Supporting Information

Permanent and Reversibly Programmable Shapes in Liquid Crystal Elastomer Microparticles Capable of Shape Switching

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Experimental

Materials

1,4-Bis-[4-(6-acryloyloxyhexyloxy)-benzoyloxy]-2-methylbenzene (RM82) was purchased from Wilshire Technologies. Pentaerythritol tetrakis(3-mercaptopropionate) (PETMP) and triethylamine (TEA), dichloromethane (DCM), polyvinylpyrrolidone (PVP), 2,2-dimethoxy-2-phenylacetophenone (DMPA), and methanol were purchased from Sigma-Aldrich. Propane dithiol (PDT) was purchased from TCI. Irgacure 819 was purchased from IGM resins. 5-micron glass rod spacers were purchased from Nippon Electric Glass Co., Ltd. Diffraction grating substrate was purchased from LightSmyth Technologies, Inc.

Allyl dithiol (ADT) synthesis

Prepared as reported by Martinez et al. – A. Martinez, M. McBride, T. White, C. Bowman, *Adv. Funct. Mater.* 2020, **30**, 35, 2003150.

Preparation of AFT-LCEMPs

The AFT-LCEMPs were prepared as follows: Reaction concentration was 1 mass % of monomers to solvent. Monomer molar ratio PETMP:ADT:RM82 1.05:2:4. With a stir bar continuously stirring to mix the system, 0.035 g (15 mass % to monomers) of PVP was dissolved in 6.73 mL of DCM. 0.157 g of RM82 was then dissolved in the solution. 13.8 mL of MeOH was added to the solution. 0.014 g of ADT was dissolved in the solution followed by 0.03 g of PETMP. 0.031 mL (10 mass % to monomers) of the catalyst TEA was then added to the reaction. The mixture turns turbid after about 15 minutes and was allowed to run overnight. The following day the product was centrifuged at 3000 RPM for 2 min and washed three times with the same MeOH/DCM mixture. Particles were stored dry in the freezer. A yield of 40 % was achieved. A 0.2 g batch of starting material yields about 0.08 g of particles. Control experiments done with non-AFT capable LCEMPs were prepared in a stoichiometric ratio of thiols to acrylates at a 1:2:4 (PETMP:PDT:RM82) monomer molar ratio, using propane dithiol instead of the ADT monomer.

Preparation of bulk LCE analog for stress-strain profile

Monomers PETMP:Propane dithiol (ADT analog):RM82 were mixed in a stoichiometric ratio of thiols to acrylates at a 1:2:4 monomer molar ratio, in 1 mL of DCM (40 mass % RM82 to DCM). 3.5 mass % to monomers of TEA was added, and the resin was then filled between two pieces of glass with 0.5 mm spacers. The resin was allowed to react overnight at 40 °C to ensure monomer RM82 remained dissolved.

Characterization of AFT-LCEMPs

Differential scanning calorimetry (DSC): The dry particles were initially heated to erase thermal history, cooled at 5 °C/min to -40 °C and the test was run from -40 to 140 °C, ramped at 20 °C/min, to generate the reported curve. DSC was run on a TA DSC 2500.
Stress-Strain profile: Stress–strain tests were done at room temperature and strained at a rate of 0.1 mm/s on rectangular samples with dimensions 13.65 mm x 4.4 mm x 0.57 mm. This results in a volume of ~34.2 mm^3 with a weight of 0.05 grams. In comparison, about 0.03 to 0.05 grams of microparticles are needed to create this same volume. Tests were run on a TA RSA-G2.
Fourier transform infrared spectroscopy (FTIR): Attenuated Total Reflectance (ATR) - FTIR was done on dried particles. ATR-FTIR was run on a Thermo Fischer Scientific Nicolet iS50 FT-IR.
Image Analysis: ImageJ was used to measure particle shape to determine coefficient of variance (150 particles analyzed) and aspect ratio from optical microscope (OM) images. For prolate programming aspect ratio measurements, 30 particles were analyzed. Out of 180 particles analyzed, 67 ± 1 % of particles casted were successfully deformed and programmed, while 32 ± 3 % remained un-deformed and un-programmed due to lack of contact with the superstrate, with these particles being 4 microns or smaller. OM and polarized optical microscopy (POM) were done with a Nikon Eclipse Ci. Field emission scanning electron microscopy (FESEM) was done with a JEOL JSM-740 1F.
AFM: Particle morphology was characterized by intermittent contact atomic force microscopy. Specialized cantilevers with a visible tip (ATEC-FMAu, Nanosensors, nominal spring constant 2.8 N/m) were used to align imaging with particles of interest. Particles were imaged at a setpoint amplitude equal to 50 % of the free amplitude. Samples were place on a custom low-expansion, low-drift hot plate inside the atomic force microscope (Cypher S, Oxford Instruments) and controlled to either 35 °C or 125 °C, as indicated.

