

## Supporting Information

# A Cut-and-Paste Strategy towards Liquid Crystal Elastomers with Complex Shape Morphing

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### *General Considerations*

Anti-parallel surface-rubbed LC cells (S100A200uG180) with ca. 20  $\mu\text{m}$  thickness were purchased from Instec Inc. Hexamethylene diacrylate, 2,5-dihydroxybenzoic acid, benzyl bromide, 4-butyloxybenzoic acid, tributylphosphine (TBP), 4-hydroxybutyl acrylate and Pd/C were purchased from Sigma-Aldrich. 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU), 2-hydroxyethyl disulfide, triethylamine (TEA), 4-dimethylaminopyridine (DMAP) and dicyclohexylcarbodiimide (DCC) were purchased from Energy Chemical Corp. Acryloyl chloride,  $\text{NaHCO}_3$  and  $\text{Mg}_2\text{SO}_4$  were purchased from Sinopharm Chemical Reagent Corp. Ltd.

All non-aqueous reactions were conducted in oven-dried glassware, under a dry nitrogen atmosphere.  $\text{CH}_2\text{Cl}_2$  was distilled from  $\text{CaH}_2$  under nitrogen. THF was distilled from sodium-benzophenone ketyl under nitrogen. All flash chromatography was performed using Macherey-Nagel MN Kieselgel 60 (0.063-1.2 mm).

All  $^1\text{H}$  NMR spectra were recorded on a Bruker HW600 MHz spectrometer (AVANCE AV-600), or a Bruker HW500 MHz spectrometer (AVANCE AV-500), or a Bruker HW400 MHz spectrometer (AVANCE AV-400), using  $\text{CDCl}_3$  as the solvent and  $\text{CHCl}_3$  ( $\delta$  7.26) as the interior reference.

Melting point analysis was performed on a microscopic melting point meter (SGW X-4).

Differential scanning calorimetry (DSC) spectra were recorded on a TA Instruments Q20 instrument (New Castle, DE) under nitrogen purge with a heating/cooling rate of  $10^\circ\text{C}/\text{min}$ .

A TU-1810 ultraviolet-visible spectrophotometer (UV/VIS spectrometer) (Beijing Purkinje General Corp., China) was adopted to obtain the UV-vis spectra of the samples.

Polarized optical microscopy (POM) observations of the liquid crystalline textures of the samples were performed on an Olympus BX53P microscope equipped with a Mettler PF82HT hot stage. The images were captured using a Microvision MV-DC200 digital camera with a Phenix Phmias 2008 Cs Ver2.2 software.

One-dimensional (1D) WAXS experiments were performed with a high-flux small angle X-ray scattering instrument (SAXSess, Anton Paar) equipped with Kratky block-collimation system and a temperature control unit (Anton Paar TCS300). At each single steady temperature, both small angle X-ray scattering (SAXS) and wide-angle X-ray scattering (WAXS) were simultaneously recorded on an imaging-plate (IP) which extended to high-angle range at 40 kV and 40 mA for 30 min. Two-dimensional (2D) WAXD experiments were performed using a Bruker D8Discover diffractometer with VANTEC 500 as a 2D detector. The diffraction patterns were recorded in the transmission mode at ambient temperature using uniaxially oriented fiber or film samples. For both the 1D and 2D WAXD experiments, the reflection peak positions were calibrated with silicon powder ( $2\theta > 15^\circ$ ) and silver behenate ( $2\theta < 10^\circ$ ). Background scattering was recorded and subtracted from the sample patterns.

The SEM images of the polysulfide LCE films were recorded on an Inspect F50 S3 field emission scanning electron microscope (FEI-SEM, America).

All mechanical property studies of elastomers were performed on a dynamic mechanical analyzer (DMA Q800, TA Instrument) with tension clamp for static stress/strain measurements.

A high-intensity ultraviolet lamp (LP-40, Shanghai Luyang Instrument Co. Ltd., emission spectral range:  $365\pm 5$  nm) was used to irradiate LC mixtures to obtain the LCE samples.

