Supporting Information for:

A Room-Temperature Two-Stage Thiol-Ene Photoaddition Approach towards Monodomain Liquid Crystalline Elastomers

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General considerations.

Poly(3-mercaptopropylmethylsiloxane) (PMMS, SMS-992, M.W. 4000~7000, 95 cst) was purchased from Gelest Inc. N,N'-dicyclohexylcarbodiimide (DCC), diethyl azodicarboxylate (DEAD), triphenylphosphine (TPP), 4-dimethylaminopyridine (DMAP) and 2,2-dimethoxy-2-phenyl acetophenone (DMPA) were purchased from Aladdin Inc. Dichloromethane (CH$_2$Cl$_2$) was distilled from calcium hydride under nitrogen. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl under nitrogen. Other chemical reagents were used without further purification. All non-aqueous reactions were conducted in oven-dried glasswares, under a dry nitrogen atmosphere. All flash chromatography were performed using Macherey-Nagel MN Kieselgel 60 (0.063-1.2 mm).

All $^1$H NMR spectra were obtained using either a Bruker HW500 MHz spectrometer (AVANCE AV-500) or a Bruker HW300 MHz spectrometer (AVANCE AV-300) and recorded in CDCl$_3$ (internal reference 7.26 ppm). Fourier transform infrared (FT-IR) spectra were obtained by applying a Nicolet 5700 FT-IR spectrometer (Thermo Electron Scientific Instruments Corp). Differential scanning calorimetry (DSC) data were recorded on a TA Q20 instrument (New Castle, DE) under nitrogen purge at a heating rate of 10 °C/min from -30 °C to +120 °C.

X-ray scattering 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 (the q range covered by the IP was from 0.06 to 29 nm\(^{-1}\), \(q = 4\pi(\sin \theta)/\lambda\), where the wavelength \(\lambda\) is 0.1542 nm of Cu K\(\alpha\) radiation and \(2\theta\) is the scattering angle) at 40 kV and 40 mA for 30 min.

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

An ultraviolet (UV) lamp (230V, 0.20A, \(\lambda\) = 365 nm, LUYOR-3109, Shanghai LUYOR Instrument Co, Ltd) was used to irradiate the samples to perform the photocrosslinking reactions. A UV intensity meter (detection-range: 0–20 mW·cm\(^{-2}\), 290-390 nm, LUYOR-34, Shanghai LUYOR Instrument Co, Ltd) was used to measure the accurate light intensity of UV light. The mechanical properties of elastomers were examined using a dynamic mechanical analyzer (DMA Q800, TA Instrument) with tension clamp for static stress/strain, isostrain, and isostress measurements.
Figure S1. One-dimensional wide-angle X-ray scattering patterns of PMMS-g-MBB LCE sample.
Figure S2. $^1$H NMR spectrum of pre-crosslinked LCE film obtained after the 1st UV illumination stage, dispersed in DMSO-$d_6$, containing imidazole as an internal standard.

In this experiment,

$I_1 = 100$,

$I_2 + I_3 = 2.65$,

$m_i = 31.5 \text{ mg}, \ M_i = 68.077 \text{ g/mol},$

$m_2 = 15.7 \text{ mg},$

$m_1 = 286.49 \text{ mg},$

$m_0 = 67 \text{ mg}, \ M_0 = 134.27 \text{ g/mol}.$
Figure S3. $^1$H NMR spectrum of LCE film obtained after the 2nd UV illumination stage, dispersed in DMSO-$d_6$, containing imidazole as an internal standard.

Figure S4. Schematic illustrations of the thermoresponsive mechanism of LCEs.
Synthesis of 4-methoxyphenyl-4-(1-buteneoxy) benzoate (MBB).

**Figure S5.** The synthetic route of monomer MBB.

DEAD (27.84 mL, 160.0 mmol) in THF (120 mL) was added dropwise into a solution containing but-3-en-1-ol (11.52 g, 160.0 mmol), 4-hydroxybenzoic acid ethyl ester (26.56 g, 160.0 mmol) and TPP (43.6 g, 160.00 mmol) in THF (120 mL) at 0 °C in 15 minutes. The reaction mixture was then stirred at room temperature for 24 h and the solvent was removed under vacuum. The crude product was purified by flash column chromatography using silica gel as the stationary phase and the mixture of ethyl acetate and petroleum ether (v/v, 1 : 6) as the eluent, to yield 4-but-3-enyloxy-benzoic acid ethyl ester (30.34 g, 137.70 mmol, yield: 86.2%) as a colorless oil.

