Supporting Information

Direct Shape Programming of Liquid Crystal Elastomers

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1 LCE Shape Programming

The 'step-function' LCE (Figure S2a) was cured by engraving rectangular wells in two pieces of 3/32-inch-thick basswood using a Universial X-660 laser cutter, as shown in Figure S1. The two halves were then clamped together with the wells slightly overlapping. LCE solution was then poured into the mold for the first cure step. After the LCE was removed, and the solvent evaporated, the LCE was stamped with a hard-plastic mold containing various geometrics patterns. The pillar-array shown in Figure S2b was made by lightly hand pressing an initially flat LCE against a comb tooth surface shown in Figure S1d.

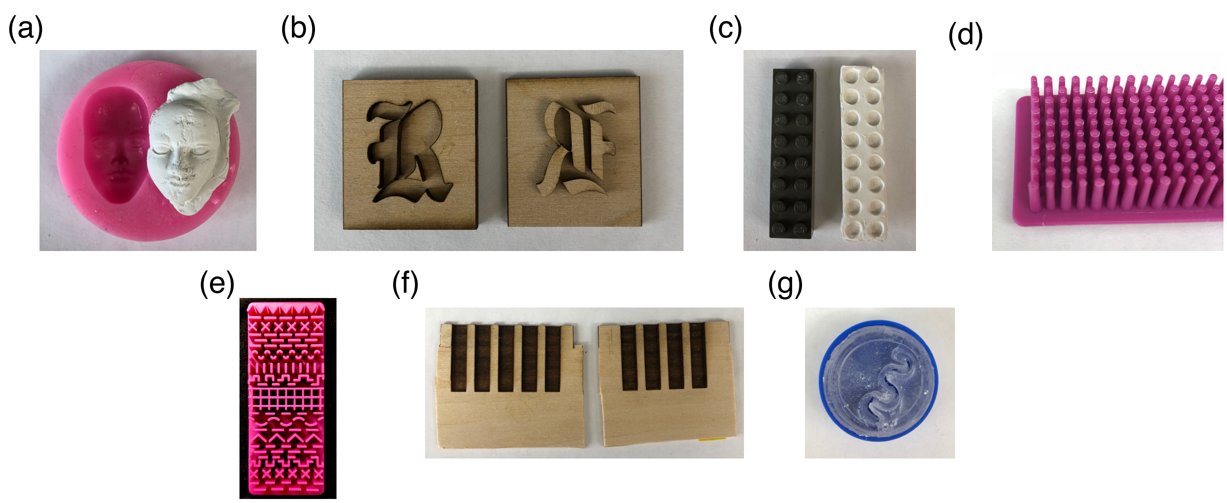


Figure S1 Molds used to mechanically deform LCEs. (a) Negative mold of a face in silicone and the positive image made in clay, (b) laser cut Rice logo embosser, (c) a LEGO and its negative counter piece made in clay used for the four-pillar LCE, (d) comb-tooth array surface used for the multi-pillar LCE, (e) plastic stamp for the 'step-function' LCE, (f) laser engraved mold for 'step-function' LCE, and (g) PDMS mold for wave LCE.