#### ***Synthesis of monomer A444 and crosslinker DSDA***

LC monomer (4''-acryloyloxybutyl)-2,5-di-(4'-butyloxybenzoyloxy)benzoate (**A444**) was synthesized following literature protocol.<sup>[1,2]</sup>  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.17 (dd,  $J = 8.7, 3.3$  Hz, 4H), 7.91 (d,  $J = 2.7$  Hz, 1H), 7.48 (dd,  $J = 8.7, 3.0$  Hz, 1H), 7.28 (t,  $J = 4.8$  Hz, 1H), 7.00 (d,  $J = 8.7$  Hz, 4H), 6.38 (d,  $J = 17.4$  Hz, 1H), 6.10 (dd,  $J = 17.4, 10.5$  Hz, 1H), 5.81 (d,  $J = 10.2$  Hz, 1H), 4.23 (t,  $J = 6.3$  Hz, 2H), 4.05 (m, 6H), 1.91 – 1.74 (m, 4H), 1.71 – 1.49 (m, 8H), 1.02 (t,  $J = 7.5$  Hz, 6H).  $^{13}\text{C}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$ : 165.5, 164.3, 164.0, 163.6, 163.3, 163.2, 147.9, 147.6, 131.9, 131.8, 129.9, 128.0, 126.6, 124.5, 124.4, 121.0, 120.7, 114.0, 113.9, 67.6, 64.4, 63.4, 30.7, 24.7, 18.7, 13.3.

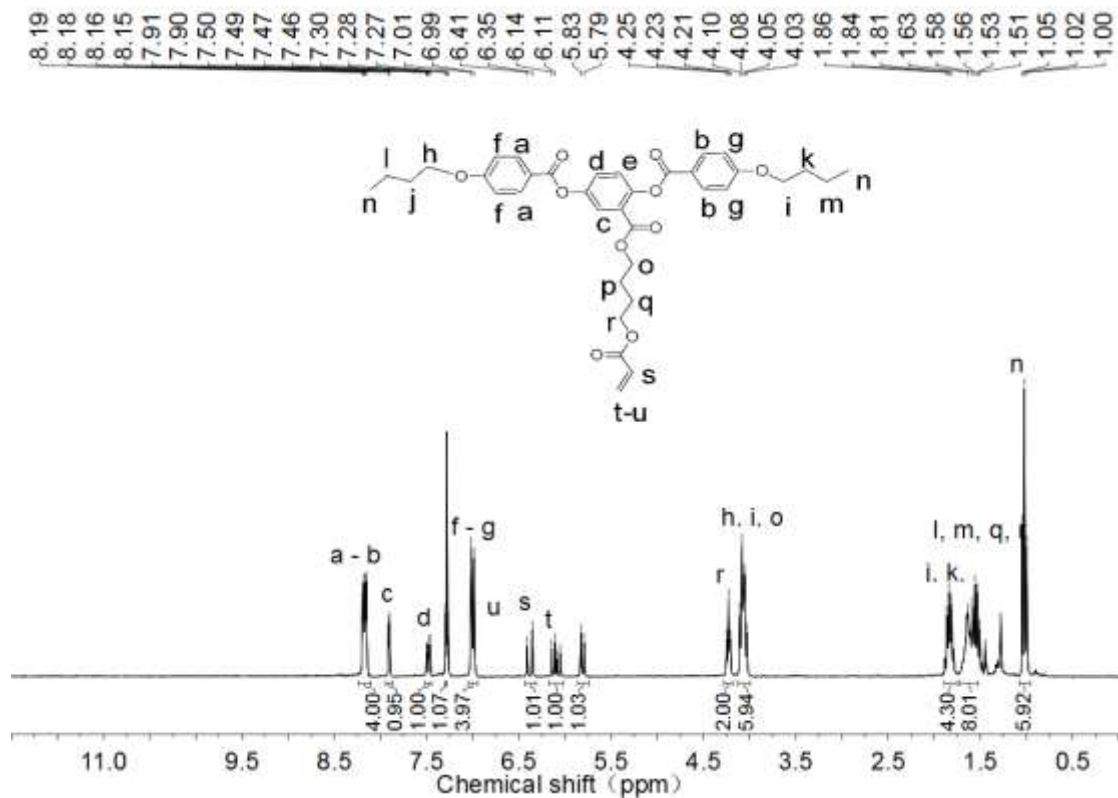


Figure S1.  $^1\text{H}$  NMR spectrum of LC monomer A444.

