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High-Energy-Density Shape Memory Materials with Ultrahigh Strain for Reconfigurable Artificial Muscles

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Experimental Section

1 Materials

PCL-diOH (M_n = 20 000 g mol^{-1}) was purchased from the Shanghai D & B laboratory. PEG-diOH (M_n = 1 000 g mol^{-1}) was purchased from Sinopharm Chemical Reagent. *N,N*-Dimethylformamide (DMF) and Hexamethylene diisocyanate (HDI) were purchased from Shanghai Titan Technology Co., Ltd. *N,N, N′,N′*-tetrakis(2-hydroxypropyl) ethylenediamine (HPED) and Triethanolamine (TEA) was purchased from Beijing Innochem Science & Technology Co.,Ltd. 4A molecular sieve was purchased from Energy Chemical Co., Ltd. Other reagents were purchased from Shanghai Macklin Biochemical Co., Ltd. Except for special instructions, all regents were used as received.

2 Preparation of Fe_3O_4 nanoparticles

The hydrothermal method is a convenient and efficient method to synthesize Fe_3O_4 NPs according to the reported literature.[1, 2] Typically, $FeCl_3 \cdot 6H_2O$ (0.01 mol) and sodium acetate (0.1 mol) was first added in ethylene glycol (140 mL) by ultrasound to obtain a dark brown solution. After that, the mixture was stirred vigorously for 1 h to ensure that they were completely dissolved. Finally, the mixture was sealed in a Teflon-lined stainless-steel autoclave, which would then be heated to 200 °C and kept for 8 h. The obtained black products were cooled to room temperature naturally and washed with ethanol three times through centrifugation, followed by drying in an oven at 80 °C for 12 h.

3 Synthesis of the PUPCLPEG

PCL-diOH, PEG-diOH, HDI, HPED and TEA should be intensively dry for the whole night. A certain amount of PCL-diOH and PEG- diOH were dissolved in DMF, stirring at 80 °C to get a homogeneous solution. (Table S1) Then HDI was added into the transparent solution and pre-polymerize for 30 min under vacuum, which was before the addition of HPED and TEA. Subsequently, the mixture was stirred for 5 min after adding ditin butyl dilaurate (DBTDL). After the pre-polymerization reaction was completed, the mixture became sticky and was decanted into poly(tetrafluoroethylene) (PTFE) molds. Finally, reacting at 80 °C for 24 h, the sample could be taken out for later use. What is more, different geometries could be achieved by using different molds such as film and strip. The whole process was finished in the nitrogen or vacuum atmosphere to avoid the side reaction of HDI and H_2O.

4 Fabrication of the PUPCLPEG/Fe_3O_4 shape memory composite

A series of PUPCLPEG/Fe_3O_4 shape memory composites with different doped amounts (0%, 0.25%, 0.5%, 1%, 2% and 5wt%) were fabricated by mixing certain amounts of Fe_3O_4 into the polyurethane matrix. Fe_3O_4 NPs were dispersed in the mixture by sonication before it became sticky. Besides, 2 wt% of fumed silica (Macklin) with an average size of 7–40 nm is added to ensure good mixing of the matrix resin with the Fe_3O_4 NPs.

5 Physicochemical Characterization

The Wide-angle X-ray diffraction (WAXD) patterns were performed by D8 ADVANCE (Da Vinci) with 2θ in the range of 5~70° with a step size of 5° min^{-1} at room temperature. The Fourier transform infrared (FT-IR) spectra of samples were

obtained by FT-IR spectrometer (Spectrum 100, USA). The microstructure and EDS mapping of the composite was observed by TESCAN Mira3 field emission scanning electron microscope (FE-SEM). Elastic modulus maps of samples were recorded by Atomic force microscope (AFM) under ambient conditions.

6 Thermodynamics Characterization

The Differential scanning calorimetry (DSC) were performed by Q2000 (TA instruments) at the heating/cooling rate of 5 °C min^{-1} under the N_2 atmosphere. The dynamic mechanical analysis (DMA) was tested using DMA Q850 (TA instruments) in tension mode at a heating rate of 5 °C min^{-1} at a constant frequency of 1 Hz with a peak-to-peak amplitude of 0.1%. The WAXD patterns with variable temperature were tested by D8 ADVANCE (Bruker) with 2θ in the range of 5 ~ 70° at a scanning rate of 5° min^{-1} and were maintained at testing temperature points (20 °C, 40 °C, 60 °C, and 80 °C) for 20 min. The polarizing optical microscopy (POM) were performed on DM LP (Leica) from 25 °C to 80 °C.

7 Mechanical Testing

Mechanical tensile tests were carried out using a microcomputer-controlled electronic universal testing machine (LD23 503, Shenzhen, China) at ambient temperature. The specifications of the tensile sample for the test were 85 × 10 × 1.5 mm^3. The strain rate was 5 mm min^{-1}

8 Shape memory and artificial muscle behavior

Shape memory performance tests were recorded by using DMA Q850 (TA instruments) through a pre-set program. The temperature range is from 10 to 60 °C at

the heating rate of 5 °C min^{-1}. (Samples: about 8 × 5 × 0.8 mm^3). And the artificial muscle behavior tests were carried out by vertically fixing the sample connected to the load with clamps on the iron platform (the weight of the clamps are 2.8400 g and 1.2800 g).

