Supporting Information

Double Network Hydrogels Based on Semi-rigid Polyelectrolyte Physical Networks

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Experimental Details

Materials: Acrylamide (AAm) (Jundei Chemical Co., Ltd) was recrystallized from chloroform. *N,N'*-Methylenebisacrylamide (MBAA; Tokyo Kasei Co., Ltd.), as a crosslinker for AAm-based gels was recrystallized from ethanol. 2-Oxoglutaric acid (α-keto) (Wako Pure Chemical Industries, Ltd.), as a UV initiator for the polymerization, was used as received. Poly(2,2'-disulfonyl-4,4'-benzidine terephthalamide) (PBDT), a water soluble, anionic, semi-rigid polymer, was synthesized by an interfacial polycondensation reaction (N. Sarkar and L. D. Kershner, *J. Appl. Polym. Sci.*, 1996, **62**, 393–408). The synthesized PBDT had a weight-average molecular weight, M_w of about 142 kDa, number-average molecular weight, M_n of about 110 kDa, and dispersity, Đ of about 1.29. These values were determined by size exclusion chromatography (column: Shodex SB-806M) with multiple angle light scattering. Acrylamide tertiary butyl sutyl sulfonic acid sodium salt (NaAMPS) was purchased from Toagosei Co., Ltd. and used as received for synthesizing the PAAm gel containing un-crosslinked poly(NaAMPS) (PNaAMPS). PNaAMPS was obtained by a UV-radical polymerization (The 0.5 M NaAMPS solution with 0.15 mol% α-keto was irradiated UV for 6 hours with stirring), then dried in a vacuum oven at 40 ℃ for 12 hours. The resulting PNaAMPS had M_w = 2,830 kDa, M_n = 392 kDa, and Đ = 7.2. For all experiments, deionized water was purified with 0.22 μm and 5 μm membrane filters prior to use.

Preparation of PAAm hydrogels containing PNaAMPS: To synthesize the hydrogel films, reaction cells were prepared by sandwiching a square framed silicone spacer (thickness: 1 mm) between two parallel glass plates. Aqueous pre-gel solutions containing 3.0 M of the neutral monomer, AAm, 3 wt% of the relatively flexible anionic polymer, PNaAMPS, 0.1 mol% of the chemical cross-linker, MBAA, and 0.5 mol% of the thermal-initiator, KPS (mol% is relative to the monomer) were prepared. After proper mixing, the pre-gel solution was poured into the reaction cells. Thermal-induced free radical polymerization was carried out in air in a temperature-controlled heat box (60℃) for 10 h. After thermal polymerization, the as-prepared sheet-like gels (about $60 \times 60 \times 1.0$ mm^3) were carefully

removed from the reaction cells.

Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy (ATR-FTIR): Measurements were carried out with a JASCO, FT / IR-6600 spectrometer. 4 wt% solutions of PBDT in water were prepared and measured as a baseline. Drops of this solution were then added to 0.15 M solutions containing $CaCl_2$, $AlCl_3$, or $ZrCl_2O$ to form a physical gel. This gel was then placed on the ATR crystal and characterized.

Measurement for optical transparency: Transmittance was measured by a Shimadzu UV-1800 Spectrophotometer at 550 nm in air at 25℃. The transparency (%) was obtained by converting the transmittance of visible light to the value per 1.0 mm thickness of the samples. Before measurement, all samples were equilibrated in a corresponding salt solution, following the preparation section above.

Supplementary Tables

Sample code	Water content [wt%]	Transparency (%)	Young's modulus [MPa]	Fracture stress [MPa]	Fracture strain [mm/mm]	Strain energy density [MJ/m^3]
PBDT(3%)/PAAm-water	97	100	0.014±0.0002	0.026±0.003	2.78±0.39	0.037±0.009
PBDT(3%)/PAAm-Na	95	98	0.017±0.001	0.035±0.015	3.34±1.2	0.065±0.04
PBDT(3%)/PAAm-Ca	93	96	0.025±0.002	0.081±0.013	4.97±0.35	0.19±0.04
PBDT(3%)/PAAm-Al	93	93	0.046±0.002	0.21±0.06	4.58±0.97	0.46±0.2
PBDT(1%)/PAAm-Zr	91	91	0.080±0.003	0.28±0.06	3.97±0.75	0.59±0.20
PBDT(2%)/PAAm-Zr	85	87	0.58±0.020	0.83±0.08	5.84±0.48	2.78±0.41
PBDT(3%)/PAAm-Zr	81	83	1.69±0.02	1.34±0.09	7.29±0.47	5.94±0.7
PBDT(5%)/PAAm-Zr	75	62	5.04±0.32	2.70±0.13	10.77±0.15	17.28±0.62
PNaAMPS(3%)/PAAm-Zr	91	-	0.029±0.0016	0.135±0.02	4.52±0.42	0.27±0.06
PAAm-water	95	100	0.17±0.0009	0.30±0.008	3.05±0.89	0.052±0.027
PAAm-Na	95	100	0.15±0.0008	0.020±0.001	2.14±0.19	0.023±0.004
PAAm-Ca	95	100	0.15±0.002	0.019±0.002	2.26±0.01	0.025±0.003
PAAm-Al	95	100	0.14±0.0009	0.020±0.001	2.11±0.08	0.023±0.002
PAAm-Zr	95	99	0.14±0.0006	0.022±0.003	2.45±0.22	0.030±0.006

Table S1. Summary of water content, transparency at 550 nm, and mechanical properties of the PBDT/PAAm and PAAm hydrogels swollen in 0.15 M $ZrCl_2O$ solution. The mechanical properties were calculated from the stress-strain curves measured by uniaxial tensile tests. The error ranges are standard deviation from the results of 3-5 samples.

Supplementary Figures

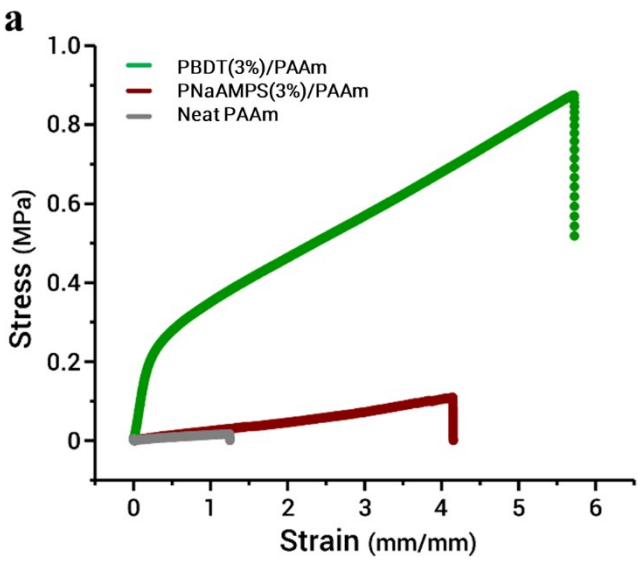

Figure S1. Stress-strain curves of composite gels formulated using polyelectrolytes of varying persistence length. When the composite gel was synthesized containing PNaAMPS, the PNaAMPS network chains cannot extend due to the presence of salt, and therefore cannot fracture sacrificially to dissipate energy.