Programming AFT-LCEMPs
Switchable prolate shape programming (**Figure 2b,c,d**): After washing, particles were dissolved in DCM with 5 mass % DMPA and left to swell overnight. Particles were then deposited onto a glass microscope slide on the benchtop. After solvent evaporation, a small piece of a microscope slide was used to compress a region of the deposited sample, and subsequently removed. The sample was then irradiated with 365 nm light at an intensity of 70 mW/cm^2, for 120 s. The sample was observed under OM and POM and heated above to 120 °C and then cooled back to room temperature.
Erasure of the prolate shape to permanent spherical shape (**Figure S10**): Particles from programming done in the above procedure were heated to 120 °C and irradiated with 365 nm light at an intensity of 70 mW/cm^2 for 5 min. They were then cooled to room temperature and observed under OM.
3-Stage programming series (**Figure 2e, S11**): Particles were dissolved in DCM with photoinitiators Irg-819 and DMPA (5 mass % of each) and left to swell overnight. Particles were cast on a glass slide and underwent - 1st Stage programming with 400 to 500 nm light at an intensity of 70 mW/cm^2 for 60 s. 2nd Stage programming; heating to 120°C and irradiated with 400 to 500 nm light at an intensity of 70 mW/cm^2 for 5 min. 3rd Stage programming; at room temperature were compressed and irradiated with 365 nm light at an intensity of 70 mW/cm^2 for 10 min and observed under OM. Lamp for programming: Exfo Acticure Hg Bulb with noted filter.
Nanoimprint Lithography (NIL): **Oblate shape programming** – Particles were dissolved in DCM with photoinitiators Irg-819 and DMPA (2.5 mass % of each) and left to swell overnight. They were then dip coated onto a silicon chip. A glass superstrate was placed on top of the coated Si

substrate to ensure light transmission for programming. The samples were run at 140 °C, 2 MPa, while exposed to 300 to 400 nm light at an intensity of 20 mW/cm^2 for 2 min. After light exposure, the samples were released from pressure and cooled. **Diffraction grating programming** – Particles were dissolved in DCM with photoinitiators Irg-819 and DMPA (2.5 mass % of each) and left to swell overnight. 5-micron rod shaped spacers were then dispersed in the mixture. Particles were dip coated onto a glass substrate. A silicon superstrate containing a diffraction grating with a line pattern (833 period, 416 nm line, 200 nm groove depth) was placed beneath the coated glass substrate and the samples were run at 140 °C, 1 MPa, while exposed to 300 to 400 nm light at an intensity of 20 mW/cm^2 for 2 min. After light exposure, the samples were released from pressure and cooled. NIL was done with an Eitre 3, Obducat imprinter machine. The low temperature diffraction grating was imprinted by performing the same steps without the 5-micron spacers.

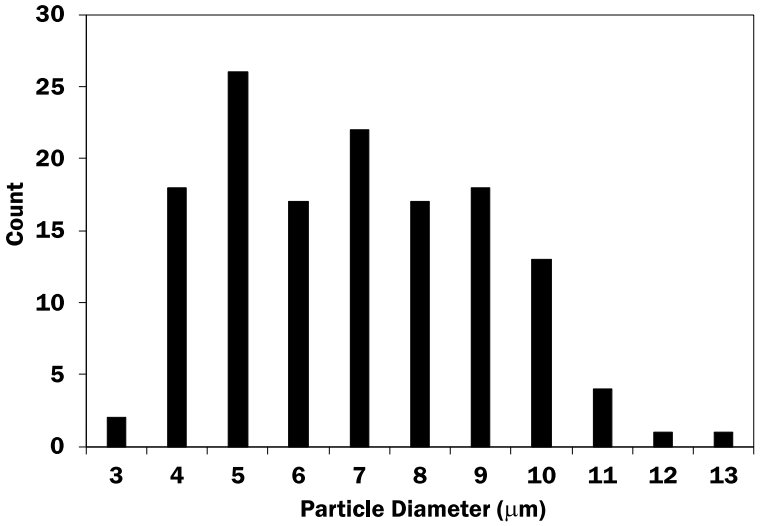
Glass and silicon substrates for NIL were prepared as follows: 5 min sonication in soap and water. 5 min sonication in isopropyl alcohol. Rinse with IPA and blow dry.