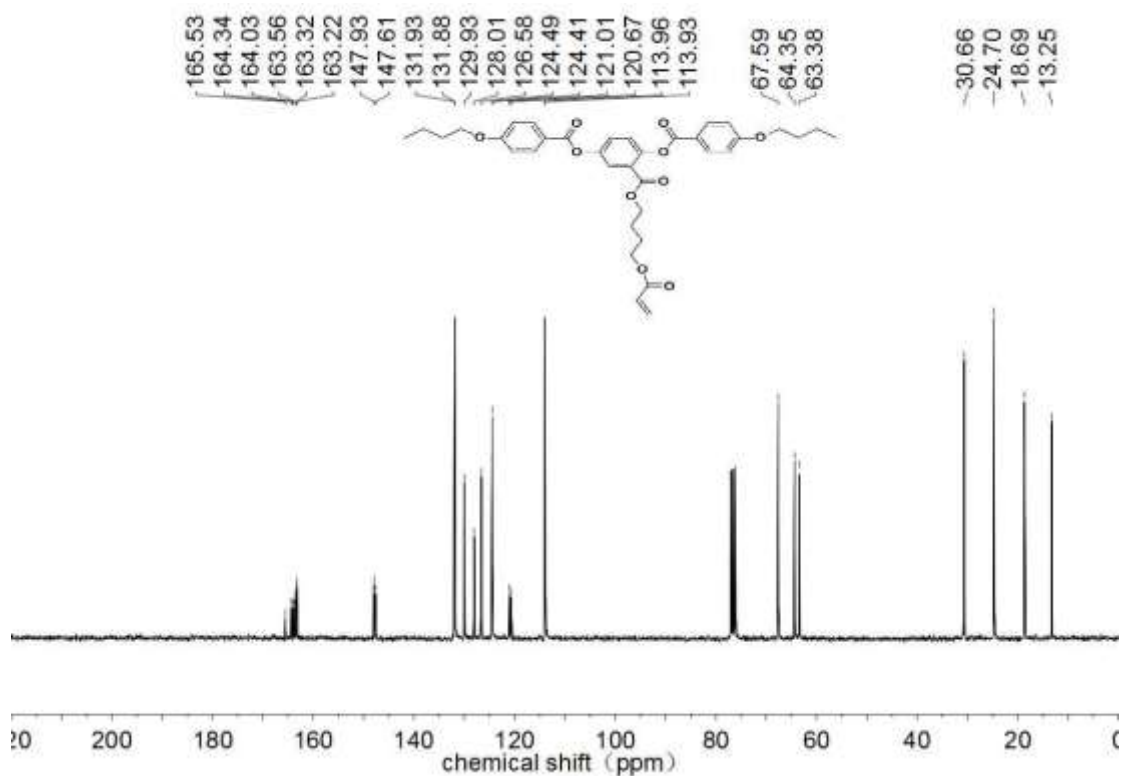
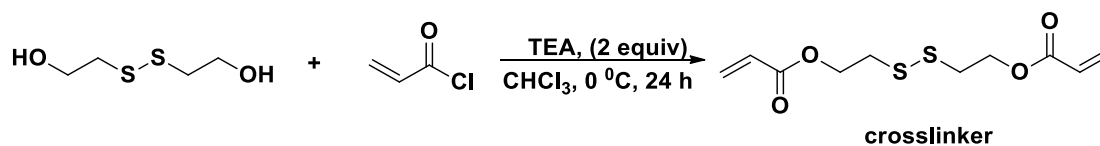


