

Supporting Information

Hydrogels with Ultra-Highly Additive Adjustable Toughness Under Quasi-Isochoric Condition

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Experimental Section

Materials

Acrylamide (AAm) was used as received from Tokyo Chemical Industry Co., Ltd.; isobornyl acrylate (IBA), 1,4-butandioldiacrylate (BDA), dimethyl sulfoxide (DMSO), salts, and acid were purchased from Macklin; hydroxyethyl acrylate (HEA), phenyl acrylate (PA), and benzyl acrylate (BA) were purchased from Macklin; N-acryloyl-glycinamide were used as received from Bide Pharmatech Ltd. α -ketoglutaric acid (α -keto) and organic additives were purchased from Aladdin. All the inorganic additives were purchased from Shanghai Macklin Biochemical Co., Ltd.

Hydrogel preparation

The P(IBA-*co*-AAm) hydrogel was prepared by one-pot radical polymerization of the monomers (AAm, IBA) in DMSO solution with BDA as a crosslinker and α -keto as an initiation. Briefly, a requested amount of AAm (2 M), IBA (38 wt%), BDA (0.5%), and α -keto (0.2%) were added into DMSO solution in succession and stirred by ultrasonic radiation for 3 min to obtain a uniform precursor solution. Afterward, the mixture solution was transferred into sandwich-like reaction cells that were assembled by two glass plates and silicone rubber (1 mm) in the middle. After UV light irradiation at 365 nm for 8 h, a transparent organogel was obtained. Thereafter, the as-prepared organogel was immersed in deionized water to afford the P(IBA-*co*-AAm) hydrogels. The water was replaced twice a day for a week to wash the organic residue and reach the swelling equilibrated state.

To investigate the influence of additives on the mechanical properties of hydrogels, the

P(IBA-*co*-AAm) hydrogels were soaked into a large amount of aqueous solution for 2 days to reach swelling equilibrium at 40 °C.

Fabrication of hydrogel sensors

The P(IBA-*co*-AAm) hydrogels with additives were cut into strip-like samples. Then two pieces of conductive copper taps were tightly adhered to the opposite ends of the hydrogel to assemble electrodes. Lastly, the transparent adhesive tapes were used to encapsulate the hydrogel into a sandwich-like sensor. The adhesive tapes could minimize the water-lose of hydrogel to ensure stable current signals.

Uniaxial tensile test

The mechanical properties of hydrogels were measured on a commercial tensile tester (Shimadzu, brand type AGX-V, Japan). For tensile tests, the samples were cut from equilibrated hydrogel sheets into dumbbell shapes with an initial gauge length of 12 mm and width of 2 mm. The tensile tests were performed at a given temperature with a fixed stretching speed of 100 mm min⁻¹. The hydrogels' surfaces were covered with silicone oil to prevent drying in the air during prolonged measurement periods. The nominal engineering stress (σ) and strain (ε) were recorded, in which the stress was defined as the tensile force divided by the original cross-section area of the sample, and the strain was defined as the displacement of the cross-head divided by the gauge length of gel sample. Young's modulus (E) was calculated from the initial slope of the stress-strain curve with a strain of about 4~10%. To explore the temperature-responsive mechanical properties of P(IBA-*co*-AAm) hydrogels, tensile tests were performed at various temperatures from 25 °C to 80 °C. In addition, cyclic tensile tests

were performed in a water bath with a certain temperature.

Rheological behavior

Rheological behaviors of the equilibrated hydrogels were analyzed using a commercial tester (TA Ares G2) under the Oscillation Temperature Ramp mode, at a fixed frequency of 1 Hz (in the linear region), a strain of 0.1%, and a heating rate of 2 °C/min. Typically, the temperature scale ranges from 5 °C to 95 °C. All the samples were cut into uniform disk-shaped specimens ($D = 7.5$ mm) at swelling equilibrated states. The transition temperature values of hydrogels are defined by the peak in $\tan\delta$.

Measurement of water content

Swollen hydrogels were tested with a Halogen moisture meter (Furbs, model FK-20A, China) for water content.

$$\text{water content} = \frac{W_0 - W_d}{W_0} \times 100\%$$

The surface water of a saturated hydrogel was carefully wiped using tissue paper and W_0 was measured. The test conditions were at 130 °C for 20 min and the final weight W_d was obtained.

Differential scanning calorimeter (DSC) test

The thermal behavior of the equilibrated hydrogels was measured by using a differential scanning calorimeter (DSC, TA, 2500). The sample with a mass of ~10 mg was sealed in an aluminum DSC pan and scanned under a nitrogen atmosphere from 10 to 150 °C with a heating rate of 10 °C/min.

Conductive performance tests

The square hydrogel with a side length of 1 cm was prepared for the measurement of

electrical conductivity (σ , S/m). Before the test, the hydrogel was assembled into a sandwich-like shape with two stainless steel sheets. The conductive performance of hydrogels was tested by Gamry electrochemical impedance spectroscopy (EIS) utilizing an electrochemical workstation (Gamry Reference 600+). EIS was performed in the frequency range from 1.3×10^6 to 5×10^0 Hz. The conductivity was calculated according to the following formula:

$$\rho = \frac{L}{S * R_L}$$

Where ρ (mS cm^{-1}), R_L (Ω), L (cm), and S (cm^2) are the conductivity, resistance obtained by the intercept with the x-axis in Nyquist fitting plots, the thickness of hydrogel, and the electrode area, respectively.

