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 $25^\circ$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 $\sigma_N$ and they can be expressed by UCM element (viscose element) and the Gent element (elastic element), respectively, 

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

where

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

for the viscoelastic stress, and

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

for the entropic elastic stress. Here, $\lambda$ 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 $G_e$, $\lambda_m$, $G_v$, 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-CMBAA are shown in Figure 5 and the fitted parameters $D_e$ and $J_m$ are summarized in Figure S2. An increase in CMBAA dramatically constrains the finite extensibility $J_m$. $D_e$ keeps a constant, independent of CMBAA.
Figure S2. Chemical cross-linker density $C_{\text{MBAA}}$ dependences of Deborah number (a) and theoretical first strain invariant value $J_m$ (b) of PA-$C_{\text{MBAA}}$ samples. The result was estimated from the tensile stress-strain curves performed at a stretching strain rate $0.011 \text{s}^{-1}$.

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

<table>
<thead>
<tr>
<th>Sample</th>
<th>$G_e$ (MPa)</th>
<th>$G_v$ (MPa)</th>
<th>$D_e$</th>
<th>$J_m$</th>
<th>$G_v/G_e$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PA*-0 (25°C)</td>
<td>0.15</td>
<td>0.46</td>
<td>0.21</td>
<td>417.2</td>
<td>3.1</td>
</tr>
<tr>
<td>PA*-0 (55°C)</td>
<td>0.006</td>
<td>0.019</td>
<td>0.21</td>
<td>2125.8</td>
<td>3.2</td>
</tr>
<tr>
<td>PA-0.1 (4°C)</td>
<td>0.105</td>
<td>0.82</td>
<td>0.13</td>
<td>216.5</td>
<td>7.8</td>
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<tr>
<td>PA-0.1 (37°C)</td>
<td>0.0017</td>
<td>0.019</td>
<td>0.46</td>
<td>149.8</td>
<td>11.4</td>
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<tr>
<td>PA-0.1 (50°C)</td>
<td>0.0019</td>
<td>0.01</td>
<td>0.47</td>
<td>136.5</td>
<td>5.4</td>
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