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Supporting Information

UV-controlled Shape Memory Hydrogels Triggered by Photoacid Generator

1 Experimental

1.1 Materials

Acrylamide (AM), ammonium persulfate (APS), tetramethylethylenediamine (TEMED), polyvinyl alcohol (PVA, M_w~74,800), sodium tetraboratedecahydrate, melamine and ethylenediaminetetraacetic acid disodium (EDTA-2Na) were purchased from Sinopharm Chemical Reagent Co. Ltd. Polyethylene glycol diacrylate (PEGDA, M_n~700) was supplied by Sigma Aldrich. Diphenyliodonium nitrate and N-vinylimidazole (VI) were obtained from Energy Chemical. Ultrapure deionized water from a Milliporewater-purification system was used.

1.2 Preparation of P (AM-*co*-VI) hydrogels

The chemical structures of the copolymer P(AM-*co*-VI) and photoacid generator are shown in Scheme 1. The hydrogels were prepared by radical copolymerization of AM and VI, using PEGDA as crosslinker, with APS (1 wt%, relative to the total monomer mass) as an initiator and TEMED (0.8wt%, relative to the total monomer mass) as an accelerator. The initial monomer concentration in the feed was kept constant at 40 wt%. The mole ratio of crosslinker in total monomers was kept at 1.27 mol%. Different compositions were obtained by varying AM: VM feed ratio and denoted as PAM-VI-x, where x represents the molar percentage of N-vinylimidazole in monomer feeds. The reaction mixtures were injected into plastic molds and the polymerization was carried out for 24 hours at 30℃. Afterwards, the hydrogels were soaked in deionized water for 24 hours to remove unreacted monomers.

1.3 Characterization of P(AM-*co*-VI) hydrogels

FTIR spectra of freeze-dried hydrogels were recorded as KBr pellets on a Nicolet 8700 FTIR spectrometer. Oscillatory shear measurements were performed on a TA AR-G2 rheometer at 25 °C with a Peltier plate for temperature control. A parallel plate was used for testing with a diameter of 40 mm and a distance of 2000-3200 μm, depending on the swelling degree of hydrogels. Frequency sweep was carried out within the linear viscoelastic range determined by dynamic strain sweep. The storage modulus G' and loss modulus G'' were measured over the frequency range from 0.5 to 100 rad/s.

Swelling behaviour of hydrogels was measured by immersing the disc samples in various pH hydrogen chloride (HCl) solutions to constant weights, then the corresponding diameters and weights were recorded. At last, the hydrogels were dried under vacuum at 40℃ to constant weight. The equilibrium water content (EWC) is defined as follows: $m_{eq} = (m_{wet} - m_{dry})/m_{wet} \times 100\%$, where m_{wet} and m_{dry} denote the wet weight and dry weight, respectively.

Atomic absorption spectroscopy assay (AA800, Perkin Elmer) was performed to study the

adsorption kinetics of Zn^{2+}. The samples were immersed into 10mM $ZnSO_4$ solution and the concentration of external solution was measured over time.

1.4 Evaluation of shape memory performance

The shape memory performance was evaluated with following A straight strip gel (length of 6 cm and a radium of 4mm) was bent into a "V"-form shape and immersed in the solution containing $ZnSO_4$ (10 mM) and PAG (20mM) for 4 hours to fix the temporary shape. Then it was subjected to UV irradiation with an Oriel 100 W mercury arc lamp. A dichroic beam turner with a mirror reflectance range of 280-400 nm was used along with a filter (<400 nm) to access the UV range of the emitted light.

2. Results

Table S1. Swelling behavior of hydrogels in water with different pH

Sample		pH			
		1.04	3.21	5.67	7.01
PAM	EWC(%)	76.6±0.3	75.7±0.2	75.6±0.1	75.5±0.1
	Radium(cm)	2.53±0.02	2.40±0.03	2.35±0.02	2.34±0.02
PAM-VI-30	EWC(%)	88.7±0.3	93.8±0.4	90.6±0.3	83.8±0.3
	Radium(cm)	3.12±0.03	4.15±0.04	3.60±0.02	2.63±0.03
PAM-VI-50	EWC(%)	96.2±0.2	99.1±0.4	98.3±0.4	87.6±0.5
	Radium(cm)	4.40±0.03	6.80±0.02	5.50±0.04	2.90±0. 02
PAM-VI-70	EWC(%)	97.3±0.4	99.3±0.6	98.8±0.3	91.4±0.3
	Radium(cm)	4.63±0.05	7.04±0.06	5.71±0.04	3.83±0.03

