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Supplementary Information

Microactuators from a main-chain liquid crystalline elastomer via thiol-ene “click” chemistry

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Table S1. *Dimensions and actuation properties of the LCE particles prepared in a 750 μm polymerization tube.*

Droplet formation	**Polymerization temperature**	**Particle diameter / μm**	**Aspect ratio at 20°C**	**Aspect ratio at 180°C**	**Relative length change**
45°C	**45°C**	284 (± 6%)	1.00 (± 3%)	1.05 (± 4%)	1.05 (± 5%)
45°C	**47°C**	200 (± 2%)	0.99 (± 2%)	1.23 (± 5%)	1.23 (± 6%)
45°C	**49°C**	166 (± 6%)	0.99 (± 3%)	1.13 (± 9%)	1.14 (± 10%)
45°C	**51°C**	170 (± 4%)	1.00 (± 1%)	1.13 (± 9%)	1.13 (± 9%)
45°C	**53°C**	136 (± 4%)	1.01 (± 3%)	1.09 (± 6%)	1.08 (± 6%)
45°C	**55°C**	133 (± 5%)	1.01 (± 4%)	1.09 (± 6%)	1.08 (± 7%)
70°C	**47°C**	308 (± 3%)	1.02 (± 3%)	1.04 (± 2%)	1.01 (± 4%)

Table S2. *Dimensions and actuation properties of the LCE particles prepared in a 500 μm polymerization tube.*

Droplet formation	**Polymerization temperature**	**Particle diameter / μm**	**Aspect ratio at 20°C**	**Aspect ratio at 180°C**	**Relative length change**
45°C	**45°C**	130 (± 8%)	1.01 (± 2%)	1.11 (± 8%)	1.10 (± 9%)
45°C	**47°C**	232 (± 4%)	1.00 (± 2%)	1.22 (± 5%)	1.22 (± 6%)
45°C	**49°C**	242 (± 3%)	0.98 (± 2%)	1.18 (± 6%)	1.20 (± 6%)
45°C	**51°C**	121 (± 2%)	1.00 (± 2%)	1.15 (± 7%)	1.15 (± 7%)

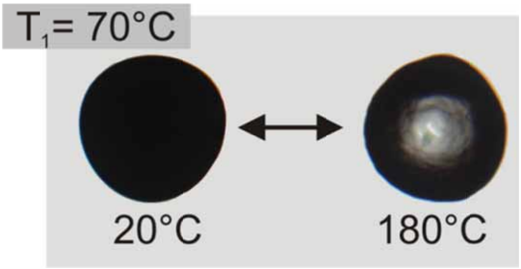

Figure S3. *Droplet formation in the isotropic phase (70°C) and its effect on the actuation behavior of the elastomer particles.*

To support our observation of a non-existent nematic phase on cooling, we prepared particles from the monomer mixture **M1** (95 mol% LC1, 2.5 mol% PETMP, 2.5 mol% GBDA and 3 wt% photoinitator Lucirin TPO). The droplet formation was conducted in the isotropic melt at T_1 = 70°C and followed by photo-polymerization of the droplets at T_2 = 47°C, well within the temperature region where a nematic phase was observed upon heating. The flow rates of the microfluidic device were set to 0.06 mL/h for the monomer phase and 1.5 mL/h for the silicone oil. The resulting elastomer particles were of spherical shape with an aspect ratio of 1.02 (± 3%) at room temperature. If the particles' mesogens were oriented along one common axis, heating the LC elastomer to its isotropic phase would result in a change of shape. When heating the particles to 180°C – well within the isotropic phase of the elastomer – the aspect ratio changes to 1.04 (± 2%) without any directed change of shape (see Figure 3 below). This confirms that the mixture was still in its isotropic phase and the mesogens randomly oriented while crosslinking. The scale bar corresponds to 200 µm.

Supplementary Discussion S4. S*tandard deviation of the particles' aspect ratios at varying temperatures.*

We note that while the standard deviation for the particles' aspect ratios at room temperature is ± 1-3%, the value increases to ± 4-9% for aspect ratios measured at 180°C. The higher uncertainty values at 180°C are mainly due to the fact that the spherical shape of the particles at room temperature makes it difficult to predict the direction of actuation. When heating the particles to their isotropic state, the shape change is not necessarily along an even plane but can be tilted towards the viewing angle. The extent of actuation in the latter direction remains unnoted. This does not only lead to an increase of the standard deviation but also causes the aspect ratio to be slightly underestimated. The values for the relative shape change given here can therefore be seen as a lower threshold of the particles' actuation.

Supplementary Discussion S5. *Degree of polymerization and sol-content of the elastomer particles.*

The degree of polymerization of the thiol-ene polymer was determined by preparation of non-crosslinked LC particles in the microfluidic device. To accommodate for the omitted crosslinkers, the amount of solvent chlorobenzene had to be increased to 17.5 wt.%. Processed with standard parameters, the monomer droplets were irradiated with UV light for several seconds. The number average molecular weight of the resulting polymer particles is 3400 g/mol, corresponding to a degree of polymerization of 8, as determined by gel permeation chromatography (GPC) in THF.