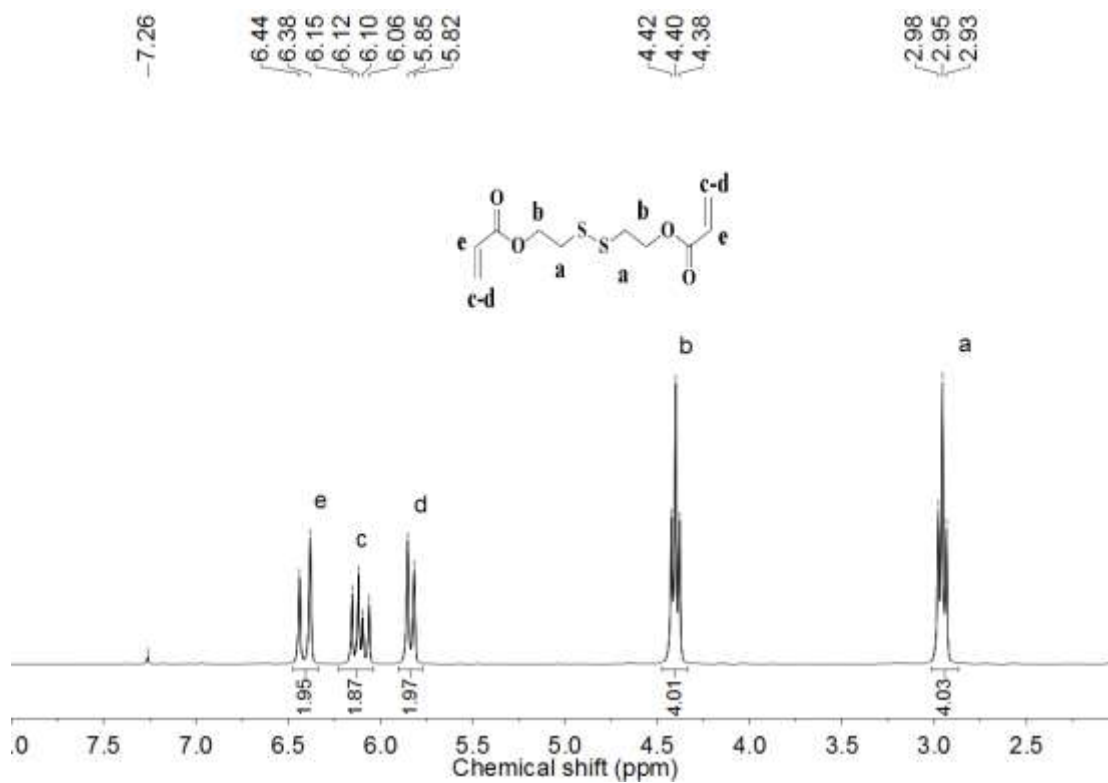
Figure S2.  $^{13}\text{C}$  NMR spectrum of LC monomer A444.

