Supplementary Material (ESI) for Soft Matter

A Functionally Graded Shape Memory Polymer

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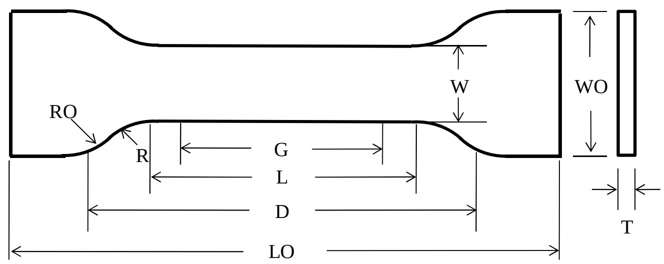
Electronic Supplementary Information



W	L	G	WO	LO	D	R	RO
1.50	8.25	6.25	4.75	28.75	16.25	3.50	6.25

Unit: mm

Scheme 2 The dumbbell geometry used for bulk shape memory characterization. **W**: width of narrow section, **L**: length of narrow section, **G**: gage length, **WO**: width overall, **LO**: length overall, **D**: distance between grips, **R**: radius of fillet, and **RO**: outer radius.

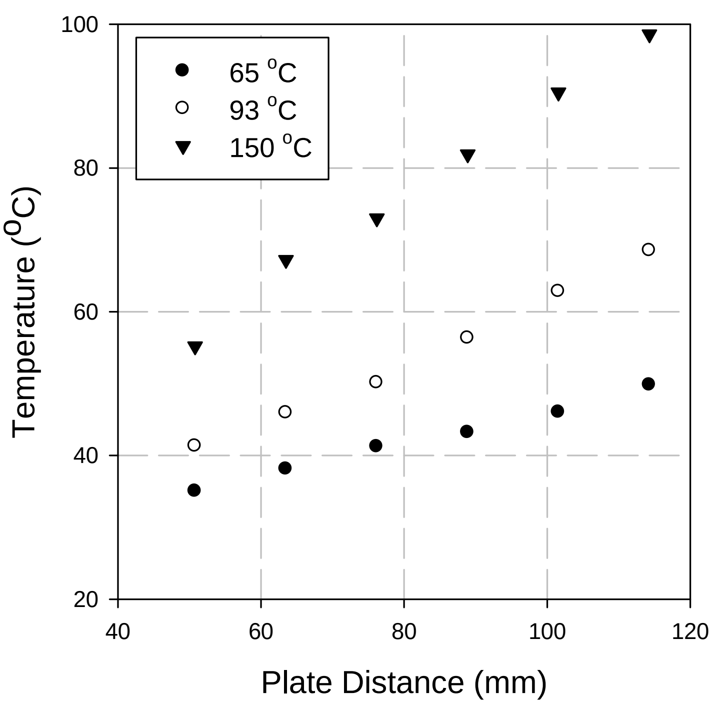


Figure S1. Different temperature gradients generated by varying the temperature (shown in the legend) of the heater unit (see Scheme 1).

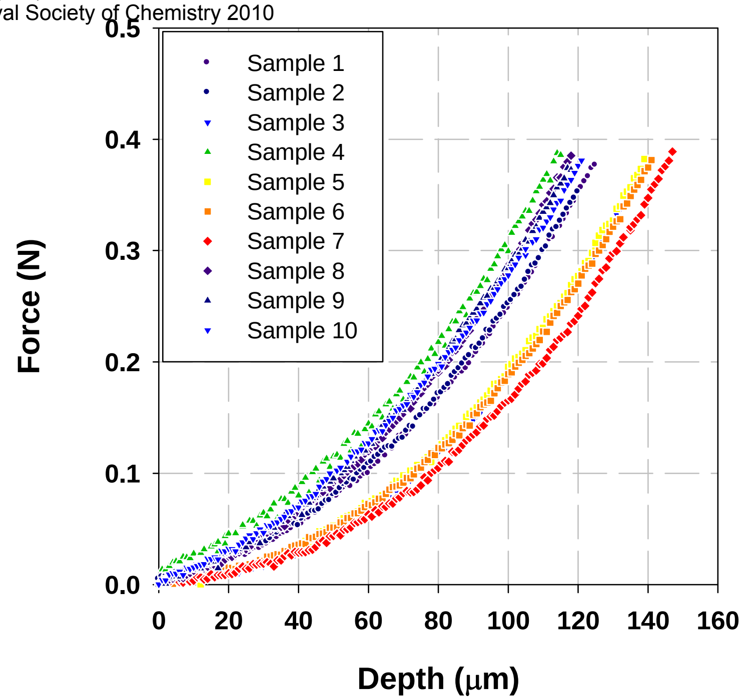


Figure S2. The force – depth plots for gradient samples 1 – 10 (see main text for details). All the indentation experiments were conducted at 80 °C (> T_g).