For the measurement of human activity-related signals, hydrogel-based sensors were attached to the corresponding epidermis parts. The Keithley DMM 6500 was connected to the hydrogel-based sensors for relative resistance changes synchronous detection.

Anti-icing tests

The anti-icing performance of hydrogel was estimated by measuring ice adhesion strength. The sample (5 mm \times 2 mm \times 0.7 mm) adhered to a glass (10 mm \times 10 mm \times 45 mm). Three independent measurement models with deionized water (1 mL) were utilized to calculate the ice adhesion strength on each sample. These samples were kept at 5 °C for 2 h to ensure the complete freezing of water. The anti-icing strength was measured by using digital dynamometers (HP-20) for removing the ice from the surfaces of the samples.

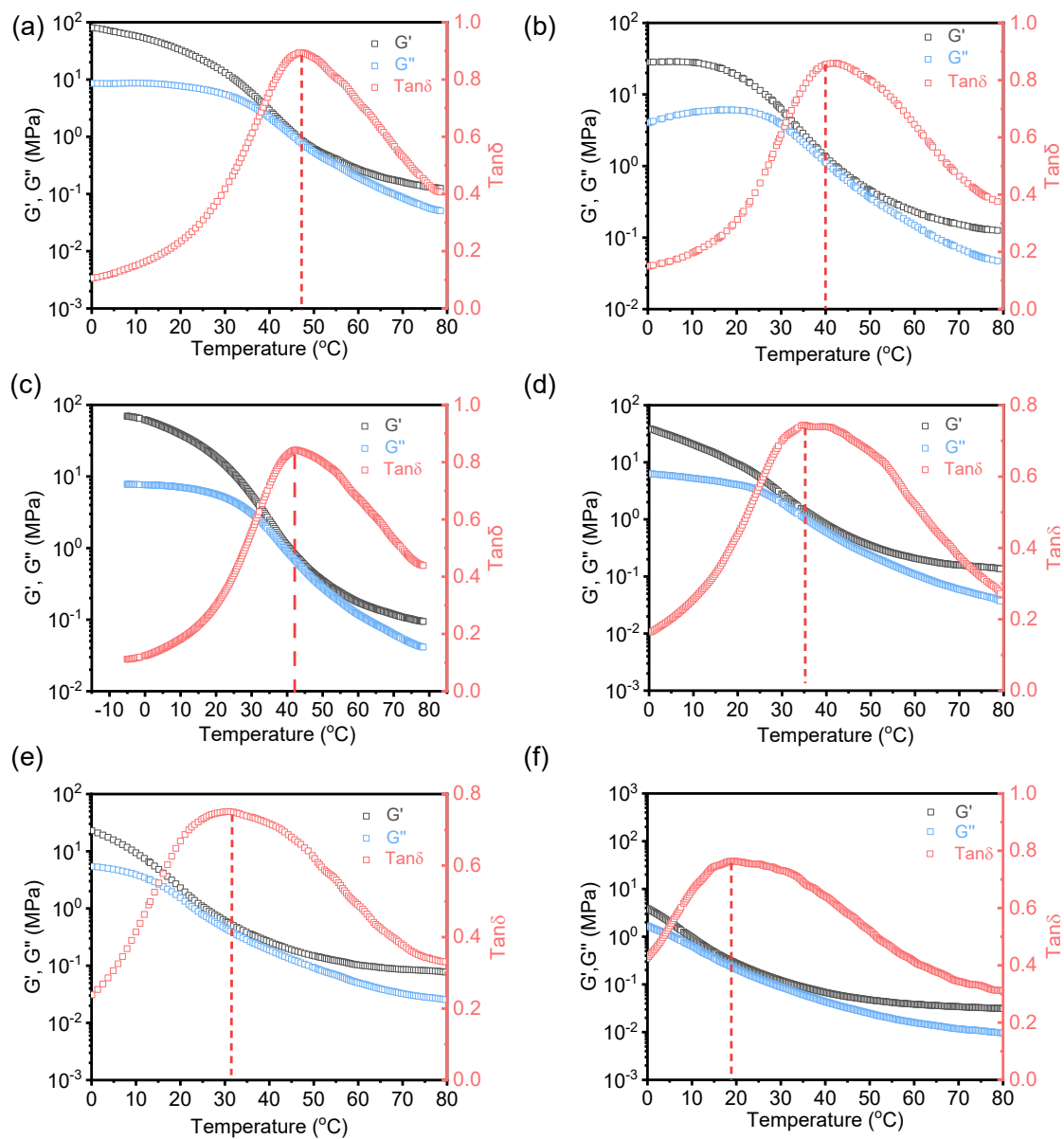


Figure S1. Variation of G' , G'' and $\tan\delta$ as a function of the temperature of P(IBA-co-AAm) hydrogels immersed in (a) K_2SO_4 , (b) KH_2PO_4 , (c) KCl , (d) KBr , (e) KI , (f) $KSCN$ solutions.

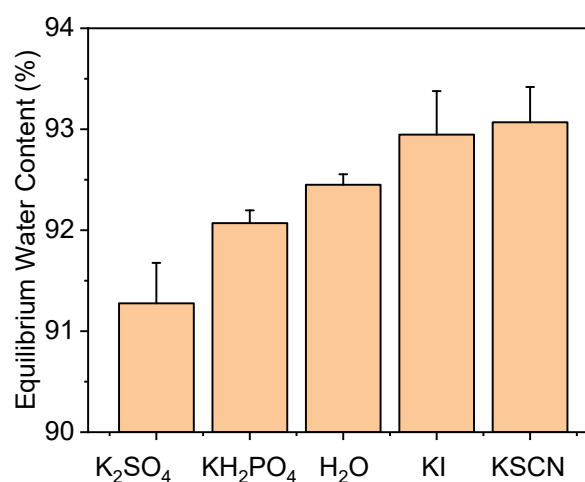


Figure S2. Hydration level of pure PAAm hydrogels in different aqueous media at swelling equilibrated states at 25 °C.

