

## Supporting Information

### **Photo-responsive Liquid Crystalline Epoxy Networks with Exchangeable Disulfide Bonds**

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Video S1 Blue light induced bending of LCEN (parallel condition)

Video S2 Blue light induced bending of LCEN (perpendicular condition)

Video S3 UV-induced shape recovery process of LCEN

### Monomer synthesis

The azobenzene-based epoxy monomer was synthesized as follows: a mixture of 4,4'-(1,2-diazenediyl)bisphenol (10.06 g), BTMAB (0.36 g) and epichlorohydrin (73.64 ml) was placed in a two-neck flask and refluxed for 60 min. NaOH (3.76 g) was dissolved in 21.3 ml of water to prepare 15% NaOH aqueous solution. The solution was added into the flask dropwise over a period of 4 hours under reflux. The reaction was carried out for an additional 12 hours at room temperature. The final product was washed with cold methanol and water. A yellow powder was obtained by recrystallization using isopropyl alcohol and chloroform (2:1). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ2.79 (2H, dd, CH<sub>2</sub> of epoxy), δ2.94 (2H, dd, CH<sub>2</sub> of epoxy), δ3.40 (2H, m, CH of epoxy), δ4.02 (2H, dd, CH<sub>2</sub> of glycidyl), δ4.33 (2H, dd, CH<sub>2</sub> of glycidyl), δ7.01 (4H, d, azobenzene), δ7.86(4H, d, azobenzene).

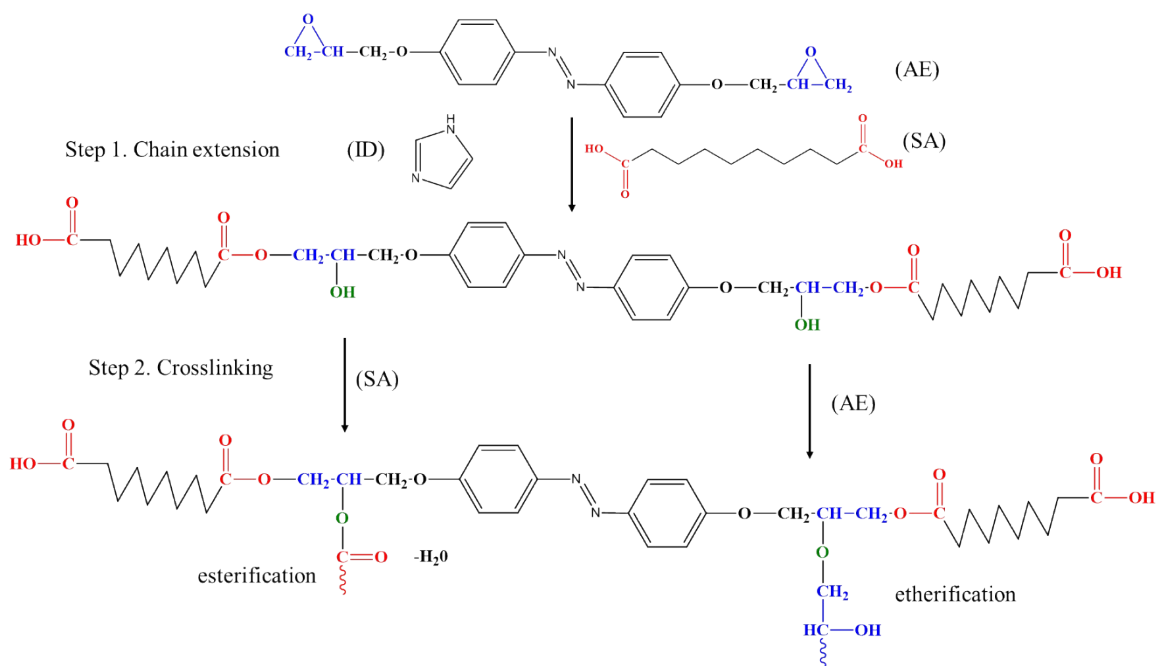


Figure S1. Reaction mechanism of LCEN.

