Supplementary Information

Converse Two-way Shape Memory Effect Through Dynamic Covalent Network Design

Guancong Chen[a], Jiante Dong[a], Xiaona Xu[a], Weike Zou[a], Binjie Jin[a-c], Wenjun peng[a], Qian Zhao[a,b], Tao Xie[a,b], Ning Zheng[a]*

[a] State Key Laboratory of Chemical Engineering, College of Chemical and Biological Engineering, Zhejiang University, Hangzhou 310027, China.

[b] ZJU-Hangzhou Global Scientific and Technological Innovation Center, Hangzhou 311215, China

[c] Center for X-Mechanics, Department of Engineering Mechanics, Zhejiang University, Hangzhou, 310027, China

E-mail: zhengning@zju.edu.cn

Materials:

Polycaprolactone diol (PCL, M_n=10000) was purchased from Sigma Aldrich. Acrylic chloride, Triethylamine (TEA), N-butyl acrylate (BA), 1,5,7-Triazabicyclo[4.4.0]dec-5-ene (TBD), and 2,2-Dimethoxy-1,2-diphenylethanone (DMPA) were purchased from TCI. Toluene and methanol were obtained from Sinopharm. All chemicals were used as received.

Synthesis of Polycaprolactone (PCL) diacrylate:

The reaction scheme is shown in Figure S1a. Polycaprolactone diol (30.0 g), acryloyl chloride (1.63 g), and TEA (1.82 g) were co-dissolved in 150 mL of toluene and reacted at 80 °C for 24

hours. After the reaction, the mixture was precipitated by cold methanol after filtration to obtain white crystals. The obtained product was vacuum dried overnight at room temperature. The polymer structures were confirmed by ^{1}H-NMR spectrum (Figure S1).

Synthesis of converse two-way SMP:

TBD (1.00 g), acetic acid (0.920 g), and toluene (3.18 g) were weighed into the glass bottle to form 20 wt% acetic acid neutralized TBD solution. Afterward, we take a sample with a BA weight percent of 70% as an example. PCLDA (3.00 g), BA (7.00 g), acetic acid neutralized TBD solution (1.00 g) and 0.5 wt% DMPA were mixed at 80 °C to obtain a precursor solution. Poured the solution into a silicone rubber mold and irradiate under UV light for 300 s for curing. The as cured sample was then vacuum dried at 40 °C for 24 hours.

Synthesis of two-way SMP fibers:

A conventional two-way SMP precursor was prepared according to reference 17 (the PPDL-15 sample). Poured the conventional and converse SMP precursors into a Teflon tube with a diameter of 1.5 mm and irradiate them under UV light for 300 s for curing. The as cured samples were then de-molded and dried in a vacuum at 40 °C for 24 hours.

Programming the reversible actuation of SMP:

The reversible actuation was programmed through the stress relaxation of the sample conducted with a dynamic mechanical analyzer (TA Q800) in an "iso-strain" mode. A rectangular sample (15 mm×5 mm×0.4 mm) was uniaxially stretched at 140 °C to an instantaneous strain of 100%. This strain was maintained constantly for 1 h. Then the stress was decreased to a negligible value of 0.001 N. At this point, the material has completed programming. For actuation, the programmed sample was subjected to a heating-cooling cycle at a temperature between 0 °C and 70 °C.

Interfacial welding:

A sample was first to cut into two halves and pushed together to thermally anneal at 160 °C for 2 h with a minimum external force. Welding of different materials was carried out similarly

except the first cutting step was not needed.

Introducing a photo-latent catalyst:

The photo-latent catalyst (Keto·TBD) was synthesized according to reference 32. The catalyst was introduced into the network through swelling. The 70% BA sample without TBD was first swollen in 1 wt% photo-latent catalyst in toluene solution for 1 h, then oven-dried at 70 °C to remove the solvent.

Light triggered release of the catalyst:

The sample was first heated on a thermal platform at 100 °C, and then exposed to UV irradiation (Tao Yuan, TY-F05-UVLEDS 100 W, 79.5 $mW \cdot cm^{-2}$) for 90 s with or without a photomask.