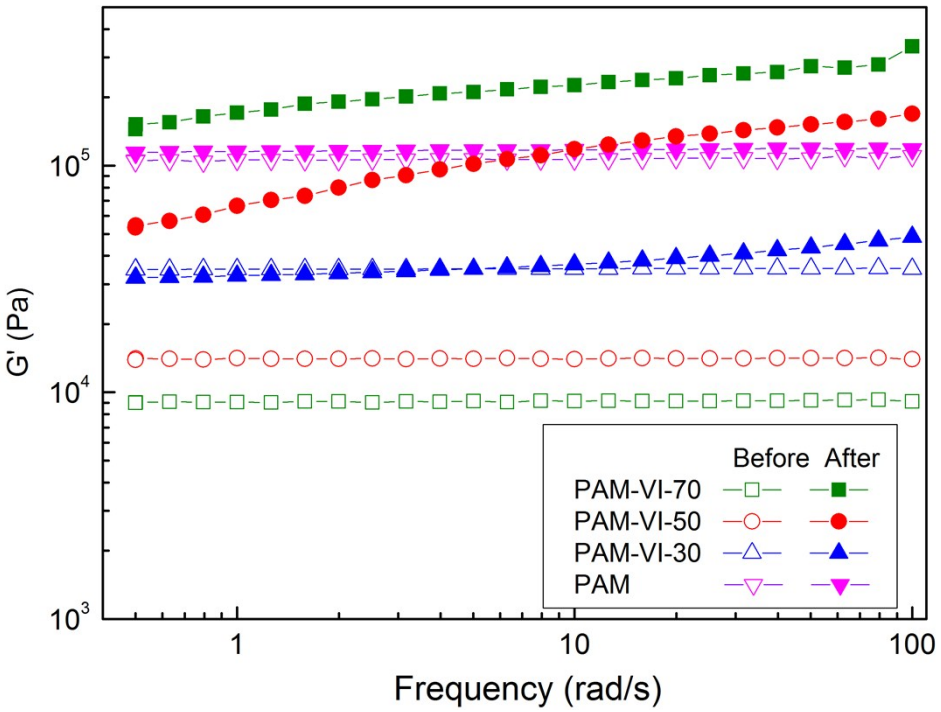

Fig. S1 Storage moduli of hydrogels with different N-vinylimidazole before and after immersion in the solution of 10 mM Zn^{2+} and 20mM PAG.

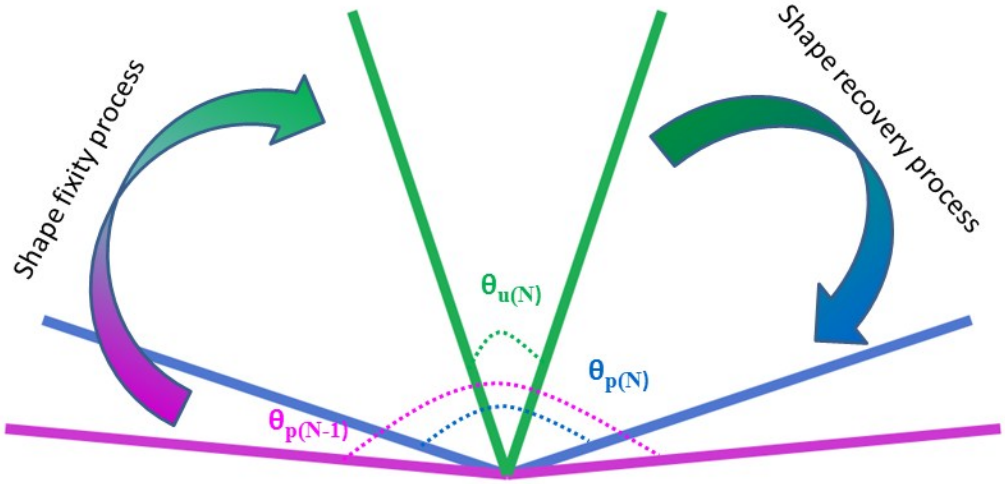

Fig.S2 Illustration of $\theta_{u(N)}$, $\theta_{p(N)}$ and $\theta_{p(N-1)}$ for the calculation of shape fixity ratio (R_f) and shape recovery ratio (R_r). Note: for clearity, the difference between $\theta_{p(N-1)}$ and $\theta_{p(N)}$ is exaggerated.

