

Supporting Information

3D-printed photothermal-responsive shape-memory polymer for soft robotic applications

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Experimental

Materials

Benzyl methacrylate (BMA), polyethyleneglycol dimethacrylate (PEGDMA), $M_n = 750 \text{ g mol}^{-1}$, diphenyl (2,4,6-trimethyl benzoyl) phosphine oxide and isopropyl alcohol (IPA) were purchased from Merck, United Kingdom.

Preparation of customized resin for mSLA 3D printing of shape memory polymers

To prepare the resins for SMP0.33, SMP0.50, SMP0.75 and SMP1.0, The required amount of BMA, PEGDMA and TPO was mixed by magnetic stirring at room temperature inside a fume cupboard for 12 h. The mixtures were stored in brown bottles to protect them from light and were subsequently used for mSLA 3D printing ('Original Prusa SL1S Speed' 3D printer). The soft-robotic tools were designed using Autodesk Fusing 360 software. The CAD model was saved as *.stl* file for 3D printing. The *PrusaSlicer* (2.7.4) software was used to fix the printing parameters such as the layer thickness and ultra-violet (UV) light exposure timings for the first layer and the subsequent layers. We kept the layer thickness of 50 μm for all our printing to obtain high resolution of printed parts. The 1st layer UV light exposure was kept 35 s and the subsequent layers were 23 s. The others parameters of the *PrusaSlicer* software were kept unchanged. The model was sliced the into a *.slls* file and inserted in the SL1S printer. The 3D model was printed filling the sufficient resin into the resin tank. We designed and printed several tools, such as a rod with spiral end, a sheet with honeycomb patterns, a pipe elbow, 4-finger grippers and a 4-legged object as shown in Fig. S1 along with ASTM D638-Type-IV specimen¹ (Fig. S2). After printing, the objects were washed for 10 min in IPA to remove all the unreacted resins still attached to the object using a washing station (Form Wash, Formlabs,

UK). After drying the objects inside a fume cupboard, the objects were cured in a UV curing station (Form Cure, Formlabs, UK) for 20 min at 40 °C.

Materials characterization

Fourier-transform infrared spectroscopy (FTIR) was carried out using Nicolet™ iS50 FTIR Spectrometer (Thermo Scientific™) in Attenuated Total Reflectance (ATR) mode to assess chemical variations in the printed material during specified cure durations. All data were acquired at ambient temperature, within a spectral range of 4000–400 cm⁻¹ at a resolution of 4 cm⁻¹, utilizing 8 scans for both sample and background. The spectra were normalized to the maximum peak. For each sample, the spectrum was analysed at three different locations.

The percentage of acrylate C=C conversion (α) can be calculated by the following Equation S1.

$$\alpha(t) = \frac{\frac{[A_{1637}]_t}{[A_{1718}]_t} - \frac{[A_{1637}]_0}{[A_{1718}]_0}}{\frac{[A_{1637}]_0}{[A_{1718}]_0}} \times 100 \quad (\text{S1})$$

The A_{1637} and A_{1718} are the area of the C=C peak and C=O peaks corresponding to the highest peak point of 1637 and 1718 cm⁻¹.

Differential Scanning Calorimetry (DSC) was carried out using DSC 2500 (TA Instruments) to characterize the printed SMPs. The sample was equilibrated first at -90 °C for 10 min and then heated at a rate of 10 °C min⁻¹ to 400 °C in nitrogen gas flowing at a rate of 25 mL min⁻¹. The typical mass of the samples was taken to be ≈8 mg.

Tensile testing was carried out using a Universal Testing Machine (UTM, Tinius Olsen, H25KS), applying 1 kN load cell, at a strain rate of 0.01 s⁻¹ following ASTM D638 method.¹ Thermomechanical testing was carried out using the same UTM with an attached temperature control unit and heater (Anglicon Solo 2). For sampling, three test samples were used for tests. The instant shape fixity ratio (R_f) and the shape recovery ratio (R_r) are determined from Equation S2 and S3, respectively.

$$R_f (\%) = \frac{\epsilon_1}{\epsilon_m} \times 100 \quad (\text{S2})$$

$$R_r (\%) = \frac{(\epsilon_2 - \epsilon_3)}{\epsilon_2} \times 100 \quad (\text{S3})$$

A heat-lamp bulb (300 W Infrared, Philips) was used to heat the printed objects to demonstrate stimulated actuation for soft-robotic applications.

