Electronic Supplementary Information

Mechanically programmed 2D and 3D liquid crystal elastomers at macro- and microscale via two-step photocrosslinking

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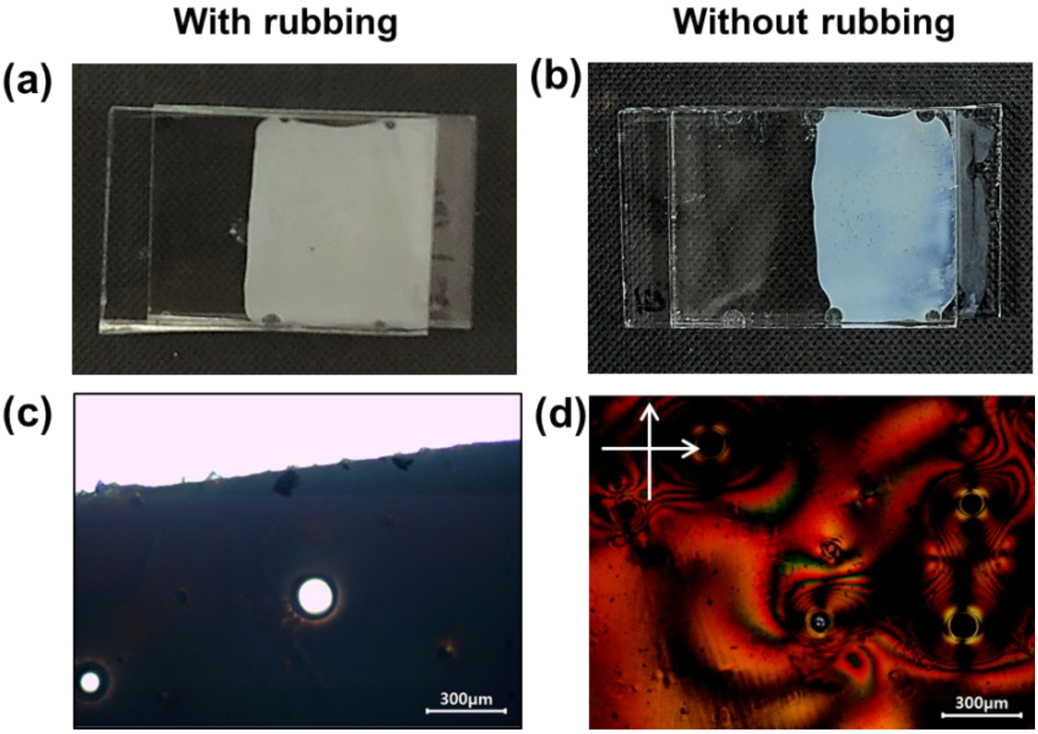


Fig. S1 Comparison of partially crosslinked polydomain LCEs oligomerized at 65 ^{o}C for 21 h followed by photopolymerization at 90 ^{o}C for 6s. (a) A photograph and (c) optical microscope image of the sample prepared inside a rubbed glass cell with Elvamide coating. (b) A photograph and (d) POM image of the sample prepared inside an unrubbed glass cell with Elvamide coating.

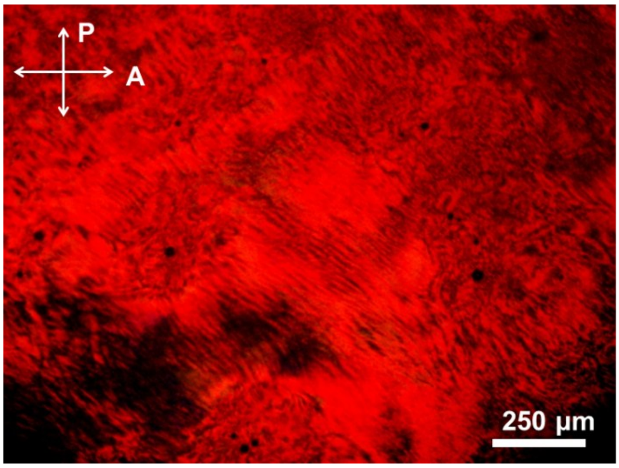


Fig. S2 Schlieren texture of LC oligomer at 70 ^{o}C obtained by POM.