Controls

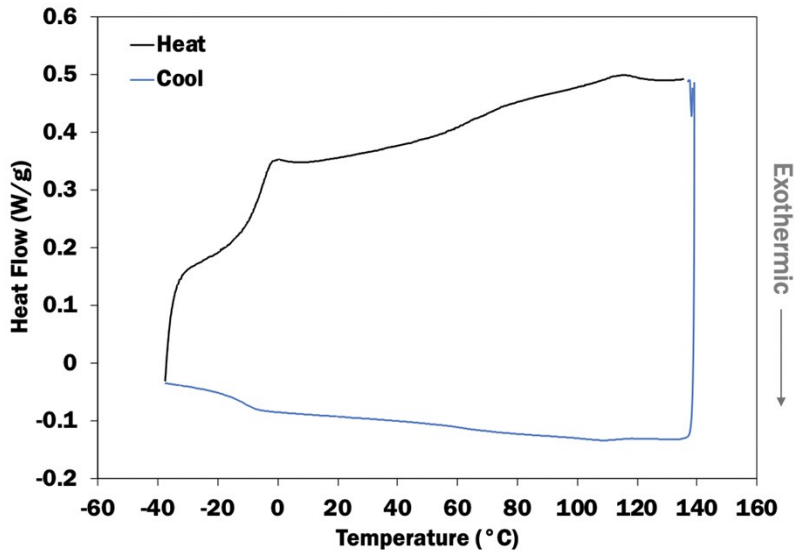
All particles were cast on a glass slide and pre-irradiated with 365 nm light at an intensity of 70 mW/cm^2 for 30 s. Non-AFT capable particles replace the ADT monomer with a non-exchangeable monomer, propane dithiol.

Control 1 – light exposed: AFT-LCEMPs not containing photoinitiator, and non-AFT capable LCEMPs prior swollen in DCM with 5 mass % DMPA, were compressed at room temperature, irradiated with 365 nm light at an intensity of 70 mW/cm^2 for 30 s, heated to 120 °C, and returned to room temperature displaying spherical shape recovery.

Control 2 – no light exposure, no photoinitiator: AFT-LCEMPs and non-AFT capable LCEMPs were compressed at room temperature, heated to 120 °C, and returned to room temperature displaying spherical shape recovery.



S1: Bar graph detailing particle size dispersity for the reported system.



S2: Differential scanning calorimetry for the AFT-LCEMPs.

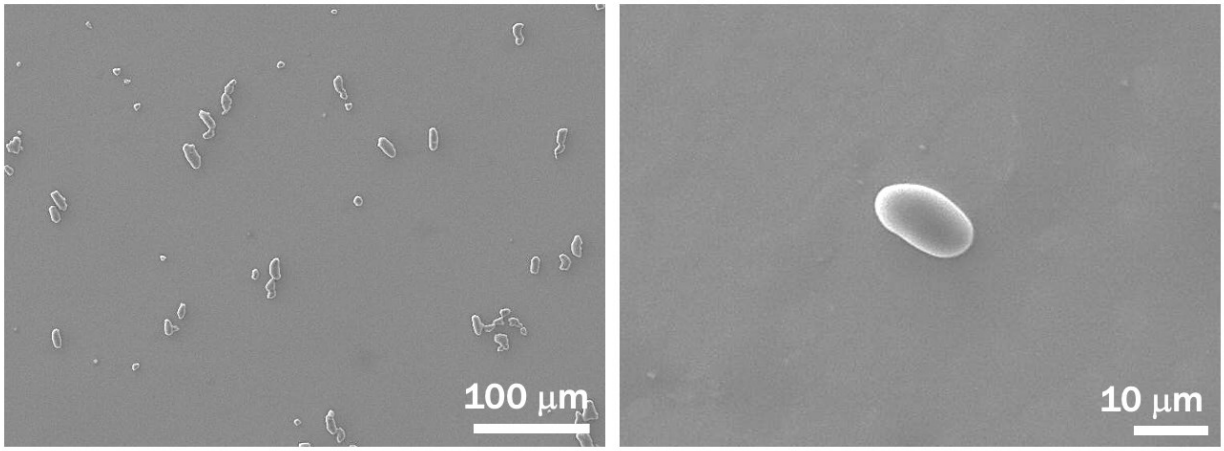


Figure S3: Scanning electron microscopy (SEM) of particles after programming displaying a prolate shape.