Crosslinked particles (parameters: T_1 = 45°C; T_2 = 47°C, d = 500 µm) were swollen in THF for 18 h and the excess solvent analyzed by GPC. Polymeric traces with a number average of 6400 g/mol were detected (degree of polymerization = 15), indicating that some fragments are not covalently bound to the LC elastomer. The conversion of the polymerization and crosslinking reactions are, however, sufficient for the formation of elastomer particles which exhibit a fully reversible actuation.

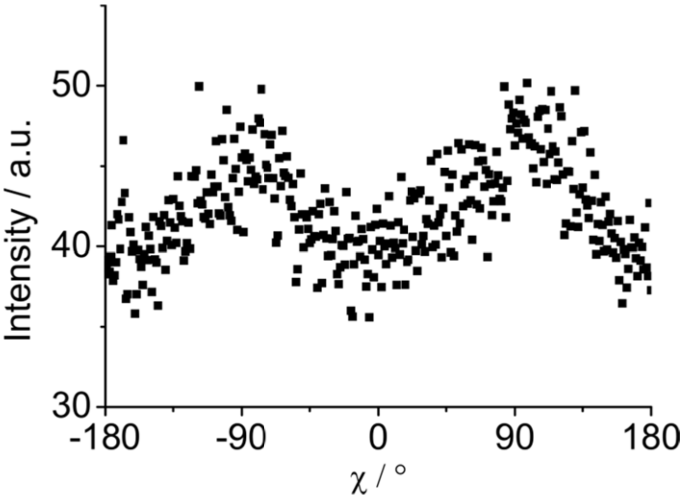

Figure S6. *WAXS (wide angle X-ray scattering) measurments on the elastomer particles.*

WAXS experiments were performed on the thiol-ene LCE particles, prepared at a polymerization temperature of 47°C in a 500 μm tube, with a Bruker NanoStar diffractometer, equipped with a HiStar area detector and crossed Goebel mirrors using the CuK_α (λ = 1.5418 Å) radiation. These particles exhibited the largest amount of actuation of 25%. A scattering pattern was obtained, exhibiting a diffuse halo in the wide-angle region with two maxima as it is typical for an oriented nematic sample. After radial integration over the wide-angle arc, we plotted the intensity I versus the angle χ. Two distinct maxima at 90° and -90° confirm a preferred alignment of the director in the elastomer particle. Evaluation of the azimuthal intensity distribution I(χ) yielded the macroscopic order parameter S = 0.3.

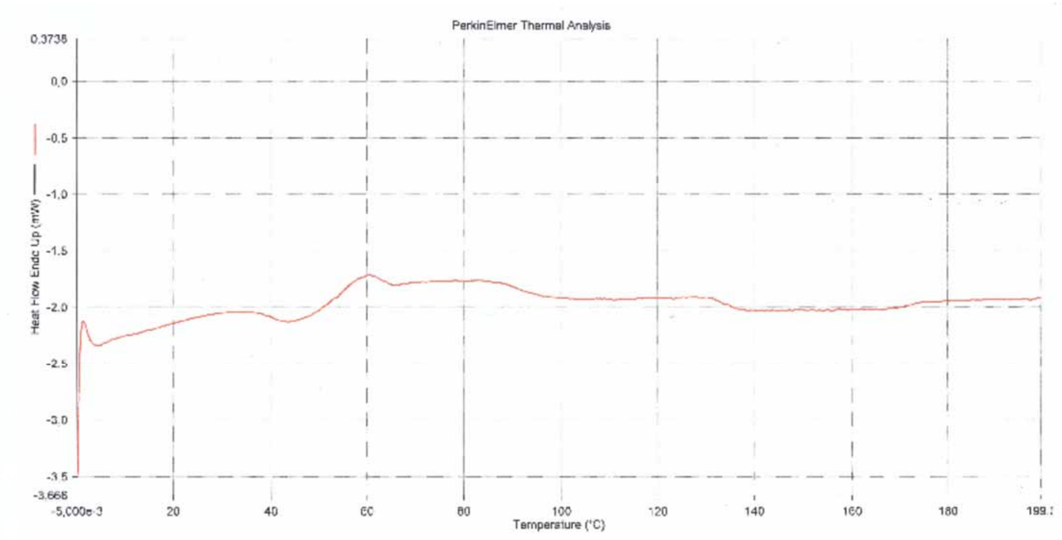

Figure S7. *DSC (differential scanning calorimetry) curve for a film sample of the LC elastomer.*

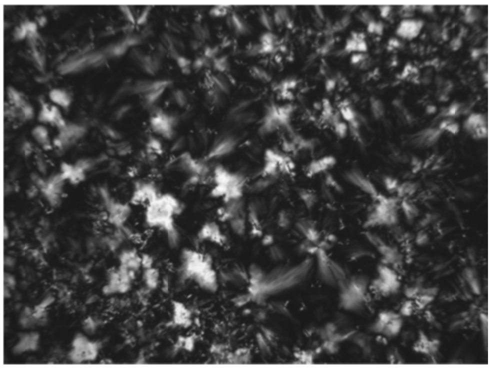

Figure S8. *Smectic phase formed on cooling of monomer LC1.*