9 Photo-responsive thermogenesis efficiency and Photo-response performance

The infrared thermal images of PUPCLPEG/Fe_3O_4 composite were taken with a visual IR thermometer (FLIR E50, FLIR Systems). The polymer films were initially synthesized in a rectangular mold of 40 × 40 mm^2 and then cut into specific shape according to the test requirements. The Xenon lamp light source with the bulb power of 300 W (Shanghai Yuming instrument co., LTD) was used for the near-infrared radiation (NIR) response test, and the output band was between 800 nm and 900 nm. 808 nm NIR laser was generated by a light source (MLD-XF-808nm-10W-BL22232) from Changchun New Industries Optoelectronics Tech Co., Ltd.

Supplementary 1: Calculation of phase domain size from SAXS

The distance between two neighboring nanoscale domains (D) can be roughly calculated by the following Equation S1.

$$D = 2\pi/q^* \quad (1)$$

Supplementary 2: Shape memory behavior and artificial muscle performance test

$$R_f = \left(1 - \frac{L_2 - L_1}{L_1}\right) \times 100\% \quad (2)$$

$$R_r = \left(1 - \frac{L_3 - L_0}{L_0}\right) \times 100\% \quad (3)$$

Where L_0 represents the initial length, L_1 represents the deformation length at the room

temperature, L_2 represents the fixation length after partial elastic contraction, and L_3 represents the final length after the recovery process.

$$W = \frac{M_{load} \times g \times \rho \times (L_2 - L_3)}{M} \quad (4)$$

Where M_{load} and M represent the mass of the load and deformation section of the sample, respectively. ρ represents the density of sample, which is measured by Archimedes method. Meanwhile, g represents the acceleration of gravity, and its value is 9.8 N kg^{-1}.

Supplementary figures, tables and movies

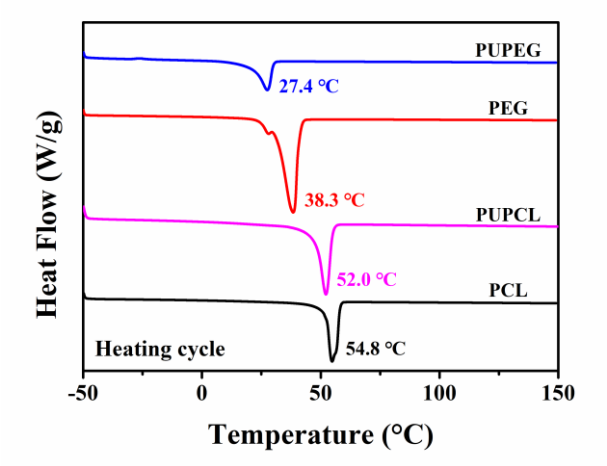

Figure S1 DSC curves in a heating cycle of PCL, PUPCL, PEG, PUPEG.

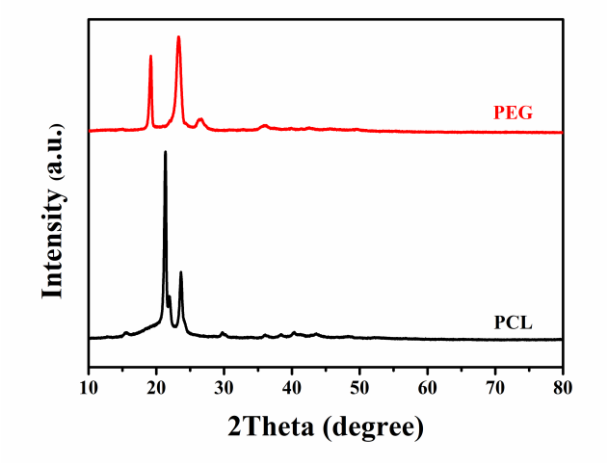

Figure S2 WAXD patterns of PCL and PEG.

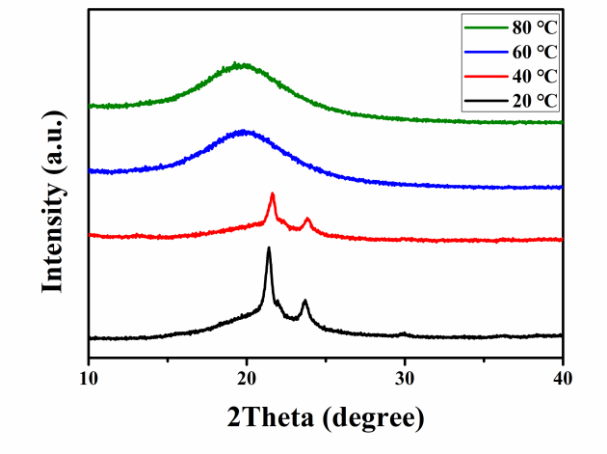

Figure S3 WAXD patterns of the PUPCLPEG under the heating circumstance.

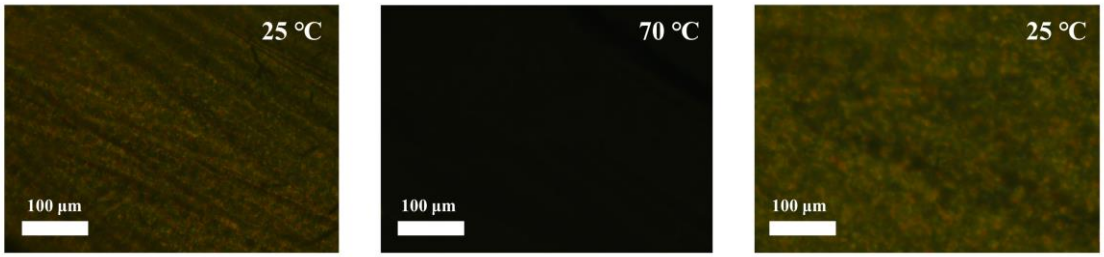

Figure S4 POM images of PUPCLPEG (7:3), recorded during the heating process and the cooling process.

