Supporting Information

Self-healing Behaviors of Tough Polyampholyte Hydrogels

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Supporting movies

Movie S1. Fast healing behavior. The fresh surfaces were brought together by pressing them slightly at room temperature and then immediately bended. It was surprisingly observed that the two pieces were self-healed immediately after joining. Sample used: PA-0.1.

Movie S2. High strength of the healed sample. After healed in water at 25 °C for 24 h, a dramatic level of self-healing was observed and the scars disappeared completely. The mended samples were able to sustain large deformations of more than 1000% and to recover their shape and size when stress was released. Sample used: PA-0.1

Supporting Table and Figures

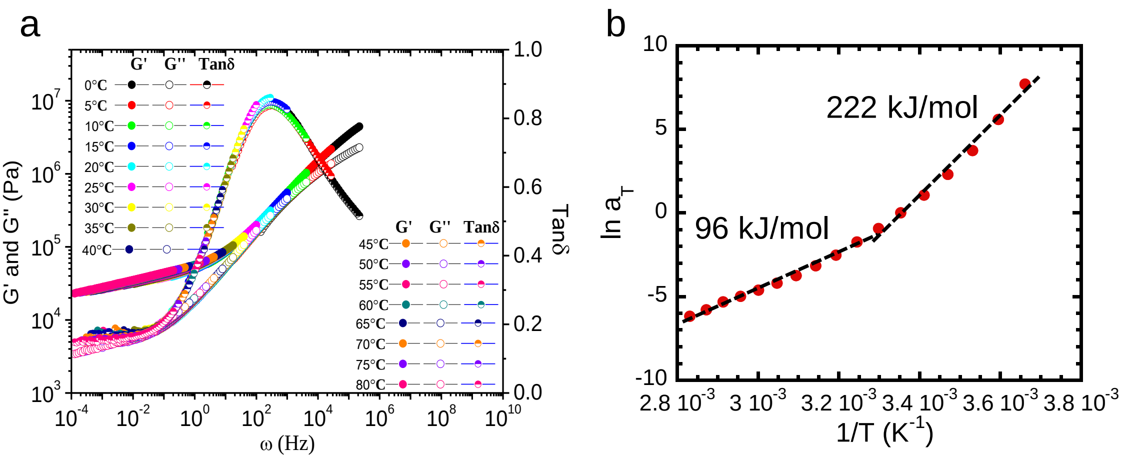

Figure S1: (a) A constructed master curve for frequency dependence of storage modulus (G′), loss modulus (G") and tanδ of PA-0.1. (**b**) Arrhenius plot depicting the temperature dependence of the shift factors for the sample.

By following the principle of time-temperature superposition, a master curve of storage modulus (G′), loss modulus (G") and tanδ over a wide frequency range for the equilibrated gel PA-0.1, was constructed at a reference temperature of 25°C, as presented in **Figure S1**. The apparent activation energy E_a is obtained from the Arrhenius equation, $a_T = Ae^{E_a/k_BT}$, where a_T is the shift factor, R is the ideal gas constant, and A is a constant. The temperature dependence of the shift factor a_T shows that the activation energy of the gel varies over a wide range, 96–222 kJ/mol.

Separation of transient bonds and permanent bonds

The transient, weak bonds and permanent, non-dynamic bonds (strong bonds, chemical and topological crosslinking) contribute to the nominal stress σ_N and they can be expressed by UCM element (viscose element) and the Gent element (elastic element), respectively,

$$\sigma_N(\lambda) = \sigma_{N,v}(\lambda) + \sigma_{N,e}(\lambda) \qquad (1)$$

where

$$\sigma_{N,v}(\lambda) = \left(\frac{2G_v D_e}{1-2D_e}\left(1-\exp\left(-\frac{(1-2D_e)}{D_e}(\lambda-1)\right)\right) + \frac{G_v D_e}{1+D_e}\left(1-\exp\left(-\frac{(1+D_e)}{D_e}(\lambda-1)\right)\right)\right)\lambda^{-1} \qquad (2)$$

