Supporting Information

to

Designing Fast-Response Porous Hydrogel Actuators with Improved Toughness

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Experimental Section

Materials.

All chemicals were obtained from Sigma-Aldrich and used as-received unless otherwise specified. Deionized water was produced by an ELGA Laboratory water station and had a resistivity of 18.2 m/cm. To remove inhibitors, oligoethyleneglycol methyl ether methacrylate [500 g/mol, OEGMA] and methacrylic acid were passed through a basic alumina column immediately before use. 1,1'-Azobis (cyclohexane carbonitrile) (AIBN) was recrystallized from ethanol and dried overnight prior to use.

Synthesis of Poly(MAA-co-OEGMA).

The poly(MAA-*co*-OEGMA) copolymer was prepared according to our previous work.¹ OEGMA 500 (1.9 mL), MAA (1.198 mL), and AIBN (1.64 mg) were dissolved in dimethyl formaldehyde (DMF) (14 mL). The flask was sealed with a rubber septum and the solution was deoxygenated by sparging with nitrogen for 20 min. After polymerizing for 24 h at 60 °C, the viscous polymer solution was precipitated into diethyl ether, and then further purified by extensive dialysis in water.

Hydrogel Preparation.

Appropriate amounts of FeCl₃ were dissolved into pure water to form an aqueous solution with varied concentrations (0.125, 0.25, 0.5, 1, 2, 4 mol/L). The FeCl₃ was then directly added into aqueous solutions of poly (MAA-*co*-OEGMA) (150 mg/mL) under stirring for 15 min.

To generate crystalline domains in hydrogel actuators, the poly(vinyl alcohol) (PVA) (Mw 146,000-186,000, 99+% hydrolyzed; Sigma-Aldrich, 363065) water solution was obtained with a concentration of 10% wt. The appropriate amount of PVA was dissolved in distilled water and stirred vigorously for 1 h at 90 °C, until the solution was homogeneous. Then, different mixtures with poly (MAA-*co*-OEGMA) were prepared with the following PVA weight ratios: (wt%: weight of PVA concerning the weight of copolymer) 0 wt%, 3.9 wt%, 7.8 wt%, and 11.7 wt%, respectively. The mixed solutions were then transferred to poly(tetrafluoroethylene) (PTFE) mold and followed by heating in an oven at 90 °C for 90 min to dry. The dried polymer films were immersed in a large amount of pure water for 1 day to produce the hydrogels and to remove excess Fe³⁺.

Before introducing PVA into the polymer solutions, we optimised the concentrations of the added FeCl₃. It should be noted that adding FeCl₃ with high concentrations of 2 mol/L and 4 mol/L could generate viscous coagulates. It was also noted that the dry films with low FeCl₃ concentrations of 0.125 mol/L and 0.25 mol/L could be easily damaged after immersion in water for several hours due to the low cross-linking densities. The hydrogel actuator prepared with a FeCl₃ concentration of 0.5 mol/L exhibited a contraction ratio of 30 % upon heating above LCST, while the sample with higher FeCl₃ concentration of 1.0 mol/L show much reduced contraction ratio of less than 20%. Based on these observations, we fixed the added FeCl₃ concentration at 0.5 mol/L for the subsequent studies unless otherwise specified.

Materials Characterization.

Infrared spectra of various samples were acquired using an IR Affinity1 Fourier transform infrared (FTIR) spectrometer fitted with an attenuated total reflectance (ATR) accessory that used a diamond internal reflection element (IRE). XRD analyses were carried out by a Bruker D8 TXS diffractometer. The rheological measurements were carried out on a MCR 102e Rheometer. Frequency sweeps were performed from 0.01 to 100 Hz using 1% strain. Confocal laser scanning microscopy (CLSM) was performed on a Leica Confocal SP8 microscope with a 40× objective. Rhodamine B treated samples were excited using a laser with wavelength of 552 nm, and the emission peak was 580 nm. Mechanical properties of the polymers were measured by tensile tests using a commercial tensile tester. The stretching rate was 50 mm/min. The nominal stress-strain curves were recorded, and Young's modulus was calculated from the initial slope of the curve with a strain below 8%.



Figure S1. UV/Vis spectra of the T-hydrogel and D-hydrogel.

Type of Hydrogels	Dry Sample	In Water after 1 hr	In Water after 4 hr	In Water after 1 day
D-Hydrogel				
T-Hydrogel				

Figure S2. Photographs showing the swelling process of D-hydrogel and T-hydrogel.



Figure S3. DSC thermograms of D-hydrogels with different PVA content. A broad peak from 60°C to 150 °C could be ascribed to the water evaporation.



Figure S4. SEM (a) and Confocal microscopy (b) image of D-hydrogel with PVA content of 0 wt%.



Figure S5. SEM images of D-hydrogel with constant Fe³⁺ concentrations of 0.5 mol/L and PVA content of 3.9 wt%, 7.8 wt% and 11.7 wt% respectively.



Figure S6. Mechanical properties of hydrogels with Fe³⁺ concentrations of 0.5 mol/L and 1.0 mol/L. The PVA content in both hydrogels is 0 wt%.



Figure S7. Diameter change over time showing the reversible actuation of a bulk cylinder hydrogel when immersed in hot water (80°C) and then cold water (25°C) at the times indicated.

Sample	Tensile Stress (MPa)	Response Time (s)
D-Fe0.125-PVA 0%	Could not be measured	102
D-Fe0.125-PVA 3.9%	Could not be measured	65
D-Fe0.125-PVA 7.8%	Could not be measured	60
D-Fe0.25-PVA 0%	Could not be measured	92
D-Fe0.25-PVA 3.9%	Could not be measured	61
D-Fe0.25-PVA 7.8%	Could not be measured	47
D-Fe0.5-PVA 0%	0.015	62
D-Fe0.5-PVA 3.9%	0.02	44
D-Fe0.5-PVA 7.8%	0.33	39
D-Fe1 -PVA 0%	0.013	73
D-Fe1-PVA 3.9%	0.014	55
D-Fe1-PVA 7.8%	0.19	52

Table S1. Tensile stress and response time of the hydrogels with varied compositions. The hydrogels were named as $D-Fe_x-PVA_y$, in which x means the concentration of Fe3+ and y means the PVA content.

The actuation speed and mechanical properties of the samples with different Fe^{3+} concentrations and PVA content. the PVAcontaining hydrogels with low Fe^{3+} concentrations of 0.125 mol/L and 0.25 mol/L were too soft to handle, which could be ascribed to the strong salvation effect of the hydrophilic ethylene glycol side chains of OEGMA. when we added the Fe^{3+} with concentrations higher than 1 mol/L into the polymer aqueous solution, heterogeneous gel precipitates were produced due to the fast binding of Fe^{3+} to the carboxyl groups. Therefore, these samples were excluded from the mechanical and actuation tests.



Figure S8. Repeated testing of the actuator multiple cycles of heating and cooling experiment, when immersed in hot water (80°C) and then cold water (25°C). d_t : diameters of hydrogel discs in the de-swollen state in hot water. d_0 : diameters of hydrogel discs in cold water. It demonstrated the reversible actuation of the hydrogel (D-Fe_{0.5}-PVA_{3.9%}).

Reference

1. Z. Jiang, S. M. Seraji, X. Tan, X. Zhang, T. Dinh, M. Mollazade, A. E. Rowan, A. K. Whittaker, P. Song and H. Wang, Chem. Mater., 2021, 33,

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