Supporting information

Mechanical and Interfacial Properties of Zwitterionic Hydrogels via High-Entanglement Network Design: A Study of Monomer and Crosslinker Synergy

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Synthesis of sulfobetaine acrylate (SBA) monomer

SBA was synthesized by the ring-opening reaction of PS with DA in the presence of acetonitrile. A mixture of PS (3.664 g, 0.03 M) and acetonitrile (5 g) was added to the mixture of DA (4.295 g, 0.03 M) and acetonitrile (10 g) with continuous stirring using a magnetic stirrer at 25 °C. After combining all components, the resultant mixture was stirred at 25 °C for 24 h and allowed to stand at 4 °C for 48 h. The resulting white precipitate was filtered, washed with acetonitrile and acetone, and dried under vacuum for 12 h.

Synthesis of sulfobetaine methacrylate (SBMA) monomer

SBMA was synthesized by the ring-opening reaction of PS with DMA in the presence of acetonitrile. A mixture of PS (3.664 g, 0.03 M) and acetonitrile (5 g) was added to the mixture of DMA (4.716 g, 0.03 M) and acetonitrile (10 g) with continuous stirring using a magnetic stirrer at 25 °C. After combining all components, the resultant mixture was stirred at 25 °C for 24 h and allowed to stand at 4 °C for 48 h. The resulting white precipitate was filtered, washed with acetonitrile and acetone, and dried under vacuum for 12 h.

Synthesis of sulfobetaine acrylamide (SBAA) monomer

SBAA was synthesized by the ring-opening reaction of PS with DAA in the presence of acetonitrile. A mixture of PS (3.664 g, 0.03 M) and acetonitrile (5 g) was added to the mixture of DAA (4.787 g, 0.03 M) and acetonitrile (10 g) with continuous stirring using a magnetic stirrer at 25 °C. After combining all components, the resultant mixture was stirred at 25 °C for 24 h and allowed to stand at 4 °C for 48 h. The resulting white precipitate was filtered, washed with acetonitrile and acetone, and dried under vacuum for 12 h.

Synthesis of sulfobetaine acrylamide (SBMAA) monomer

SBMAA was synthesized by the ring-opening reaction of PS with DMAA in the presence of acetonitrile. A mixture of PS (3.664 g, 0.03 M) and acetonitrile (5 g) was added to the mixture of DMAA (5.108 g, 0.03 M) and acetonitrile (10 g) with continuous stirring using a magnetic stirrer at 25 °C. After combining all components, the resultant mixture was stirred at 25 °C for 24 h and allowed to stand at 4 °C for 48 h. The resulting white precipitate was filtered, washed with acetonitrile and acetone, and dried under vacuum for 12 h. All spectra of all monomers were recorded at 600 MHz with 256 scans, and all the ^{1}H NMR sample was prepared by dissolving into D_2O.