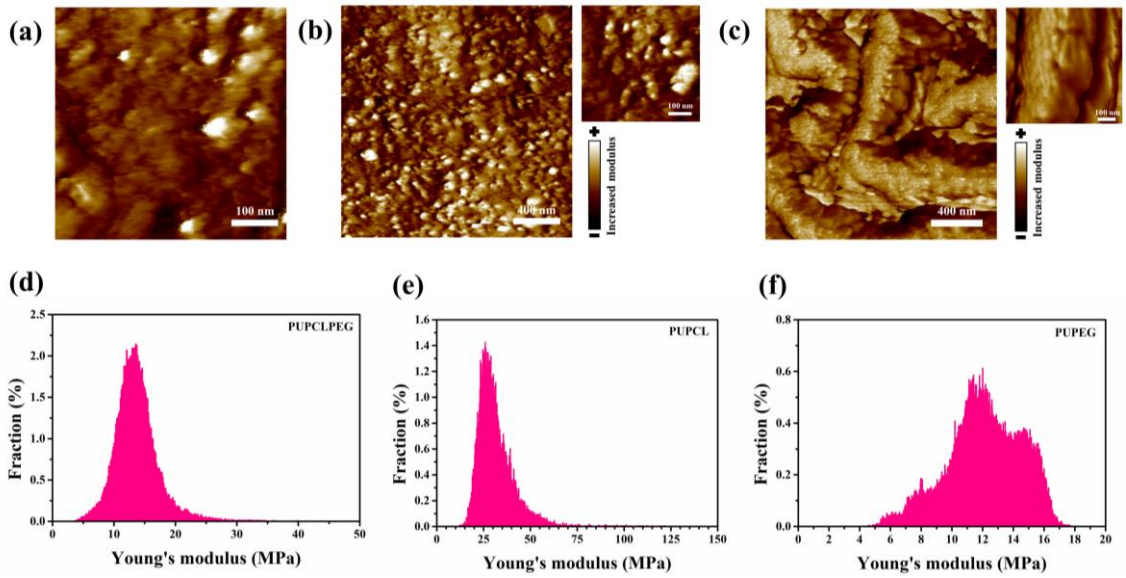

Figure S5 Elastic modulus maps of PUPCLPEG (7:3) (a), PUPCL (b), PUPEG (c), and Elastic modulus histograms of PUPCLPEG (7:3) (d), PUPCL (e), PUPEG (f) recorded by AFM.

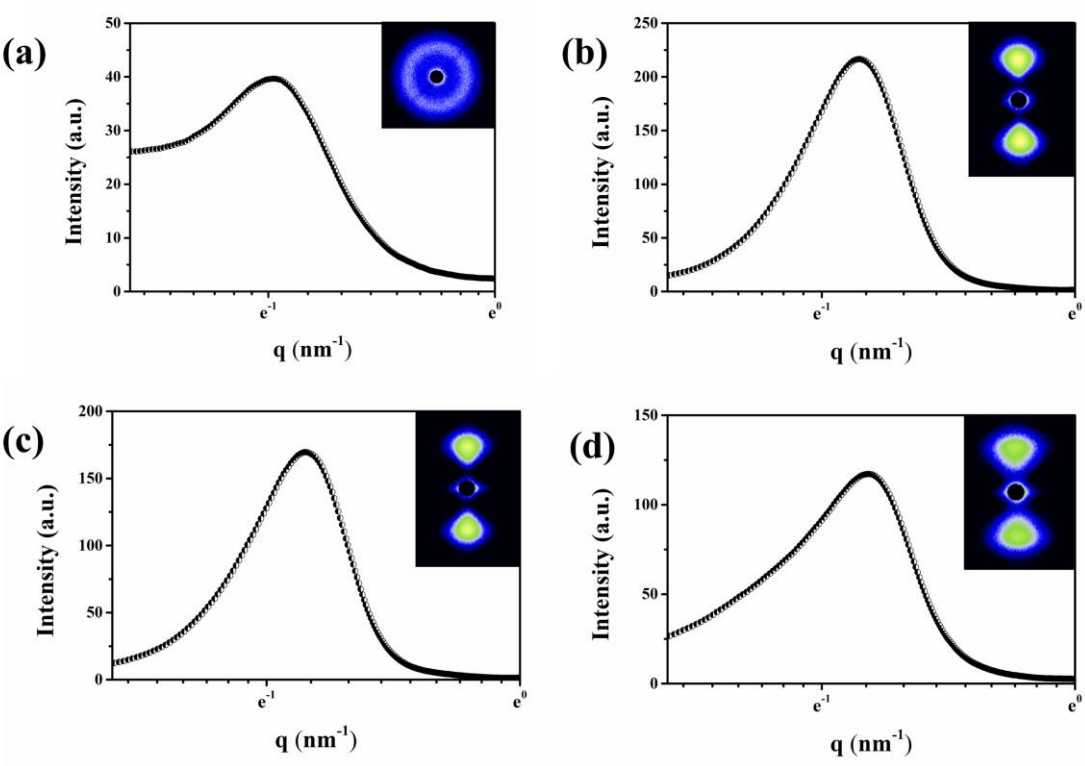

Figure S6 SAXS patterns and 2D-SAXS images (inset) of PUPCLPEG (7:3) at strains of 0% (a), 200% (b), 400% (c), 600% (d).