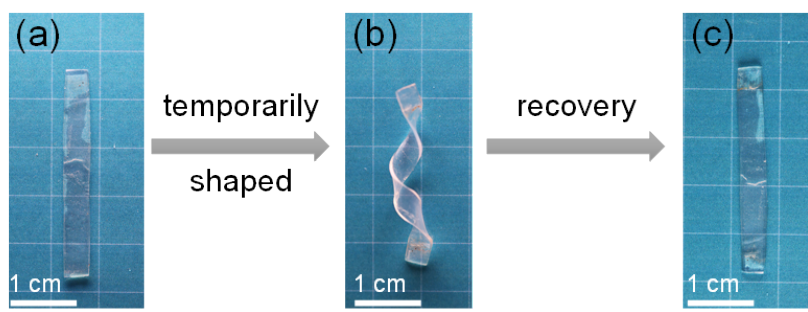


Figure S3. Shape memory property of P(IBA-*co*-AAm) hydrogels at 25 °C. (a) A hydrogel strip was cut and immersed in KSCN solutions (1 M). (b) The hydrogel strip was temporarily shaped by fixed at a specific shape and immersed in K_2SO_4 (0.7 M) solutions overnight. (c) The shape sample was readily recovered to its original shape by another immersion process in KSCN solutions (1 M) for 4 h.

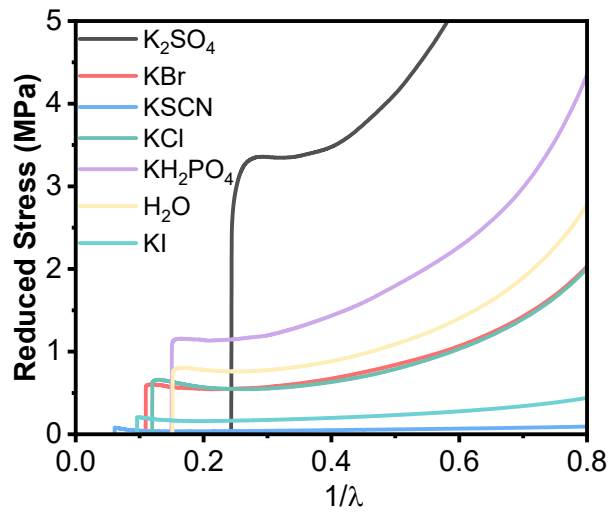


Figure S4. The Mooney-Rivlin plot of P(IBA-co-AAm) hydrogels treated with various potassium solutions. The reduced stress is defined as the ratio between the nominal stress with $(\lambda - 1/\lambda^2)$, where the λ is specified as the deformed length divided by the initial length ($\lambda = \text{strain} + 1$).

