Supplementary Information (SI) for Materials Horizons.

Supporting information

Molecular engineering of backbone rotation in an energy-dissipative hydrogel for combining ultra-high stiffness and toughness

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Materials and Methods

Materials. Methacrylamide (MAAm), ammonium persulfate (APS) and chitosan oligosaccharide lactate (M_n = 5000 g mol^{-1}) were purchased from Sigma Aldrich. Acrylamide (AAm) and acrylic acid (AAc) were purchased from Merck. $Fe(NO_3)_3 \cdot 9H_2O$ was purchased from Fisher Scientific and Na_2SO_4 from Bio-lab ltd. N,N,N',N'-tetramethylethylenediamine (TMEDA) from Acros Organics. Deionized water (Merck Millipore) was used for all experiments. All the chemicals were used as received.

Hydrogel preparation. Dual cross-linked hydrogels were synthesized using conventional three-step method.[1] Various molar ratios of acrylic acid (AAc: 10%, 15% and 20%, relative to methacrylamide), chemical crosslinker MBAA (0.06 mol% relative to total monomer) were dissolved in 2.4 M MAAm solution in deionized water. The solutions were purged with nitrogen gas, initiator APS (1 wt%, relative to total monomer) accelerator TMEDA (20 μL) were added under vigorous stirring. The resulting solutions were quickly transferred into Petri dish and allowed to polymerize for 12 h at room temperature, leading to the chemically crosslinked hydrogels. Then the hydrogels were immersed in a 0.06 M $Fe(NO_3)_3 \cdot 9H_2O$ solution for 24 h, followed by immersion in deionized water for 48 h to form the dual cross-linked hydrogels. Subsequently, these hydrogels were soaked in varying concentration of Na_2SO_4 solution to produce the final hydrogels.

Similarly, the acrylamide variant of dual cross-linked hydrogels was synthesized, substituting methacrylamide (MAAm) with acrylamide (AAm). Pure PAAm and PMAAm hydrogels were prepared using same polymerization process from a 2.4 M monomer solution in the presence of 0.06 mol% MBAA.

Double-network hydrogels were synthesized in a single step.[2] A solution of acrylamide (2.03 g) and chitosan oligosaccharide lactate (0.1g) was prepared in deionized water (total volume: 10 mL). The solution was purged with nitrogen gas, followed by addition of APS (1 wt% of monomer) and TMEDA (20 µL) under vigorous stirring. The mixture was then transferred into a Petri dish and left for 12 h to form a double-network hydrogels.

The methacrylamide variant was synthesized similarly by replacing acrylamide with methacrylamide. Both hydrogel variants were immersed in different concentrations of Na_2SO_4 solution to obtain the final hydrogels.

Characterization.

The hydrogels' tensile and compressive mechanical properties were tested at room temperature using a Zwick/Roell Z050 Universal Testing Machine. Samples were coated with thin layer of silicon oil prior to tests to prevent water loss. For tensile testing, hydrogel sheets (~ 1 mm thick) were cut into rectangular strips (~ 40 mm in length and ~ 4 mm in width) and subjected to a grip-to-grip separation of ~10 mm. The extension rate was set to 100 mm min^{-1} for both tensile and cyclic tensile loading-unloading experiments. Compression tests were conducted on cylindrical samples (~ 8 mm in diameter, ~ 12 mm in height) at a crosshead speed of 3 mm min^{-1}.

The engineering stress was (σ) was calculated using the following equation:

$$\sigma = F/A_0$$

Where F is the applied force and A_0 is the initial cross-sectional area.

The storage and loss moduli of the cylindrical samples (~ 8 mm in diameter, ~ 5 mm in height), coated with silicone oil, were measured in compression mode using NETZSCH DMA-242 E Artemis, Germany. Measurements were taken at 1 Hz over a temperature range of 30 to 90 °C at a heating rate of 5 °C min^{-1}, under nitrogen atmosphere.

Surface morphologies of fractured surfaces were observed using Carl Zeiss Ultra Plus HRSEM at 1 keV acceleration voltage. Samples were prepared by freeing the hydrogels at -80 °C, followed by freeze-drying at this temperature of one day (VirTis Bench Top Pro, SP Scientific, USA). Freeze-dried samples were fractured and coated with Iridium for 5 min. For cryo-SEM, samples were prepared using Leica EM ICE High-pressure Freezing System and fractured with the Leica EM ACE900 Freeze fracture system.

The microstructure of the hydrogels was characterized using small-angle X-ray scattering (SAXS) on a Molecular Metrology SAXS system (JJ X-ray A/S, Denmark), utilizing CuKα radiation (λ = 0.1542 nm). Wide-angle X-ray diffraction (WAXD) was performed using the Rigaku SmartLab 9 kW high-resolution instrument.

The thermogravimetric analysis (TGA) of the as-prepared hydrogels was examined by TGA/DSC 3+ STARe system (Mettler Toledo) under N2 atmosphere (flow rate = 25mL/min) at a temperature range of 25 to 800 °C.

A Discovery DHR-2 rotational rheometer (TA Instruments) was used to study the rheological properties of hydrogels. A parallel plate (diameter 20 mm) setup with a ~ 1 mm gap was used. Waterproof sandpaper (600-grit) was attached to both plates to prevent slippage.

Polarized optical microscopy (POM) was conducted using Olympus BX51 microscope under different strain.

The hydrodynamic radius of pure polymer solution was measured using a Zetasizer Ultra (Malvern Panalytical, UK). Dynamic scanning calorimetry (DSC) experiments were conducted using a DSC 2500 (TA instruments) at cooling rate of 10 °C min^{-1}.

