Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

A multi-functionally zwitterionic hydrogel with unique micro-structure, high elasticity and low modulus

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This PDF file includes:

Other Supplementary Material for this manuscript includes the following:

Materials and Experimental Methods

Materials.

Dimethylaminoethyl methacrylate (DMAEMA; 98%), 1,3-propane sultone (PS; 98%), acrylamide (AM; 99%), *N,N*-methylene-bisacrylamide (Bis; 99%), ammonium peroxydisulfate (APS; 98%) and *N,N,N',N'*-tetramethyl-ethylenediamine (TEMED; 99%), phosphate-buffered saline (PBS) were purchased from Sigma-Aldrich Chemical Reagent Co., Ltd, Bovine Serum Albumin (BSA), fluorescein isothiocyanate (FITC; 97%), ammonium chloride (NH_4Cl; 99.5%), sodium carbonate (99.5%), sodium bicarbonate (99.5%), anhydrous dimethylsulfoxide (DMSO; 99.7%) were purchased from Maikelin Chemical Reagent Co., Ltd. All the chemicals were used without further purification. Dialysis bag (MW=3500) was purchased from Spectrum Laboratories. In all experiments, deionized water was used.

Synthesis of SBMA.

A certain amount of DMAEMA was put into a round-bottom flask, then PS (molar ratio of DMAEMA and PS is 1.15:1) was dropped into the flask slowly at room temperature under stirring. After that, the reaction was continuously stirred for 1h at room temperature and the product was obtained without any after-treatment. The structure of the product was characterized by nuclear magnetic resonance spectrometer (Bruck Ascend 400) operating at 400 MHz.

Preparation of PSBMA hydrogel.

The monomer SBMA and crosslinker Bis were mixed with deionized water and stirred for 0.5h at the temperature of 0 ^{o}C, then the initiator APS and the accelerator TEMED were added into the mixture and stirred for 10 min. The mixture was poured into a mold and kept in an ice bath for another 5 h to complete gelation, then the hydrogel was obtained after taking out from the mold. The mass ratio of H_2O/SBMA/Bis/APS/TEMED is 15 g/15 g/20 mg/20 mg /5 μl. The crosslinking ratio is 0.066%.

Characterization of the structure of PSBMA hydrogel.

The structure of the freeze-dried PSBMA xerogel was characterized by a high-resolution scanning electron microscope (FESEM, Zeiss Sigma, operation voltage of 2 keV). The sample was sputtered with gold with a thickness of deposition as a conductive coating for imaging purposes.

Mechanical tests.

Mechanical tests were conducted at 25 °C using an MTS (model E44, EXCEED) testing machine. For the tensile test, the samples were of rod-like shape 50 mm in length and 3.26 mm in diameter. The stretched portion of the samples between the two clamps was 10 mm, and the samples were elongated at a loading rate of 10 mm/min. For the compression tests, cylindrical samples of the as-prepared hydrogels were used, with dimensions of 10 mm in diameter and 8.8 mm in height, speed was 1 mm/min, and stopped at the height of 8.8 mm.

Self-healing of PSBMA hydrogel: hydrogel was cut into two pieces firstly, then two fractured hydrogels were pressed to contact with each other and packaged by foil, finally heated in an oven for 12 h at the temperature of 90 °C.

Protein adsorption experiment.

Preparation of FITC-BSA solution [1]: Firstly, a solution of 20 mL sodium carbonate-sodium bicarbonate buffer in 0.1 mol/L (pH=9) was prepared. Then 4 mg BSA was added into 2 mL sodium carbonate buffer and placed in the dark. 1 mg FITC was dissolved in 1 mL anhydrous DMSO under ice bath and then added into 2 mL BSA solution. After storing for 8h in the dark under ice bath, 8.04 mg NH_4Cl was added into the mixture and stirred for 2h in the dark under an ice bath. The mixture was then dialyzed against deionized water using dialysis bag for 3 days in the dark (deionized water was changed every 6 h). Finally, the FITC labelled BSA solution (FITC-BSA) was obtained.

Preparation of PAM hydrogel: The monomer AM and the crosslinker Bis were mixed with deionized water and stirred for 0.5h at the temperature of 0°C, then the initiator APS and the accelerator TEMED were added into the mixture and stirred for 10 min. The liquid was poured into the mold and stood for 24h at room temperature. The mass ratio of H_2O/SBMA/Bis/APS/TEMED is 6 g/1.5 g/2 mg/2 mg/1 μL.