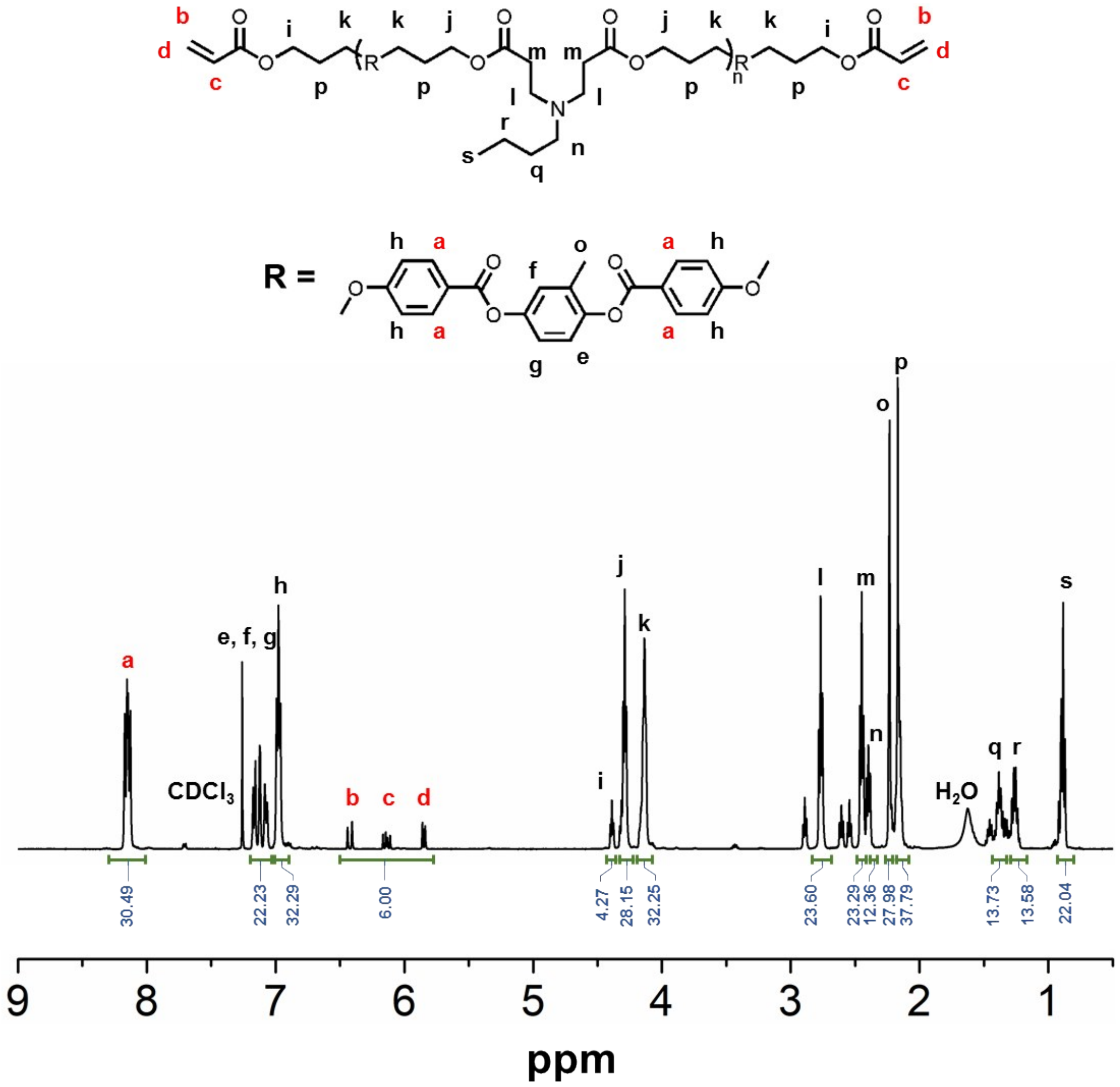


Fig. S3 ^{1}H NMR spectra of LC oligomer in CDCl$_3$.