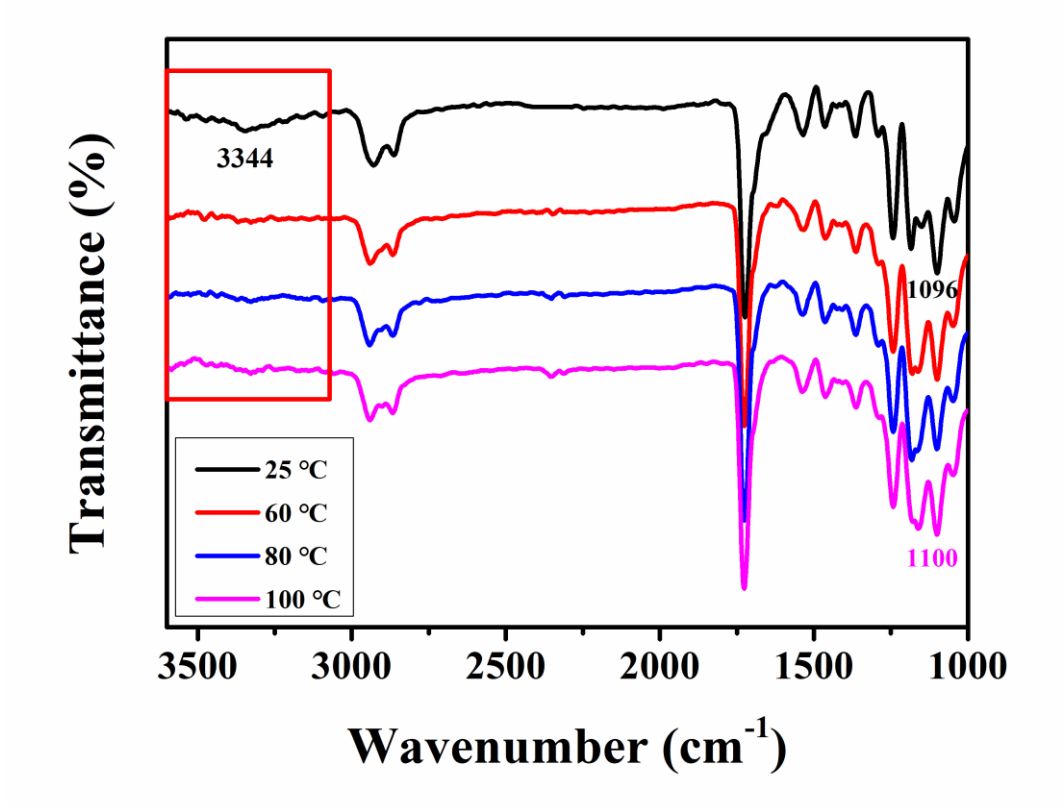

Figure S7 FTIR spectra of PUPCLPEG at different temperatures.

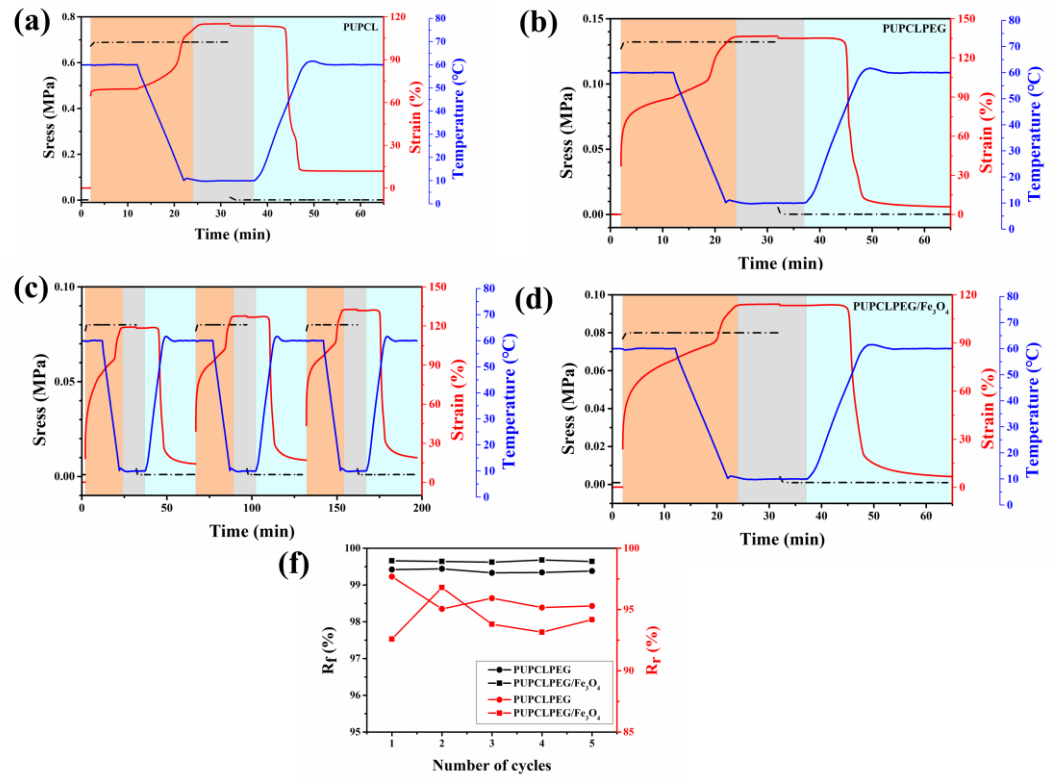

Figure S8 Characterization of shape memory behavior using DMA. Temperature, strain, and stress as functions of time for (a) PUPCL in one cycle (b) PUPCLPEG in one cycle and (c) PUPCLPEG in three cycles (d) PUPCLPEG / Fe_3O_4 in the first cycle. (f) Rf and Rr as functions of cycle number for PUPCLPEG and PUPCLPEG / Fe_3O_4 . In (a-d), black dashed lines: stress; red solid lines: strain; blue solid lines: temperature.