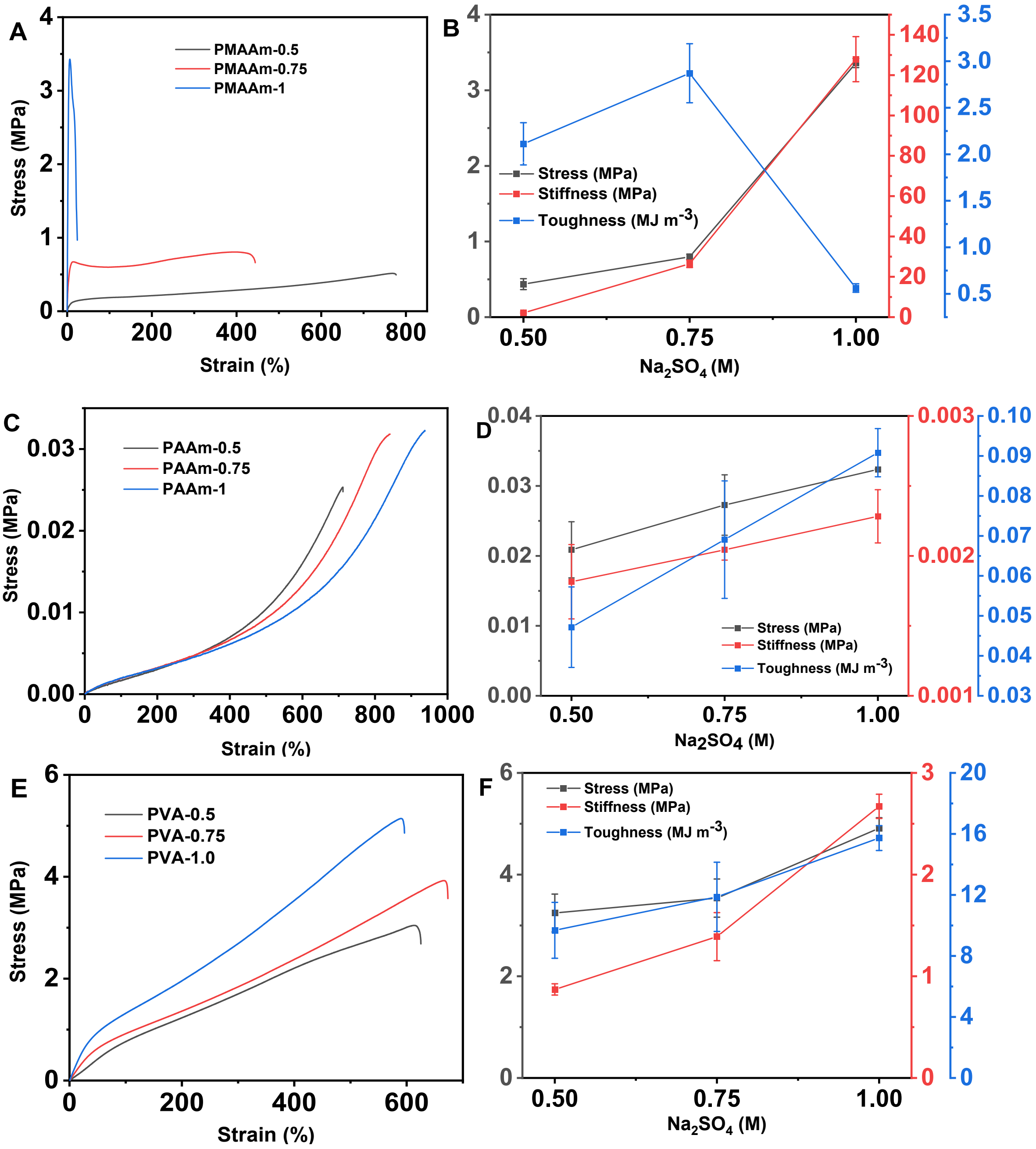


Figure S1. Tensile stress-strain curve of A) PMAAm and B) corresponding detailed mechanical parameters, C) PAAm and D) corresponding detailed mechanical parameters, and C) PVA and D) corresponding detailed mechanical parameters at different Na_2SO_4 concentration.