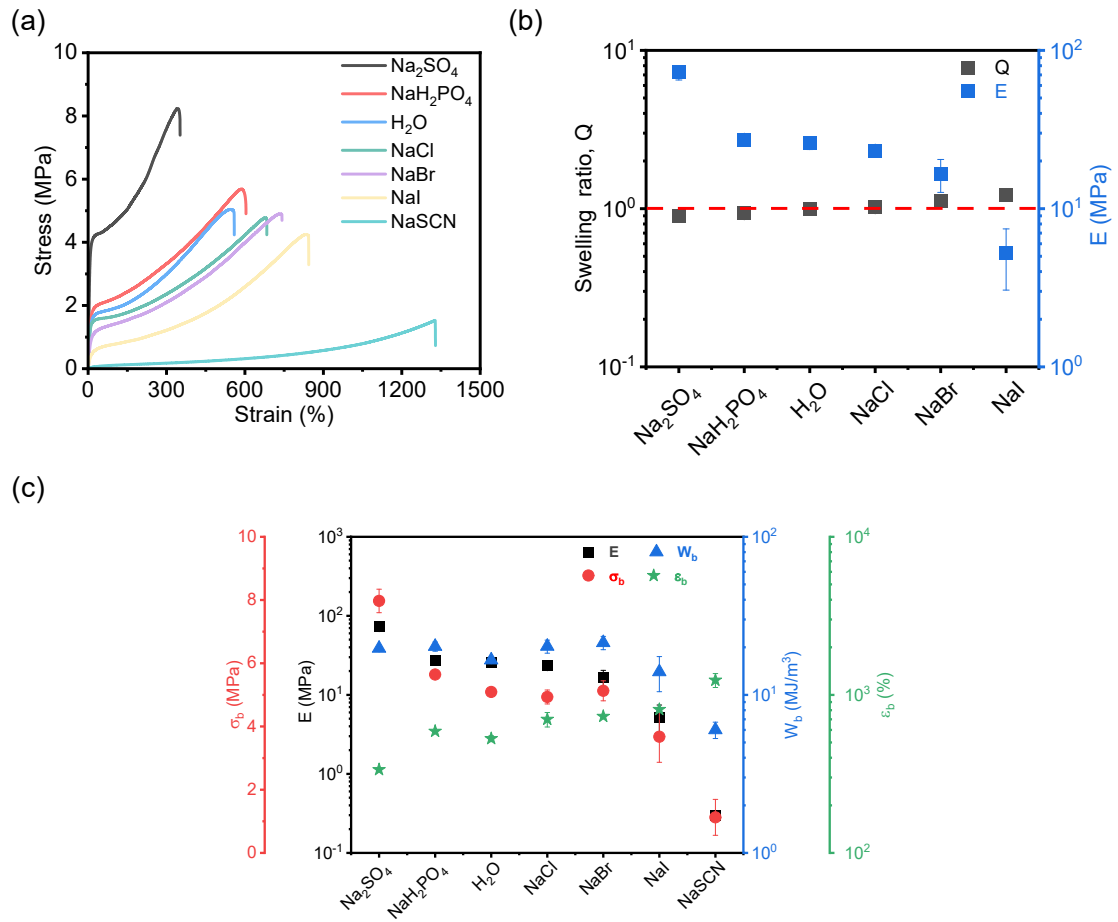


Figure S5. (a) uniaxial tensile stress-strain curves, (b) the corresponding swelling degree, and (c) the mechanical properties of P(IBA-co-AAm) hydrogels immersed in various sodium solutions (1 M).

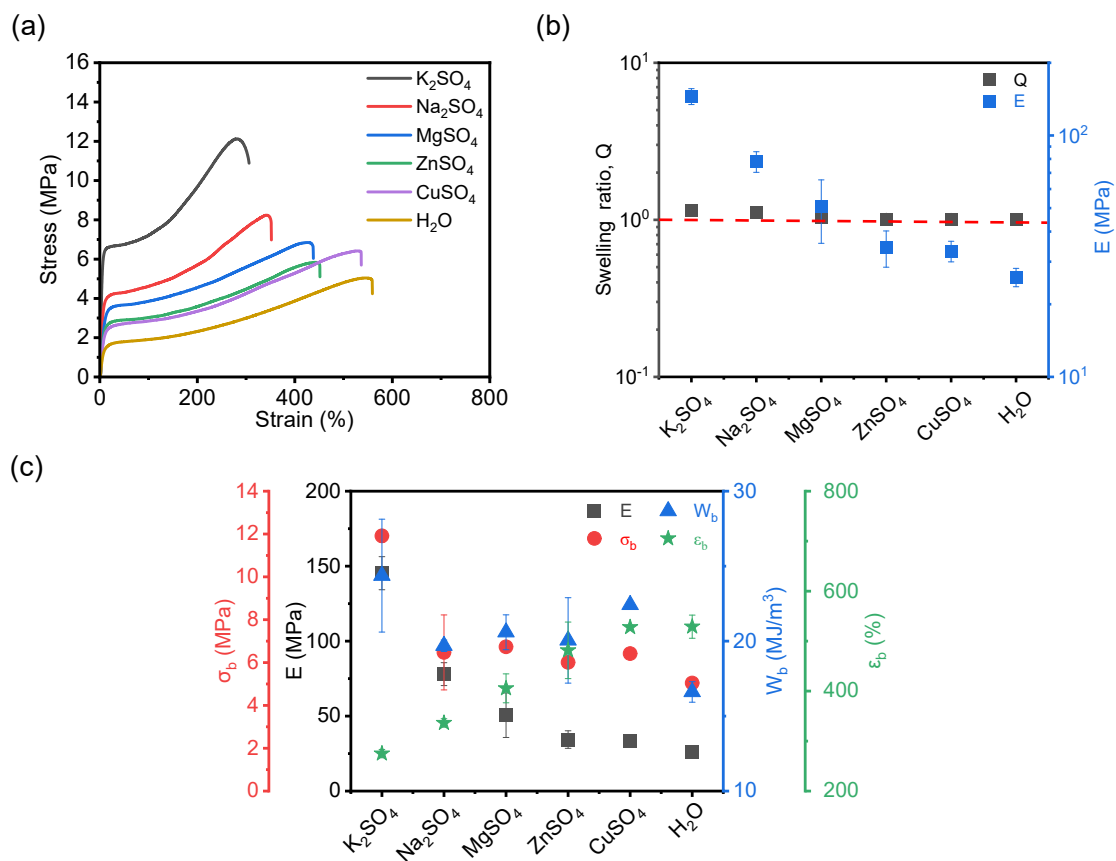


Figure S6. Mechanical parameters and uniaxial tensile performance of the P(IBA-co-AAm) hydrogels equilibrated in different sulfate aqueous solutions (1 M, 25 °C, stretch rate: 100 mm.min⁻¹).

