scientific) and all the solvents are used as received without further purification. Hot-compression is conducted on Carver Hot Embossing System with operating temperature as 180 °C and applied force as 1 ton. The uniaxial mechanical tests are conducted using Universal Mechanical Testing System (5965 Dual Column Testing systems, Instron) with a 1000 N loading cell. The ends of the samples are glued onto acrylic plates which are clipped by the clamps of the Instron machine. The testing LCE samples are cut into a rectangular shape with a size of 30 mm×10 mm×0.4 mm. The engineering strain rate is set as 0.1 min⁻¹. The polarized optical microscope (POM) images are taken on ZESIS polarized optical microscope. Differential scanning calorimetry (DSC) measurement is conducted on the Mettler Toledo differential scanning calorimeter. The sample is encapsulated in hermetically sealed aluminum pans. The heating rate is set as 5 °C/min. Male and female molds used for room temperature embossing techniques are made by 3D printing (Objet 350 Connex3, Stratasys) with VeroClear as the printing material.

Synthesis of disulfide LCEs.

The disulfide LCEs are synthesized following the modified procedures reported by our group previously¹. Three entries of disulfide LCEs with different crosslinking densities are synthesized, named as LCE-Mn. n is denoted as the average number of liquid crystal mesogen RM257 between two crosslinking points. The larger value of n, the lower crosslinking density. The value of n is controlled by the feed ratio between RM257 and chain extender. The synthetic routes are shown in Figure S1. Take LCE-M4 as an example. First, RM257 (9.42 g, 16 mmol) and HDT (3.00 g, 20 mmol) are dissolved in 50 mL acetone. Then, the catalyst DPA (0.2 g, 2 mmol) is added into the solution. The mixture is stirred overnight and turns into

turbid, indicating the formation of LCE oligomer. Then, the solvent is evaporated and the concentrated oligomer solution is dissolved in 50 mL THF. After that, the crosslinker PETMP (0.98 g, 2 mmol) with equivalent amount as the thiol group of oligomers is added into the THF solution. Then, oxidized reagent 30% hydrogen peroxide (1 mL) and catalyst NaI (0.04 g, 0.26 mmol) are added into the mixture. The mixture is stirred for 24 hours and the gelation forms. Then, the gel is cut into pieces and washed with 5% sodium thiosulfate solution and water for 3 times. The LCE-Mn sample is obtained as yellow pieces and dried in the oven at 85 °C overnight. The polymeric particles are subject to hot-compression at 180 °C for 1 hour with a force of 1 ton to get a thin yellow film with smooth surface.

Room-temperature processing of LCE.

We process LCE-Mn from polydomain into monodomain through the steps illustrated in Figure 1c. The LCE film is heated to 180 °C for 1 h and cooled to room temperature. Then, the LCE film is stretched with a prestretch of λ_p . After holding the stretch for a certain period of time, the LCE film is released to be free standing, heated to 100 °C and cooled to room temperature for 3 cycles to remove the thermal history before measuring the temperature-dependent actuation stretch. To study the effect of stretch holding time, we stretch the LCE specimen immediately after it is cooled to room temperature. The prestretch is set as 2. After holding the stretch for a certain period of time, the LCE specimen is released to be free standing, heated to 100 °C and cooled to room temperature for 3 cycles to remove the thermal history before measuring the temperature-dependent actuation. To study the effect of storage time, the LCE specimen is placed in room temperature for certain storage time and then stretched. The prestretch is set as 2. The stretch holding time is set as 24 h. After that, the LCE specimen is released to be free standing, heated to 100 °C and cooled to room temperature for 3 cycles to remove the thermal history before measuring the temperature-dependent actuation. For other processing steps, we stretched or compressed the LCE film after it was cooled to room temperature immediately (i.e. the storage time is equal to 0.). The stretch holding time is set as 24 h, unless specifically stated.

Room-temperature embossing fabrication of LCE 3D structures.

Here we use LCE-M4 to fabricate the LCE with various shapes. First, we make a pair of male and female molds through 3D printing (Objet 350 Connex3, Stratasys) using VeroClear as the printing material. The LCE-M4 film is obtained from hot-compression. Then, the as-prepared LCE-M4 film is compressed by a pair of male and female molds at room temperature and kept between the two molds for 24 hours. After that, the film is taken out from the molds and the LCE film with desired 3D structures can be obtained.