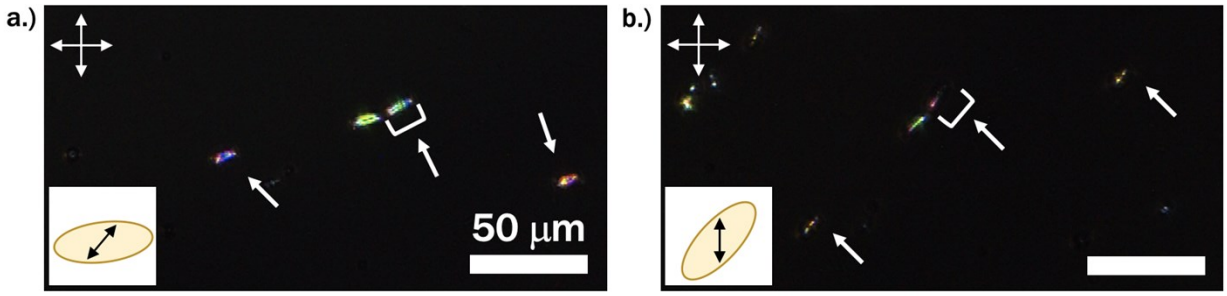


Figure S4: Compressed AFT-LCEMPs under POM. Inset represents a microparticle and the LC alignment director within. a.) Particles aligned with polarizers displaying a skewed alignment

along the particle long axis b.) Particles 45 degrees to polarizers displaying a disappearance of birefringence.

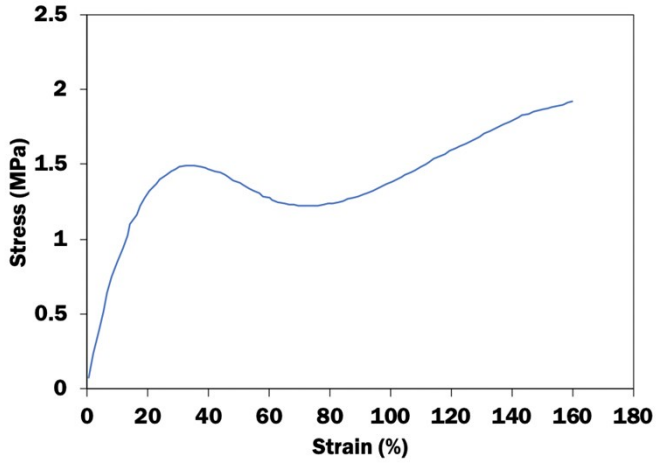


Figure S5: Stress-Strain profile for bulk LCE analog of the LCEMPs. Data taken until sample slipped or broke.

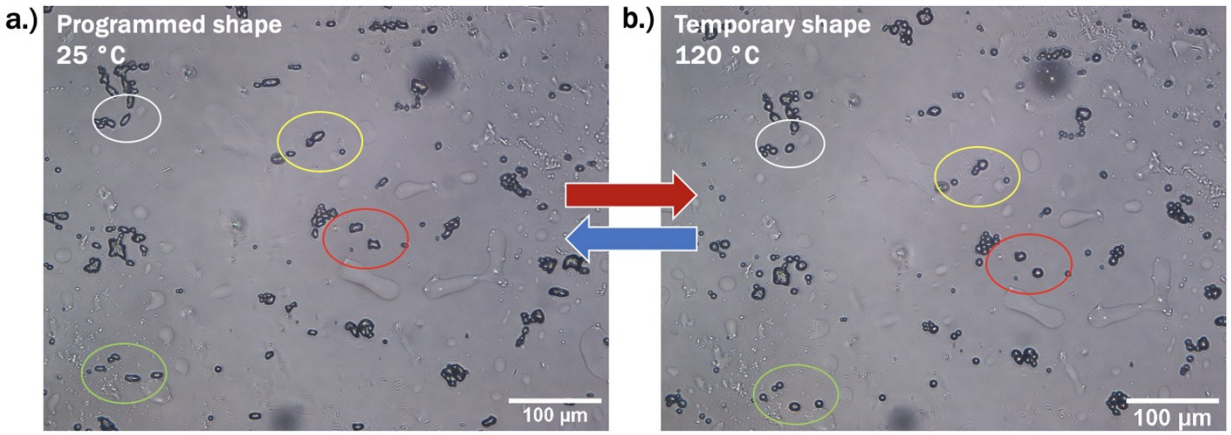


Figure S6: Particles after programming. a.) Programmed particles display a permanent prolate shape. b.) Particles recover temporarily to their initial shape when heated above their T_{NI}.