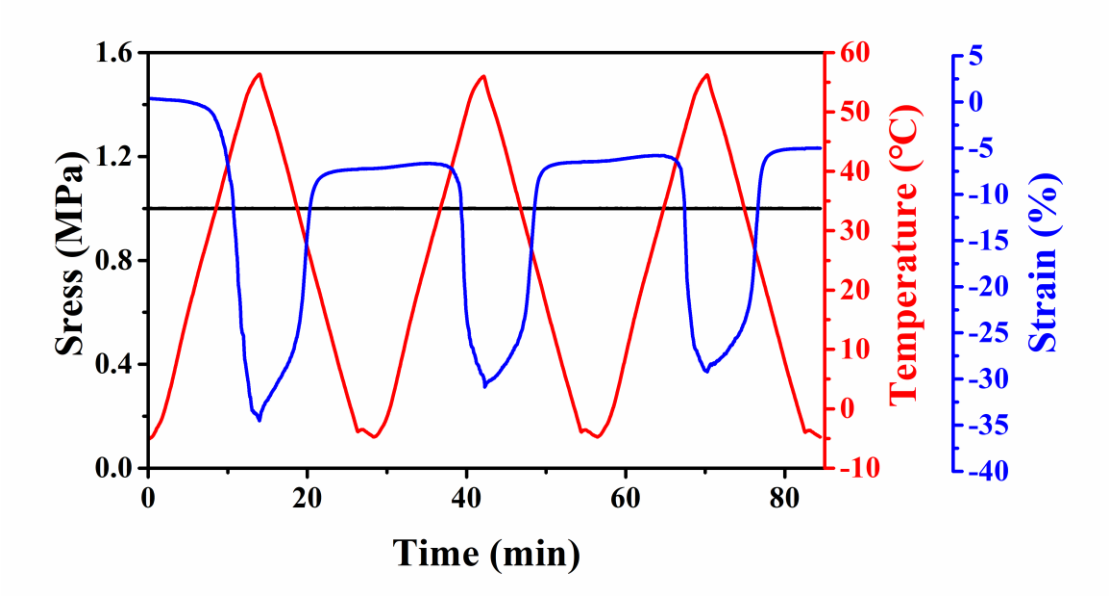

Figure S9 Reversible shape memory effect of PUPCLPEG under the stress of 1.0 MPa recorded by DMA

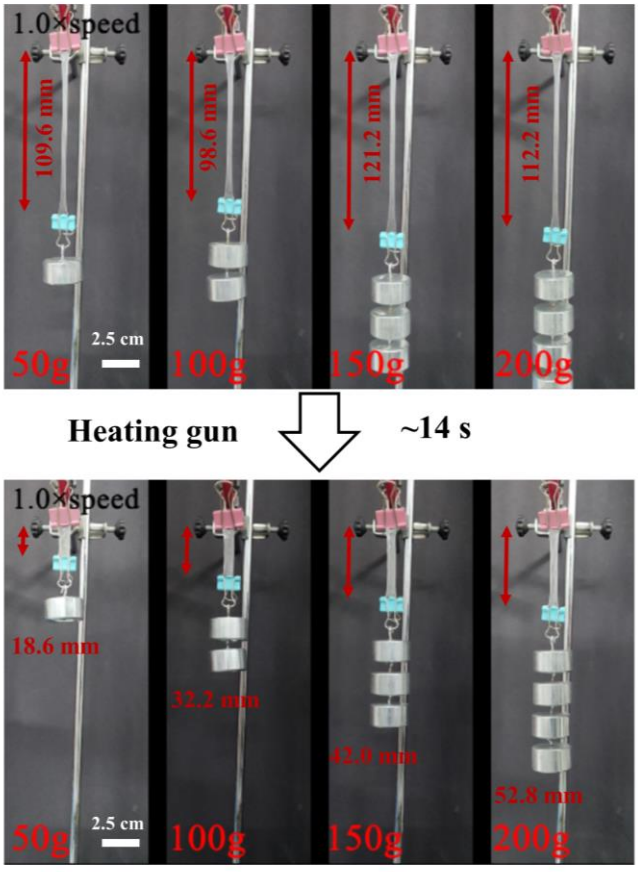

Figure S10 Photos of a PUPCLPEG (7:3) strip lifting different weight load by

employing a heating gun.