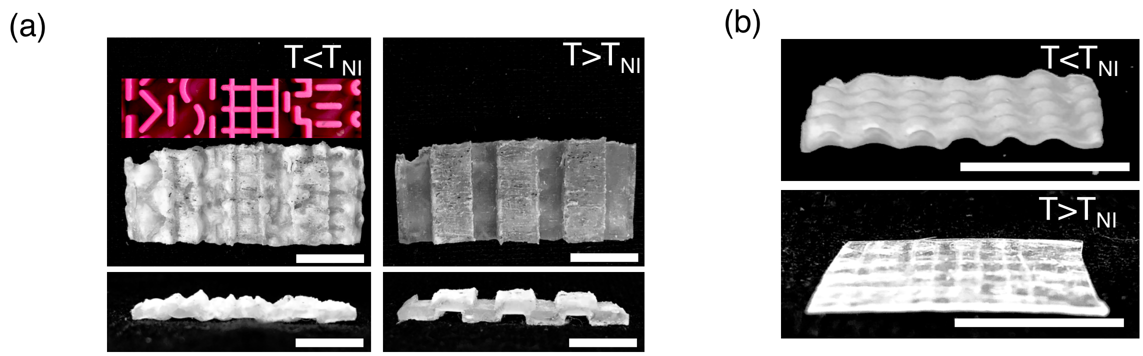


Figure S2 (a) 'Step-function' (thickness t = 2 mm) LCE pressed with the shown pink stamp and cured, and (b) multi-pillar array LCE (t = 0.25 mm) at $T < T_{NI}$and $T > T_{NI}$. (scale bars = 10 mm)

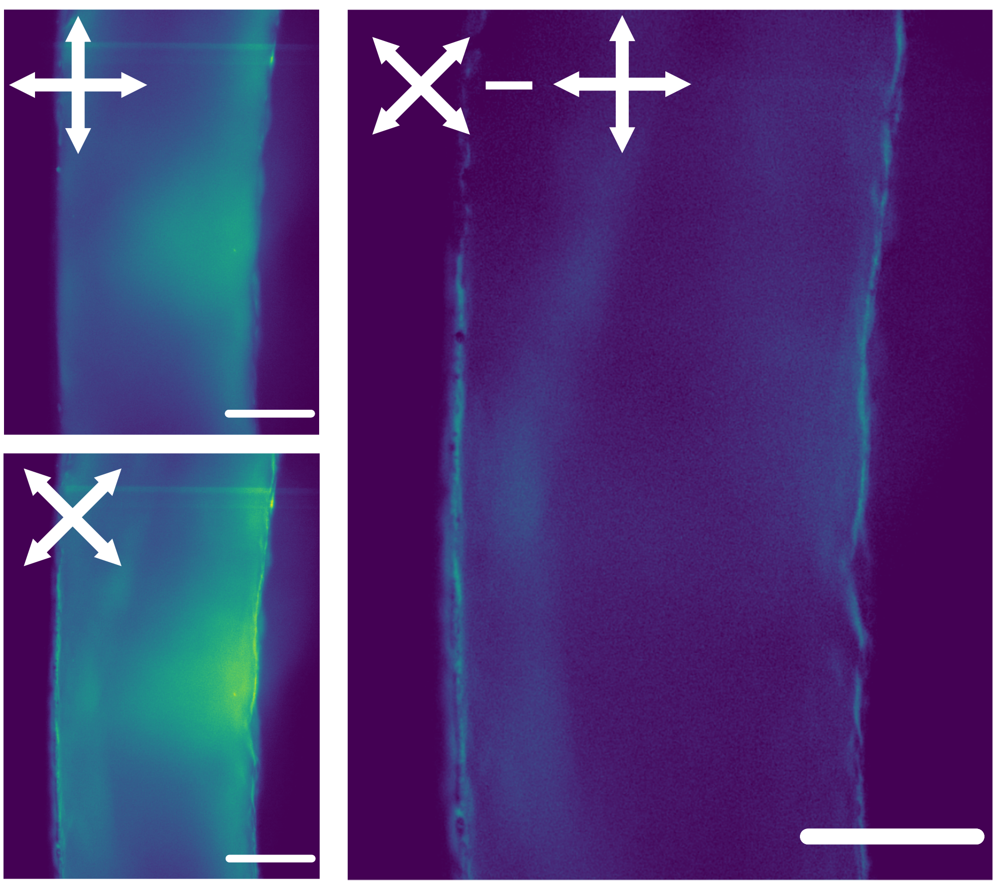


Figure S3 Cross-polarized optical micrographs imaged through the thickness of a curved LCE (t = 0:25mm, cure = 2:455mm). The right image is the top left image subtracted from the bottom right image to accentuate the birefringence at the inner and outer edges, which confirms partial mesogen alignment near the sample edges shown schematically in Figure 1a. (scale bar = 100 m)

