Supporting Information

Elastic-Plastic Transformation of Polyelectrolyte Complex Hydrogels from Chitosan and Sodium Hyaluronate

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1. Characterization of the degree of deacetylation of chitosan

The degree of deacetylation (DD) of chitosan was determined by NMR using chitosan aqueous solution containing trace of deuterium chloride (DCl), and calculated by the following equation[43]: $\mathrm{DD}\ (\%) = \left[1 - \left(\frac{1}{3} \times I_{CH3}\right) / \left(\frac{1}{6} \times I_{H2\sim H6}\right)\right] \times 100$, where, I_{CH3} is the integral intensity of H from CH_3 in the residual acetyl group, and $I_{H2\sim H6}$ is the summation of integral intensity of H2, H3, H4, H5, H6 and H6', as shown in **Scheme 1** .

2. Yield strain and failure strain

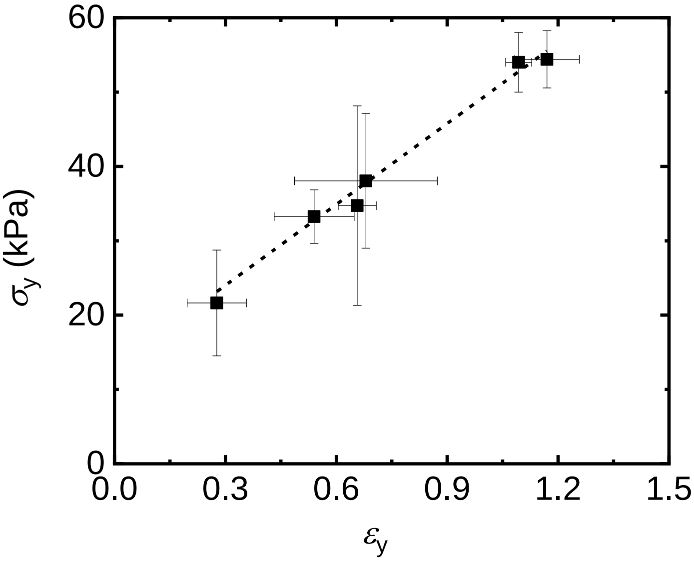

Figure S1 The dependence of yield stress σ_y on yield strain ε_y.

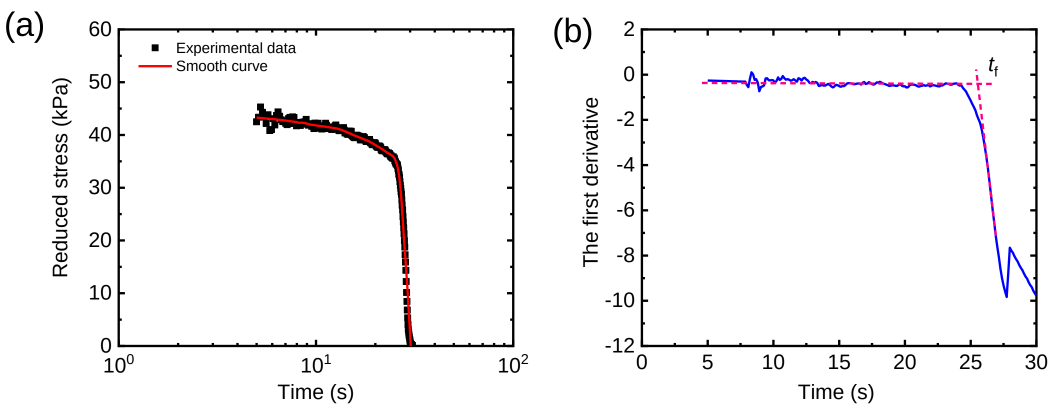

Figure S2 (a) Stretching time dependence of reduced stress $\sigma_{red} = \sigma/(\lambda - \lambda^{-2})$ at a strain rate $\dot{\varepsilon}$ of 0.014 s^{-1}. (b) The first derivative of reduced stress respect to the stretching time.