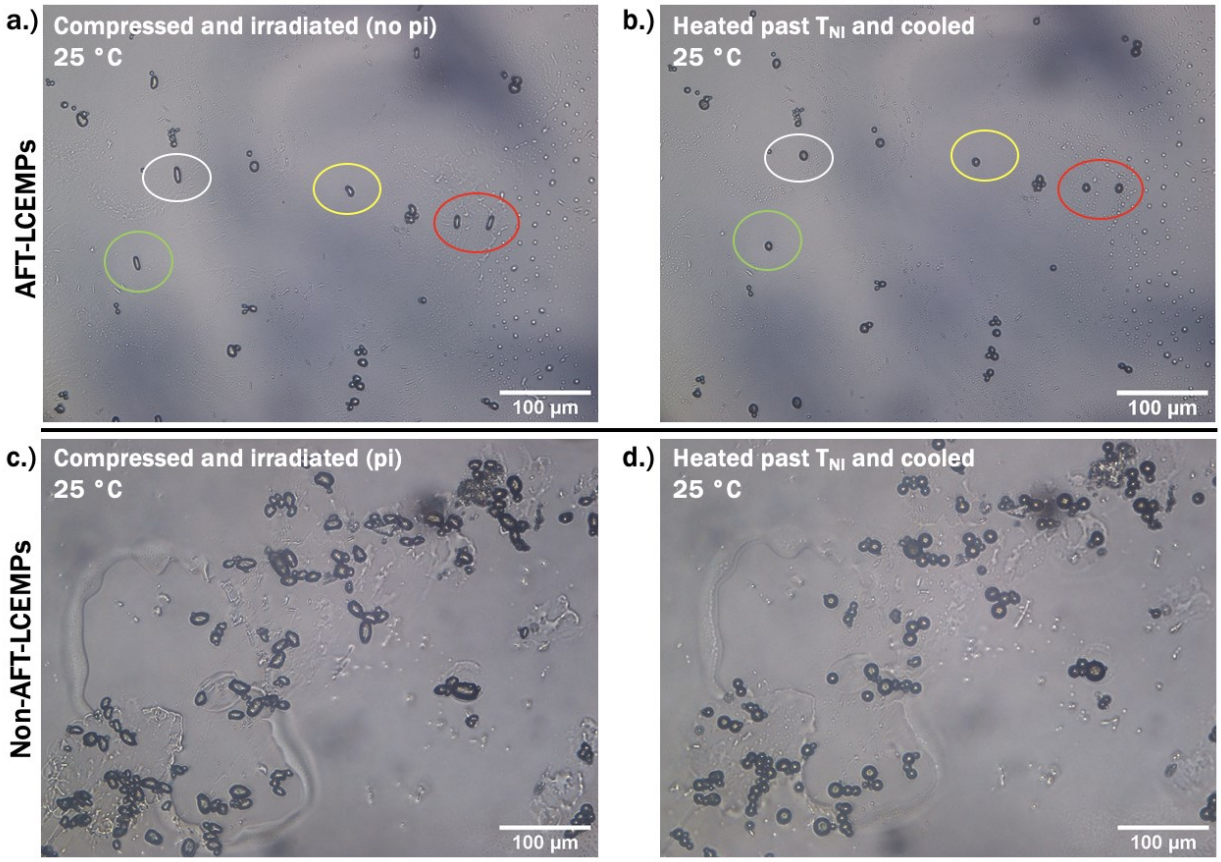


Figure S7: Control 1: light exposed - Particles were pre-irradiated with UV light for 30 s to ensure any excess acrylates and thiols were reacted. AFT-LCEMPs without photoinitiatior (no pi) a.) Particles were compressed and exposed to light for 30 s. b.) Particles were heated past the T_{NI} and returned to room temperature displaying the recovered original spherical shape. Non-AFT capable LCEMPs swollen with photoinitiator (pi) c.) Particles were compressed and exposed to light for 30 s. b.) Particles were heated past the T_{NI} and returned to room temperature displaying the recovered original spherical shape.