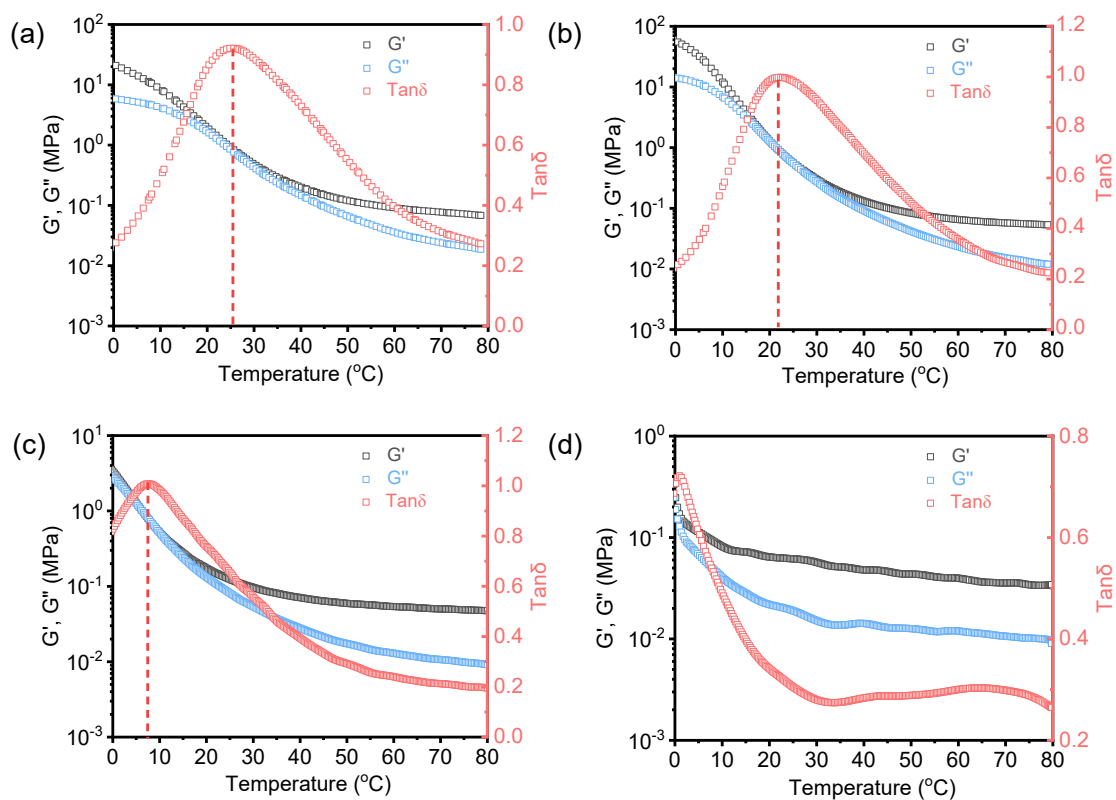


Figure S7. Variation of G' , G'' and $\tan\delta$ as a function of the temperature of P(IBA-co-AAm) hydrogels soaked in 1 M (a) formic acid (FAC), (b) acetic acid (AAc), (c) propionic acid (PAc), (d) butyric acid (BAc) solution.

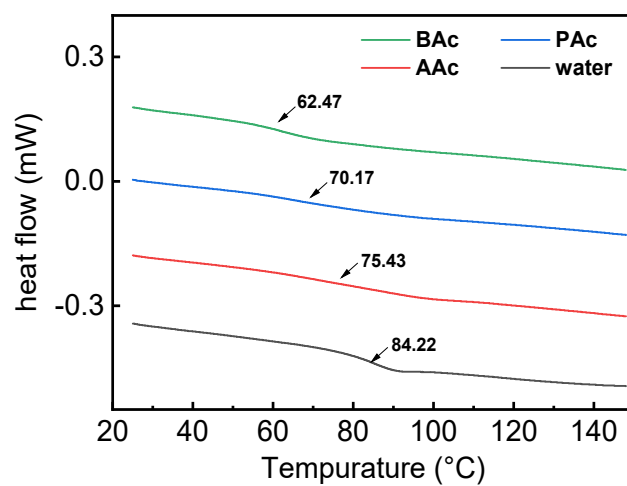


Figure S8. Glass transition of PolyIBA network with small amount of organic additives. (determined by DSC, additive concentration: 10 wt%). Note that no solvent is integrated in the systems.