*Synthesis of disulfanediybis(ethane-2,1-diyl) diacrylate (DSDA)*<sup>[3]</sup>

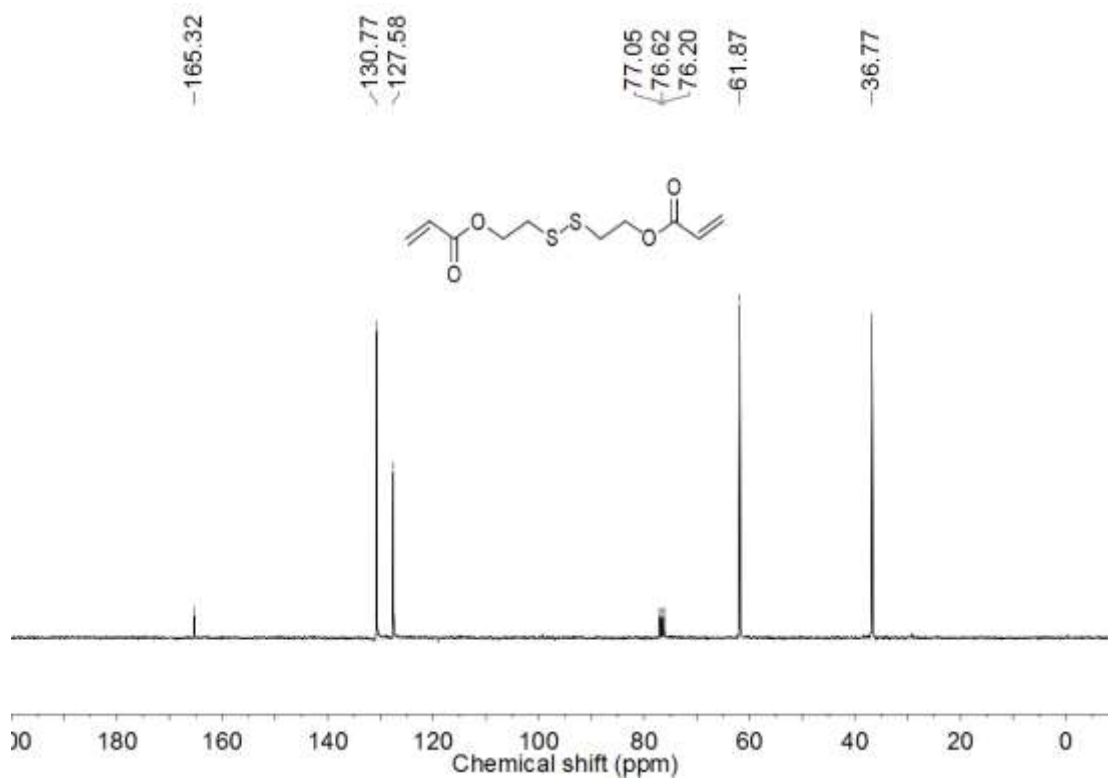


**Scheme S1.** The synthetic route of crosslinker **DSDA**.

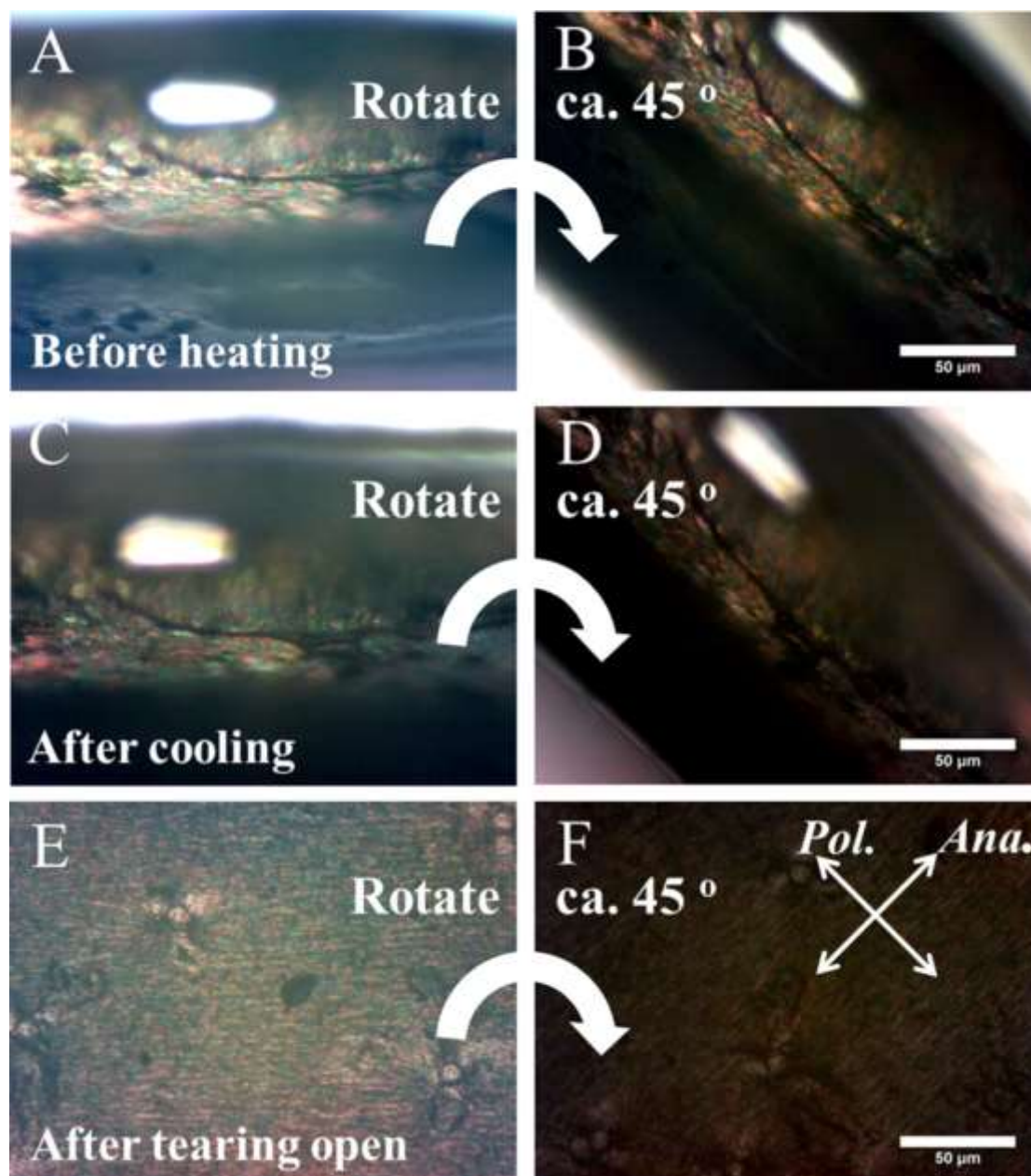
Bis(2-hydroxyethyl) disulfide (250 mg, 1.62 mmol), TEA (330 mg, 3.24 mmol) and dry CHCl<sub>3</sub> (4.0 mL) were added into a 25 mL Schlenk flask. Acryloyl chloride (590 mg, 6.40 mmol) was dropwisely added into the above solution under nitrogen atmosphere. The flask was sealed and the reaction mixture was stirred at 0 °C for 24 h. The mixture was allowed to be warmed to room temperature. The resulting precipitated salt was removed through filtration, the filtrate was washed by sodium carbonate aqueous solution (0.1 M). The organic layer was dried over MgSO<sub>4</sub> and concentrated on a rotary evaporator. The crude oil was purified by flash column chromatography (petroleum ether : ethyl acetate = 30/1) to afford the desired product (400 mg, 97 %). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ: 6.41 (d, *J* = 17.4 Hz, 2H), 6.11 (dd, *J* = 17.4, 10.5 Hz, 2H), 5.84 (d, *J* = 10.5 Hz, 2H), 4.40 (t, *J* = 6.6 Hz, 4H), 2.95 (t, *J* = 6.6 Hz, 4H). <sup>13</sup>C NMR (300 MHz, CDCl<sub>3</sub>) δ: 165.3, 130.8, 127.6, 61.9, 36.8.