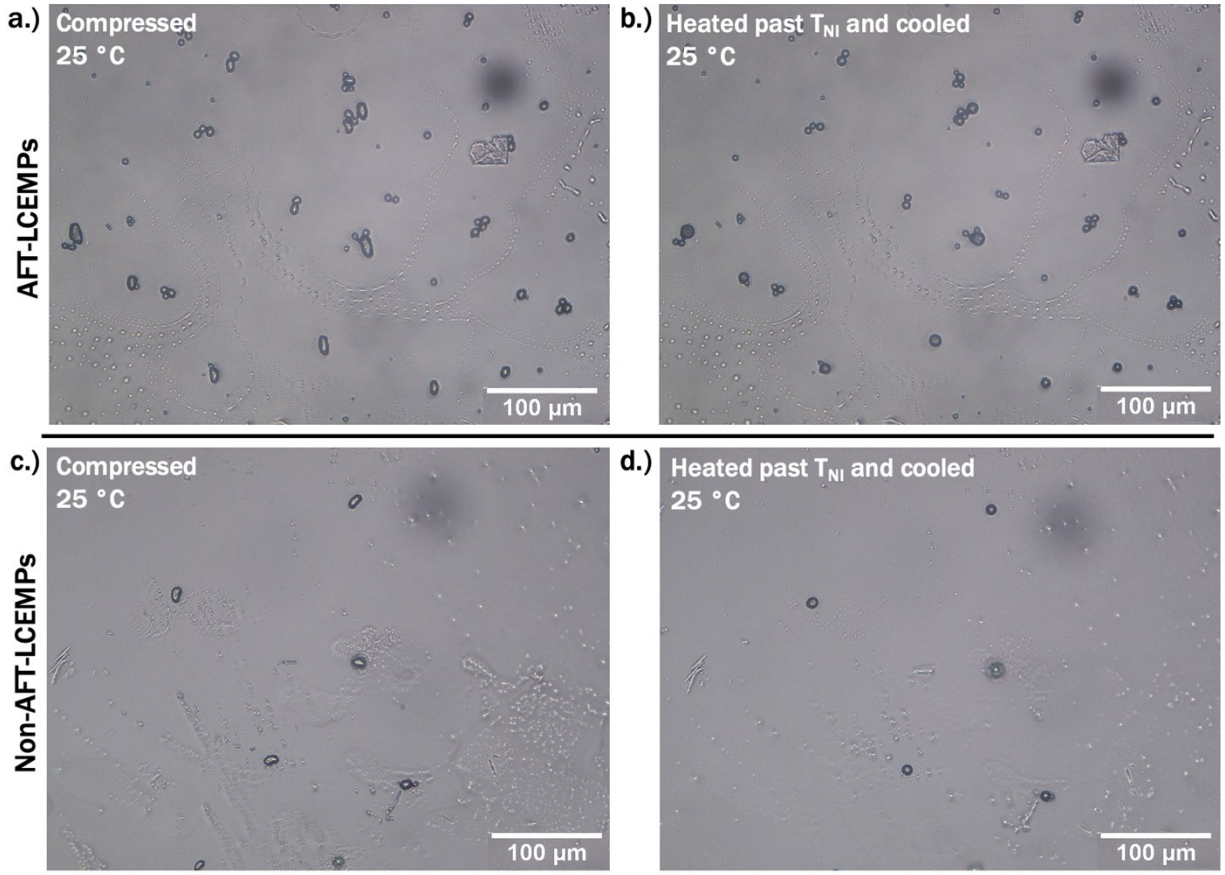


Figure S8: Control 2: no photoinitiator, no light exposure - Particles were pre-irradiated with UV light for 30 s to ensure any excess acrylates and thiols were reacted. AFT-LCEMPs without photoinitiatior a.) Particles were compressed at room temperature. b.) Particles were heated past the T_{NI} and returned to room temperature displaying the recovered original spherical shape. Non-AFT capable LCEMPs without photoinitiator c.) Particles were compressed at room temperature. d.) Particles were heated past the T_{NI} and returned to room temperature displaying the recovered original spherical shape.