2. Synthetic routes of disulfide LCEs.

Synthesis of LCE-Mn

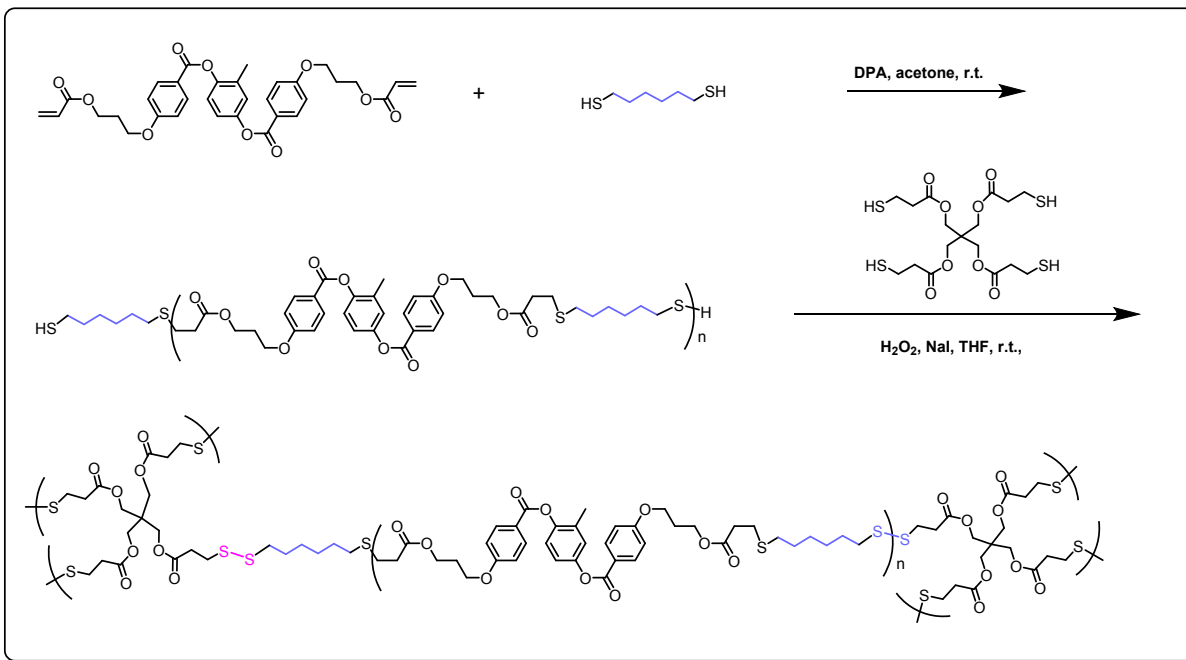


Figure S1. Synthetic route of LCE-Mn.

Table S1. Recipe for the preparation of LCE-Mn.

	RM257 (mmol)	HDT (mmol)	PETMP (mmol)	30 % H ₂ O ₂ (mL)
LCE-M1	16	32	8	4
LCE-M2	16	24	4	2
LCE-M4	16	20	2	1

3. Mechanical properties of LCE-Mn.

Table S2. Mechanical properties of as-prepared LCE-Mn.

	$E_{5\%}$ (MPa)	Strength (MPa)	Rupturing strain (%)
LCE-M1	1.07	1.07	91
LCE-M2	0.78	1.30	234
LCE-M4	0.60	1.69	285