Incubation and reincubation of hydrogels in FITC-BSA solution [2]: PAM hydrogel and PSBMA hydrogel (diameter in 3.5 mm and thickness in 1 mm) were individually taken into 1 mL FITC-BSA solution and incubated for 48h in the dark. Then the hydrogels were taken out and reincubated in 10 mL PBS solution. The hydrogels were photographed by a confocal laser microscope (Leica TCS-SP8) every 30 min. The normalized fluorescence intensity for the square (50 μm × 50 μm) of hydrogel was obtained by the integration of the fluorescent profiles by NIS Elements.

Electromechanical response tests of PSBMA hydrogel

Electromechanical response tests were conducted by machine of precision source (Angilent KEYSIGHT 2902B). During the tests, setting voltage to 1V, changes of current were recorded by the machine while the hydrogels were stretched or compressed (Fig. S3a).

Fasten of hydrogel on stretching instrument: firstly, hydrogel with 30 mm in length, 10 mm in width and 1 mm in thickness was fixed on the substrates of the stretching instrument (the stretched portion of the hydrogel between the two substrates was 4 mm), and the Pt electrodes were attached on both endings of the hydrogel. The endings of the hydrogel and the Pt electrodes were fixed by ive copper foil tape. During the tests, the stretching pace of the hydrogel was controlled by the knob of the stretching instrument (Fig. S3 b).

Electromechanical response test to stepwise deformation of 500% stretch: During the test, the hydrogel was stretched at a stretching rate of 1mm/s, and the stretching would be stopped for several seconds every time when the stretching length was increased for 100% original length. The test was completed when the hydrogel was stretched to 500% strain.

Electromechanical response test to cyclic deformation of 100% stretch: hydrogel was subjected to cyclic stretching by 100% strain at a stretching rate of 1 mm/s and recovery.

Electromechanical response test to compressive deformation: firstly hydrogel with 10 mm in length, 10 mm in width and 1 mm in thickness was fixed under the keyboard panel of the keyboard test machine (1001V10), then the Pt electrodes were attached on the top and bottom of the hydrogel, and the edges of the keyboard panel were fixed by adhesives (Fig. S3 c-d). During the test, the compression bar was cyclically compressed and rise at a frequency of 5000 times/h and with medium compressive strength.

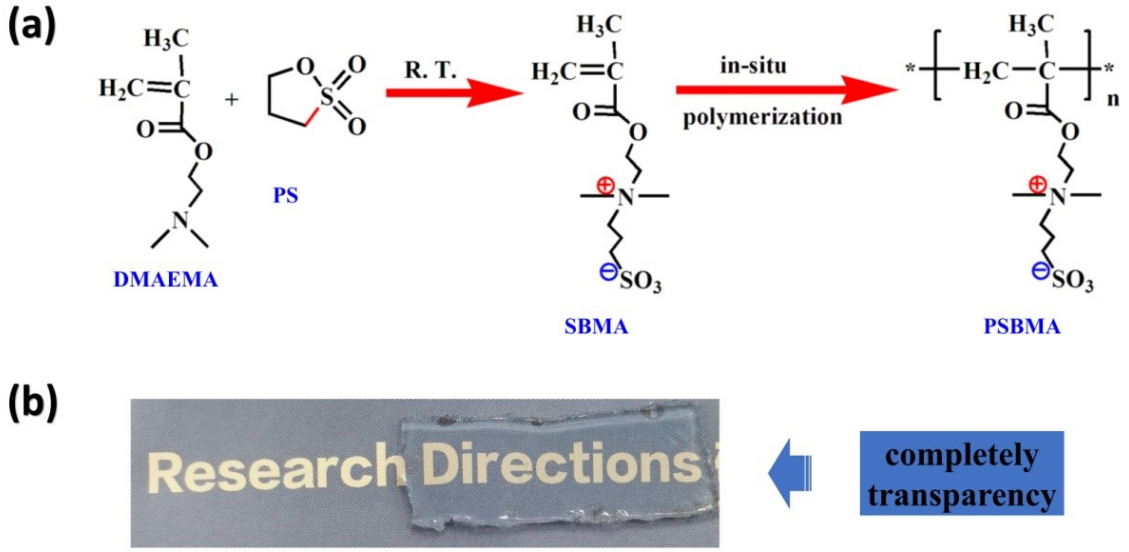

Fig. S1 (a) Synthetic route of PSBMA; **(b)** Appearance of PSBMA hydrogel.