Other characterizations:

A commercial UV chamber (Uvitron Intelliray 600, 66 mW/cm^2, 265-700 nm) was used for all UV irradiations except the release of the photo-latent catalyst. Differential scanning calorimetry (DSC) measurements were conducted using a TA Q200 machine at a temperature ramping rate of 5 °C/min. Mechanical tests were performed using a Zwick/Roell tensile machine at a stretching speed of 10 mm/min with a sample dimension of 25 mm×5 mm×0.3 mm. The wide-angle X-ray diffraction (WAXS) patterns were collected by a Nano-inXider vertical WAXD system (Xenocs, Sassenage, France) equipped with a Pilatus 100K (for WAXS) semiconductor pixel detector (Dectris, Swiss). The experiments were conducted at room temperature with a wavelength of 0.154 nm. The sample-to-detector distance is 79 mm for WAXS.

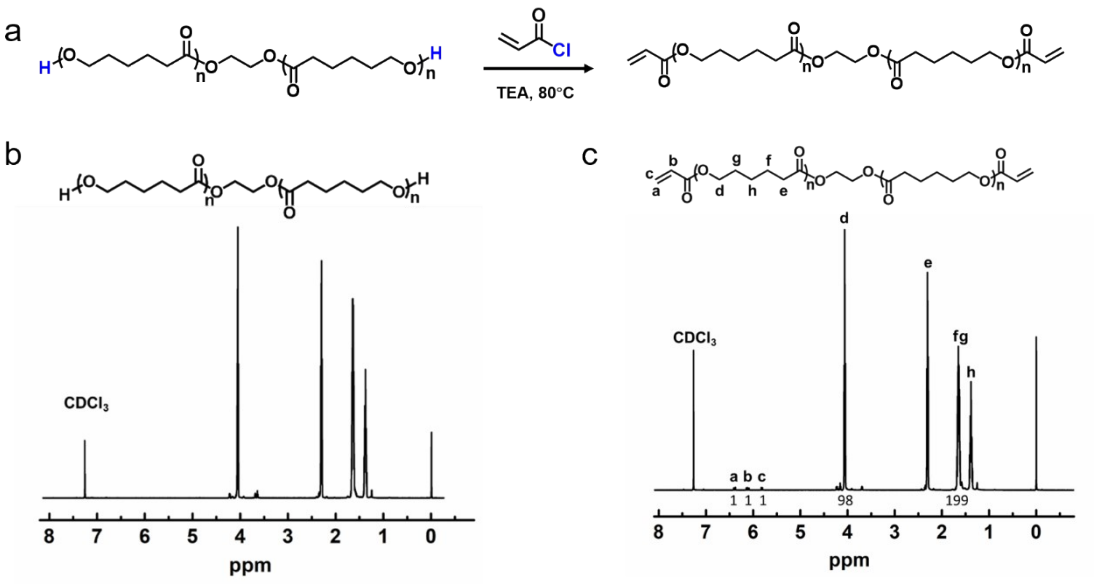

Figure S1. Synthesis of PCL diacrylate. a) Synthetic scheme for PCL diacrylate. b) ^{1}H-NMR spectrum of PCL. c) ^{1}H-NMR spectrum of the synthesized PCL diacrylate.

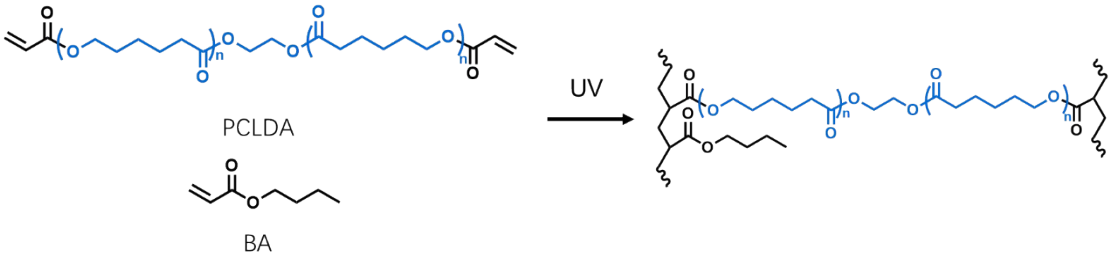

Figure S2. Synthetic scheme for the converse two-way SMP.

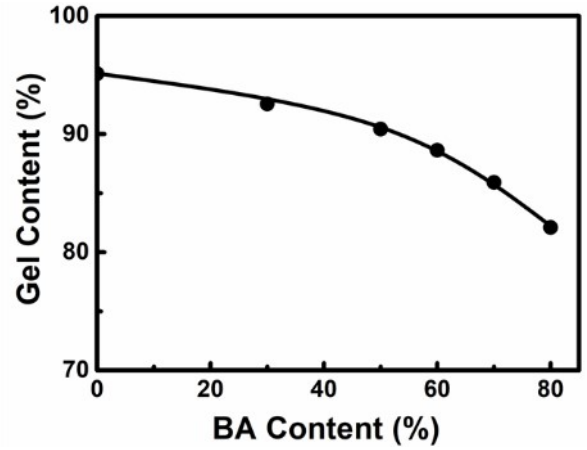

Figure S3. The gel content of the samples with different BA contents.