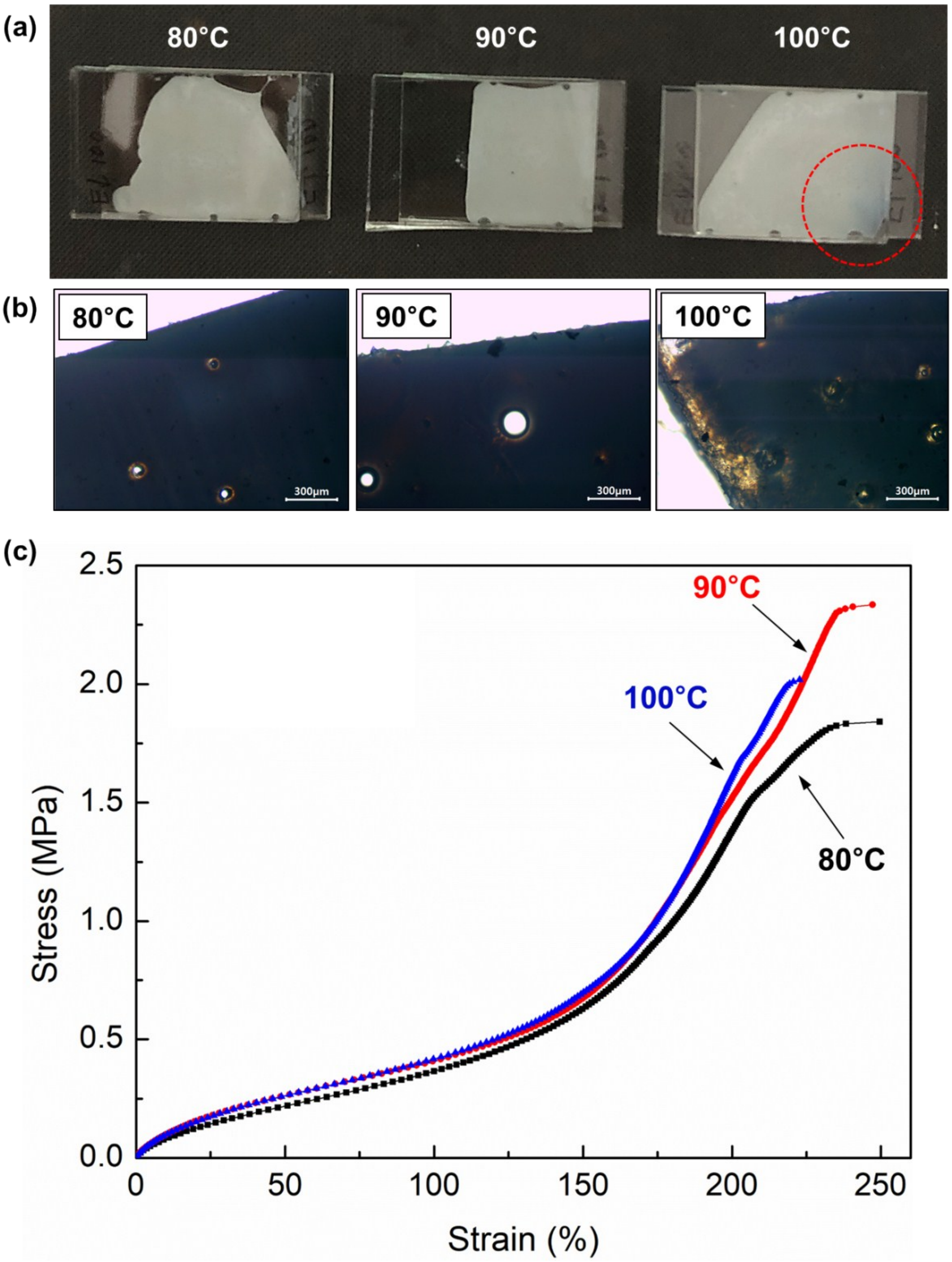


Fig. S4 Polydomain LCEs photopolymerized at different isotropic temperatures. (a) Photographs of three polydomain LCEs photopolymerized at 80 °C (left), 90 °C (middle) and 100 °C (right). Higher transparency (red circled region) observed in the sample polymerized at 100 °C suggests the formation of optically and structurally less uniform polydomain LCE for this sample. (b) Optical microscope images of three polydomain LCEs photopolymerized at 80 °C (left), 90 °C (middle) and 100 °C (right). (c) Stress-strain curves of three polydomain LCEs photopolymerized at different isotropic temperatures.

Calculating degree of polymerization (DP) and number average molecular weight (M_n) by ^{1}H NMR end-group analysis

The three peaks in the ^{1}H NMR spectrum (**b, c, d** in Figure S2) appearing at 5.85-6.45 ppm correspond to six protons in the diacrylate end groups of the LC oligomer (CH_2=CHCOO-). The integration value of these peaks was used to calibrate other peaks, and set as six. The peak at 8.15 ppm (**a** in Figure 2) correspond to the four aromatic protons in the LC oligomer, and its integration value was 30.25. Therefore, the number of repeating unit (i.e., DP) was calculated by (30.25 / 4) – 1 = 6.6, and the M_n was calculated by DP × M_n of repeating unit (6.6 × 661.8 g/mol) + M_n of end-group (588.6 g/mol) = ~5000 g/mol.

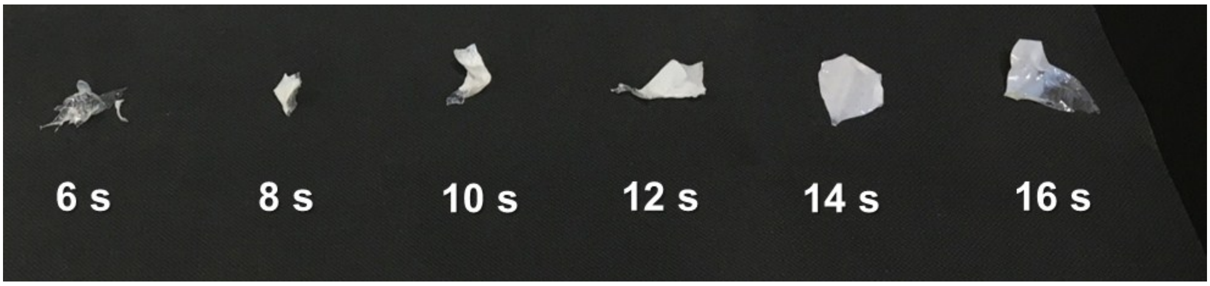


Fig. S5 Photographs of partially crosslinked polydomain LCEs after extracted with $CHCl_3$ for 48 h, followed by vacuum drying. Each LCE were prepared by UV crosslinking with different exposure time as indicated in the image.

Table S1. Gel fraction values of the partially crosslinked polydomain LCEs after different UV exposure time.

UV Exposure Time (s)	2	4	6	8	10	12	14	16
Gel Fraction (%)	N/A	N/A	45	54	62	66	72	80