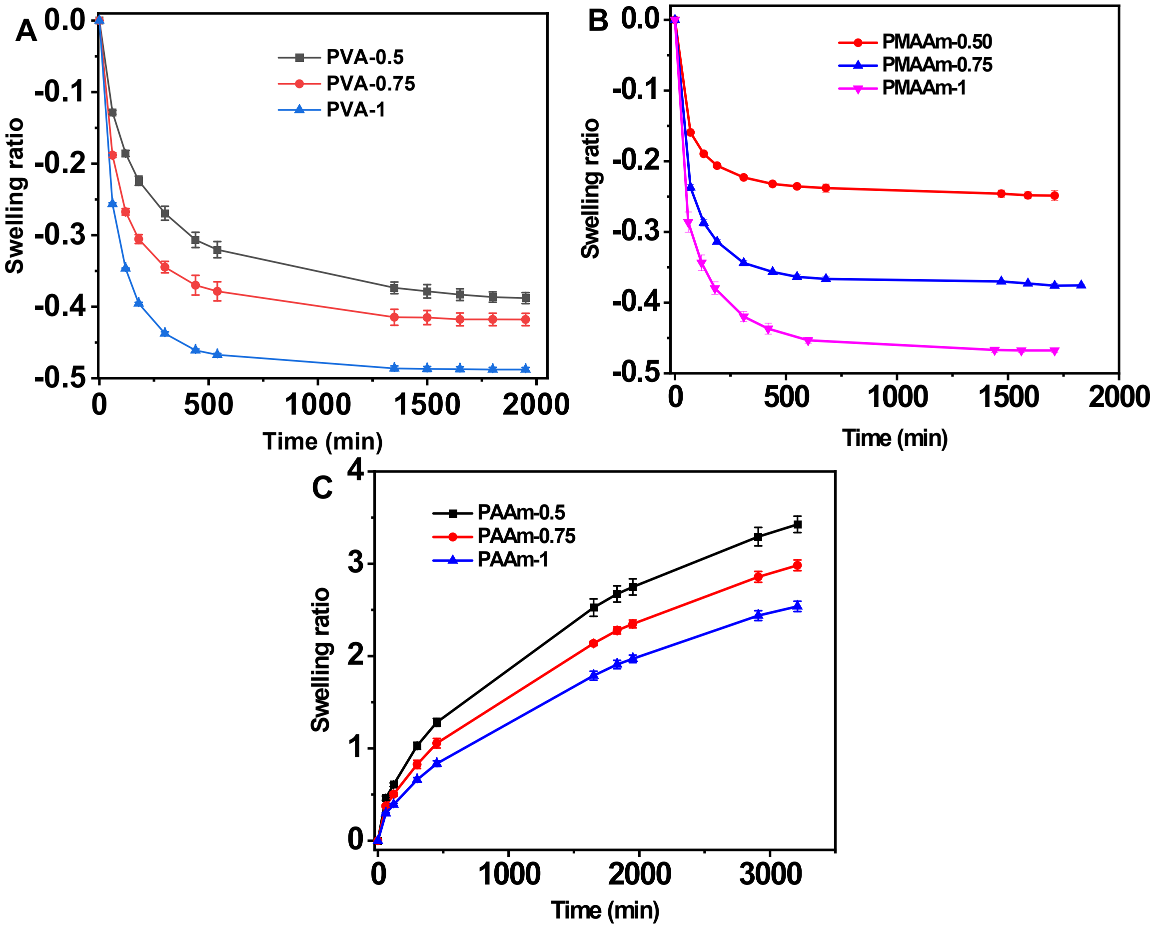


Figure S2. Swelling kinetics of A) PVA, B) PMAAm, C) PAAm at different Na_2SO_4 salt concentrations.

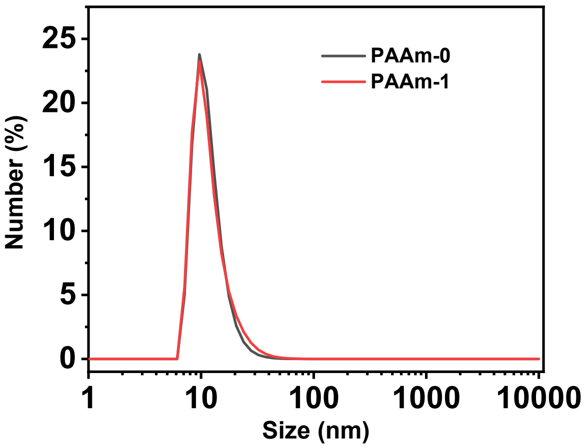


Figure S3. DLS measurements of linear PAA at different salt concentration.

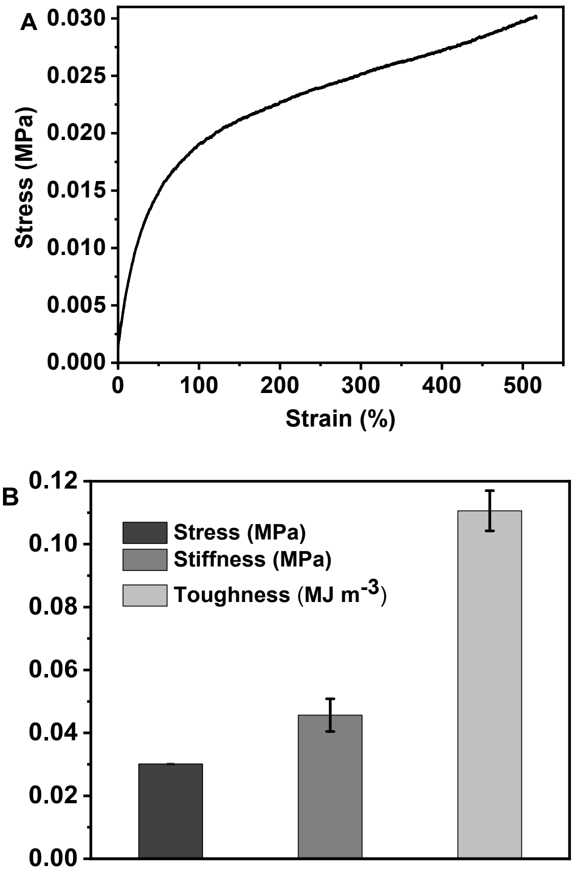


Figure S4. Tensile stress-strain curve of A) PMA-10-S and B) corresponding detailed mechanical parameters.