The reduced stress-time curve was smoothed by the Savitzky–Golay filter method in the Origin 9.0 software, with 50 data points used to obtain a smooth curve (Figure S2a). The smooth curve (red line) overlapped well with the original experimental data. The first derivative of the reduced stress with respect to time (blue line, Figure S2b) was calculated from the smooth curve. The derivative was almost constant and slightly negative at short times, and then sharply decreased at the onset of the failure. The first derivative curve can be roughly divided into two almost linear regions with the crossover in-between. Time to failure (t_f) was determined from the intersection of the two linear extrapolations (pink lines) of the first derivative curve in the slow varying and the sharply decreasing regions.

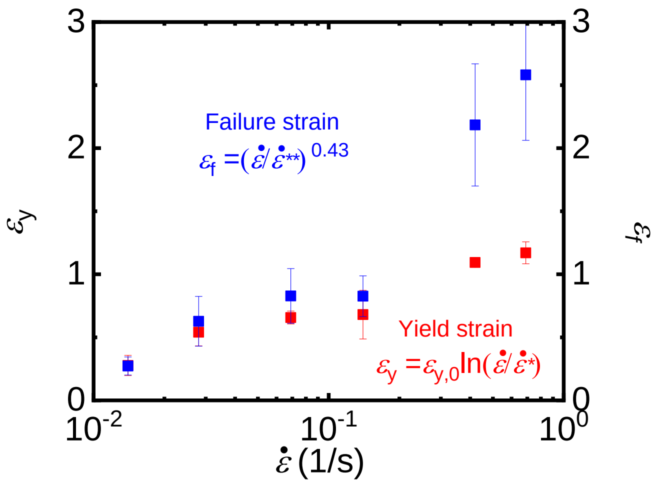

Figure S3 Strain rate $\dot{\varepsilon}$ dependence of yield strain ε_y and failure strain ε_f.

3. Structure parameters of PMPTC/PNaSS hydrogel

Table S1. Structure parameters of individual PMPTC and PNaSS chains.

Polymer	Molecular weight, M (g/mol)	Mass of repeat unit, m (g/mol)	Number of repeat units, n	Length of repeat unit, l (nm)	Distance between charges, d (nm)	Persistence length, l_p (nm)	Contour length, L_c (nm)
PMPTC	3.75×10^6	220.74	17,000	0.25	0.25	1	4250
PNaSS	-	206.19	-	0.25	0.25	1	-

Table S2. Structure parameters of PMPTC/PNaSS double-strands between entanglements.

	Entanglement molecular weight, M_e (g/mol)	Mass of the repeated unit m (g/mol)	Number of repeat units between entanglements, n_e	Persistence length, l_p (nm)	Contour length between entanglements, L_e (nm)
PMPTC/PNaSS double-strand gel	7×10^4	426.9	164	2	41

Here, we assume that the plateau modulus (~ 2×10^4 Pa) at low frequencies is due to the contribution from entanglements. Therefore, the entanglement molecular weight is calculated as ~ 7×10^4 g/mol from the equation of $G_e \cong \phi\rho RT/M_e$, using ϕ=0.45 and ρ=1.2 g/m^3.[20]

References

(20) Luo, F.; Sun, T. L.; Nakajima, T.; King, D. R.; Kurokawa, T.; Zhao, Y.; Ihsan, A. Bin; Li, X.; Guo, H.; Gong, J. P. Strong and Tough Polyion-Complex Hydrogels from Oppositely Charged Polyelectrolytes: A Comparative Study with Polyampholyte Hydrogels. *Macromolecules* **2016**, *49* (7), 2750–2760.

(43) Hirai, A.; Odani, H.; Nakajima, A. Determination of degree of deacetylation of chitosan by ^{1}H NMR spectroscopy. *Polymer Bulletin* **1991**, *26* (1), 87-94.