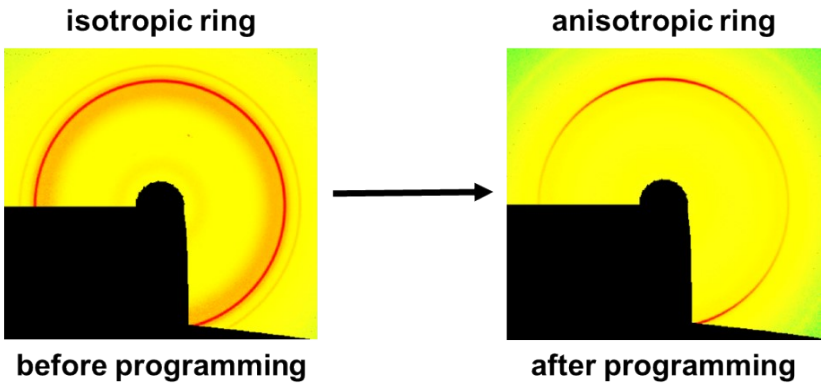

Figure S4. The 2D-WXRD figures of the sample before and after programming. The anisotropic ring after programming is contrary to the conventional result (reference 1) that the orientation is parallel to the programming, proving the perpendicular orientation.

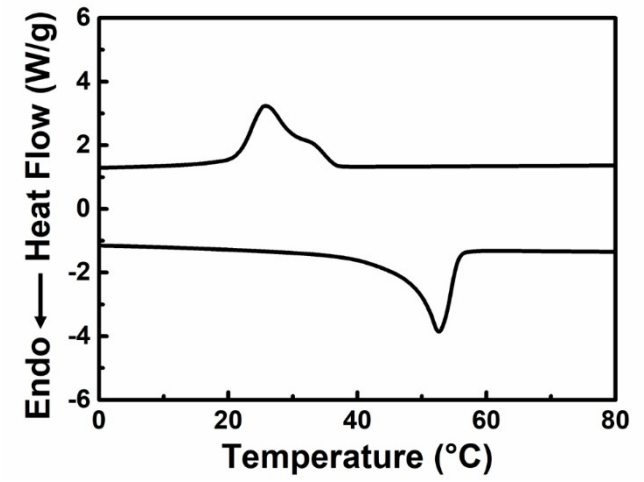

Figure S5. DSC curve of the sample with 70% BA.

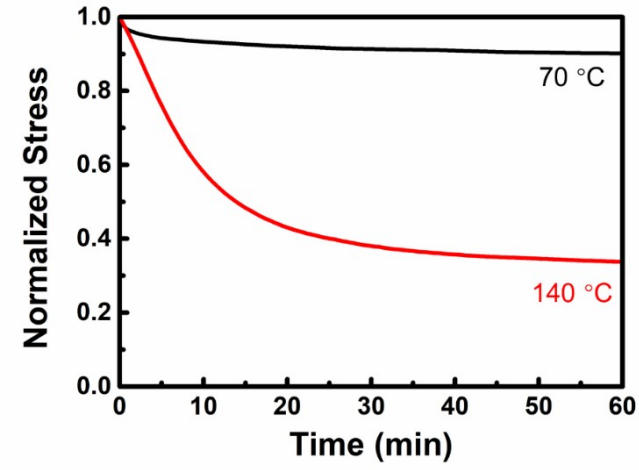

Figure S6. Typical stress relaxation curves of the sample at 70 °C and 140 °C.