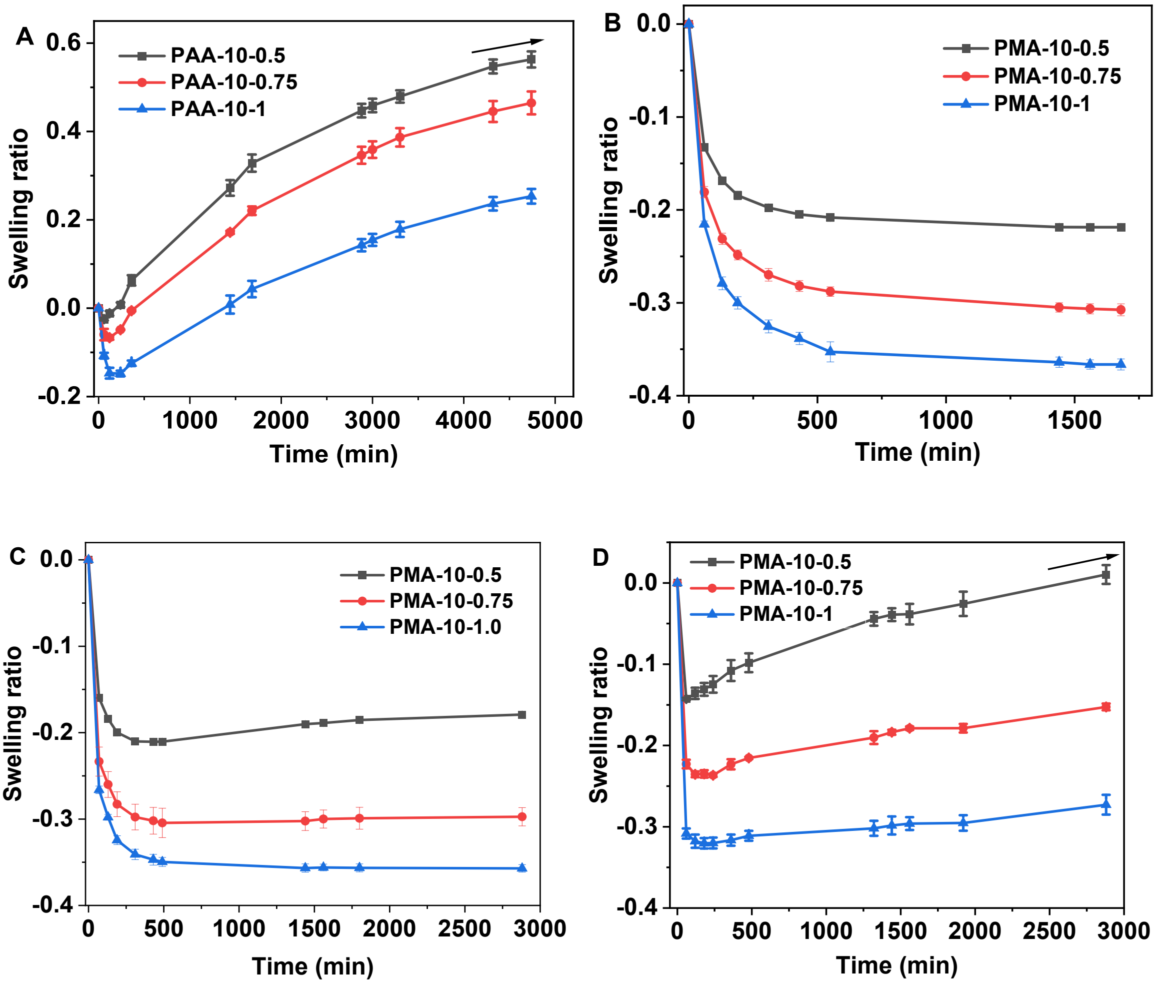


Figure S5. Swelling kinetics of A) PAA-10 at room temperature at different Na_2SO_4 salt concentrations. Swelling kinetics of PMA-10 hydrogels at B) room temperature, C) 50 °C and D) 70 °C at different Na_2SO_4 salt concentrations.

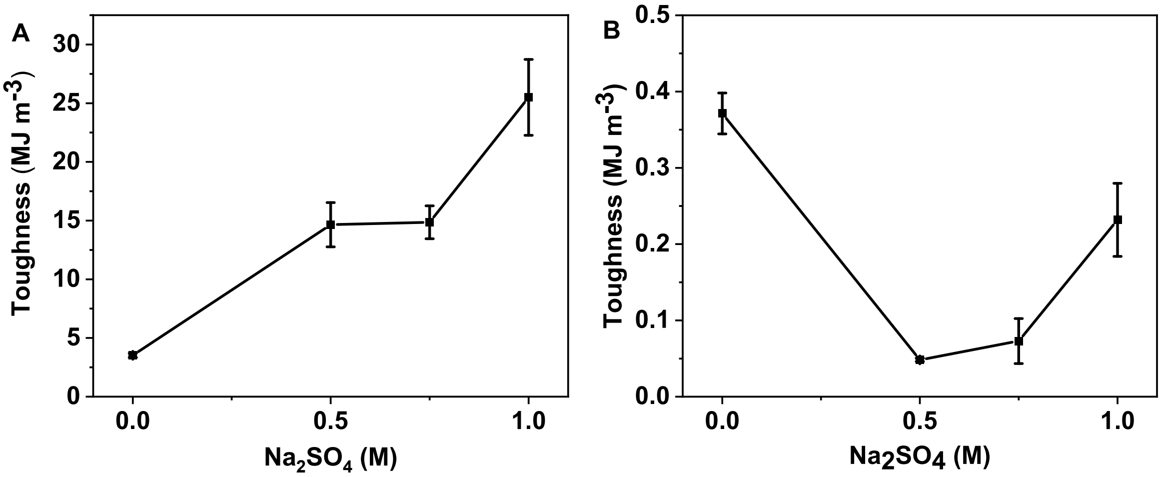


Figure S6. Tensile toughness of A) PMA-10-Y and B) PAA-10-Y at different Na_2SO_4 concentrations.