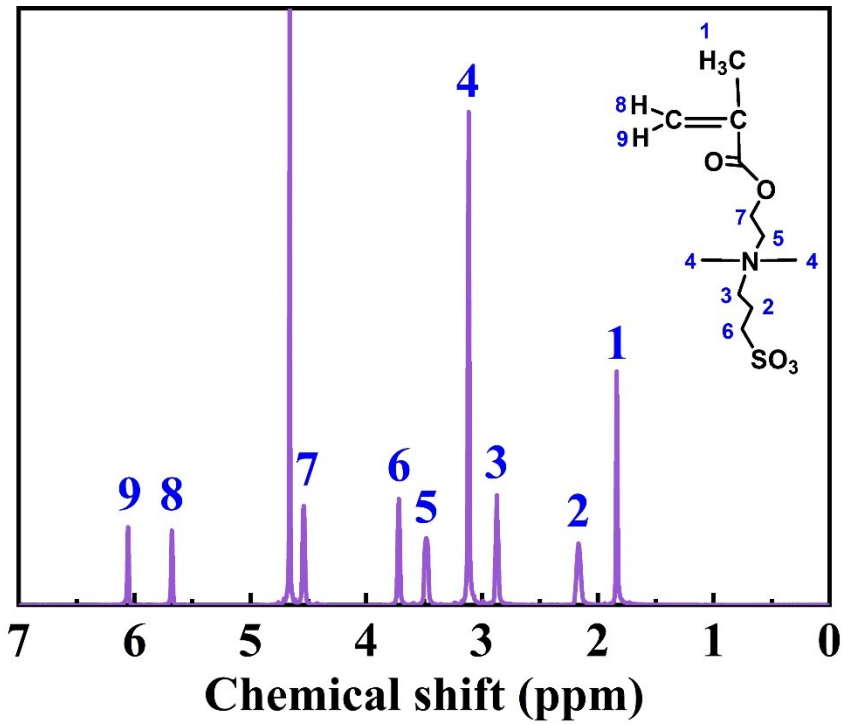

Fig. S2 ^{1}H NMR spectra of SBMA.