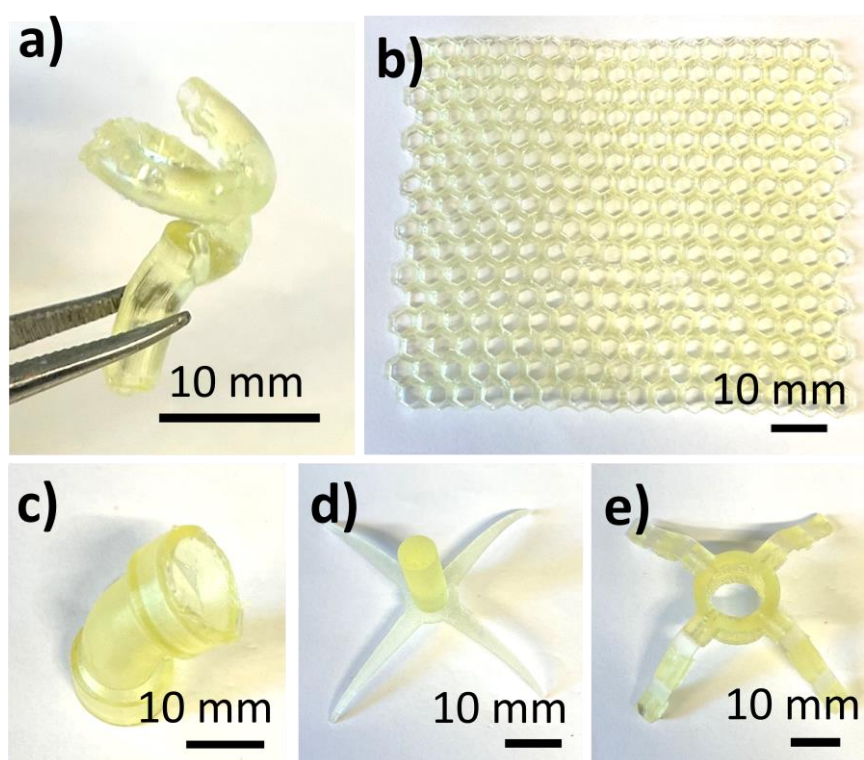


Fig. S1 Masked stereolithography (mSLA) printed tools using SMP_{0.50} resin. (a) a rod with spiral end, (b) a sheet with honeycomb patterns, (c) a pipe elbow, (d) a 4-finger gripper and (e) a 4-legged object.

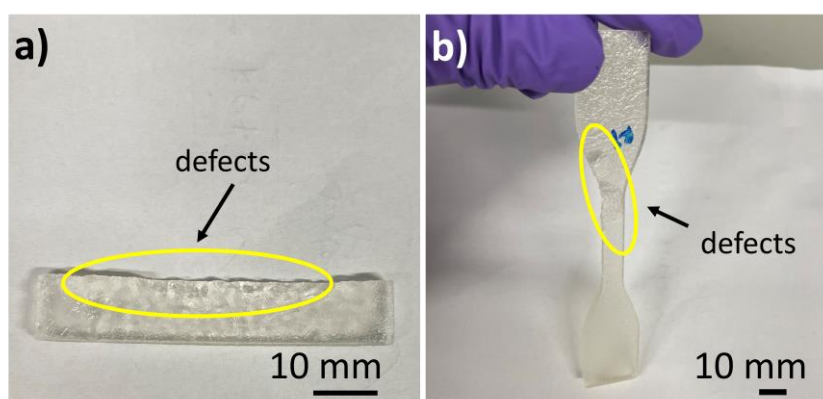


Fig. S2 (a) and (b) printed parts using SMP_{0.33} resin.