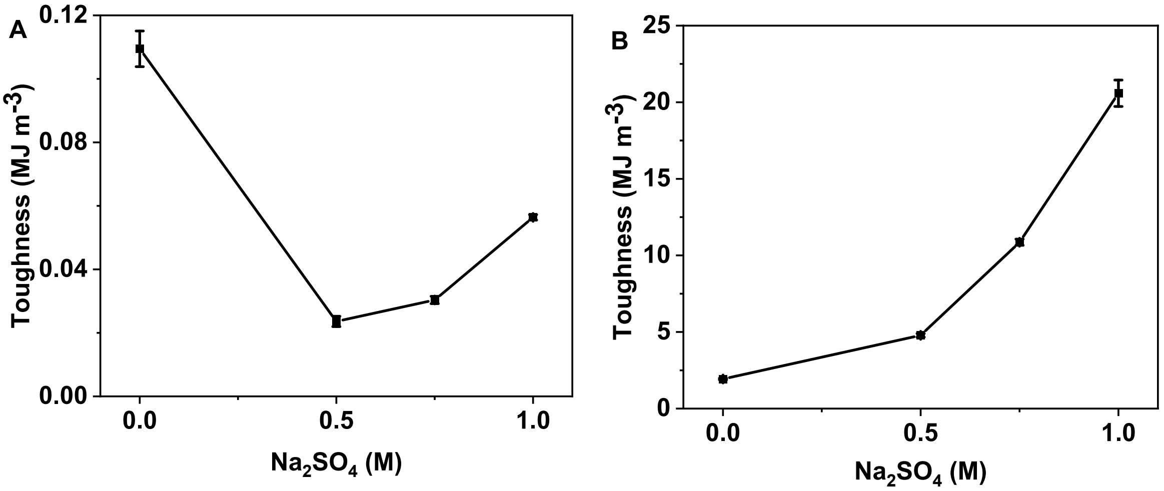


Figure S7. Compressive toughness of A) PAA-10-Y and B) PMA-10-Y at different Na_2SO_4 concentrations.

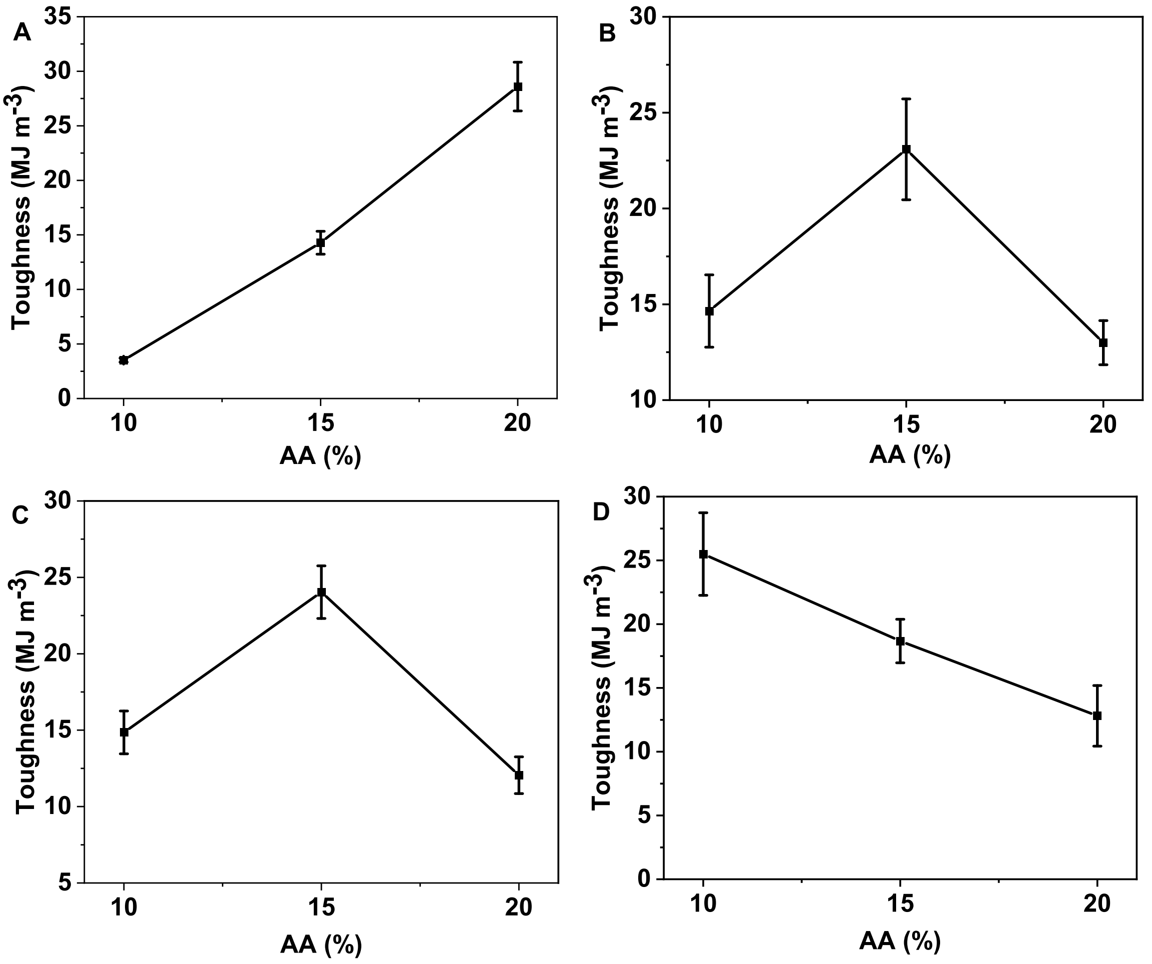


Figure S8. Toughness of A) PMA-X-0, B) PMA-X-0.5, C) PMA-X-0.75 and D) PMA-X-1 at varied acrylic acid (AA) concentrations.