**Figure S3.**  $^1\text{H}$  NMR spectrum of crosslinker **DSDA**.

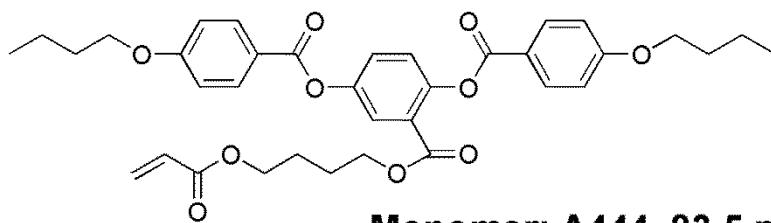


**Figure S4.**  $^{13}\text{C}$  NMR spectrum of crosslinker **DSDA**.

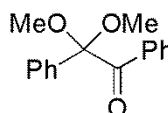
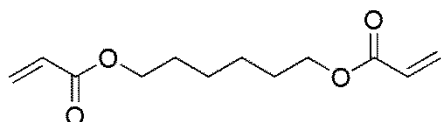


**Figure S5.** POM side-view images of the interface between two overlapped polydisulfide LCE films after TBP/DBU treatment oriented at (A)  $45^\circ$  or (B)  $0^\circ$  from the polarizer's transmission. POM side-view images of the same interface region between the two overlapped polydisulfide LCE films oriented at (C)  $45^\circ$  or (D)  $0^\circ$  from the polarizer's transmission after a heating-cooling cycle treatment of the sample. POM top-view images of the surface of one tearing-open LCE film, oriented at (E)  $45^\circ$  or (F)  $0^\circ$  from the polarizer's transmission.