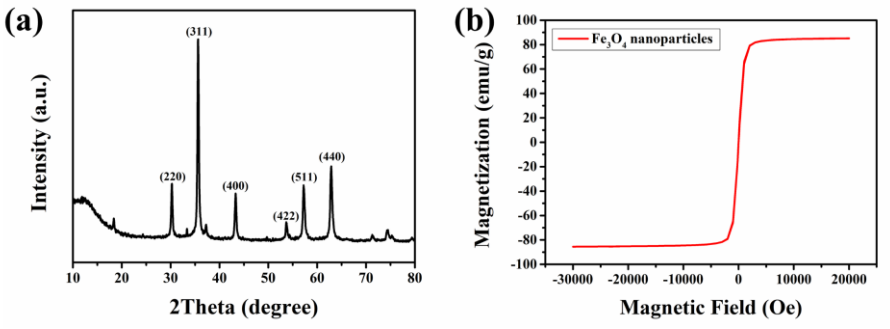

Figure S11 XRD patterns (a) and static magnetic hysteresis loops (b) of Fe_3O_4 nanoparticles.

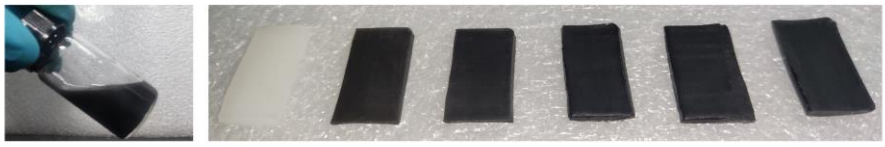

Figure S12 (a) Photograph of the mixture of polymer and Fe_3O_4 nanoparticles before polymerization. (b) Photograph of the PUPCLPEG/Fe_3O_4 shape memory composites with different doped amount (0%, 0.25%, 0.5%, 1%, 2% and 5wt%).

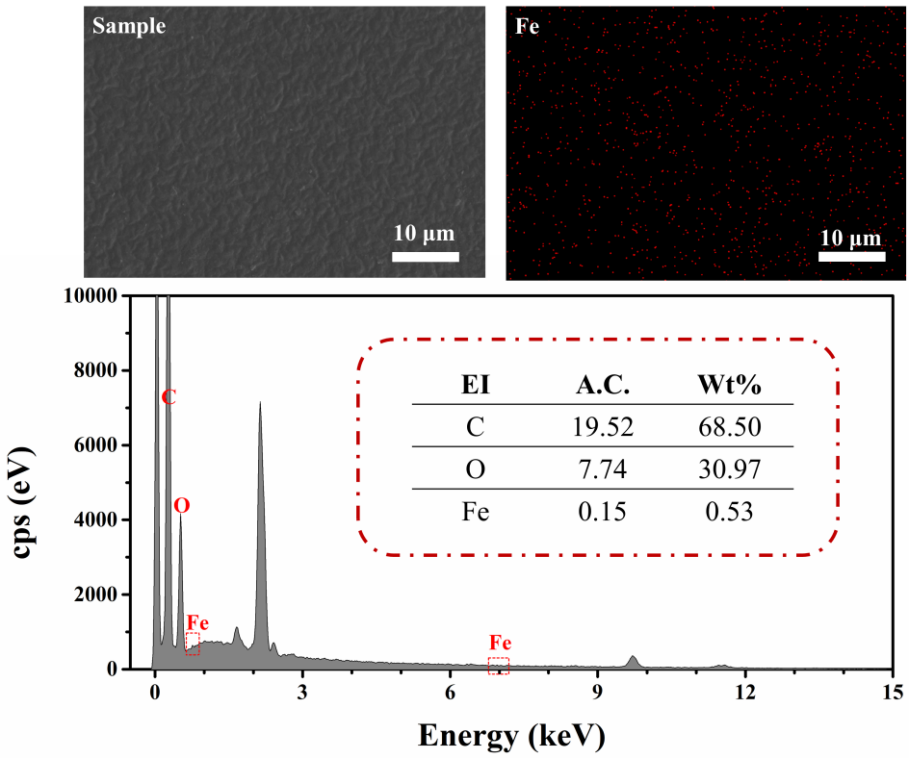

Figure S13 SEM image of the surface and EDS analysis of the component of 0.5 % PUPCLPEG/Fe_3O_4 shape memory composite (El for element, A.C. for apparent concentration).