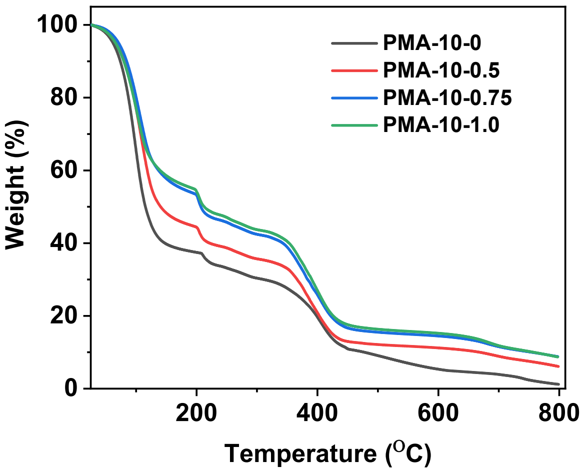


Figure S9. TGA of PMA-10 hydrogel swelled at different salt concentrations.

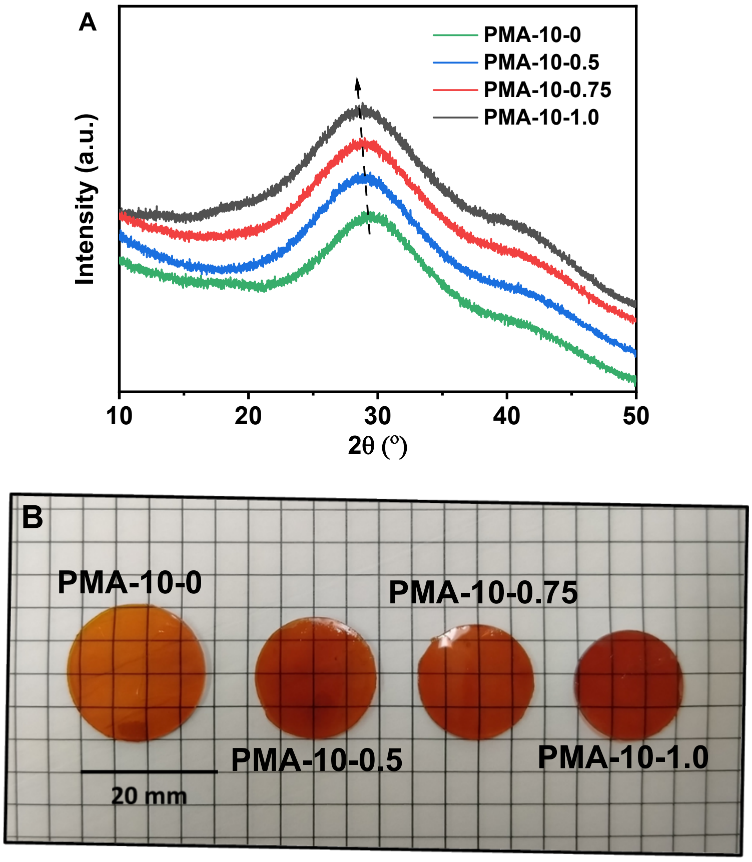


Figure S10. A) WAXD of PMA hydrogels and B) photographs of PMA-10 hydrogel at different Na_2SO_4 salt concentrations.