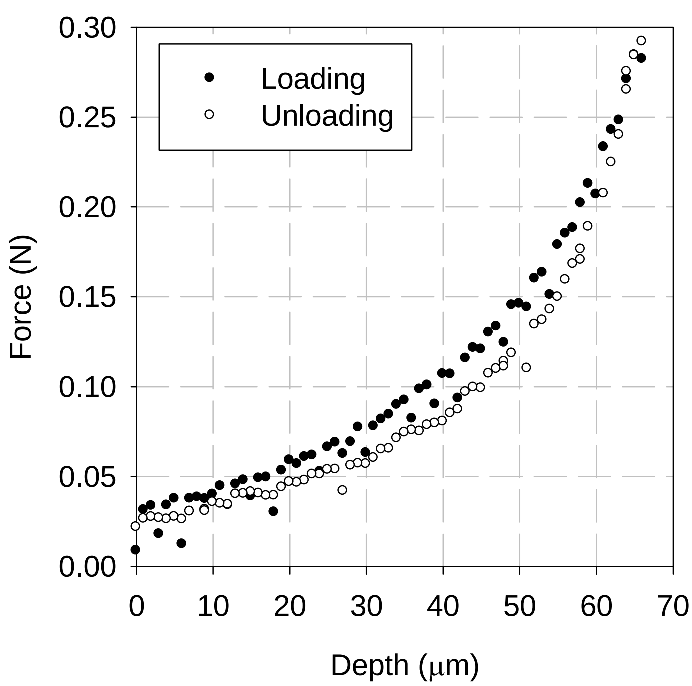


Figure S3. The loading – unloading curves for a NOA63 sample indented at $T > T_g$. The sample shows very elastic behavior, evident from the small hysteresis between loading and unloading.

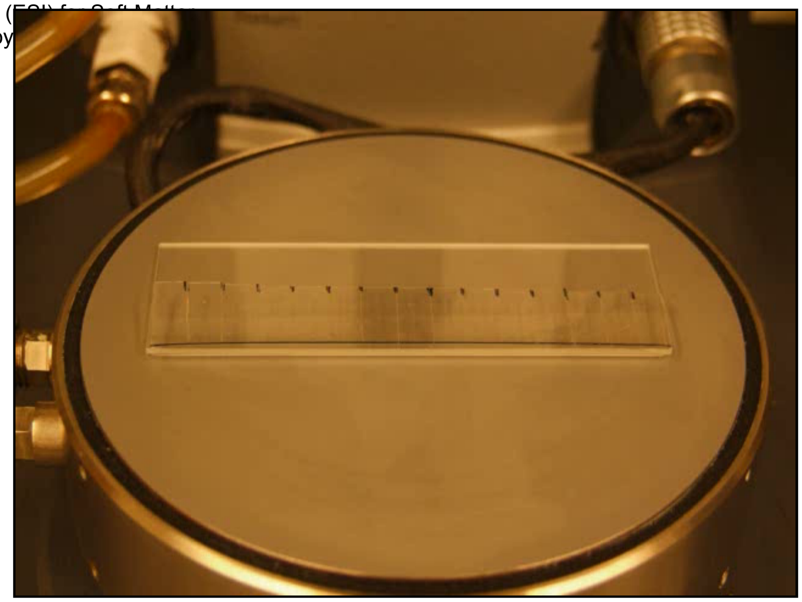


Figure S4. A continuous movie showing the macroscopic recovery of a graded NOA63 (Figure 6)