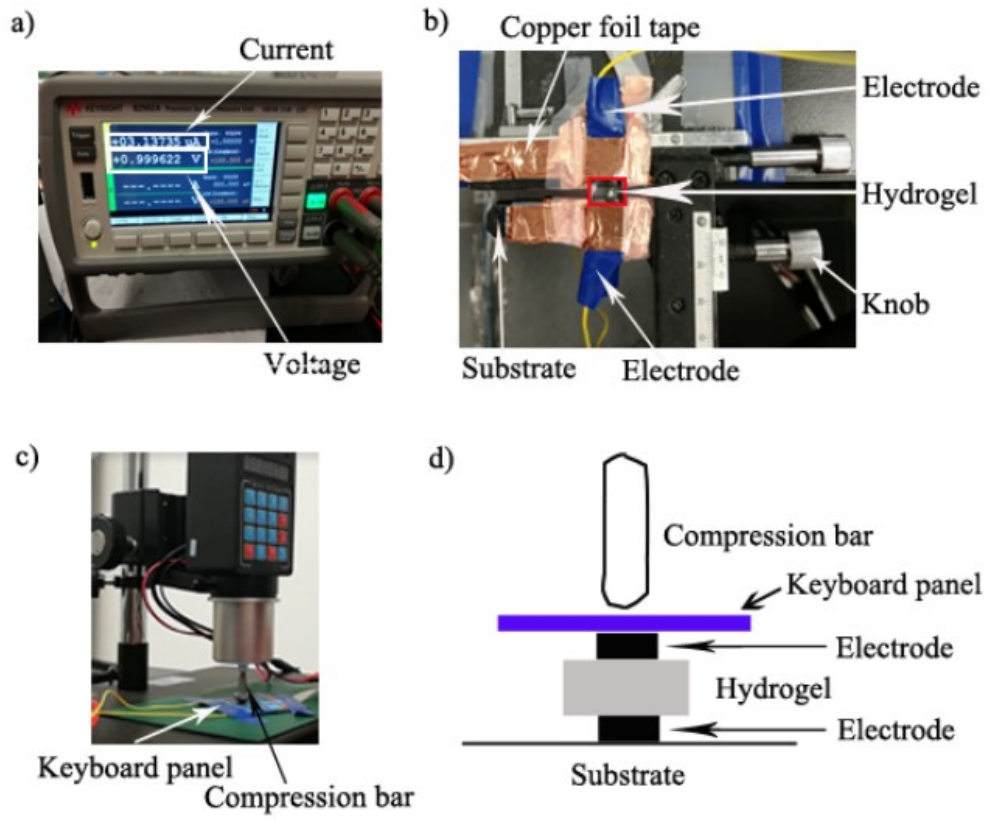

Fig. S3 Electromechanical response tests of PSBMA hydrogel. **a)** the machine of precision source for electromechanical response tests; **b)** Fasten of hydrogel on stretching instrument; **c)** compressive instrument; **d)** the cross section under keyboard panel.

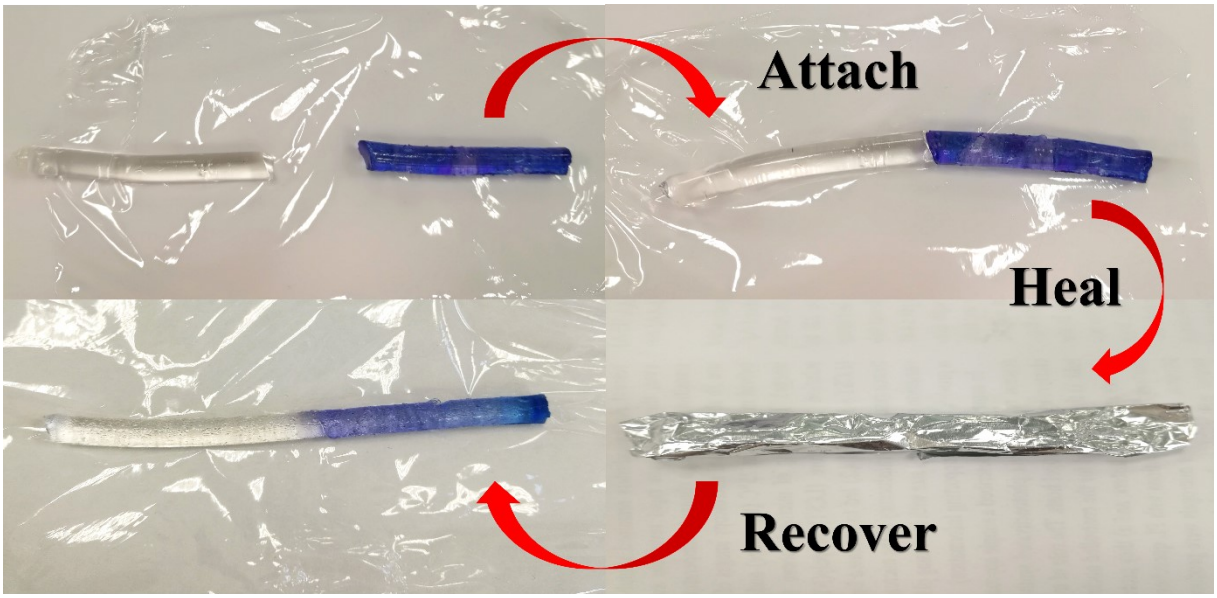

Fig. S4 The healing procedures of PSBMA hydrogel.

Table S1 Mechanical properties comparison of PSBMA hydrogel with other hydrogels.

Hydrogel	Tensile		Compressive			Ref.
	Stress (KPa)	Strain	Stress (MPa)	Strain	Modulus (KPa)	
PSBMA	53	1211%	7.19	100%	8.79	This work
PAM	110	700%	0.8	65%	39	[3]
PMAEMA	7	80%	0.25	60%	7	[4][5]

Movie S1

A hair was folded in half and compressed into PSBMA hydrogel.

Movie S2

The hydrogel was compressed by 100% strain under loading and then recovered to original size while loading was removed.

References

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