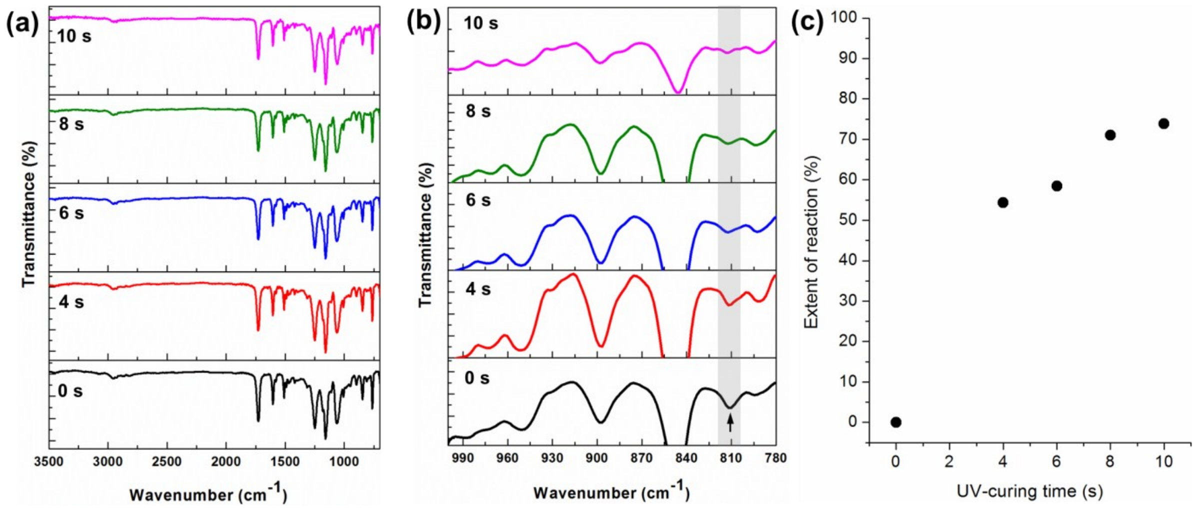


Fig. S6 FT-IR spectra of partially cured polydomain LCEs at different UV exposure times: (a) full spectra and (b) magnified region of spectra from 780 to1000 cm^{-1}, and (c) the extent of acrylate reaction as a function of UV curing time.

The extent of reaction by FT-IR

The extent of acrylate reaction was determined by the following equation.[1]

$$The\ extent\ of\ reaction\ (\%) = 1 - \frac{(\frac{A_{810,t}}{A_{1730,t}})}{(\frac{A_{810,0}}{A_{1730,0}})} \times 100$$

, where $A_{810,0}$ and $A_{810,t}$ refer to the areas of acrylate peak for uncured polydomain and partially cured polydomain after a certain time, respectively. $A_{1730,0}$ and $A_{1730,t}$ indicate the areas of the reference peak for uncured polydomain and partially cured polydomain after a certain time, respectively.