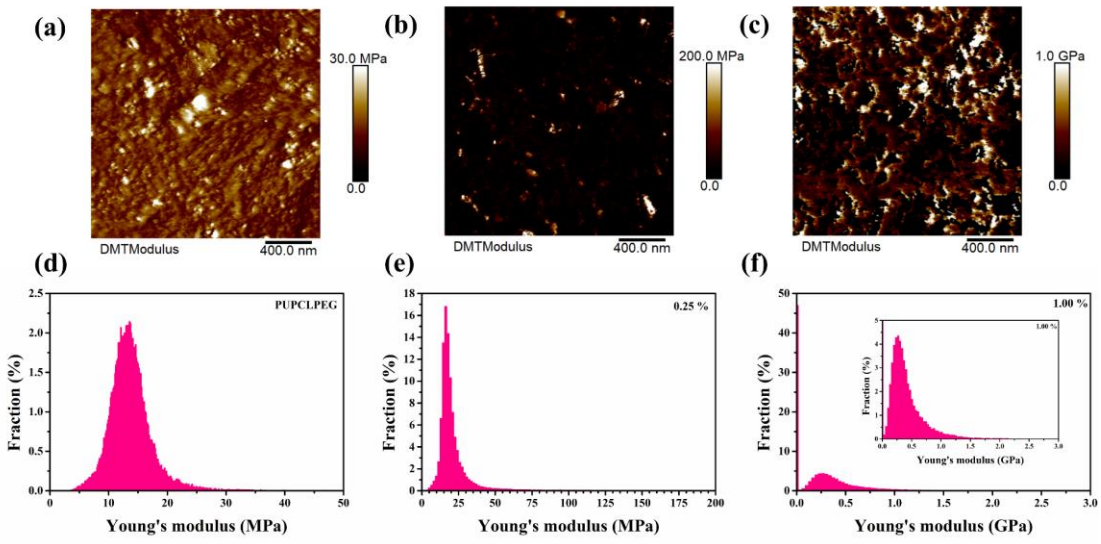

Figure S14 Elastic modulus maps of PUPCLPEG(7:3) (a), 0.25 % PUPCLPEG/Fe_3O_4 (b), 1.0 % PUPCLPEG/Fe_3O_4 (c) and Elastic modulus histogram of PUPCLPEG(7:3) (d), 0.25 % PUPCLPEG/Fe_3O_4 (e), 1.0 % PUPCLPEG/Fe_3O_4 (f).

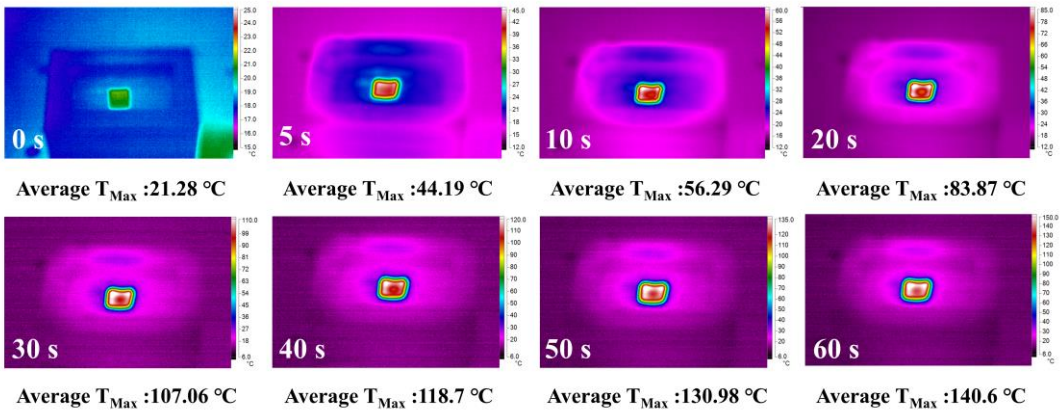

Figure S15 The IR mapped temperature distribution of 0.5 % PUPCLPEG/Fe_3O_4 shape memory composite, the surface temperatures change with irradiation time. The light intensity is 1000 mW cm^{-2}.

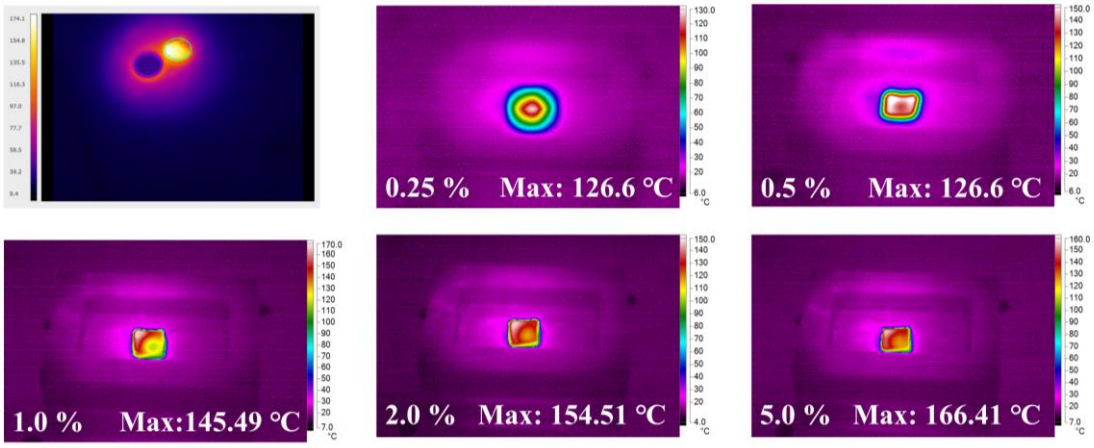

Figure S16 The IR mapped temperature distribution of Fe_3O_4 and PUPCLPEG/Fe_3O_4 shape memory composite with different doped amount (0.25%, 0.5%, 1%, 2% and 5wt%). The light intensity is 1000 mW cm^{-2}.

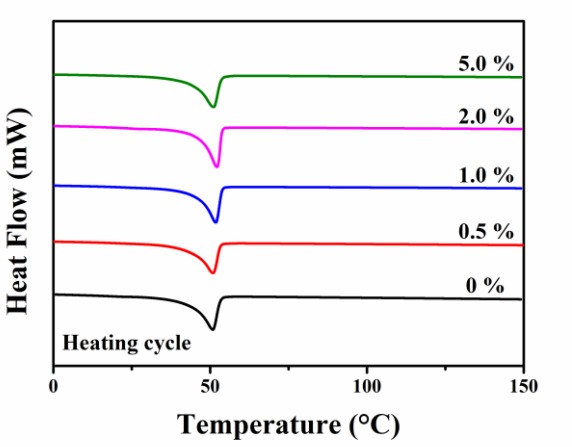

Figure S17 DSC curves in a heating cycle of PUPCLPEG/Fe_3O_4 shape memory composite with different doped amount (0%, 0.5%, 1%, 2% and 5wt%).