A solution of 4-but-3-enyloxy-benzoic acid ethyl ester (30.34 g, 137.70 mmol), sodium hydroxide (11.02 g, 275.46 mmol) in ethanol (200 mL) and water (200 mL) was heated under reflux for 12 h. The reaction mixture was cooled to room temperature and acidified to pH~2 by adding hydrochloric acid (1M) solution. The white precipitate was collected and washed with water. The product was recrystallized from ethanol to give 4-but-3-enyloxy-benzoic acid as a white solid (25.25 g, 131.50 mmol, yield: 95.50%, m.p. = 116 °C).
A mixture of 4-but-3-enyloxy-benzoic acid (25.25 g, 131.50 mmol), 4-methoxy phenol (17.94 g, 144.65 mmol), DMAP (8.02 g, 65.75 mmol) and DCC (19.88 g, 157.8 mmol) in dry dichloromethane (250 mL) was stirred at room temperature for 18 h. The solvent was removed under vacuum and the resulting white solid was purified by flash column chromatography using silica gel as the stationary phase and dichloromethane as the eluent to give the crude product, which was further recrystallized from ethanol to provide the desired monomer MBB (31.94 g, 107.17 mmol, yield: 81.5%) as a white solid. $^{1}$H NMR (300 MHz, CDCl$_3$) $\delta$ 8.16 and 8.13 (d, $J = 6.0$ Hz, 2H), 7.14 – 7.11 (m, 2H), 6.99 – 6.92 (m, 4H), 5.97 – 5.88 (m, 1H), 5.23 – 5.13 (m, 2H), 4.12 – 4.08 (t, $J = 9.0$ Hz, 2H), 3.82 (s, 3H), 2.62 – 2.56 (dt, $J = 6.0$, 6.0 Hz, 2H).

Figure S6. $^1$H NMR spectrum of monomer MBB in CDCl$_3$. 
Synthesis of 1,4-bis-undec-10-enyloxy-benzene (BUEB).1-4

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\text{HO-} + \text{CH}_2=\text{C(H}_2)_9\text{CH}_2\text{Br} \rightleftharpoons \text{H}_2\text{C=HC(H}_2)_9\text{H}_2\text{CO-} \quad \text{EtOH, 18 h}
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**Figure S7.** The synthetic route of crosslinker BUEB.

A solution of hydroquinone (4.65 g, 42.27 mmol) and potassium carbonate (20.42 g, 147.93 mmol) in 80 mL ethanol was heated under reflux. Then this suspension was added with a solution of 11-bromo-1-undecene (24.9 g, 101.44 mmol) in ethanol (80 mL) dropwise in 10 minutes. The reaction mixture was stirred under reflux at 80 °C for 18 h, and was then poured into 400 mL of iced water. This solution was extracted twice with diethyl ether (400 mL in total). The organic layer was washed twice with saturated aqueous solution of sodium carbonate (200 mL in total) and once with water (200 mL), followed by drying over anhydrous magnesium sulfate. The diethyl ether was removed under vacuum, and the precipitate was subsequently purified by flash column chromatography using silica gel as the stationary phase and a mixture of ethyl acetate and petroleum ether (v/v, 1 : 10) as the eluent, followed by solvent removal in vacuum to yield BUEB as a white solid. The product was further recrystallized from ethanol (13.69 g, yield: 78.16%, measured m.p. = 56 °C, m.p. = 56 °C reported in the literature.2). 1H NMR (300 MHz, CDCl\textsubscript{3}) \( \delta \) 6.82 (s, 4H), 5.86 – 5.75 (m, 2H), 5.02 – 4.91 (dd, \( J = 15.0, 21.0 \) Hz, 4H), 3.92 – 3.87 (t, \( J =6.0, 4H \)), 2.08 – 2.01 (m, 4H), 1.77 – 1.72 (m, 4H), 1.44 – 1.30 (m, 24H).
Figure S8. $^1$H NMR spectrum of crosslinker BUEB in CDCl₃.

References