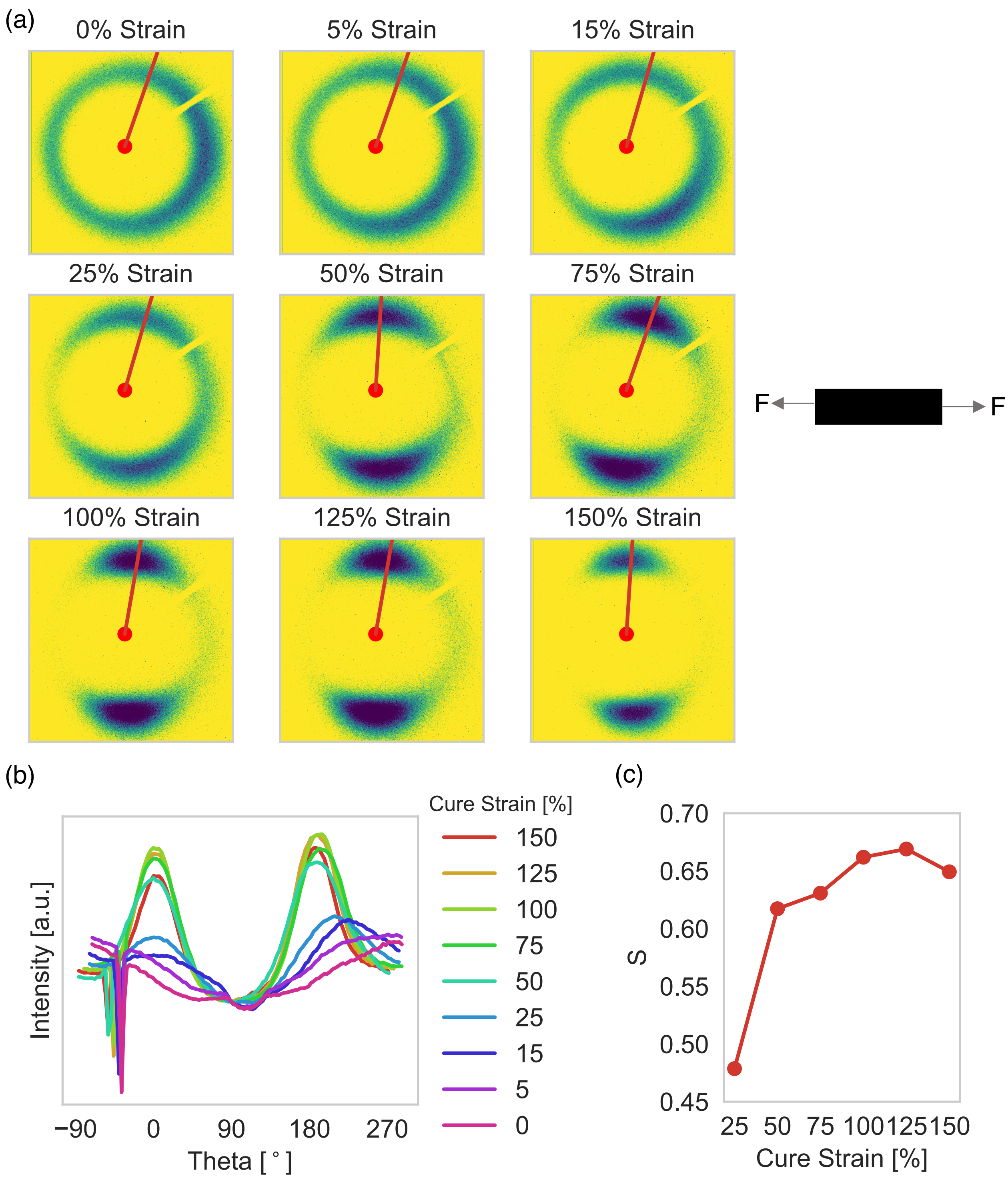


Figure S4 Wide angle X-ray scattering (WAXS) data from LCEs uniaxially stretched and UV-cured from 0 to 150% strain. (a) 2D diffraction images of LCEs. The red lines indicate the reference 0° theta position for the intensity plot. Samples were stretched approximately in the direction shown in the schematic on the right. (b) Intensity plotted as a function of azimuthal angle theta for all samples. (c) Calculated order parameter as a function of cure strain for samples with 25 % or greater cure strains.