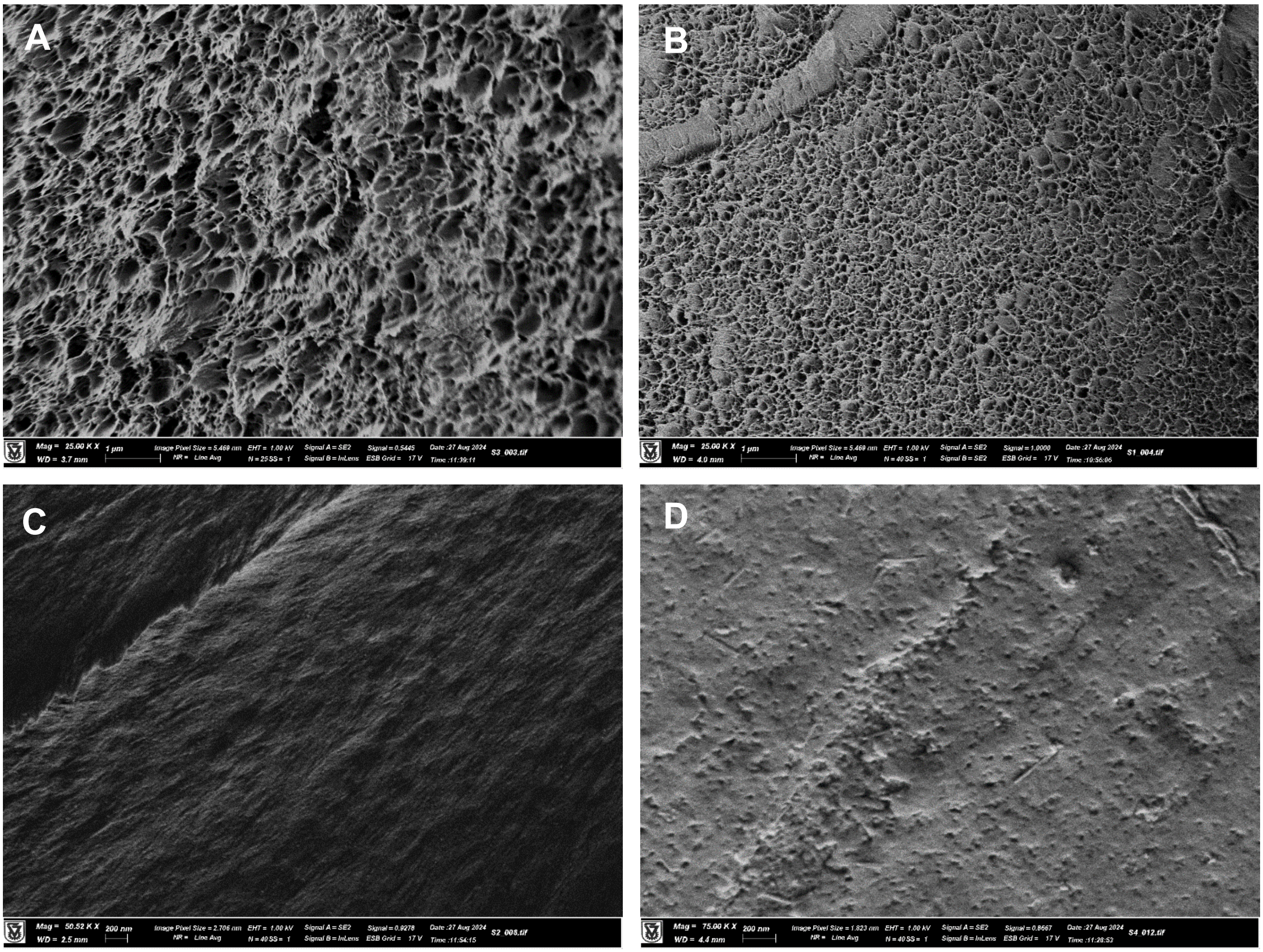


Figure S11. FESEM image of A) PMA-10-0, B) PMA-10-0.5, C) PMA-10-0.75 and D) PMA-10-1

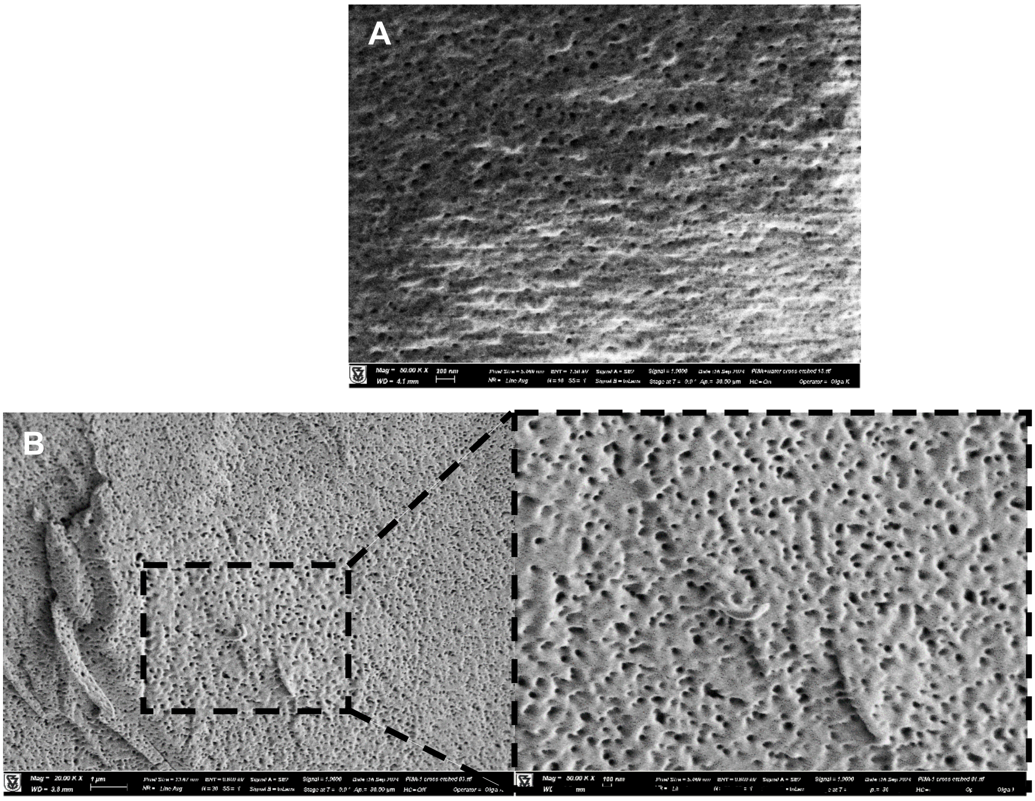


Figure S12. Cryo-SEM image of A) PMA-10-0, and B) PMA-10-1.

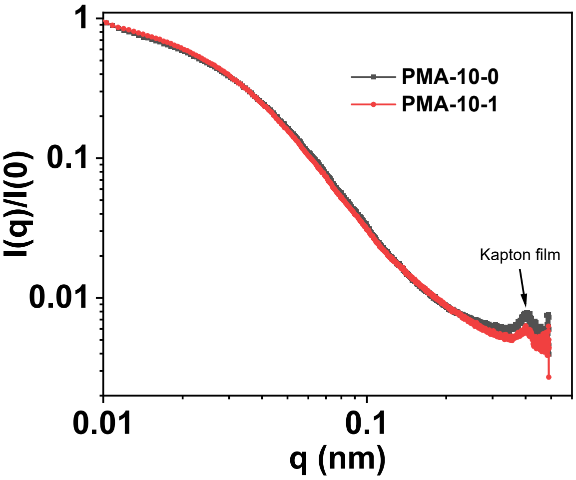


Figure S13. Normalized SAXS profile of PMA-10-0 and PMA-10-1.