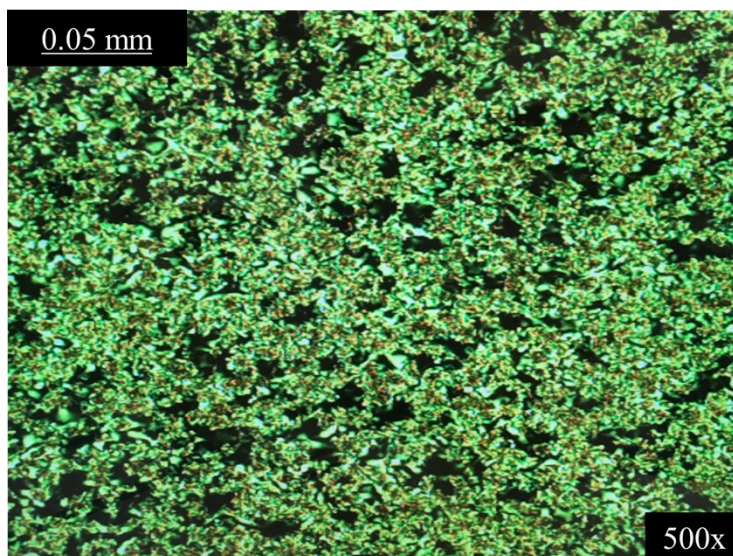


Figure S2. Polarized optical microscopy images of fully cured LCEN at room temperature.

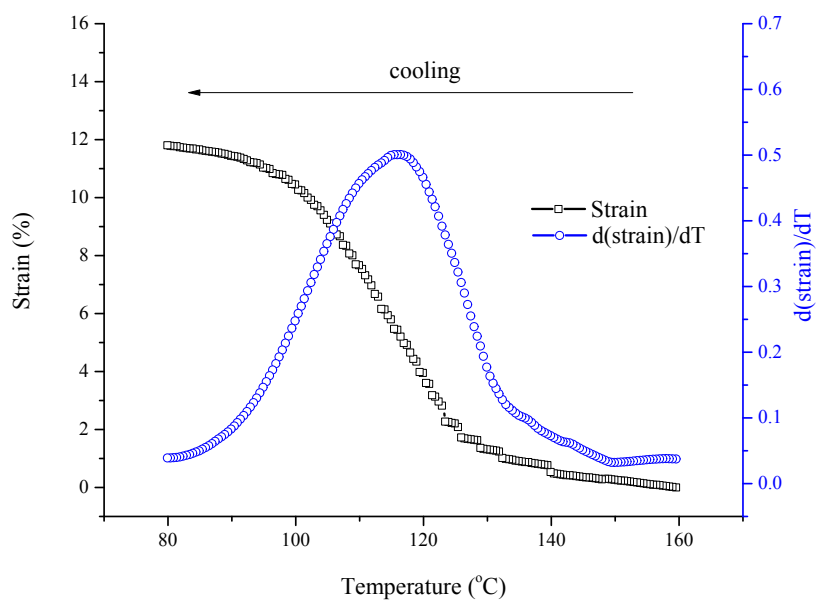


Figure S3. LC formation and macroscopic orientation induced elongation of LCEN during the cooling process in a cyclic thermomechanical tensile test.

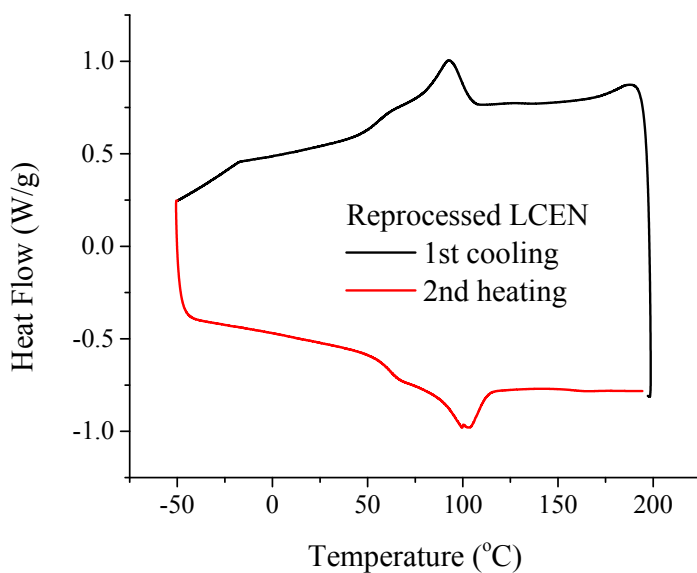


Figure S4. Thermal and LC properties of reprocessed LCEN films.