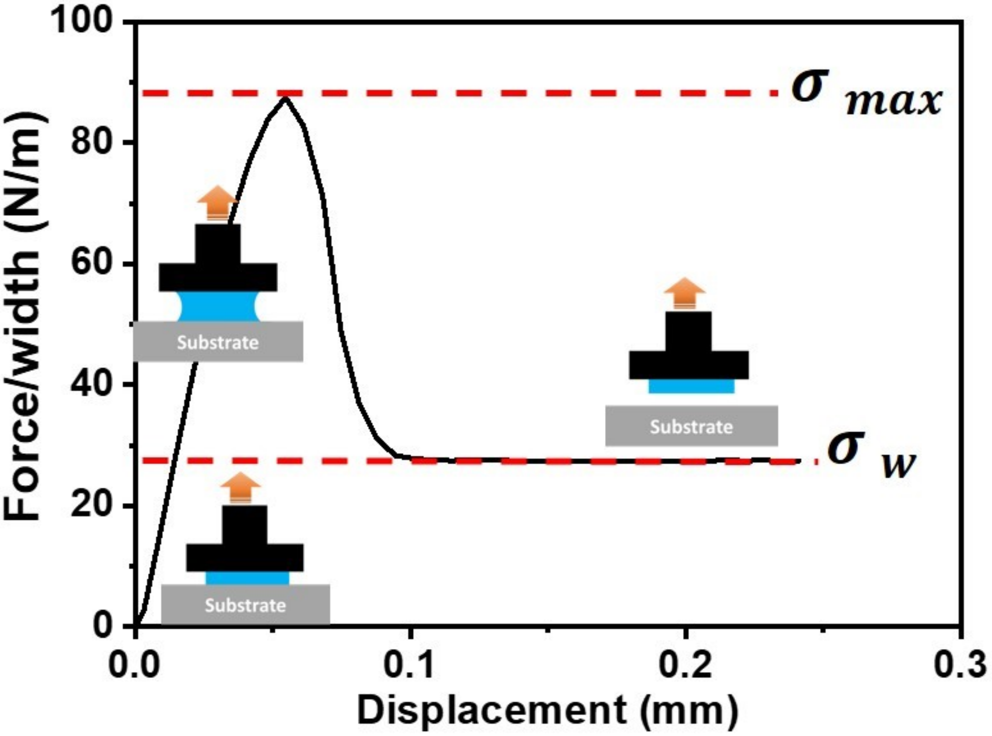

Figure S1. Schematic illustration of the adhesion strength test to quantify the detachment stress between hydrogels and different substrate surfaces using a universal testing machine in reverse compression mode.

The SBA monomer was prepared via the reaction between 2-(dimethylamino)ethyl acrylate (DA) and 1,3-propane sultone (PS) in acetonitrile as the solvent. The crude product was purified by precipitation in excess acetone, yielding approximately 99%. The obtained product was dissolved in deuterium oxide (D_2O) to prepare the NMR sample, and the ^1H NMR spectrum was recorded at 600 MHz using D_2O as the solvent. The residual solvent peak of D_2O was used for chemical shift calibration. The characteristic peaks of the synthesized SBA monomer were observed as follows: δ (ppm) = 2.23–2.35 (j, 2H), 2.94–3.03 (i, 2H), 3.17–3.26 (f, g, 6H), 3.54–3.63 (h, 2H), 3.79–3.86 (e, 2H), 4.63–4.71 (d, 2H), 6.03–6.09 (b, 1H), 6.22–6.31 (c, 1H), 6.45–6.52 (a, 1H).