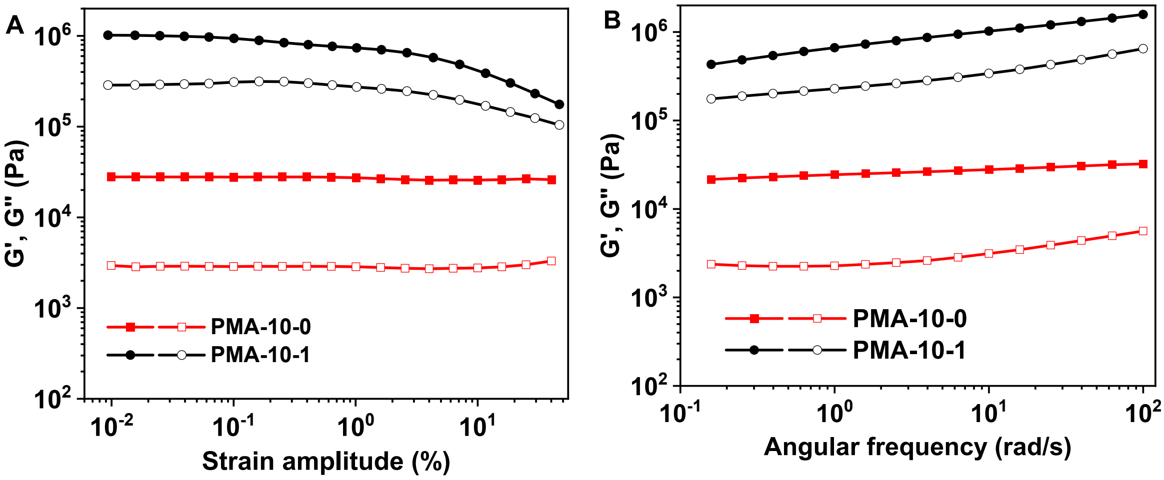


Figure S14. Storage (G') and loss (G") moduli as a function of A) strain amplitude and B) angular frequency for PMA-10-0 and PMA-10-1.

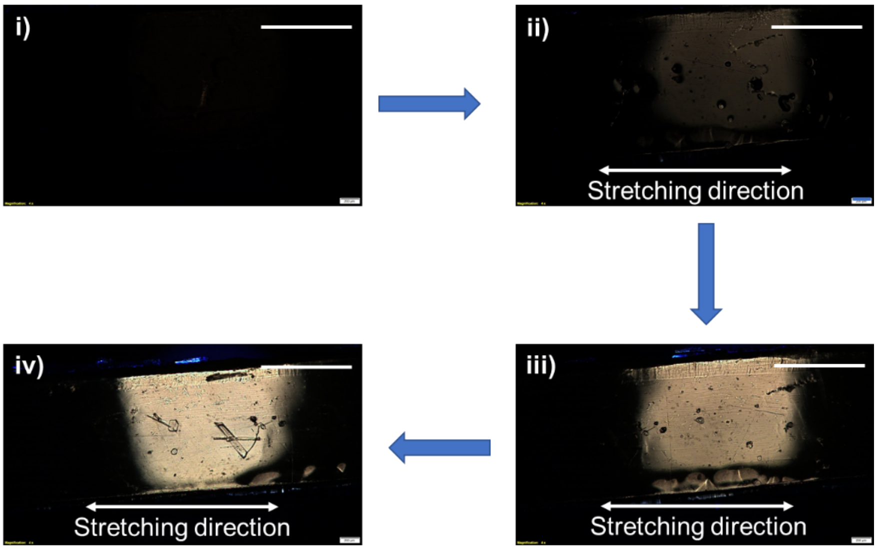
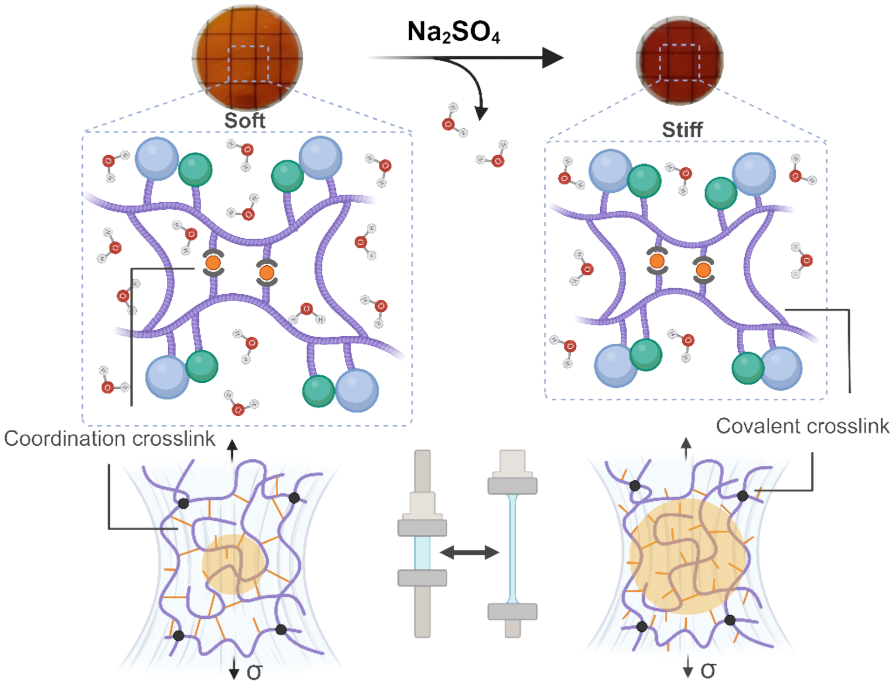


Figure S15. Polarized optical microscopy images of PMA-10-1, i) unstretched and under ii) 10%, iii) 30% and iv) 50% tensile strain. Scale bar 1 mm.



Scheme 2. Schematic illustration of hydrogel deswelling due to Hofmeister effect. The bottom panel shows the energy dissipation under tensile stress.

References

1. Lin, P., Ma, S., Wang, X. & Zhou, F. Molecularly engineered dual-crosslinked hydrogel with ultrahigh mechanical strength, toughness, and good self-recovery. *Advanced Materials* **27**, 2054–2059 (2015).

2. Dutta, A., Maity, S. & Das, R. K. A Highly Stretchable, Tough, Self-Healing, and Thermoprocessable Polyacrylamide–Chitosan Supramolecular Hydrogel. *Macromol Mater Eng* **303**, 1800322 (2018).