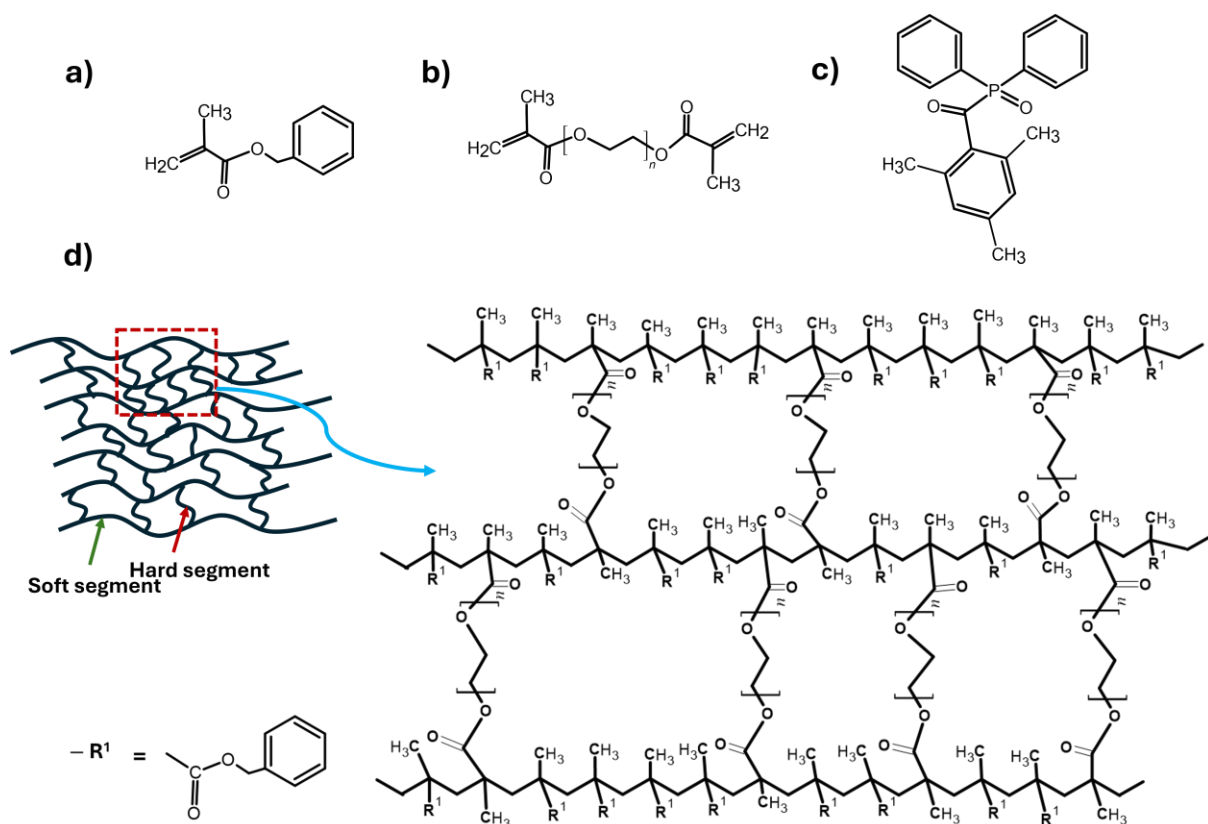


Fig. S3 Chemical structure of (a) benzyl methacrylate (BMA), (b) polyethyleneglycol dimethacrylate (PEGDMA), (c) diphenyl (2,4,6-trimethyl benzoyl) phosphine oxide (TPO), and (d) schematic presentation of photopolymerized polymer network and its chemical structure.

FTIR spectroscopy study was carried out on all the printed parts that were obtained from the exposure of UV light from 11 to 25 s, along with raw liquid resin and a fully post-cured printed part. The FTIR spectra from 2000 to 400 cm^{-1} of all the samples are presented in Fig. S4. To determine the percent of reaction conversion the region of interest is 1600 – 1800 cm^{-1} , wherein the peak at 1637 cm^{-1} is related to the C=C stretching of acrylate carbon-carbon double bond of BMA and PEGDMA and the peak at 1718 cm^{-1} corresponds to the C=O stretching of the acrylate ester group. The C=C stretching band intensity decreased with increasing the exposure time while the C=O stretching band intensity almost remained unchanged providing an internal reference for quantification of reaction conversion.²