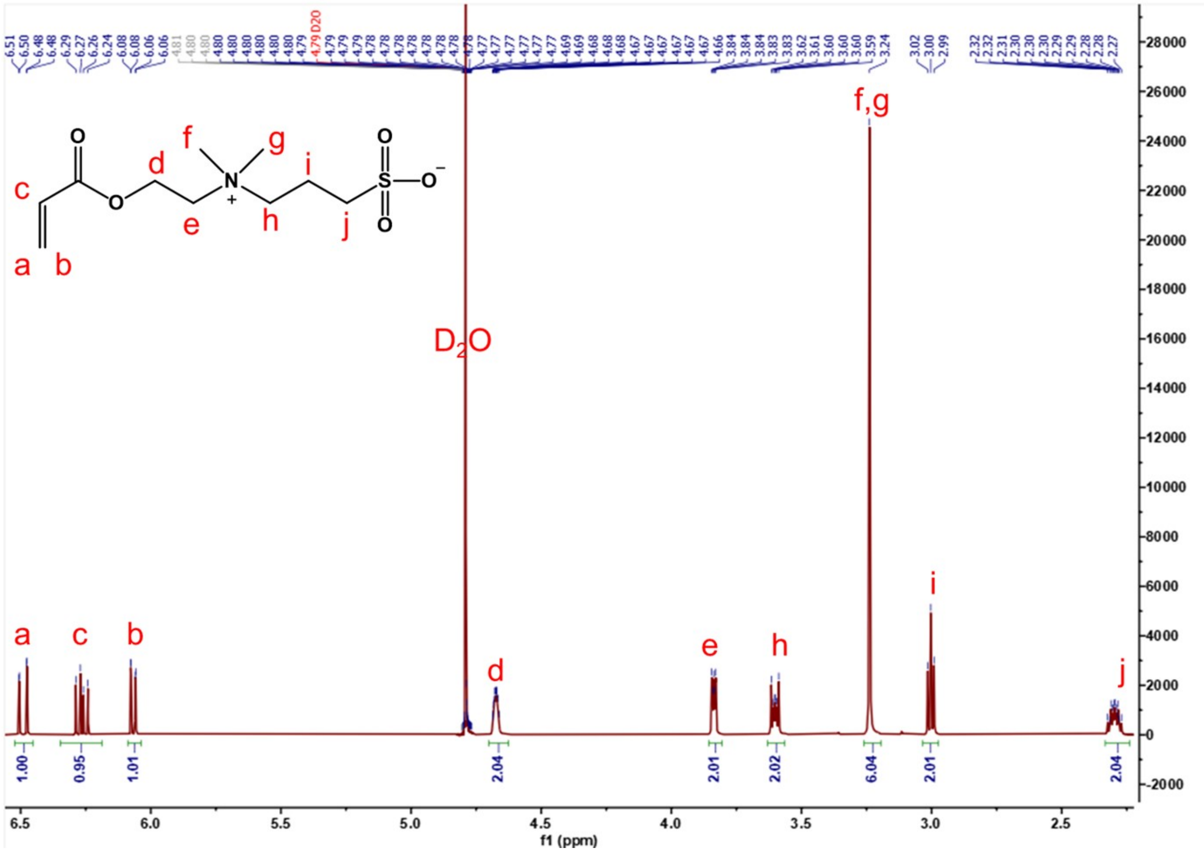

Figure S2. ^{1}H NMR spectrum and assignment of SBA monomer.

The SBMA monomer was prepared through the reaction of 2-(dimethylamino)ethyl methacrylate (DMA) with 1,3-propane sultone (PS) in acetonitrile as the solvent. The crude product was purified by precipitation in excess acetone, affording a yield of approximately 99%. The purified SBMA product was dissolved in deuterium oxide (D_2O) to prepare the NMR sample. The ^{1}H NMR spectrum was recorded at 600 MHz using D_2O as the solvent, with the residual D_2O peak used for chemical shift calibration. The characteristic proton signals of the synthesized SBMA monomer were observed as follows:

δ(ppm)=1.92-1.99(c；2H)、2.22-2.33(i；2H)、2.95-3.03(j；2H)、3.21-3.29(f, g；6H)、3.57-3.64(h；2H)、3.81-3.87(e；2H)、4.62-4.69(d；2H)、5.77-5.83(b；1H)、6.16-6.21(a；1H)