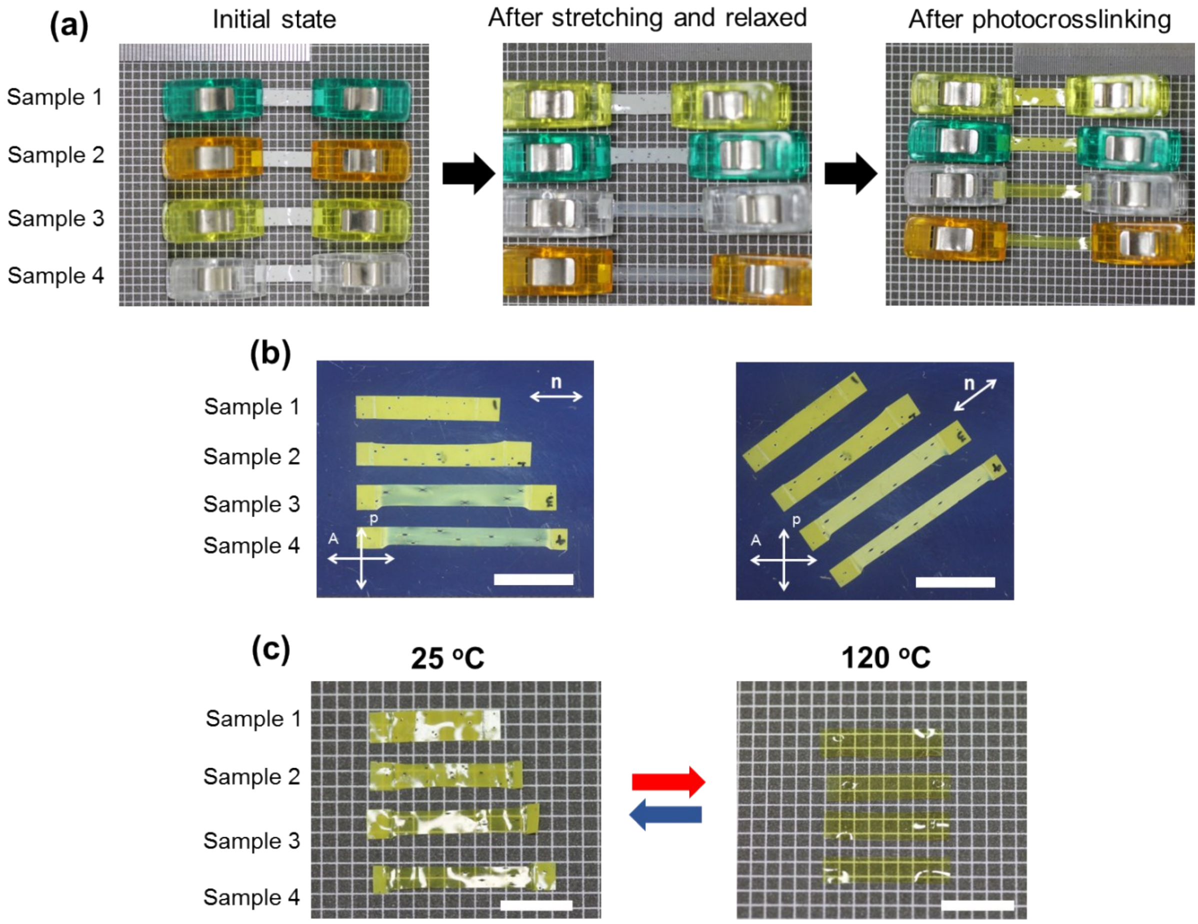


Fig. S7 (a) Mechanical programming process of polydomain LCEs with different extent of elongation. (b) Photographs of uniaxially-aligned monodomain LCEs between cross polarizers. (c) Thermal actuation of the monodomain LCEs programmed by different extent of elongation. Scale bars indicate 10 mm.