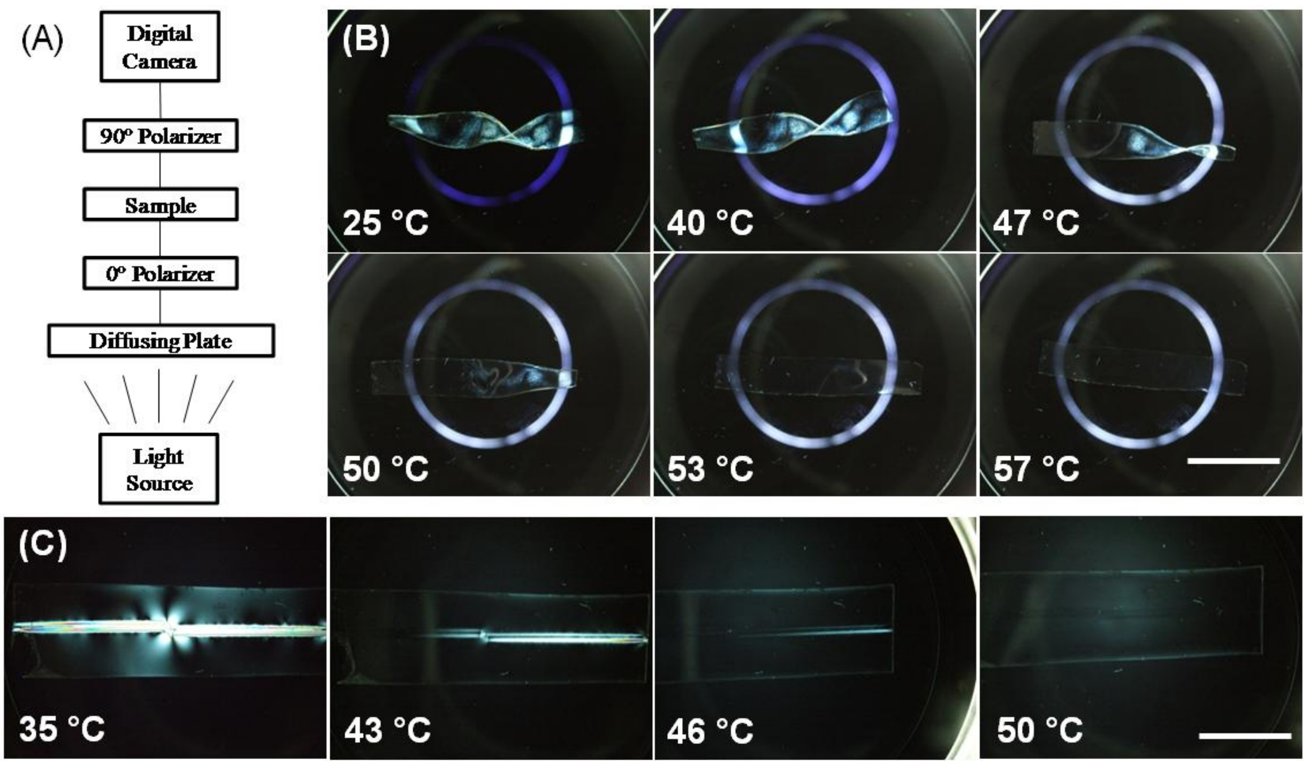


Figure S5. Recovery of functionally graded NOA63, demonstrated using the photoelastic effect. (A) schematically shows the optical setup for the demonstration. For (B), the temporary shape was fixed by hand twisting a heated sample then allowing it to cool to room temperature. For (C), a straight line-indent along the gradient direction was produced by gently pressing the blunt edge of two razor blades in series onto the sample surface. Recovery was triggered by stepping the temperature from room temperature to 60 °C at 1 °C steps. Images were taken at each step temperature and are shown in (B) and (C). For both cases, the disappearance of birefringence propagated from the left (T_g minimum) to the right (T_g maximum) with increasing temperatures. The scale bar represents 2 cm.

Table S1. Summary of studies on indentation based shape memory.

Reference	Materials	Indenter Geometry	Indentation Temperature	Observation
Gall et al. (29)	A commercial, two-part epoxy SMP with a T_g = 67 °C (from loss tangent peak). The chemical composition is not disclosed.	Vickers indenter (four sided pyramid with a face angle of 136°)	Indented at 5 different temperatures, between $0.37T_g$ and $1.27T_g$ (c.a. 25 to 85 °C), then cooled to $0.37T_g$ (25 °C) for indent "fixing"	(1) Complete recovery was achieved regardless of indentation temperature; (2) Recovery temperatures increased with higher indentation temperatures.
Xu et al. (30)	Glassy PU (MM5520 from Mitsubishi Heavy Industries) reinforced with thermally treated attapulgite clay T_g of neat PU = 34.3 °C T_g of nanocomposites ~ 40 °C	Vickers indenter (same as above)	Not mentioned; presumably at ambient temperature	(1) Complete recovery was observed for both neat PU and the nanocomposite; (2) Nanocomposite showed slower recovery kinetics.
Wornyo et al. (31)	tBA photo-crosslinked with different amounts of DEGDMA and PEGDMA (M_w = 550 g/mol)	Berkovich indenter	Indented at ambient temperature	Complete recovery was observed for all the samples with different crosslink densities;
Yang et al. (32, 33)	tBA photo-crosslinked with DEGDMA	A custom-made cantilever with a heated tip; tip geometry not specified	Indented at different tip temperatures of 150, 192 and 250 °C; two "cold indents" were also introduced by using a unheated tip	(1) All indents showed almost complete recovery upon heating; (2) The indents formed at room temperature recovered at lower temperatures.

SMP: shape memory polymer; PU: polyurethane; tBA: tert-butyl acrylate; DEGDMA/PEGDMA: di-/poly-(ethylene glycol) dimethacrylate; M_w: molecular weight.