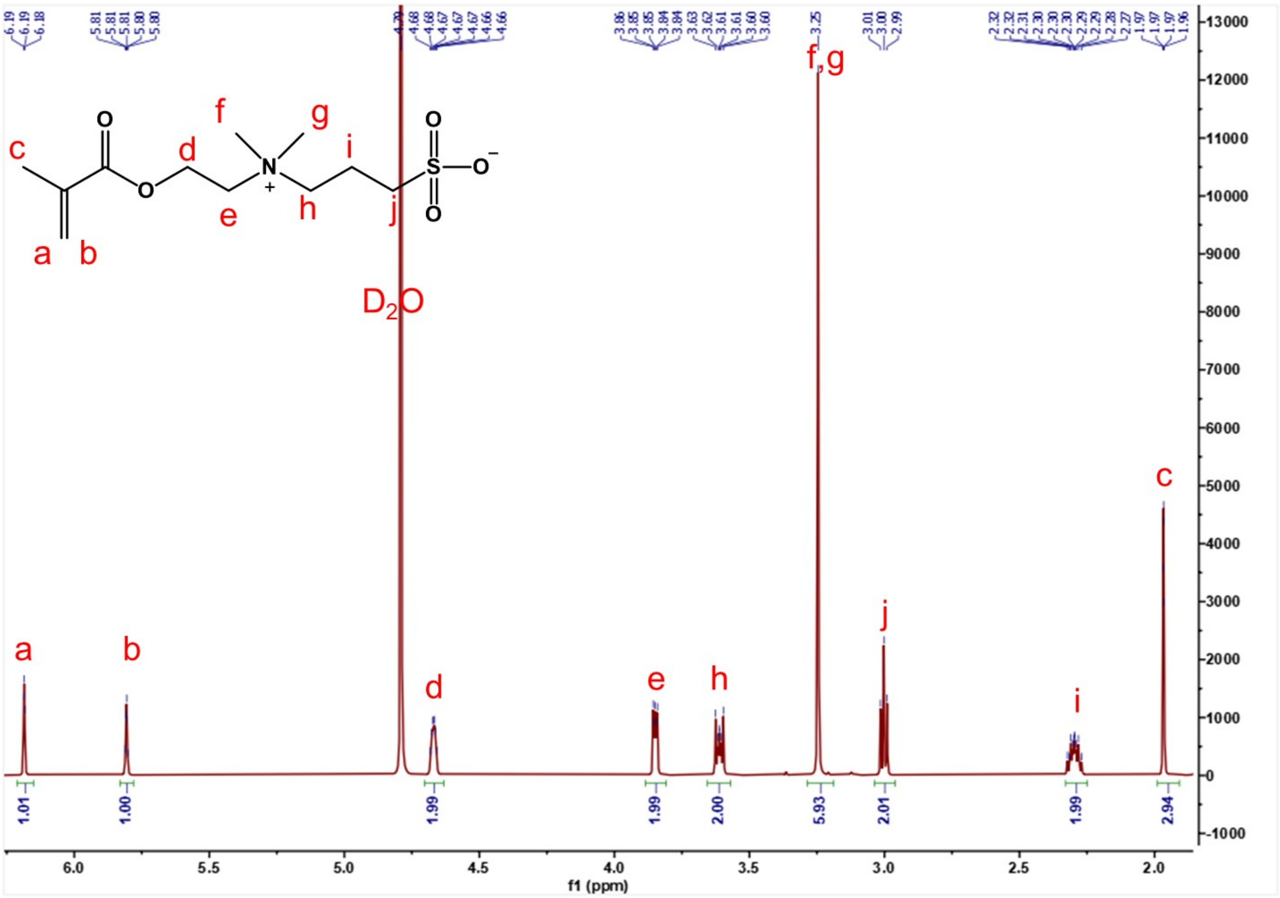

Figure S3. ^{1}H NMR spectrum and assignment of SBMA monomer.

The SBAA monomer was obtained through the reaction between N-[3-(N,N-dimethylamino)propyl]acrylamide (DAA) and 1,3-propane sultone (PS) in acetonitrile. The resulting product was purified by precipitation with excess acetone, yielding approximately 99%. The purified SBAA was dissolved in deuterium oxide (D_2O) to prepare NMR samples and characterized by ^{1}H NMR spectroscopy (600 MHz, D_2O). The spectrum of SBAA exhibited characteristic signals at δ (ppm): 2.02–2.12 (j, 2H), 2.19–2.27 (k, 2H), 2.94–3.03 (e, 2H), 3.08–3.17 (g, h, 6H), 3.33–3.45 (f, i, 4H), 3.47–3.53 (d, 2H), 5.76–5.83 (c, 1H), and 6.18–6.32 (a, b, 2H).