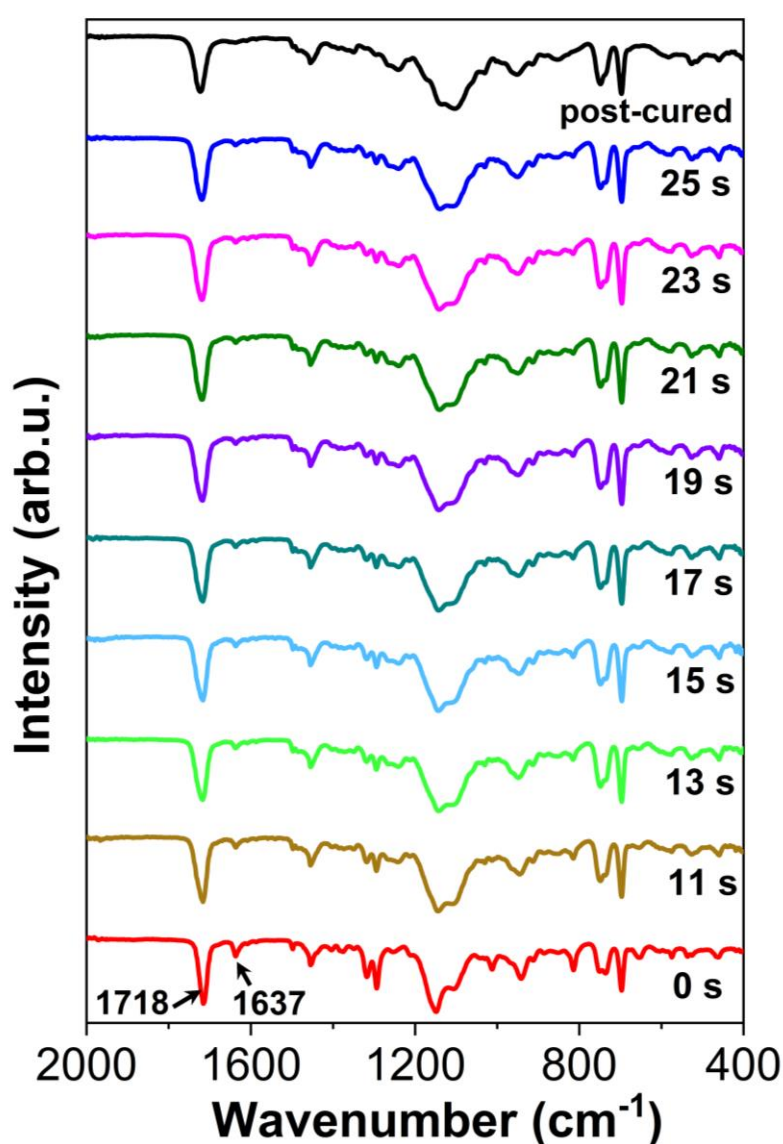


Fig. S4 FTIR spectra of the liquid resin (0 s), printed samples with UV light exposure time from 11 to 25 s, and post-cured sample of SMP_{0.50}.

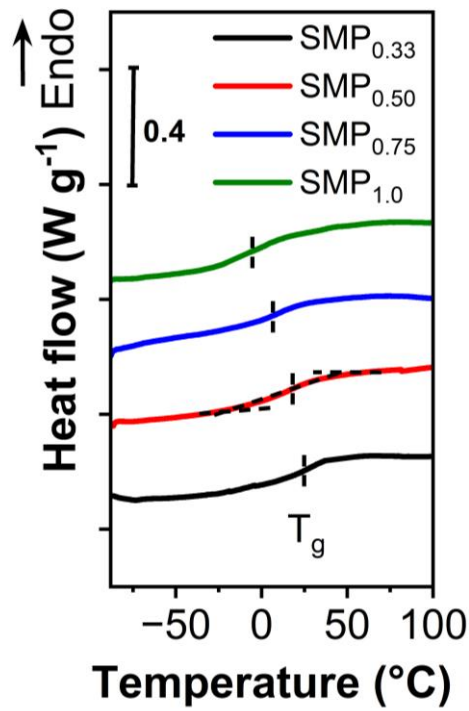
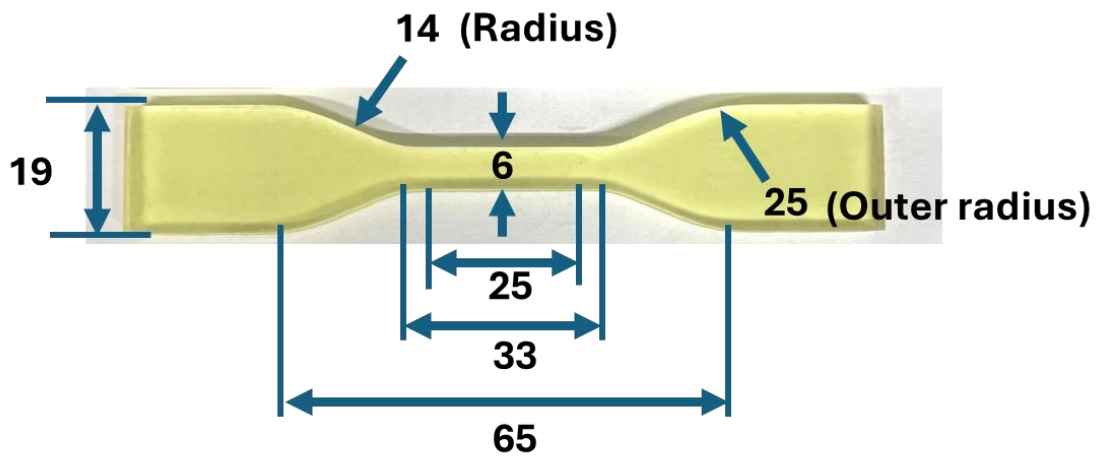