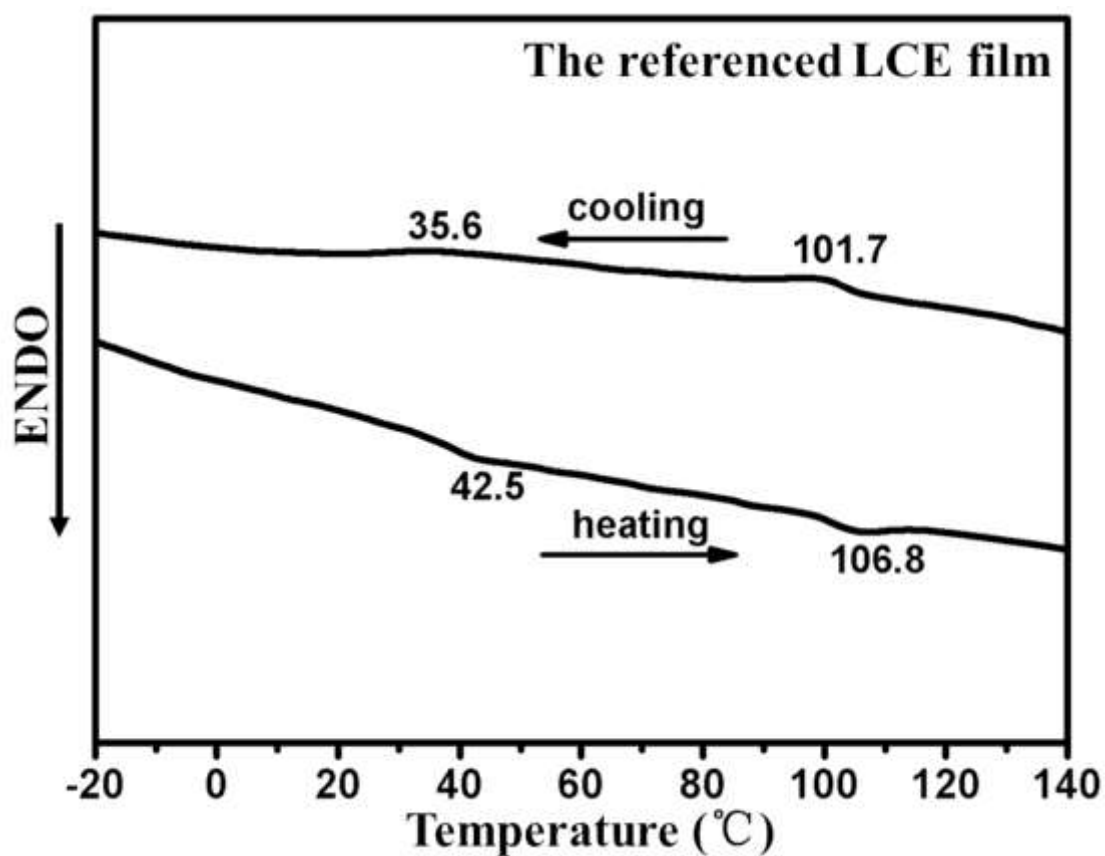


**Monomer: A444, 83.5 mol%**



**Crosslinker, 15 mol% Photo-initiator, 1.5 mol%**

**Scheme S2.** The chemical composition of the reference LCE film containing 1,6-hexanediol diacrylate crosslinker.



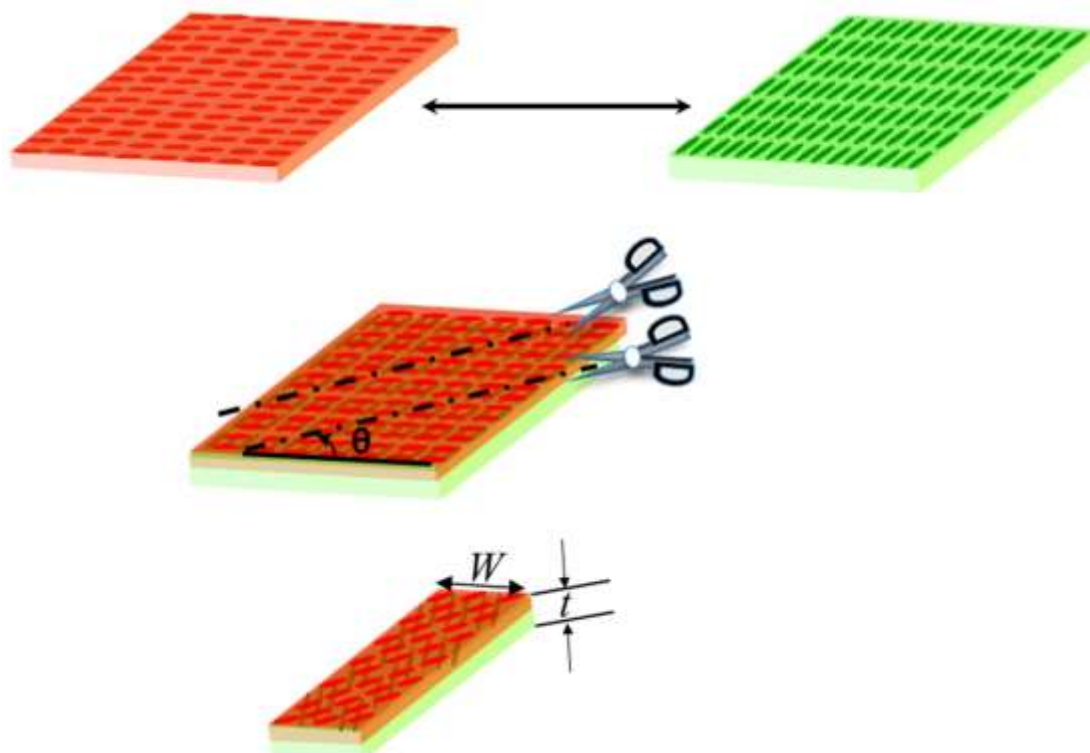
**Figure S6.** DSC curves of the referenced LCE film containing 1,6-hexanediol diacrylate crosslinker during the first cooling and second heating at a rate of 10 °C/min under nitrogen atmosphere.