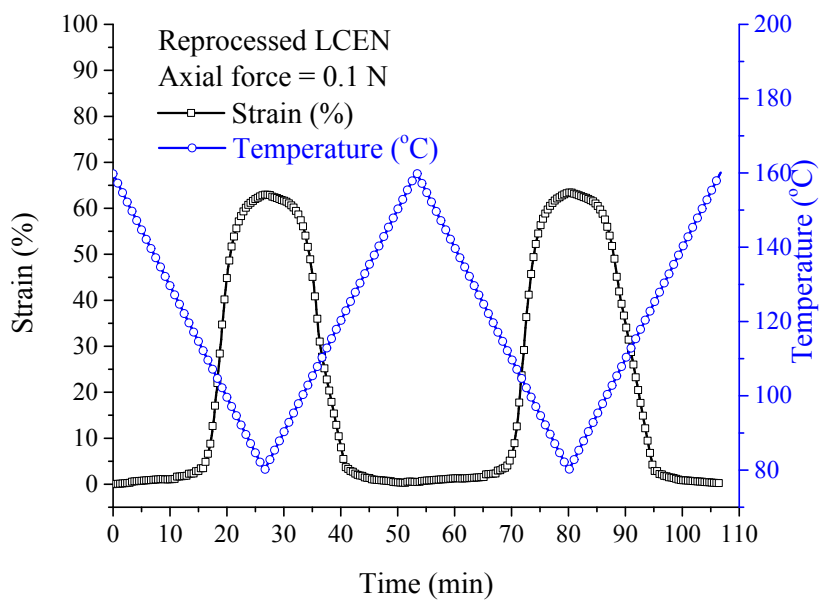


Figure S5. Cyclic thermomechanical tensile test of reprocessed LCEN films.

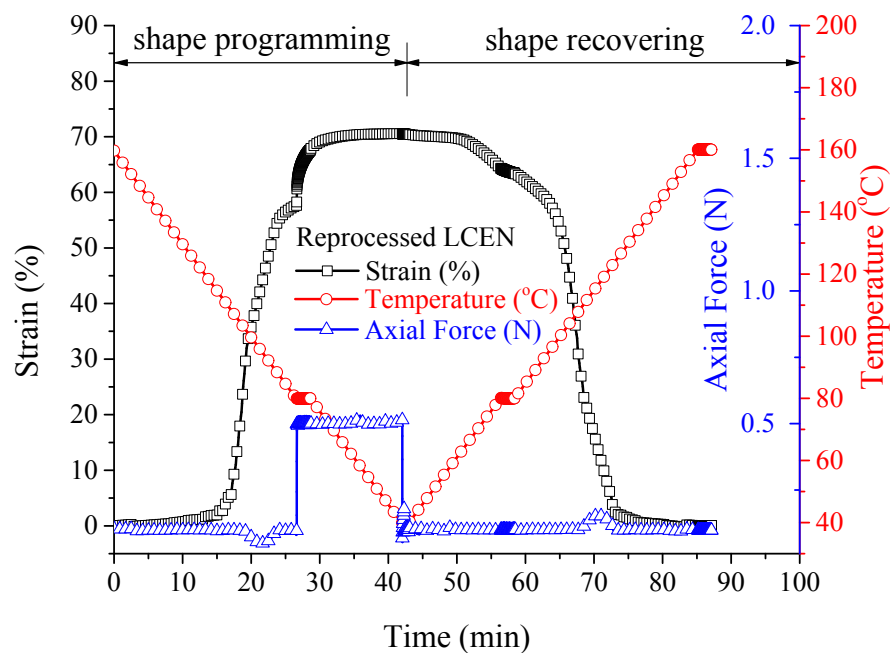


Figure S6. Triple shape memory test of reprocessed LCEN films.