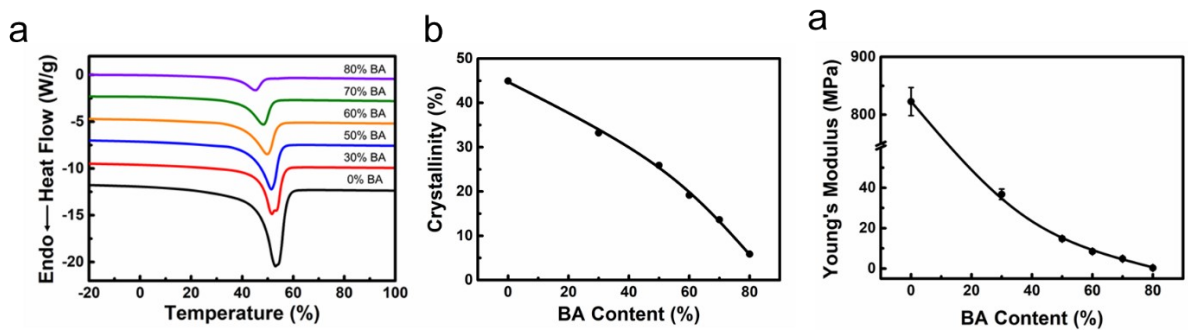

Figure S7. Thermal analysis and modulus of the samples with different BA contents. a) The DSC curves; b) The corresponding crystallinity; c) Young's modulus. The crystallinity is calculated as $X_c=H_m/H_0$, the H_m is the melting enthalpy, H_0 is the ideal melting enthalpy of PCL.

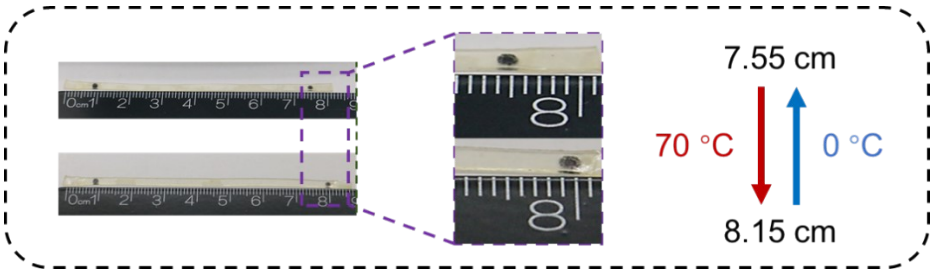

Figure S8. The visual demonstration of reversible actuation.

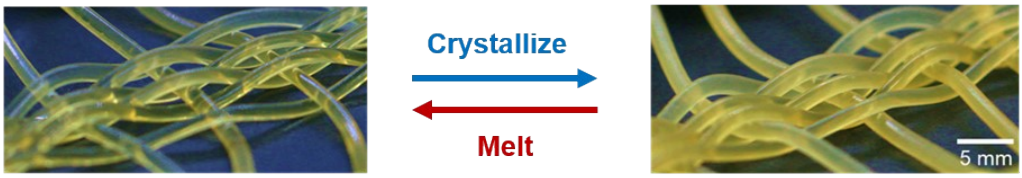

Figure S9. The reversible actuation of multi-strand fibers.

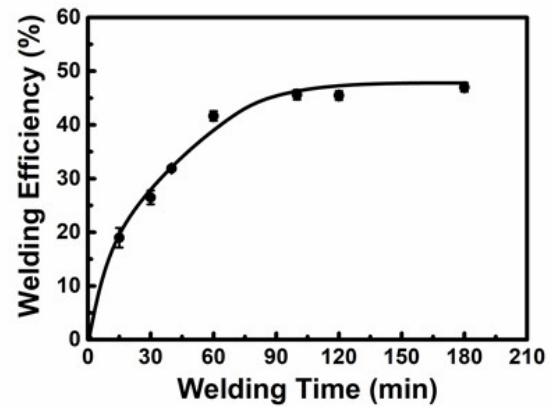

Figure S10. The welding efficiency of the sample with 70% BA. The welding efficiency is calculated by dividing the strain at break of the welded sample by the original sample.

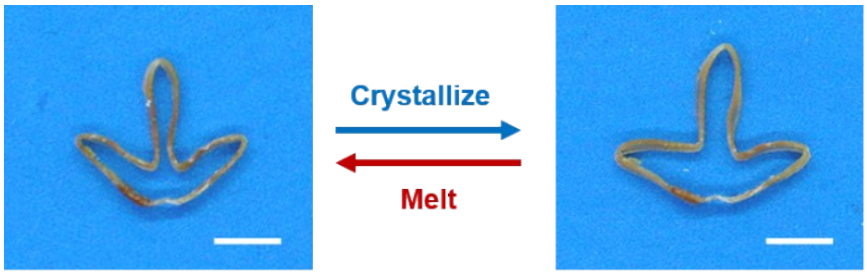

Figure S11. The reversible actuation of the welded "bird pawn" sample (scale bar is 1 cm).