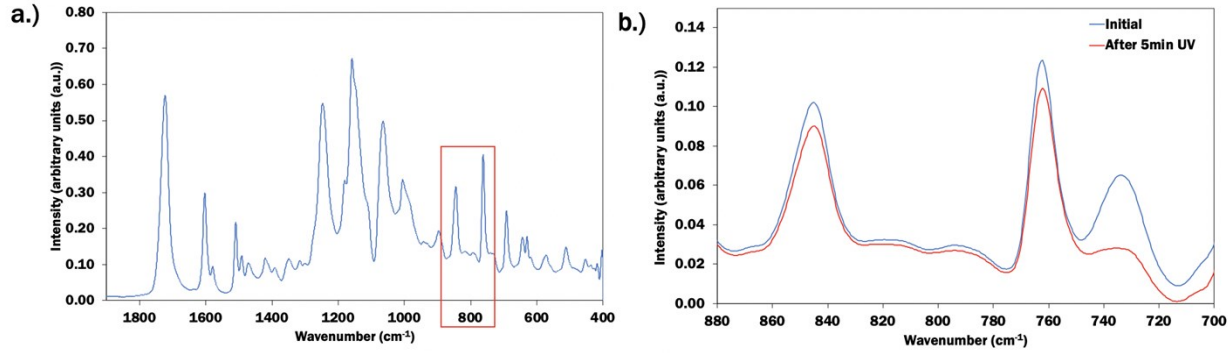


Figure S9: Fourier Transform Infrared Spectroscopy for a.) Dried AFT-LCEMPs not containing photoinitiator b.) Zoomed in on the faint acrylate region at 800 to 830 cm^{-1}.

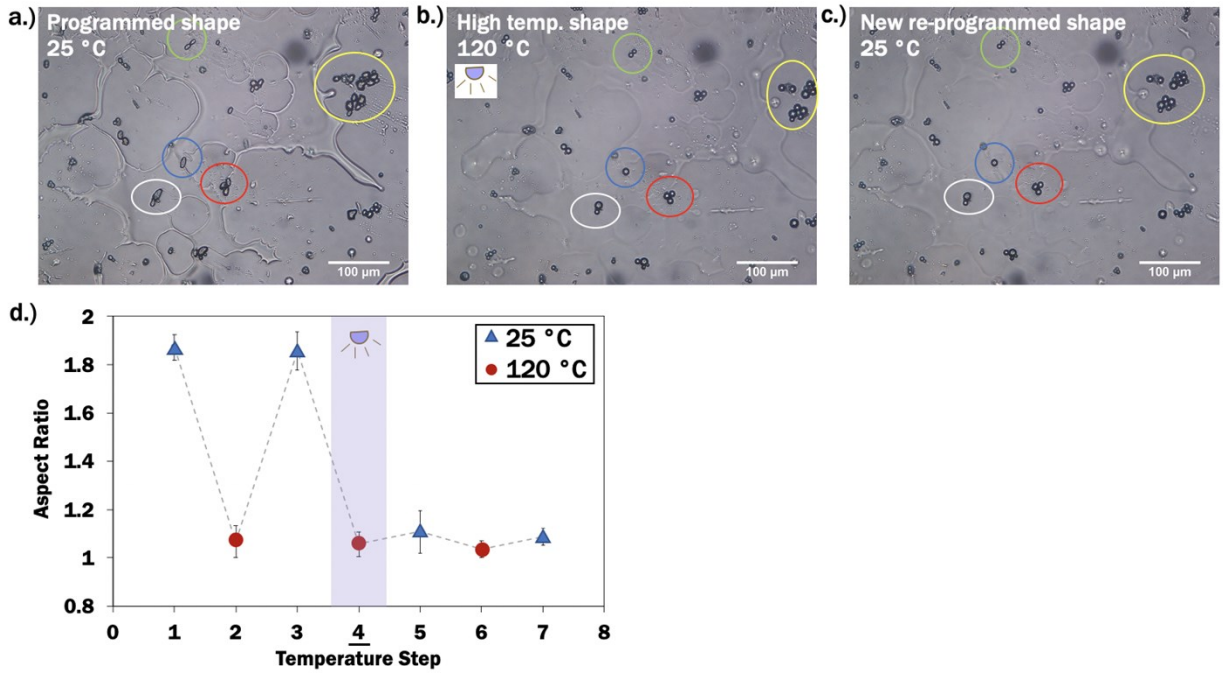


Figure S10: Particles undergoing reverse programming. a.) Programmed particles display a permanent prolate shape. b.) Particles recover temporarily to their initial shape when heated above their T_{NI} and are exposed to light again c.) Particles are cooled back to room temperature displaying their re-programmed permanent spherical shape. d.) Aspect ratio for particles during temperature steps demonstrating the initial prolate shape is re-programmed to a permanent sphere. Dotted line for ease of viewing.