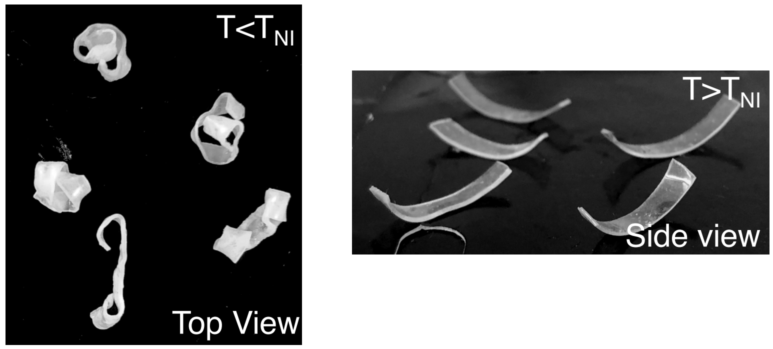


Figure S5 Curled LCE that was UV cured at $T > T_{NI}$ at both $T < T_{NI}$ and $T > T_{NI}$.

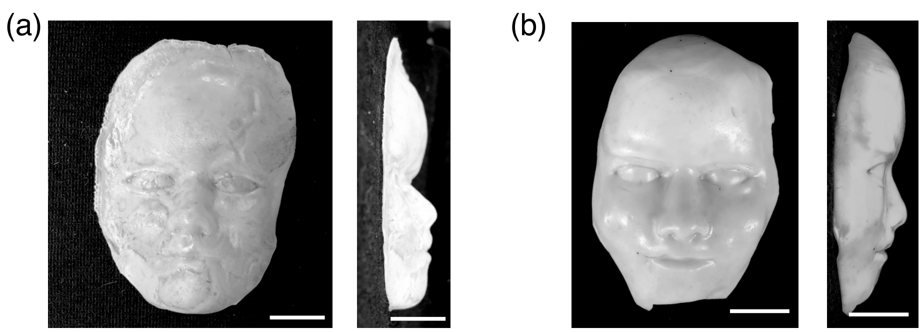
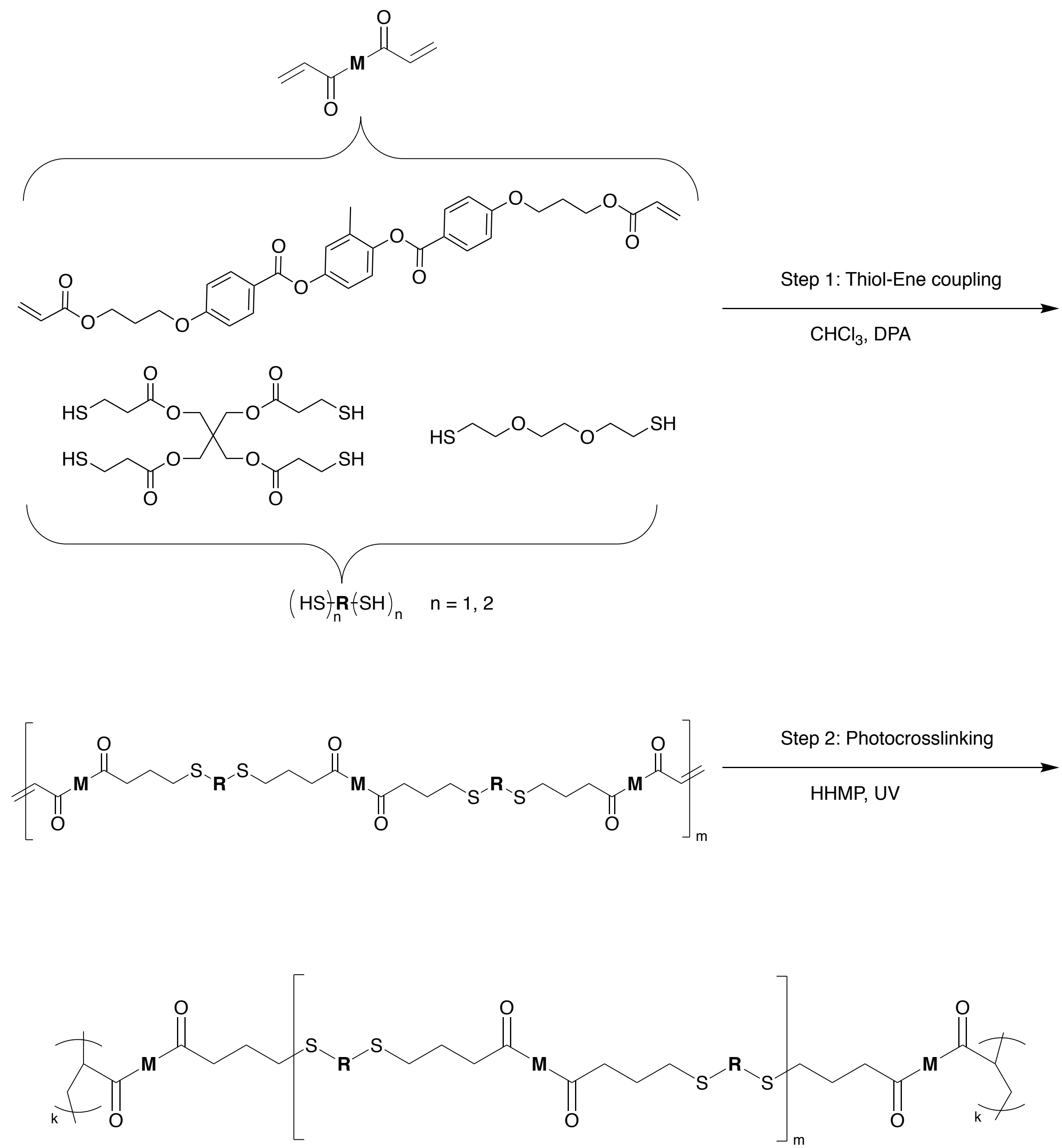


Figure S6 Comparison of LCE programmed using the same mechanical deformation at (a) $t = 0.2$ mm, and (b) $t = 0.45$ mm. The thinner sample is capable of retaining features with tight curvatures, i.e. nose, eyes, but is less able to retain the large curvature of the forehead and cheeks.



Scheme 1 Reaction Scheme for the thiol-ene coupling of the first network and the photocrosslinking of the second network.

PETMP Thiol Content (mol %)	Excess Acrylate (mol %)	EDDET (mg)	PETMP (mg)	DPA* (mg)
10	5	79.59	11.86	49.01
	10	75.97	11.32	48.02
20	5	70.75	23.71	47.85
	10	67.53	22.63	46.85
	15	64.60	21.65	45.93
25	5	66.33	29.64	47.24
	10	63.31	28.29	46.26
	15	60.56	27.06	45.37
40	5	53.06	47.42	45.40
	15	48.45	43.30	43.69
	25	44.57	39.84	42.26
60	5	35.37	71.14	42.94
	15	32.30	64.95	41.45
	25	29.71	59.76	40.19
80	5	17.69	94.85	40.49
	15	16.15	86.60	39.21
	25	14.86	79.67	38.13

*DPA added as 2 wt % solution in $CHCl_3$

Table S1 Quantities of EDDET, PETMP, and DPA used to synthesize LCEs reported. The PETMP thiol content is the mol % thiol from PETMP, and the excess acrylate is the mol % excess acrylate relative to all thiol functional groups. All reactions were conducted using 300 mg RM257, 1.5 mg HHMP, 0.75 mg MEHQ and 120 mg of $CHCl_3$.