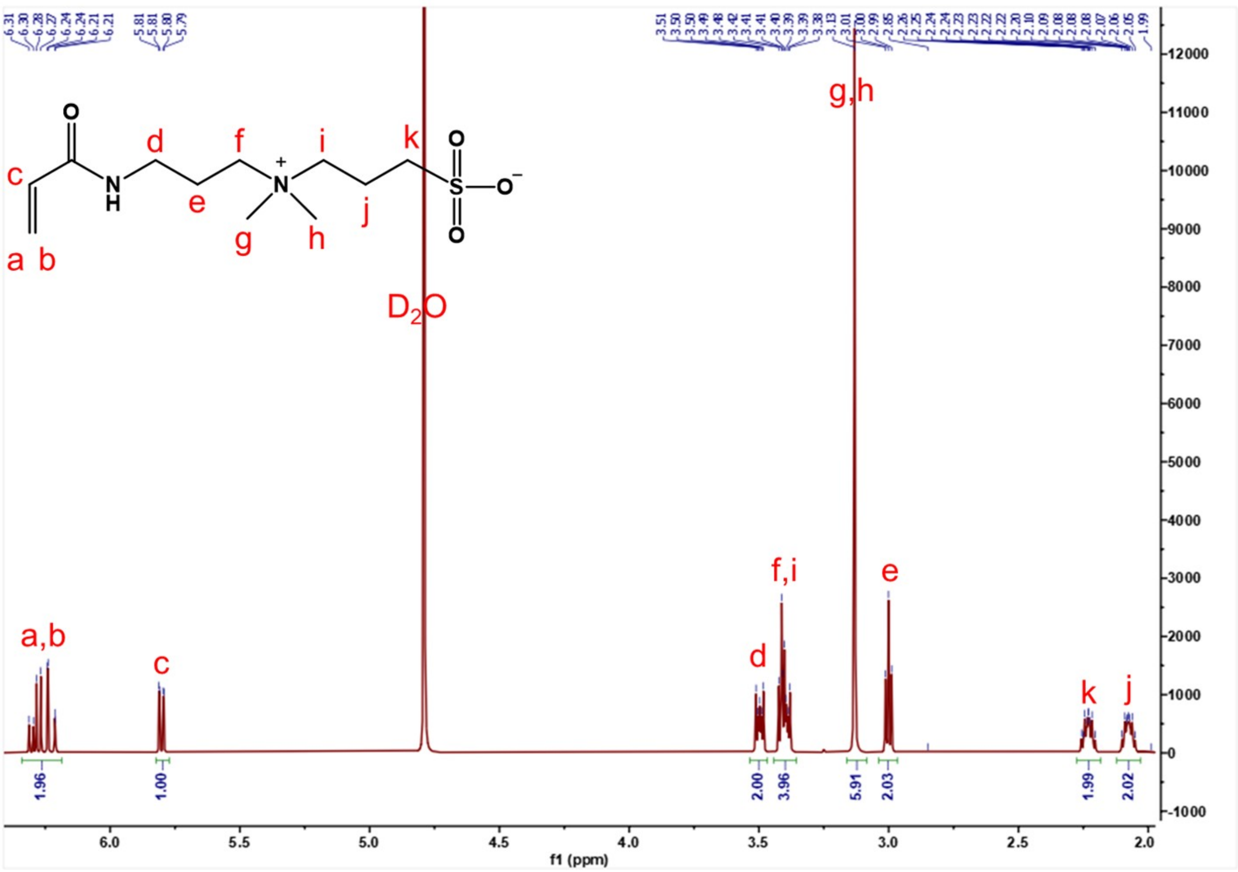

Figure S4. ^{1}H NMR spectrum and assignment of SBAA monomer.

The SBMAA monomer was prepared via the reaction between N-[3-(N,N-dimethylamino)propyl]methacrylamide (DMAA) and 1,3-propane sultone (PS) in acetonitrile, followed by purification with excess acetone to afford a yield of approximately 99%. The resulting product was dissolved in deuterium oxide (D_2O) and characterized by ^1H NMR spectroscopy (600 MHz, D_2O). The spectrum of SBMAA displayed characteristic peaks at δ (ppm): 1.91–1.97 (c, 3H), 2.02–2.12 (k, 2H), 2.18–2.26 (j, 2H), 2.96–3.03 (i, 2H), 3.08–3.16 (g, h, 6H), 3.35–3.42 (f, e, 4H), 3.47–3.53 (d, 2H), 5.48–5.52 (b, 1H), and 5.72–5.75 (a, 1H).