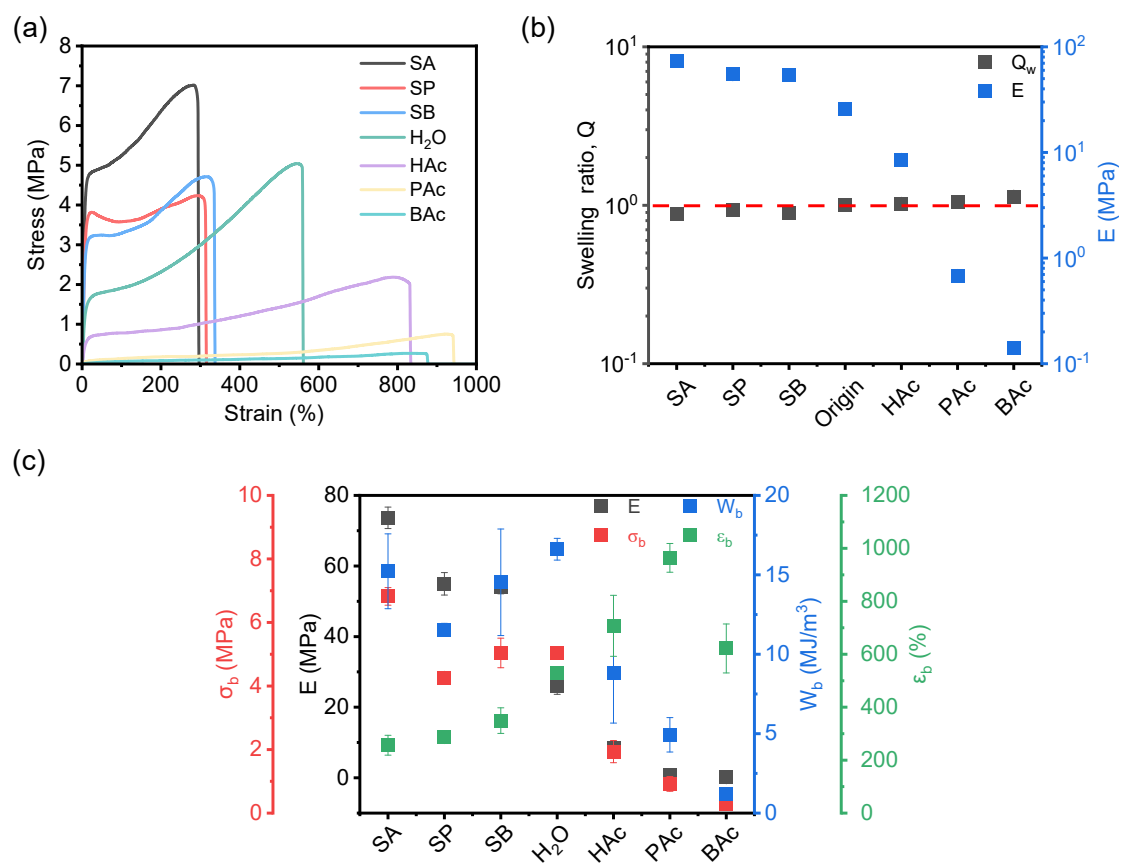


Figure S9. (a) uniaxial tensile stress-strain curves, (b) the corresponding swelling degree, and (c) the mechanical properties of P(IBA-co-AAm) hydrogels treated with different organic acid sodium and organic acid solution (1 M).

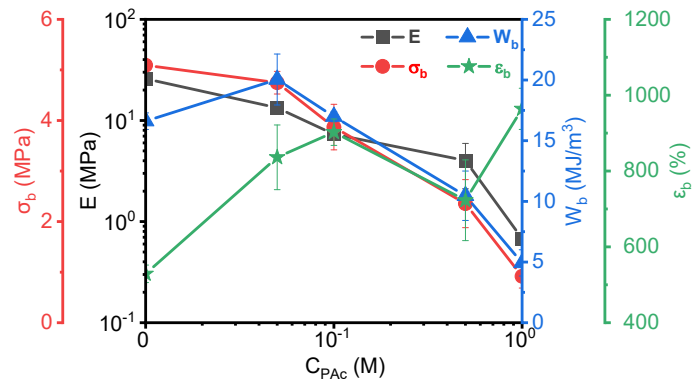


Figure S10. The mechanical properties of P(IBA-co-AAm) hydrogels soaked in 0, 0.05, 0.1, 0.5, and 1 M propionic acid (PAC) solutions.

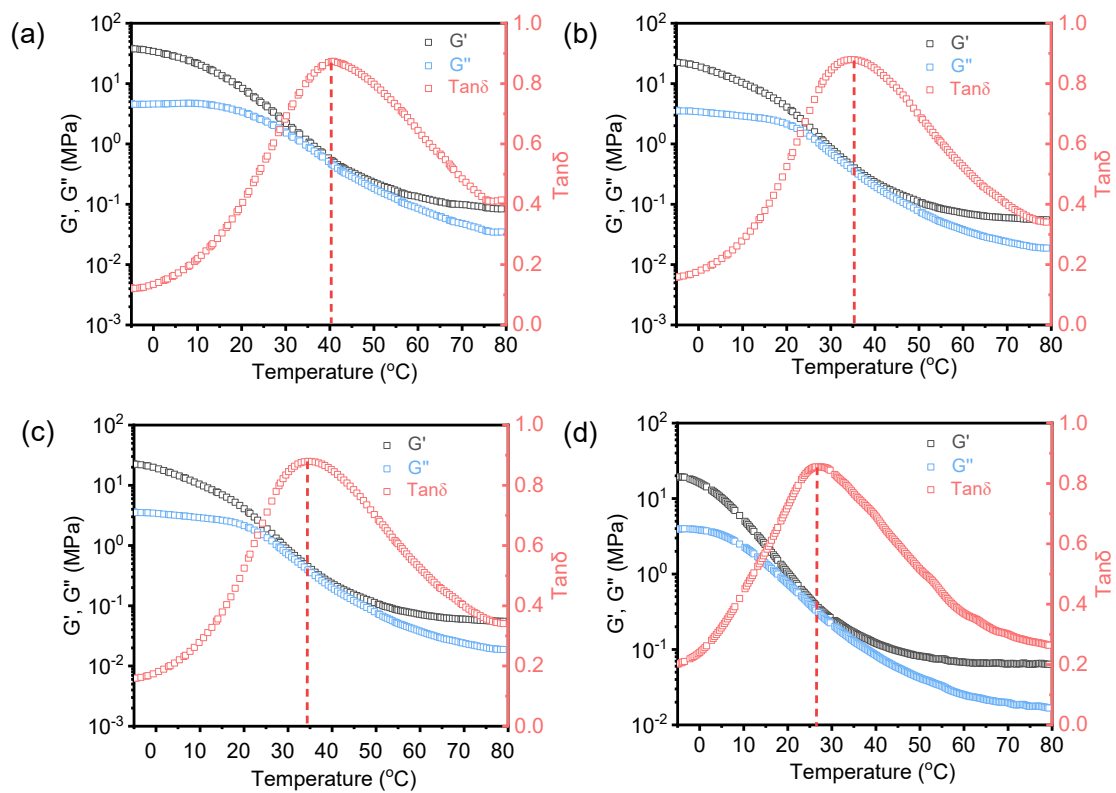


Figure S11. Variation of G' , G'' and $\tan\delta$ as a function of the temperature of hydrogels soaking in (a) 0.01 M, (b) 0.05 M, (c) 0.1M, (d) 0.5 M propionic acid solution.