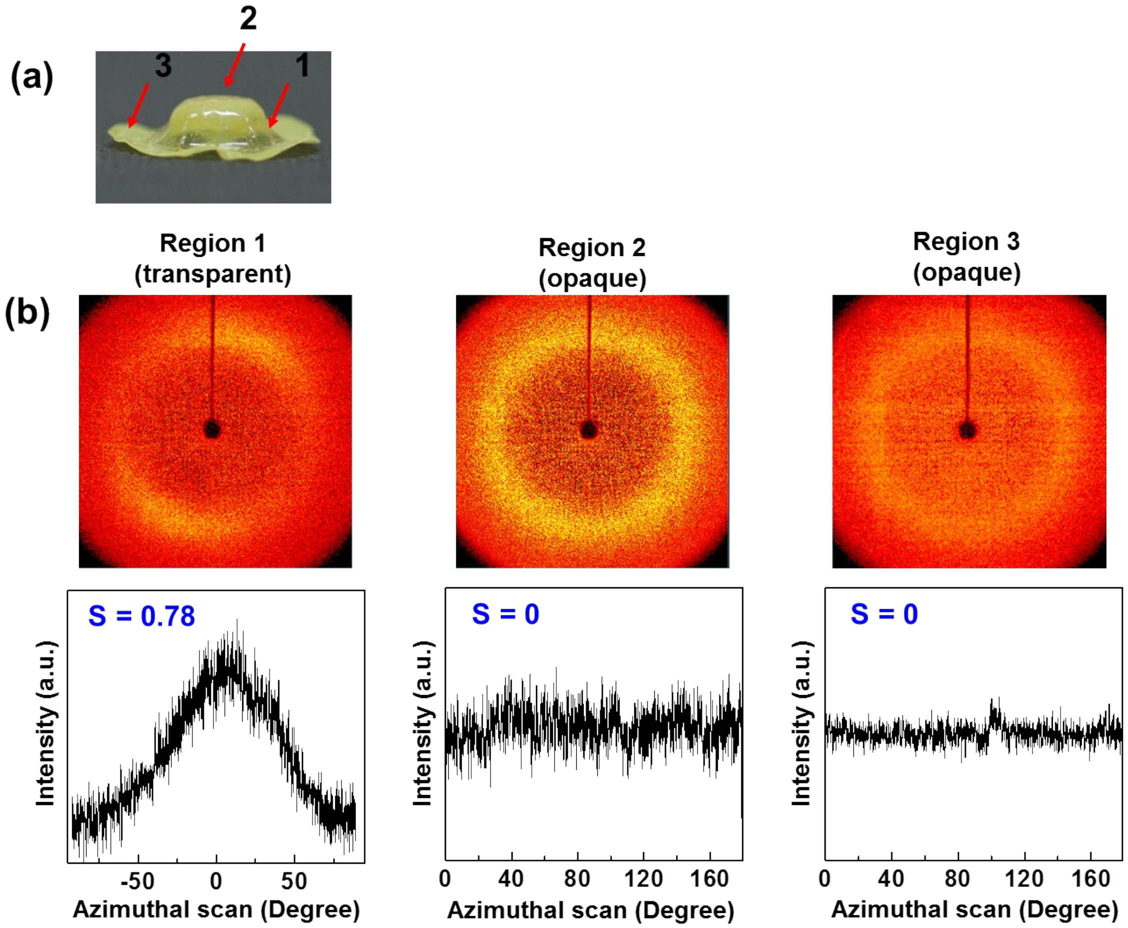
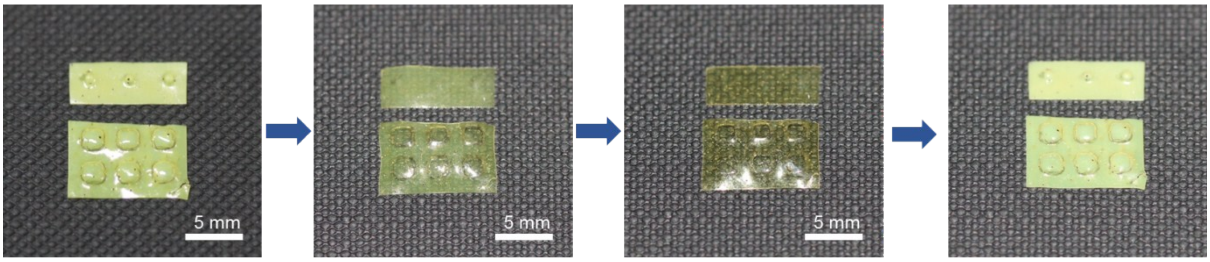


Fig. S8 (a) The photograph of the hat shaped LCE showing both transparent and opaque regions indicated by arrows. (b) 2D-WAXD patterns and order parameters of the hat-shaped LCE obtained at different regions.



Initial state

After 10 min

After 20 min

After evaporation of THF

Fig. S9 Chemoresponsive behavior of patterned LCEs. LCE films were fully swelled after 20 min when exposed to THF vapor, and the initial shapes were recovered when THF was completely evaporated

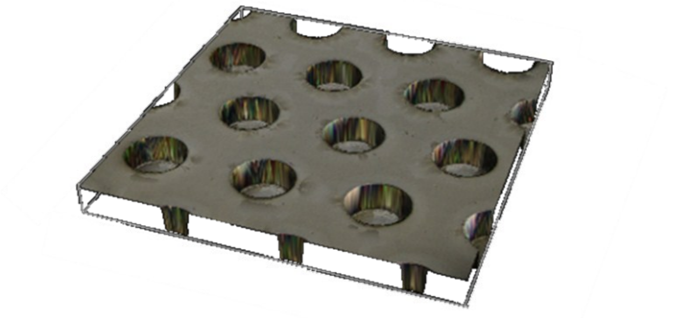


Fig. S10 Laser scanning confocal microscope image of the micropatterned mold made by acryl resin. The diameter and height of the cylindrical holes is 91 and 96 μm, respectively.