Table S1. Sample numbers with various proportions and mechanical properties of SMPUs (*f*: number of functional groups) tested by tensile test

	PCL(*f*=2) [mmol]	PEG(*f*=2) [mmol]	HPED(*f*=4) [mmol]	TEA(*f*=3) [mmol]	HDI(*f*=2) [mmol]	Young's Modulus E[MPa]	Strain at break ε_B[%]	Tensile strength σ_B[MPa]
PUPCL	0.05 (1.0 g)	-	0.2	0.1	0.6	133.98	221.8	9.39
9:1	0.045 (0.9 g)	0.1 (0.1 g)	0.2	0.1	0.695	39.12	706.6	12.18
8:2	0.04 (0.8 g)	0.2 (0.2 g)	0.2	0.1	0.790	33.17	779.7	10.96
7:3	0.035 (0.7 g)	0.3 (0.3 g)	0.2	0.1	0.885	17.94	947.0	11.68
6:4	0.03 (0.6 g)	0.4 (0.4 g)	0.2	0.1	0.980	13.21	729.2	6.84
5:5	0.025 (0.5 g)	0.5 (0.5 g)	0.2	0.1	1.075	11.45	486.7	4.78
PUPEG	-	1.0 (1.0 g)	0.2	0.1	1.550	0.49	299	$1.1*10^{-3}$

Table S2. Shape memory performance of PUPCL, PUPCLPEG, and PUPCLPEG/ Fe_3O_4.

No.	sample	L_0[mm]	L_1[mm]	L_2[mm]	L_3[mm]	R_f[%]	R_r[%]
1	PUPCL	8.051	17.268	17.134	8.930	99.22	89.08
2	PUPCLPEG(7:3)	8.048	17.013	16.915	8.235	99.42	97.68
3	PUPCLPEG(7:3)	8.026	17.887	17.787	8.423	99.44	95.05
4	PUPCLPEG(7:3)	8.499	18.522	18.398	8.846	99.33	95.92
5	PUPCLPEG(7:3)	8.075	18.147	18.028	8.466	99.34	95.16
6	PUPCLPEG(7:3)	8.509	17.328	17.220	8.910	99.38	95.29
7	PUPCLPEG/ Fe_3O_4	8.490	18.425	18.363	9120	99.66	92.58
8	PUPCLPEG/ Fe_3O_4	8.504	16.591	16.532	8.777	99.64	96.79
9	PUPCLPEG/ Fe_3O_4	7.931	16.915	16.850	8.423	99.62	93.80
10	PUPCLPEG/ Fe_3O_4	6.497	13.173	13.131	6.942	99.68	93.15
11	PUPCLPEG/ Fe_3O_4	7.925	16.395	16.336	8.837	99.64	94.17

Table S3. Artificial muscle behavior test of PUPCLPEG. (g = 9.8 N kg^{-1})

No.	L_0[mm]	L_2[mm]	L_3[mm]	ΔL[mm]	M_{load}[g]	M[g]	ρ[g cm^{-3}]	W[kJ kg^{-1}]
1	10.2	65.0	16.2	48.8	52.840	0.170	1.137	169.013
2	10.2	55.0	19.5	35.5	102.840	0.170	1.137	239.292
3	10.2	53.4	33.0	20.4	152.840	0.170	1.137	204.364
4	10.2	62.5	51.0	11.5	202.840	0.170	1.137	152.894
5	10.0	100.0	41.0	59.0	151.280	0.186	1.137	534.696
6	10.5	98.6	32.2	66.4	101.280	0.186	1.137	402.870
7	12.0	109.6	18.6	91.0	51.280	0.186	1.137	279.552
8	13.8	121.2	42.0	79.2	151.280	0.186	1.137	717.762
9	13.8	112.2	52.8	59.4	201.280	0.186	1.137	716.243

Movie S1. Shape memory behavior induced by heat at 60 ℃. The movie is shown with 1.0 × speed.

Movie S2. Artificial muscle performance induced by heat at 60 ℃ with the varied load. The movie is shown with 1.0 × speed.

Movie S3. The reversible actuation of the artificial muscle materials induced by heating at 60 ℃ and cooling at 0 ℃. The movie is shown with 1.0 × speed.

Movie S4. The application of the artificial muscle materials on a puppet arm. The movie is shown with 1.0 × speed.

Movie S5. Photothermal-driven contraction of the composite induced by NIR at 800~900 nm. The movie is shown with 1.0 × speed.

Movie S6. Photothermal-driven reversible bending of the composite induced by NIR laser at 808 nm. The movie is shown with 1.0 × speed.

Movie S7. The programmable deformation process of "S J T U" induced by NIR laser at 808 nm. The movie is shown with 1.0 × speed.

Movie S8. The blending process with different loading induced by NIR laser at 808 nm. The movie is shown with 1.0 × speed.

Movie S9. The programmed and precise folding of a box induced by NIR laser at 808 nm. The movie is shown with 2.0 × speed.

1. J. Liu, Z. Sun, Y. Deng, Y. Zou, C. Li, X. Guo, L. Xiong, Y. Gao, F. Li and D. Zhao, *Angew Chem Int Ed Engl*, 2009, **48**, 5875-5879.
2. K. Wang, Y. Chen, H. Li, B. Chen, K. Zeng, Y. Chen, H. Chen, Q. Liu and H. Liu, *ACS Applied Nano Materials*, 2019, **2**, 8063-8074.