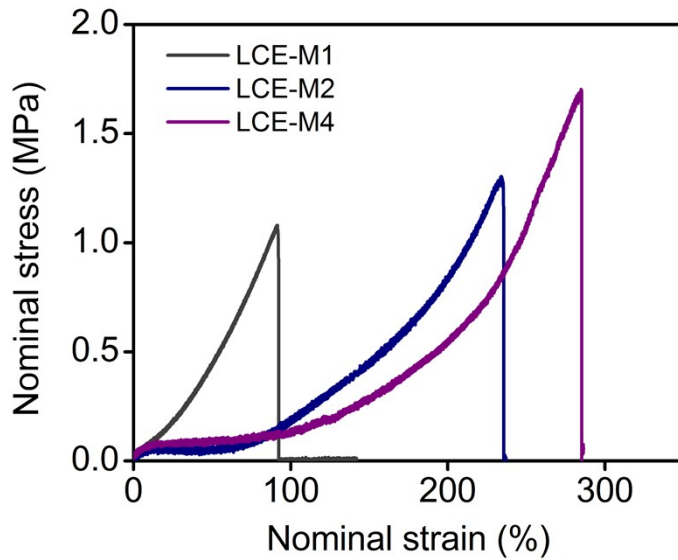


Figure S2. Uniaxial tensile tests of LCE-Mn. The sample specimen is 30 mm×10 mm×0.4 mm and the strain rate is 0.1 min⁻¹. The rupturing strain increases from 91% for LCE-M1 to 285% for LCE-M4. The strength also increases from 1.07 MPa to 1.69 MPa for LCE-M1 and LCE-M4, respectively. We calculate the tangential modulus of LCE-Mn when the engineering strain is 5%. The modulus decreases from 1.07 MPa for LCE-M1 to 0.60 MPa for LCE-M4.

4. DSC measurement of LCE-Mn.

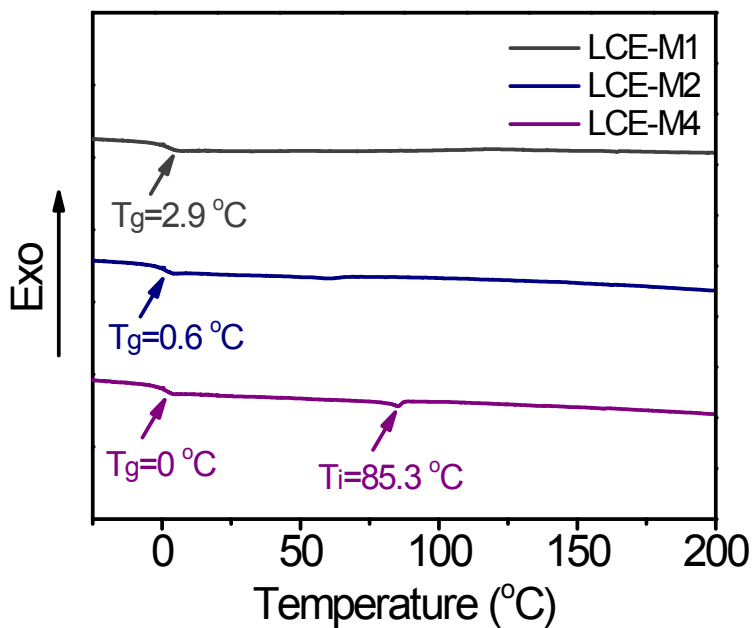


Figure S3. DSC measurements of LCE-Mn samples in the second heating scan at a heating rate of 5 °C/min under nitrogen atmosphere. The glass transition (T_g) increases from 0 °C for LCE-M4 to 2.9 °C for LCE-M1. The isotropic transition temperature T_i of LCE-M4 is detected as 85.3 °C. However, the isotropic transition temperature cannot be detected in either LCE-M2 or LCE-M1 with high crosslinking density.

5. Cyclic actuation of monodomain LCE-Mn.

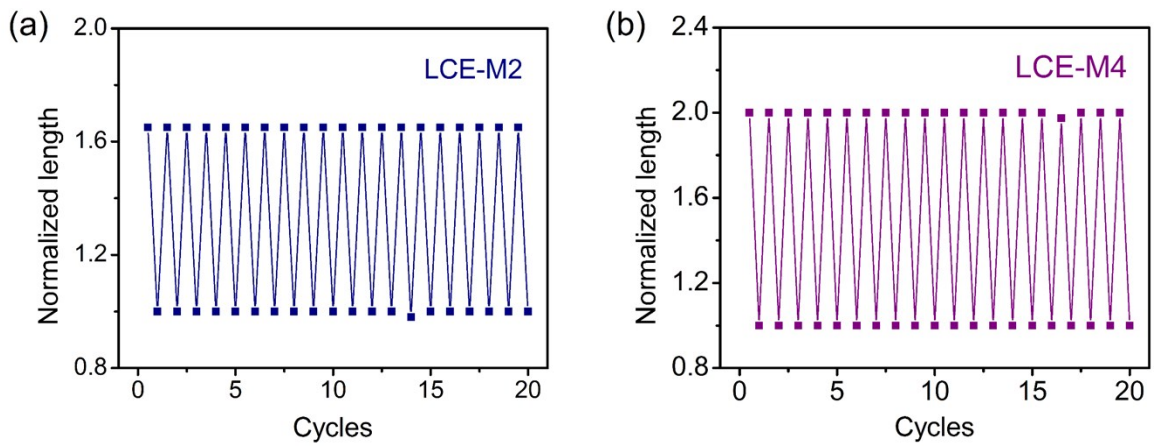
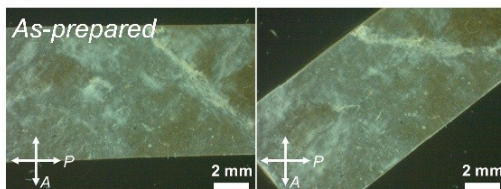