% PETMP Content	% Excess Acrylate	Modulus after 1st Cure (kPa)	Modulus after 2nd cure (kPa)	Modulus Ratio	κ_n	f
10	5	5.09 ± 1.35	5.58 ± 0.71	1.21	0.14	0.05
	10	2.43 ± 0.77	7.75 ± 0.93	3.58	0.70	0.10
20	5	10.08±2.97	12.27 ± 2.20	1.29	0.39	0.05
	10	1.98±0.22	19.22 ± 3.39	9.76	0.95	0.13
	15	2.91±0.93	11.86 ± 5.27	4.29	0.93	0.16
25	5	7.49±1.48	8.45 ± 1.84	1.23	0.49	.04
	10	3.07±0.27	17.77 ± 1.96	5.78	0.95	0.09
	15	1.96±0.22	17.03 ± 0.58	8.78	0.90	0.17
40	5	24.09±2.74	29.88 ± 8.11	1.22	0.31	0.04
	15	14.73±3.60	25.11 ± 1.66	1.83	0.66	0.10
	25	1.79±0.22	19.44 ± 4.49	10.94	0.95	0.69
60	5	38.63± 8.05	43.39 ± 6.66	1.14	0.29	0.05
	15	40.38± 2.18	53.10 ± 4.30	1.32	0.31	0.08
	25	14.22± 1.99	30.39 ± 3.18	2.21	0.87	0.62
80	5	74.98 ± 7.54	76.01 ± 5.39	1.02	0.07	0.04
	15	69.71 ± 6.50	82.62 ± 16.16	1.18	0.15	0.05
	25	39.29 ± 5.16	76.31 ± 5.98	1.96	0.50	0.31

Table S2 Numerical data for graphs in Figure 2. Young's modulus for LCEs after the first and second cure (n = 3, error indicate 95% confidence intervals of the mean), the mean modulus ratio of the second cure to the first, mean κ_n, and mean f are listed for varying LCE compositions.

ρ (mm)	t (mm)	κ_n	Calculated Strain (%)
6.580	0.25	0.06 ± 0.05	1.86
4.350	0.25	0.49 ± 0.15	2.83
6.580	0.44	0.86 ± 0.03	3.35
2.695	0.25	0.92 ± 0.06	4.66
6.580	0.56	0.97 ± 0.08	4.66
2.015	0.25	0.99 ± 0.05	6.33

Table S3 Numerical data for graphs in Figure 3. Normalized curvature, κ_n, and calculated strain for LCEs with 25% PETMP content and 10% excess acrylate at varying cure radius and thickness. (n = 5, error indicates 95% confidence intervals of the mean)

Cure Strain (%)	Elongation Fixity	Contraction Fixity	Actual Actuation (%)	Normalized Actuation (%)
50	1.00 ± 0.00	1.01 ± 0.02	47.40 ± 2.87	94.80 ± 5.74
75	1.00 ± 0.01	1.01 ± 0.01	71.79 ± 2.30	95.72 ± 3.06
100	0.99 ± 0.02	1.03 ± 0.03	91.87 ± 3.15	91.87 ± 3.15
125	0.91 ± 0.02	1.02 ± 0.02	100.15 ± 2.38	80.12 ± 1.91
150	0.81 ± 0.01	1.07 ± 0.02	90.36 ± 4.52	60.24 ± 3.01

Table S4 Numerical data for graphs in Figure 4. Contraction fixity, elongation fixity, actual actuation, and normalized actuation for LCEs with 25% PETMP content and 10% excess acrylate. (n = 5, error indicates 95% confidence intervals of the mean)