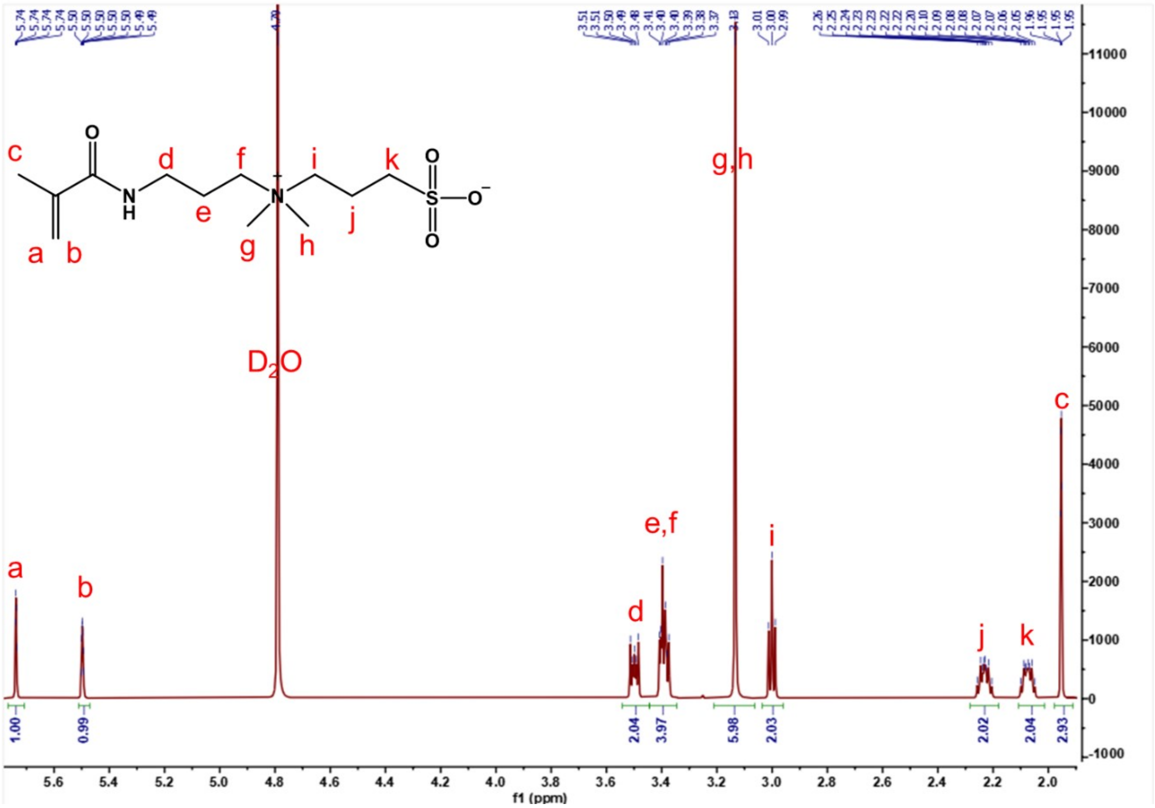

Figure S5. ^1H NMR spectrum and assignment of SBMAA monomer.

Table S1. The Comparative Mechanical Properties of EZHs and ZHs.

Sample name	Stress (KPa)	Strain (%)	Elastic modulus (KPa)
pSBA_EZH	77.2 ± 10.0	672.4 ± 26.3	32.9 ± 2.7
pSBMA_EZH	29.5 ± 83.4	1160.7 ± 83.4	4.5 ± 0.9
pSBAA_EZH	18.6 ± 5.4	523.0 ± 13.7	13.2 ± 0.7
pSBMAA_EZH	18.1 ± 2.0	620.7 ± 7.5	6.2 ± 0.9
pSBA_ZH	54.8 ± 6.7	84.7 ± 8.2	82.8 ± 6.6
pSBMA_ZH	33.7 ± 8.6	44.0 ± 4.4	81.4 ± 15.9
pSBAA_ZH	49.7 ± 6.1	83.9 ± 10.5	69.1 ± 7.2
pSBMAA_ZH	17.2 ± 1.0	67.1 ± 8.3	27.0 ± 2.0