for the viscoelastic stress, and

$$\sigma_{N,e}(\lambda) = \left(\frac{G_e}{1-\frac{\lambda^2+2\lambda^{-1}-3}{J_m}}(\lambda^2-\lambda^{-1})\right)\lambda^{-1} \qquad (3)$$

for the entropic elastic stress. Here, λ is the elongation ratio, G_v is the initial shear modulus of the viscoelastic part, stemming from the contribution of weak inter-chain bonds that rupture during deformation. D_e is the Deborah number (the product of the relaxation time of the viscous component and the strain rate). G_e is the shear modulus at small strain from the elastic part, stemming from the contributions of strong inter-chain bonds, the topological inter-chain entanglement, and the chemical cross-linking that do not flow during the deformation. J_m is the maximum allowable value of the first strain invariant representing the theoretical finite extensibility of the network chains. **Eq. 1** is determined by four parameters G_e, λ_m, G_v, and D_e. Since the Young's modulus $E = 3(G_e + G_v)$, we can fit the tensile stress-strain data with the model using 3 independent parameters and the Young's modulus E estimated from the tensile behaviour. The fitted G_e and G_v for the samples PA-C_{MBAA} are shown in **Figure 5** and the fitted parameters D_e and J_m are summarized in **Figure S2**. An increase in C_{MBAA} dramatically constrains the finite extensibility J_m. D_e keeps a constant, independent of C_{MBAA}.

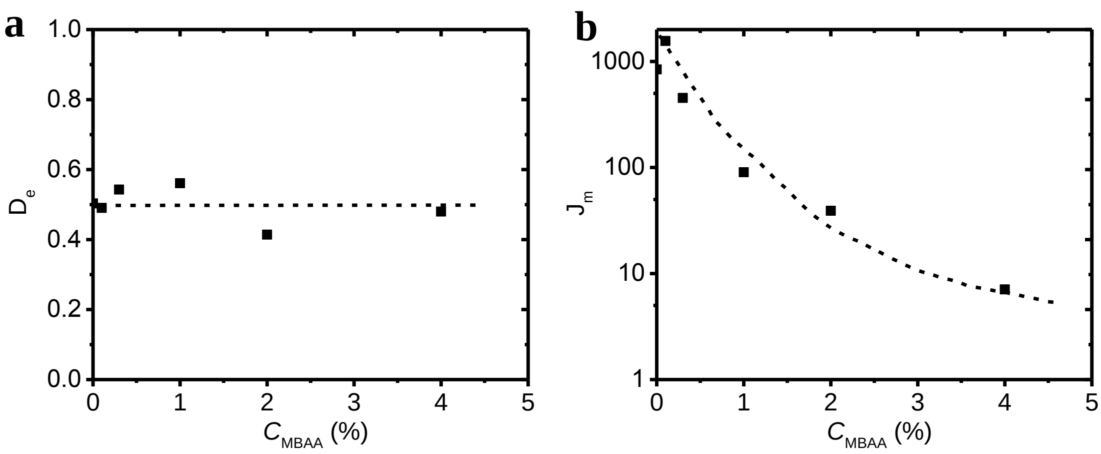

Figure S2. Chemical cross-linker density C_{MBAA} dependences of Deborah number (a) and theoretical first strain invariant value J_{m} (b) of PA-C_{MBAA} samples. The result was estimated from the tensile stress-strain curves performed at a stretching strain rate $0.011 s^{-1}$.

Table S1 Fitted parameters of polyampholyte gels PA-0.1 and PA*-0.

Sample	G_e (MPa)	G_v (MPa)	D_e	J_m	G_v/G_e
PA*-0 (25℃)	0.15	0.46	0.21	417.2	3.1
PA*-0 (55℃)	0.006	0.019	0.21	2125.8	3.2
PA-0.1 (4℃)	0.105	0.82	0.13	216.5	7.8
PA-0.1 (37℃)	0.0017	0.019	0.46	149.8	11.4
PA-0.1 (50℃)	0.0019	0.01	0.47	136.5	5.4