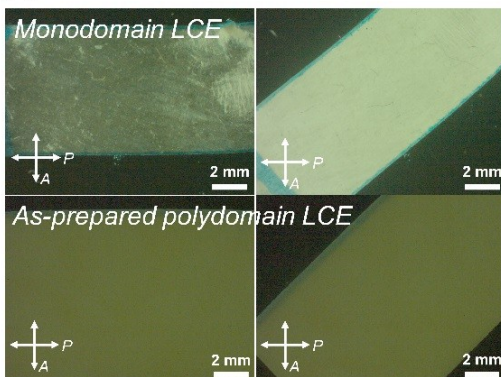
Figure S4. Cyclic actuation performance of room-temperature processed (a) monodomain LCE-M2 and (b) monodomain LCE-M4. The specimen is heated to 100 °C and then cooled down to room temperature cyclically.

6. Polarized microscope images of LCE-Mn.

(a) LCE-M1



(b) LCE-M2



(c) LCE-M4

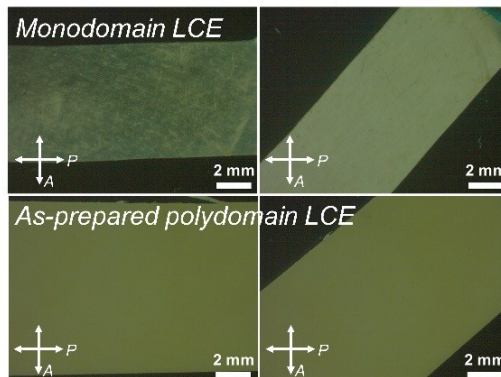


Figure S5. POM images of (a) LCE-M1, (b) LCE-M2 and (c) LCE-M4 at different angles with respect to the analyzer. (a) Images of LCE-M1 always dark at different angles, indicating that the LCE-M1 stays in isotropic state at room temperature. (b) For monodomain LCE-M2, the brightness changes with the variation of the angle. In polydomain state, the brightness of the LCE changes little with the variation of the angle. (c) For monodomain LCE-M4, the brightness changes with the variation of the angle. In polydomain state, the brightness of the LCE changes little with the variation of the angle.

7. Processing of LCE-M4 in the presence of radical scavenger.

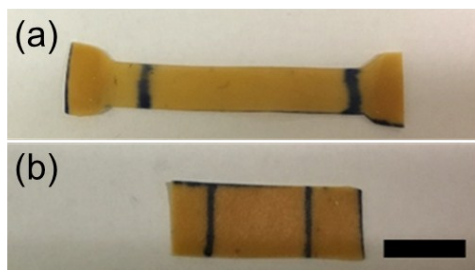


Figure S6. Photographs of room-temperature processed LCE-M4 in the presence of radical scavenger hydroquinone (a) before heating and (b) after heated to 100 °C and then cooled down to room temperature. Scale bar: 1 cm. In the experiment, an LCE-M4 sample was first immersed in the hydroquinone/THF solution (0.01 g/mL) for 1 h and dried in the room temperature for 1 day. The dried LCE sample was subjected to 180 °C for 10 min. After that, the sample was cooled to room temperature and stretched for 24 h with a prestretch of 2. The processed LCE is shown in Figure S6a. Then the sample is heated to 100 °C and cooled down to room temperature. The LCE would contract upon heating. However, the LCE would not expand to the stretched length after further cooling to room temperature, indicating that the LCE is not fixed in monodomain state.

8. Actuation performance of twisting LCE stripe.

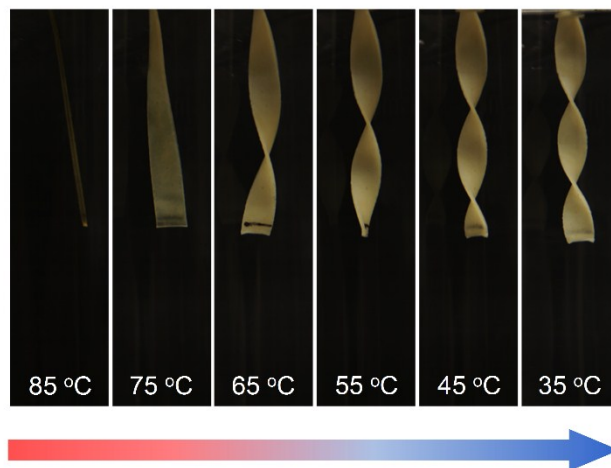


Figure S7. Temperature-dependent actuating performance of a twisting LCE stripe. The LCE stripe changes to flat shape with high transparency at high temperature and twists gradually with the decrease of the temperature.