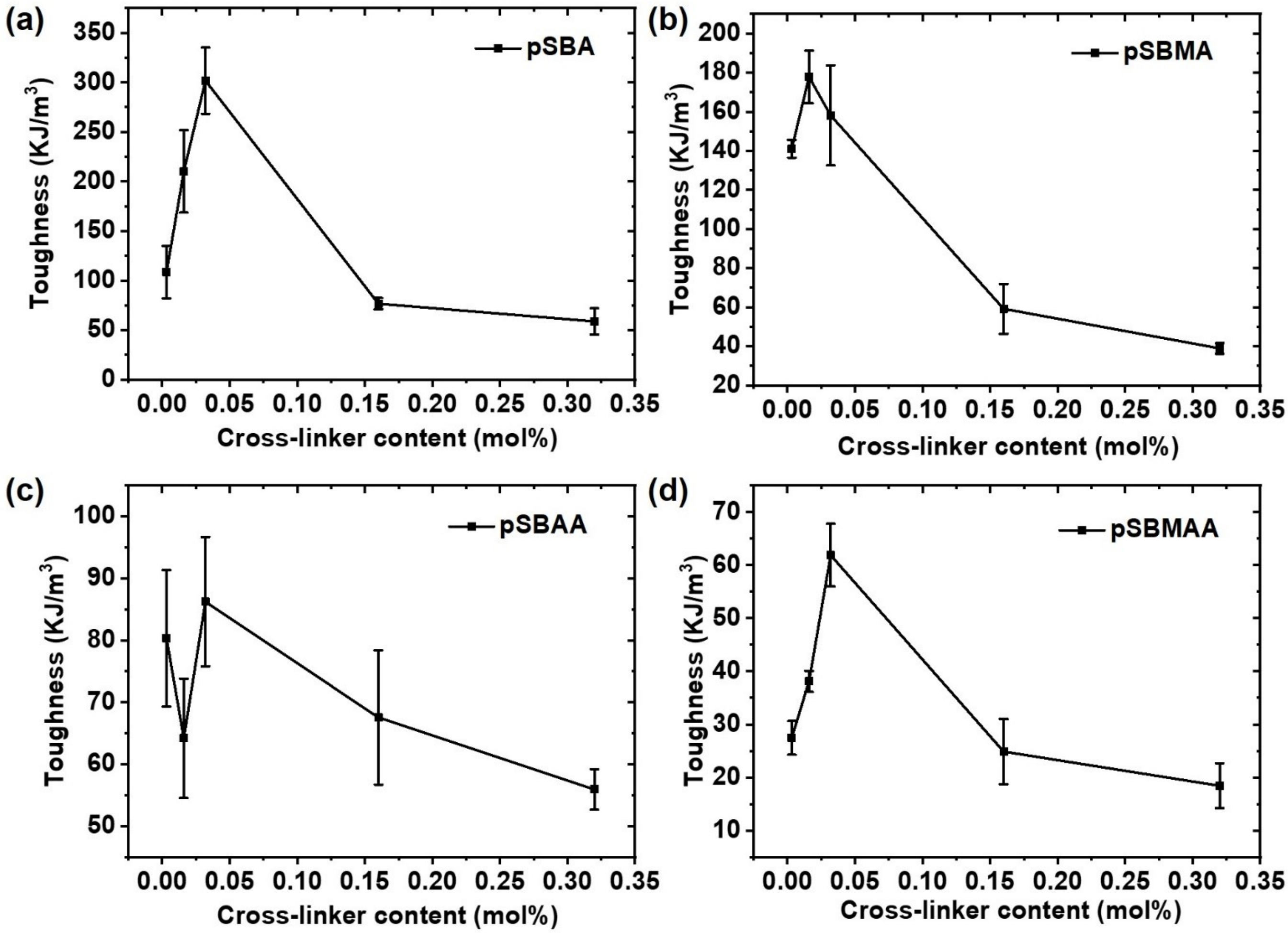

Figure S6. Toughness of highly entangled zwitterionic hydrogels with various cross-linked ratios. The EZHs include pSBA (a), pSBMA (b), pSBAA (c) and pSBMAA (d).