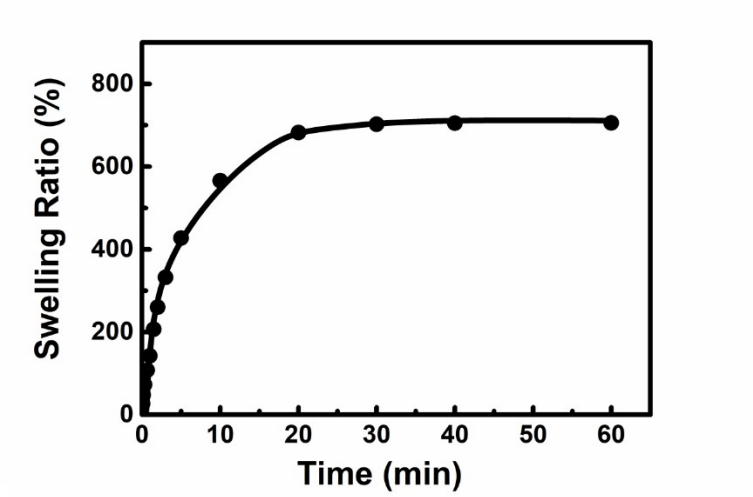

Figure S12. Swelling kinetics of the sample with 70% BA in photo-latent catalyst solution (mass ratio).

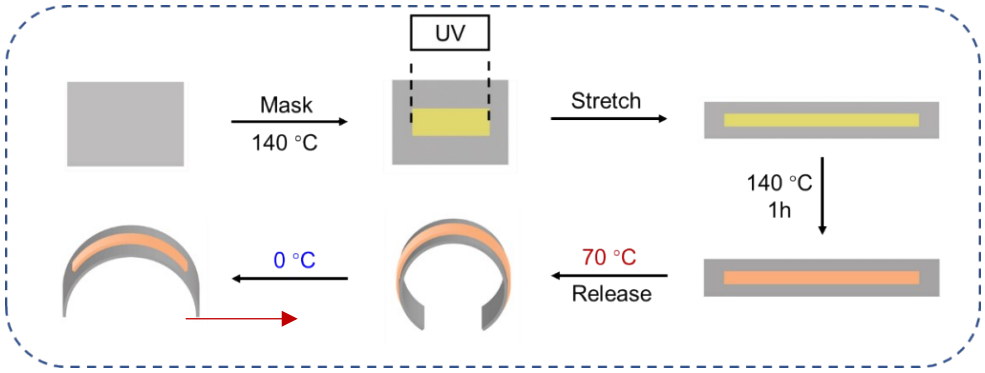

Figure S13. Schematic illustration of spatio-temporal programming reversible actuation by UV irradiation. (reversible actuation)

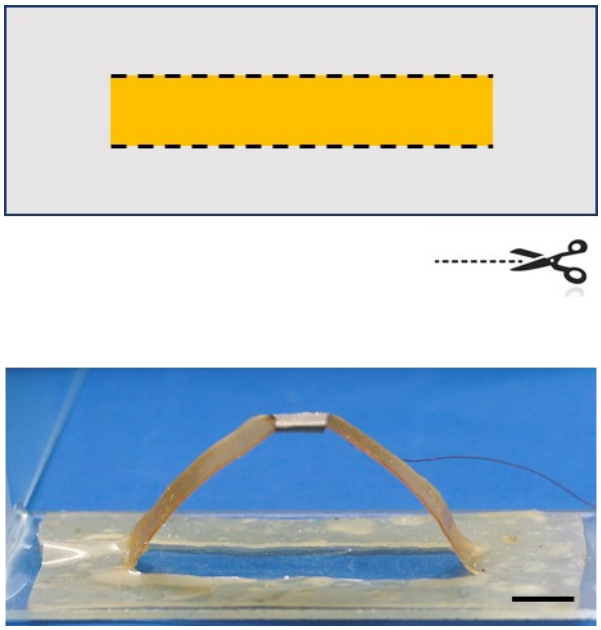

Figure S14. The photo-pattern 2D pattern with the strategic cutting and the corresponding thermosensitive switch after programming (scale bar is 1 cm)

Reference

[1] B. Jin, J. Liu, Y. Shi, G. Chen, Q. Zhao, S. Yang.* Adv. Mater. 2022, **34**, 202107855

Supporting Videos

Movie S1: The live action of this soft machine.
Movie S2: The thermosensitive switch for high-temperature warnings.