Fig. S5 DSC study of the SMP_{0.33}, SMP_{0.50}, SMP_{0.75}, and SMP_{1.0} at the temperature range -88 to 100 °C pointing to their glass transition temperatures (T_g).



All dimensions are in mm

Fig. S6 3D-printed ASTM D638-Type-IV specimen for tensile testing.

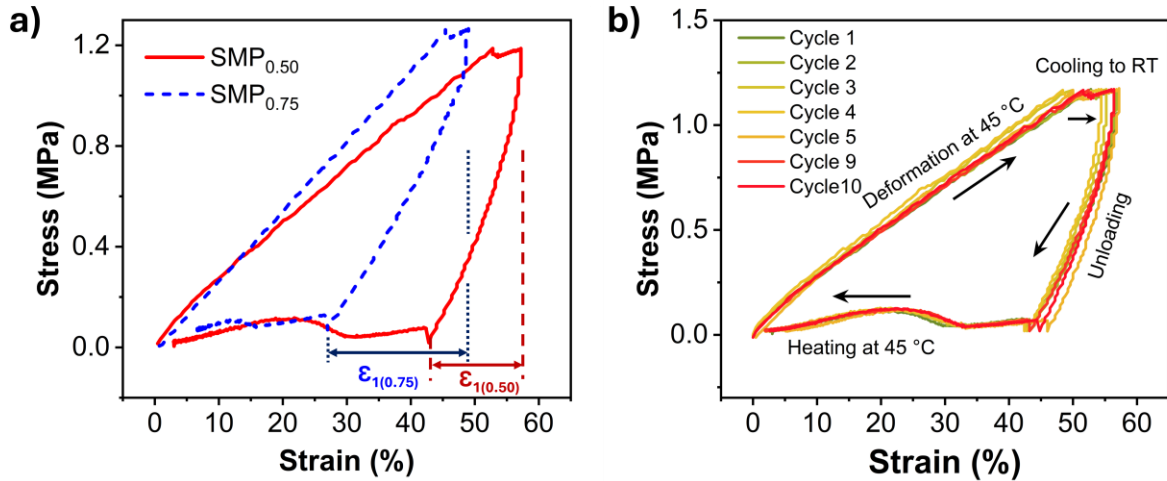


Fig. S7 (a) Comparison of cyclic thermomechanical test of SMP_{0.50} and SMP_{0.75} and (b) cyclic thermomechanical test for 10 cycles of a specimen of SMP_{0.50}.

The shape recovery behaviour of SMP_{0.50} and SMP_{0.75} is compared using a cyclic thermomechanical test. The stress vs strain plots from the cyclic thermomechanical test are shown in Fig. S7a. The SMP_{0.75} shows a lower shape fixity ratio of $57 \pm 2\%$ as compared to SMP_{0.50} of $78 \pm 3\%$. Due to higher amount crosslinkers in SMP_{0.75}, the specimen shows higher creep recovery and thus, it became unsuitable for soft robotic applications. Cyclic thermomechanical testing was performed for 10 continuous cycles as shown in Fig. S7b. The stress vs strain plots followed a similar path as of cycle-1 with trivial deviation.

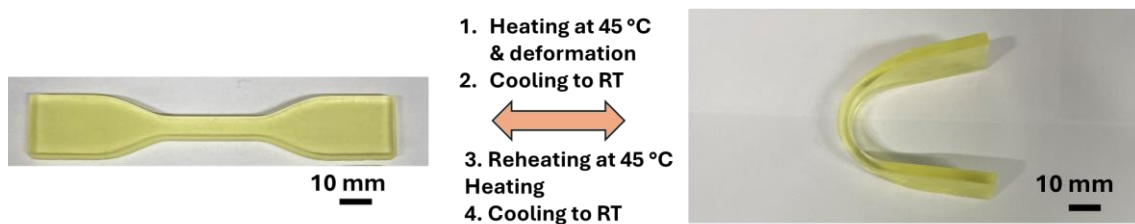


Fig. S8 Shape transformation for cyclic stability test for 100 times.