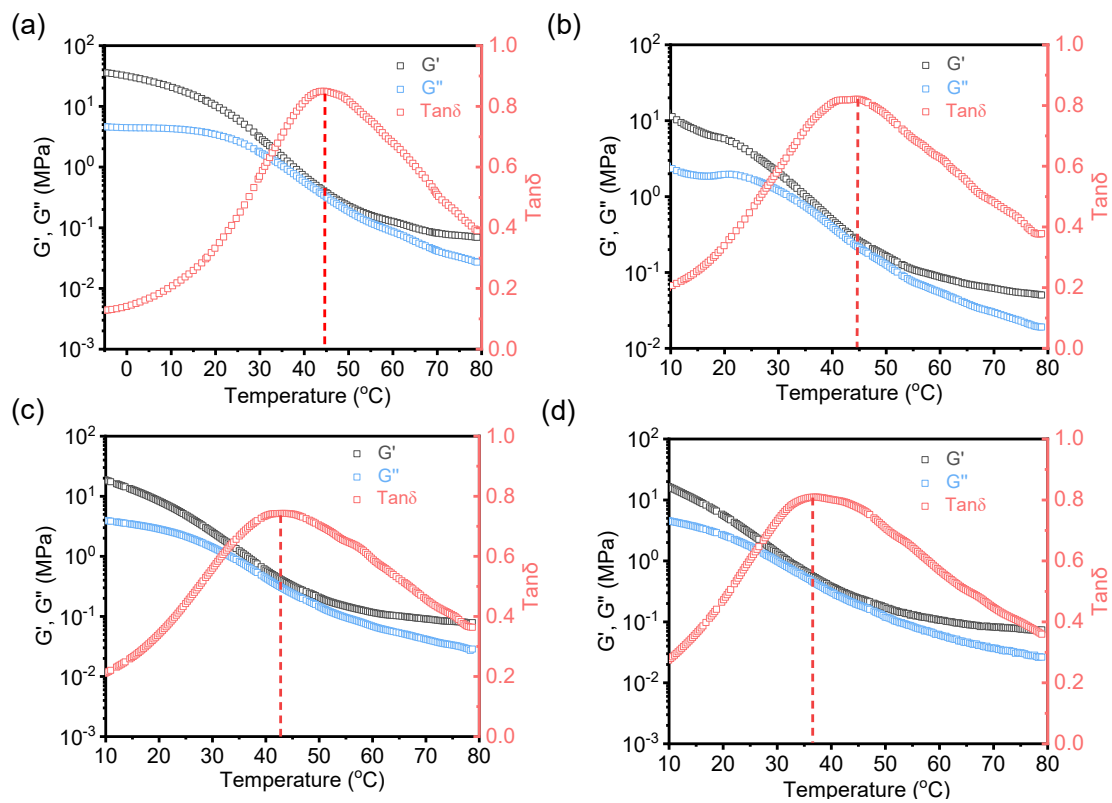


Figure S12. Variation of G' , G'' and $\tan\delta$ as a function of the temperature of hydrogels immersed in (a) 0.05 M, (b) 0.1 M, (c) 0.5 M, (d) 1 M KSCN solutions.

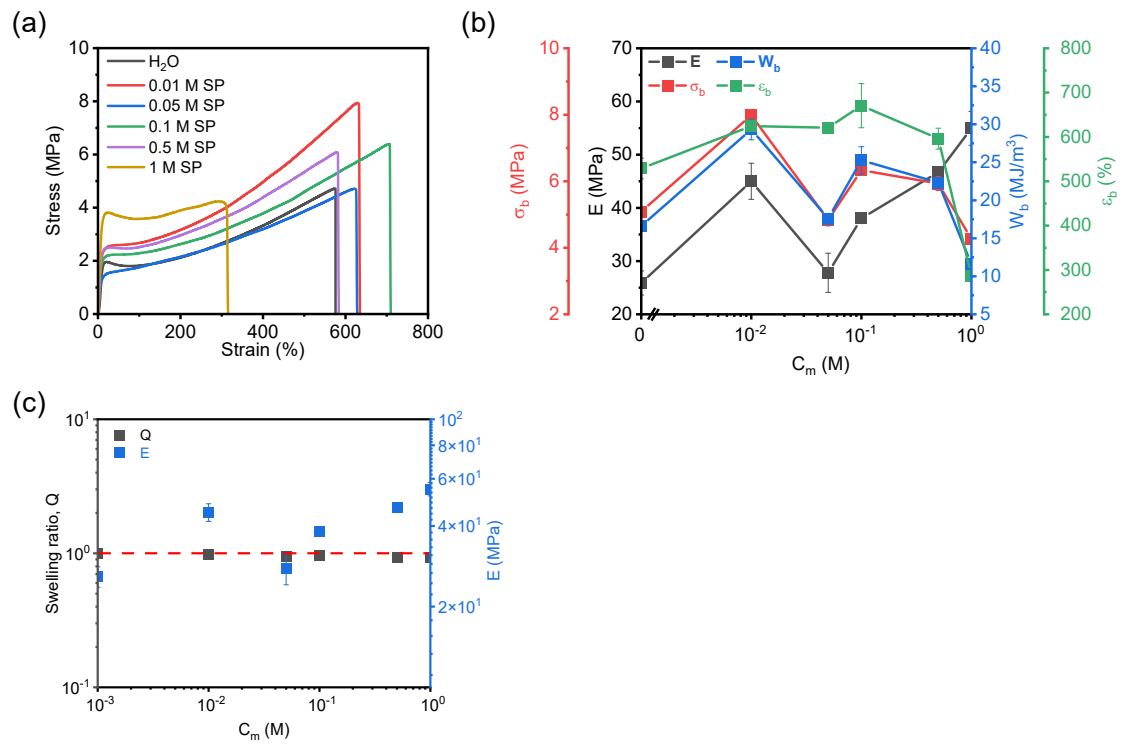


Figure S13. (a) Uniaxial tensile stress-strain curves, (b) the corresponding mechanical properties, and (c) the swelling ratio of P(IBA-co-AAm) hydrogels soaked in sodium propionate (SP) solutions.