9. DSC measurements of semi-crystalline phase of LCE-Mn.

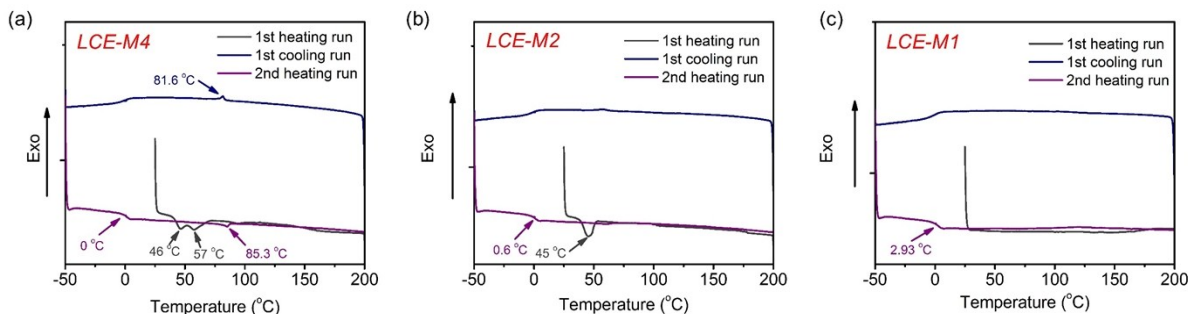


Figure S8. DSC curves of (a) LCE-M4, (b) LCE-M2 and (c) LCE-M1 at a heating/cooling rate of 5.0 °C/min under nitrogen atmosphere. The samples are stored at room temperature for 1 week before the measurement. The LCE-M4 and LCE-M2 show endothermic peaks around 50 °C in the first heating run (46 °C, 57 °C for LCE-M4 and 45 °C for LCE-M2), indicating the crystallization in the samples stored at room temperature for 1 week. No endothermic peaks around 50 °C are observed in LCE-M1. This is because the high crosslinking density of LCE-M1 limits the formation of semicrystalline phase. No endothermic peaks are observed in the second heating run for both LCE-M4 and LCE-M2 samples, implying that the crystalline phase cannot form during a short period.

10. Uniaxial tensile tests of LCE-Mn.

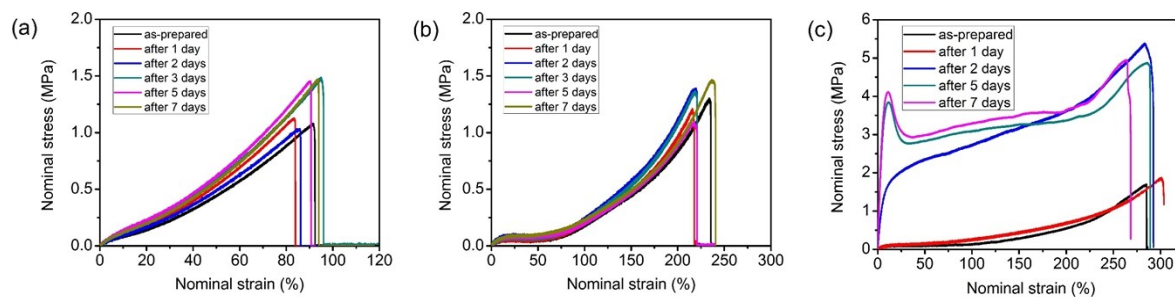


Figure S9. Uniaxial tensile tests of polydomain (a) LCE-M1, (b) LCE-M2 and (c) LCE-M4 with various storage times. The specimen is 30 mm×10 mm×0.4 mm and strain rate is 0.1 min⁻¹. The LCE-M4 shows time-dependent stiffening effect due to the crystallization of the polymer chain.

Reference

(1) Z. Wang, H. Tian, Q. He, S. Cai, *ACS Appl. Mater. Interfaces* 2017, **9**, 33119-33128.