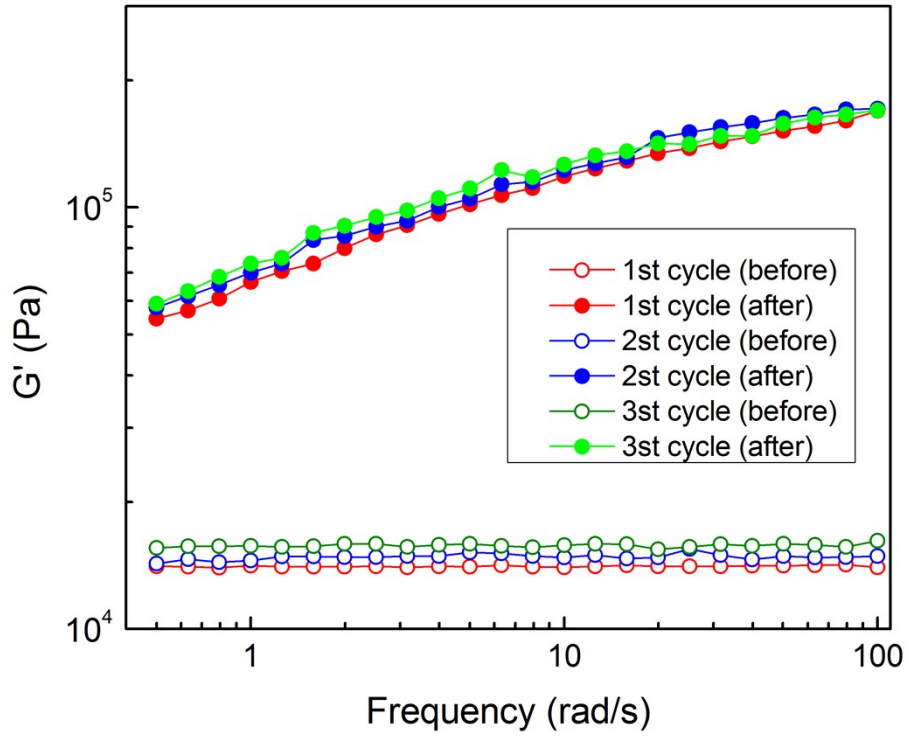

Fig.S3 Frequency sweep of G' of the PAM-VI-50 hydrogel before and after immersion in ZnSO4-PAG solution in three cycles.

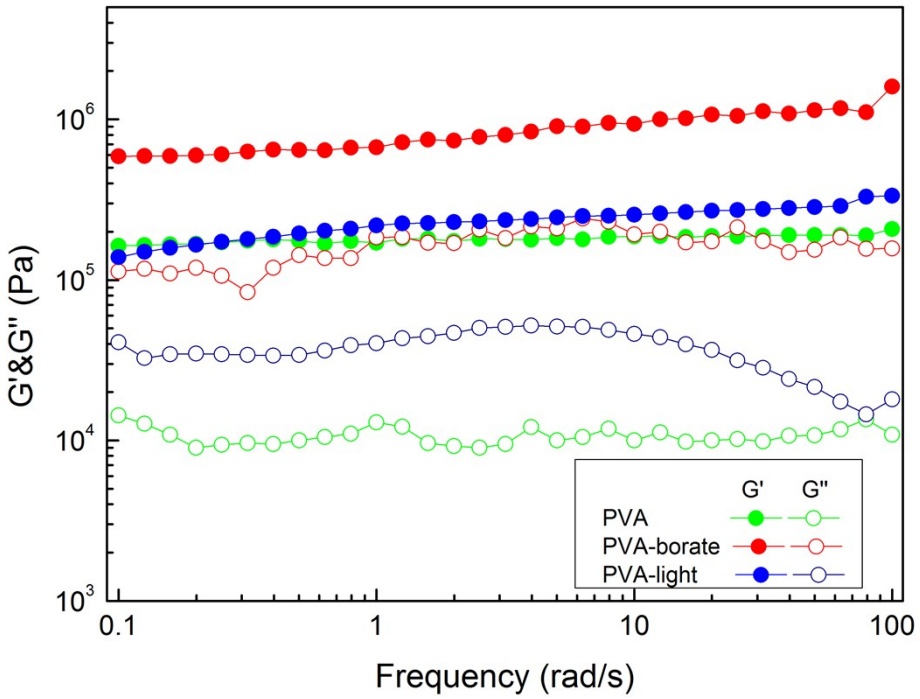

Fig.S4 Frequency sweep of three hydrogels: pristine PVA hydrogel, PVA hydrogel cross-linked with 10 mM borax and UV treated PVA-borate hydrogel.