*Calculation of order parameter S*

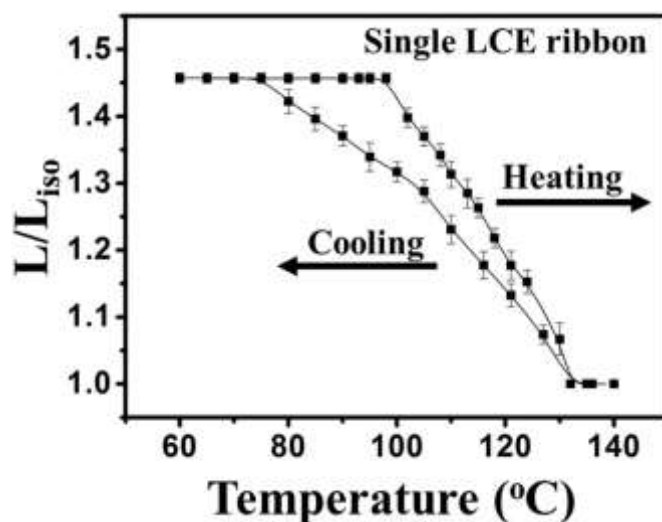
$$S = \frac{1}{2}(3\langle \cos^2 \alpha \rangle - 1) \quad (1)$$

$$\langle \cos^2 \alpha \rangle = \frac{\int_0^\pi I(\alpha) |\sin \alpha| \cos^2 \alpha d\alpha}{\int_0^\pi I(\alpha) |\sin \alpha| d\alpha}$$

The order parameter  $S$ , defined as Equation (1),<sup>[4]</sup> is calculated from the WAXS patterns to determine the uniorientation extent of the mesogenic groups. The intensity profiles  $I(\alpha)$  in azimuthal angle  $\alpha$  are integrated according to the WAXS patterns.



**Figure S7.** Schematic illustration of the preparation protocol of a bilayer LCE film with complex shape morphing.



**Figure S8.** The shape deformation  $L/L_{iso}$  of single LCE ribbon along stretching direction during the heating and cooling circles (heating rate = 15 °C/min).

### Reference

- [1] D. L. Thomsen, P. Keller, J. Naciri, R. Pink, H. Jeon, D. Shenoy and B. R. Ratna, *Macromolecules*, 2001, **34**, 5868-5875.
- [2] A. Buguin, M. H. Li, P. Silberzan, B. Ladoux and P. Keller, *J. Am. Chem. Soc.*, 2006, **128**, 1088-1089.
- [3] T. Y. Zhao, H. Zhang, B. Newland, A. Aied, D. Z. Zhou and W. X. Wang, *Angew. Chem. Int. Ed.*, 2014, **53**, 6095-6100.
- [4] C. Ortiz, M. Wagner, N. Bhargava, C. K. Ober and E. J. Kramer, *Macromolecules*, 1998, **31**, 8531-8539.