This shape-changing mechanism is explained by a schematic presentation in Fig. S9. The crosslinked polymer possesses an entangled molecular chain with some covalent “net-points”. The net-points determine the shape of the polymer and possibility of shape switching. The domain with net-points acts as a hard segment and the flexible chain acts as a soft segment or switching segment. When the polymer is heated above its T_g , the polymer becomes softened and can be mechanically deformed (step-1, Fig. S9). The net-points hold the polymer chains and act as memory sites. At the temporary state, when the polymer is cooled below the transition temperature, the switching segments keep the temporary position (step-2, Fig. S9). Later in (step-3, Fig. S9) when the polymer is heated again above the transition temperature, the switching segments move to the original shape to reach the highest level of entropy.³

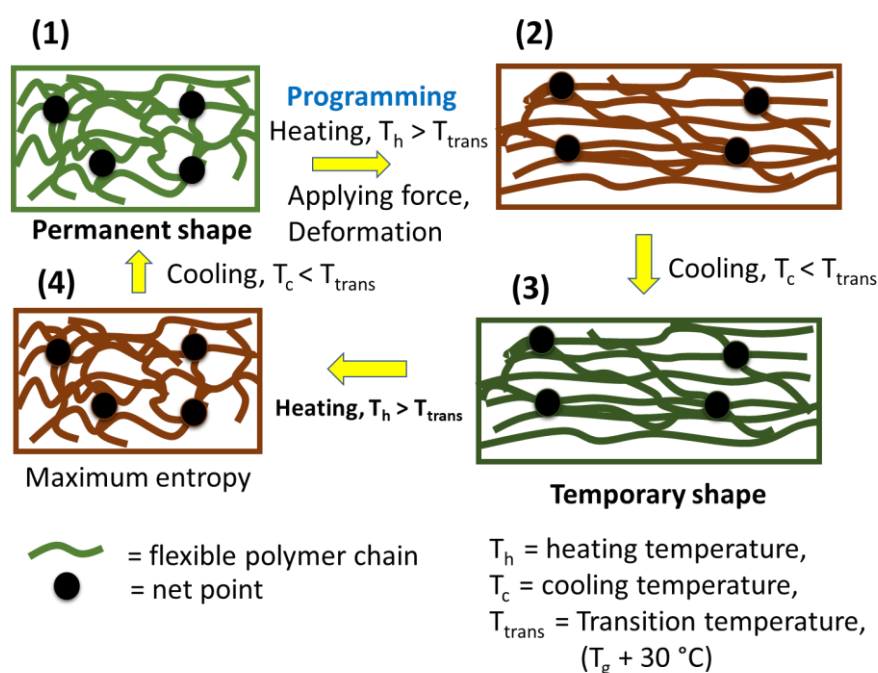


Fig. S9 Schematic diagram showing the molecular mechanism of the shape-memory effect.

Cyclic thermomechanical test steps are stated in Table S1.

Table S1 Steps involved cyclic thermomechanical study

Steps	Experimental condition	Activity
Step 1	Heating the sample at 45 °C	Heating
Step 2	Elongation at 15 mm/min until stress reached 1.18 MPa (30 N load) at isothermal condition of temperature 45 °C for 2 min	Deformation
Step 3	Holding the specimen at 30 N load for 3 min while cooling the sample to Room temperature (20 °C)	Cooling
Step 4	Quick unloading the load to 0.5 N at a rate 60 N/min, at RT	Unloading
Step 5	Holding the specimen with 0.5 N load for 1 min showing the stability of the temporary shape and the degree of shape deformation.	Stability at temporary shape and creep recovery
Step 6	Heating the specimen to 45 °C while holding it at 0.5 N load and kept for 3 min isothermal condition to recover the temporary shape	Reheating and shape transformation to the original shape
Step 7	Cooling the sample to RT while holding it at 0.5 N load.	The sample is stable in its original shape

References

- 1 ASTM International, *ASTM standard*, D638-22. <https://www.astm.org/d0638-22.html>
- 2 K. C. Wu and J. W. Halloran, *J. Mater. Sci.*, 2005, 40, 71–76.
- 3 M. Behl and A. Lendlein, *Mater. Today*, 2007, 10, 20–28.