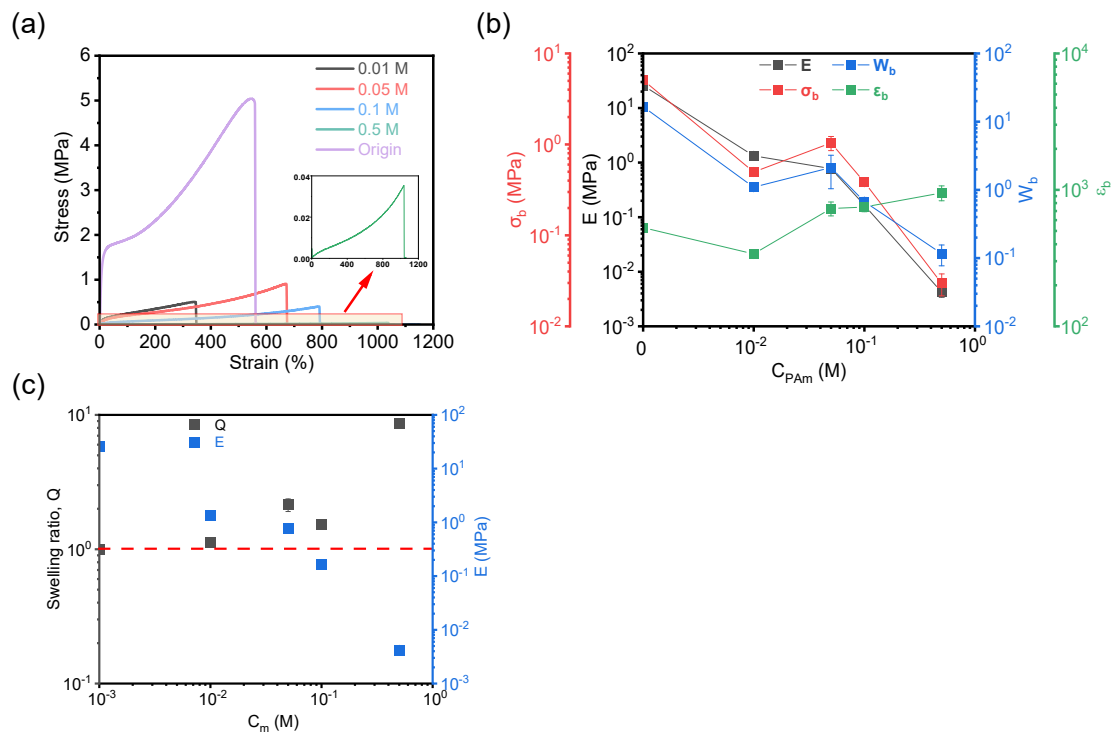


Figure S14. (a) Uniaxial tensile stress-strain curves, (b) the corresponding mechanical properties, and (c) the swelling ratio of P(IBA-co-AAm) hydrogels soaked in an *n*-propylamine (PAm) solutions.

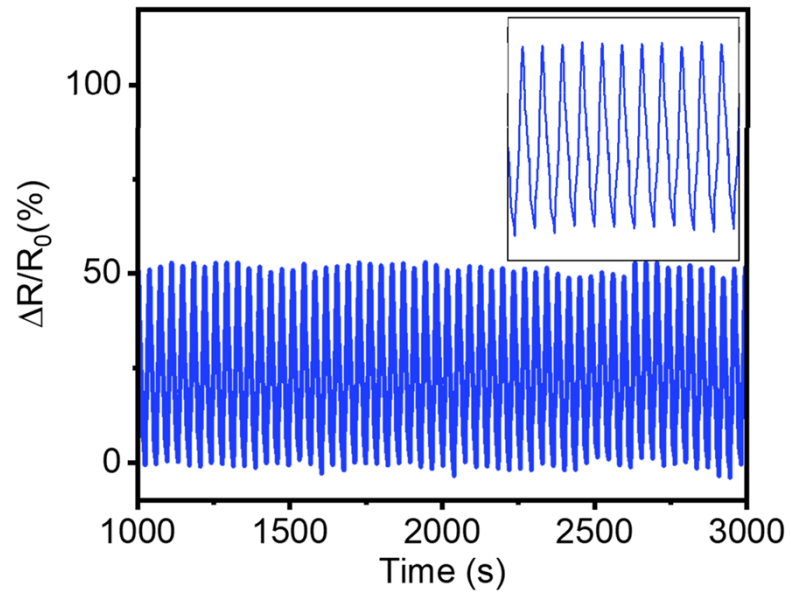


Figure S15. Response of the P(IBA-*co*-AAm) hydrogels with KSCN to repeated loading and unloading of 200% strain for 3000 s. Part of the result is zoomed in for clarification.