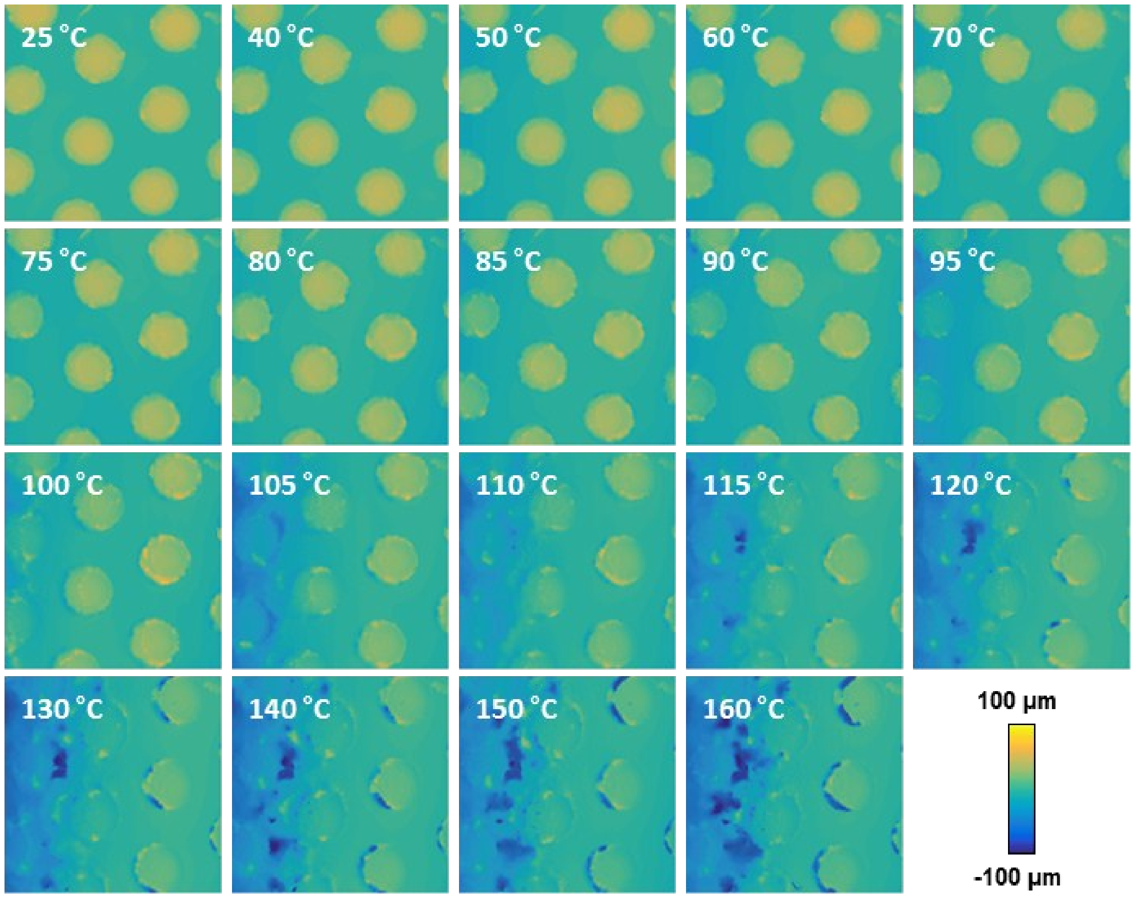


Fig. S11 Confocal microscope images as a function of the heating temperature.

Reference

(1) Rigail-Ceden˜o, A.; Sung, C. S. Paik. Fluorescence and IR characterization of Epoxy Cured with Aliphatic Amines. *Polymer*, **2005**, *46*, 9378-9384.