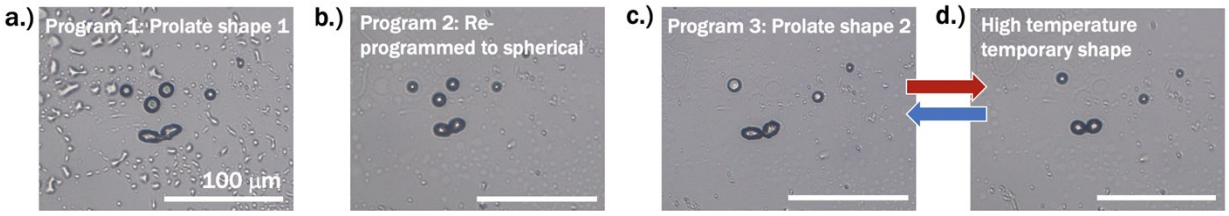


Figure S11: Particles undergoing 1st through 3rd Stage programming. Particles were initially swollen with Irg-819 and DMPA a.) Programmed particles display a permanent prolate shape. b.) Particles recover temporarily to their initial spherical shape when heated above their T_{NI} and are exposed to light again at high temperature, followed by cooling to room temperature, maintaining a spherical shape c.) Particles are compressed and exposed to light again to re-program the prolate shape. d.) Particles are heated above the T_{NI} and are cooled back to room temperature to recover the prolate shape and demonstrate shape switching. The shape can be toggled between prolate and spherical by thermally cycling past the T_{NI}.

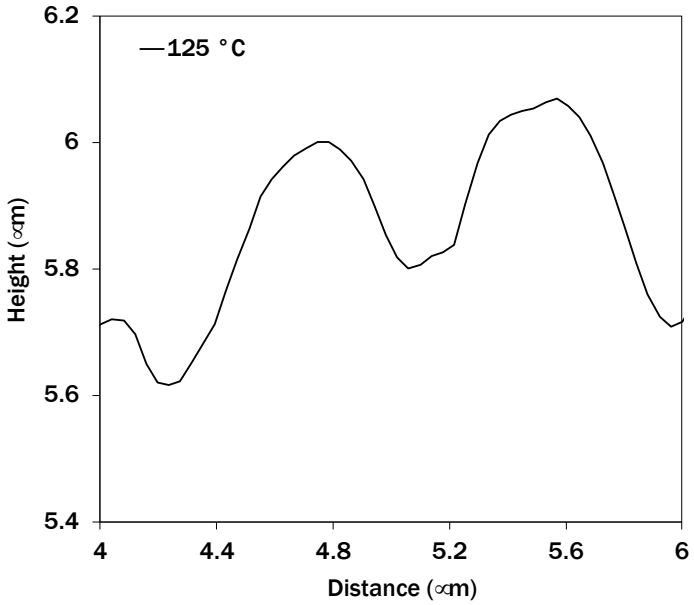


Figure S12: Zoomed in AFM cross-section of a single particle surface after undergoing NIL programming with a diffraction grating mold utilizing spacers, imaged at 125 °C displaying pattern profile.

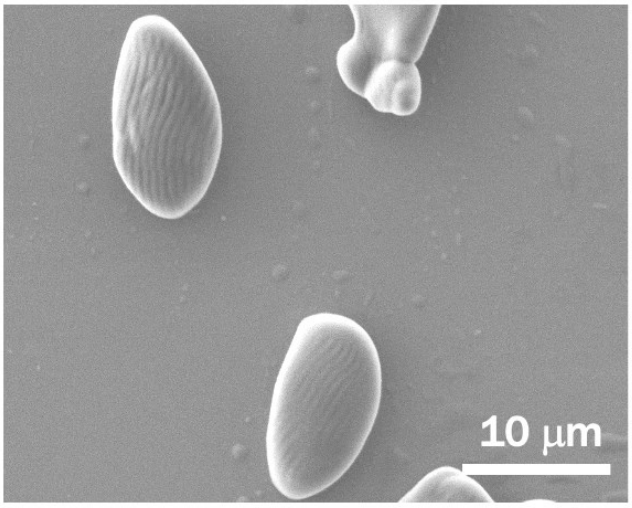


Figure S13: SEM of particles after NIL programming at high temperature with a diffraction grating mold, without the use of spacers, yielding a complex surface topography.