Title	Inverse mechanical-swelling coupling of a highly deformed double-network gel
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Supplementary Materials for

Inverse mechanical-swelling coupling of a highly deformed double-network gel

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This PDF file includes:

Supplementary Text
Figs. S1 to S6

Supplementary Text

Determination of φ_1 and φ_2 of the PNaAMPS/PAAm DN gel

The first network of the PNaAMPS/PAAm DN gels was prepared by the radical polymerization of 1.4 M NaAMPS with small amount of cross-linker. We assume the conversion ratio of the reaction is 100%. Since the DN gels swelled 10.9 times in volume in comparison with the as-prepared first network, molar concentration of the AMPS monomeric unit in the swollen DN gels is 1.4/10.9 = 0.128 M. Given the molecular weight of the AMPS unit of 207.25 and density of dried PAMPS of 1.74 g/ml, volume fraction of the AMPS monomeric unit in the as-prepared PNaAMPS/PAAm DN gels, φ_1, is estimated as 0.0152. The second network was prepared by the radical polymerization of 2 M AAm with small amount of cross-linker in the presence of the first network. Since the DN gels swelled 1.52 times in volume in comparison with the as-prepared DN gels, molar concentration of the AAm monomeric unit in the swollen DN gels is 2/1.37 = 1.46 M. Given the molecular weight of the AAm unit of 71.08 and density of dried PAAm of 1.44 g/ml, volume fraction of the AAm monomeric unit in the as-prepared PNaAMPS/PAAm DN gels, φ_2, is estimated as 0.0721.

The swelling model based on the Neo-Hookean hyperelastic model

Π_{el} of the Neo-Hookean model upon the stress relaxation experiment is derived by substitution of Eq. 8 into Eq. 20 as

$$\Pi_{\mathrm{el}} = -2{\Lambda_{\mathrm{x}}}^{-1} c_{10}. \tag{S1}$$

This is a monotonically increasing function of Λ_{x}. The corresponding equation of state of a DN gel is

$$-2{\Lambda_{\mathrm{x}}}^{-1} c_{10} - \frac{kT}{v_s}\big(\ln(1-\phi_1-\phi_2) + \phi_1 + \phi_2 - \chi_{12}\phi_1\phi_2 + \chi_{1s}\phi_1(\phi_1+\phi_2) + \chi_{2s}\phi_2(\phi_1+\phi_2)\big) + \frac{\alpha\phi_1}{v_1} = 0. \tag{S2}$$

This swelling model always predicts extension-induced swelling regardless of Λ_{x}, as shown in fig. S5.

Comparison of various hyperelastic models

The following hyperelastic models were used to describe stress-strain curves and the experimental stress relaxation results of the pre-treated DN gels.

Abbreviations:

I_2: ${\Lambda_x}^2{\Lambda_y}^2 + {\Lambda_y}^2{\Lambda_z}^2 + {\Lambda_x}^2{\Lambda_z}^2$

N: number of segments in a single network strand

β: $\mathcal{L}^{-1}\left(\frac{I_1}{\sqrt{N}}\right)$, where $\mathcal{L}^{-1}$ is the inverse Langevin function.

c_{ik}: materials constants, where i and k are arbitrary numbers.

Mooney-Rivlin model

$$\Delta F^{\mathrm{el}} = c_{10}(I_1 - 3) + c_{01}(I_2 - 3) \tag{S3}$$

$$\sigma_{\mathrm{x}} = 2\left(\Lambda_{\mathrm{x}} - \frac{{\Lambda_{\mathrm{y}}}^2}{\Lambda_{\mathrm{x}}}\right)c_{10} + 2\left(2\Lambda_{\mathrm{x}} - \Lambda_{\mathrm{x}}{\Lambda_{\mathrm{y}}}^2 - \frac{{\Lambda_{\mathrm{y}}}^4}{\Lambda_{\mathrm{x}}}\right)c_{01} \tag{S4}$$

Arruda-Boyce model

$$\Delta F^{\mathrm{el}} = 2c_{10}\sqrt{N}\left[\beta I_1 + \sqrt{N}\ln\frac{\beta}{\sinh\beta}\right] \tag{S5}$$

$$\sigma_{\mathrm{x}} = \frac{2}{3}\left(\Lambda_{\mathrm{x}} - \frac{{\Lambda_{\mathrm{y}}}^2}{\Lambda_{\mathrm{x}}}\right)c_{10}\left(\frac{9N - {\Lambda_{\mathrm{x}}}^2 - 2{\Lambda_{\mathrm{y}}}^2}{3N - {\Lambda_{\mathrm{x}}}^2 - 2{\Lambda_{\mathrm{y}}}^2}\right) \tag{S6}$$

(Padé approximation)

Yeoh model

$$\Delta F^{\mathrm{el}} = c_{10}(I_1 - 3) + c_{20}(I_1 - 3)^2 + c_{30}(I_1 - 3)^3 \tag{S7}$$

$$\sigma_{\mathrm{x}} = 2\left(\Lambda_{\mathrm{x}} - \frac{{\Lambda_{\mathrm{y}}}^2}{\Lambda_{\mathrm{x}}}\right)\left(c_{10} + 2c_{20}(I_1 - 3) + 3c_{30}(I_1 - 3)^2\right) \tag{S8}$$

Extended Gent model

$$\Delta F^{\mathrm{el}} = -c_{10}J_{\mathrm{m}}\ln\left(1 - \frac{I_1 - 3}{J_{\mathrm{m}}}\right) + c_{01}(I_2 - 3) \tag{S9}$$

$$\sigma_{\mathrm{x}} = 2\left(\Lambda_{\mathrm{x}} - \frac{{\Lambda_{\mathrm{y}}}^2}{\Lambda_{\mathrm{x}}}\right)c_{10}\frac{J_{\mathrm{m}}}{J_{\mathrm{m}} - I_1 + 3} + 2\left(2\Lambda_{\mathrm{x}} - \Lambda_{\mathrm{x}}{\Lambda_{\mathrm{y}}}^2 - \frac{{\Lambda_{\mathrm{y}}}^4}{\Lambda_{\mathrm{x}}}\right)c_{01} \tag{S10}$$

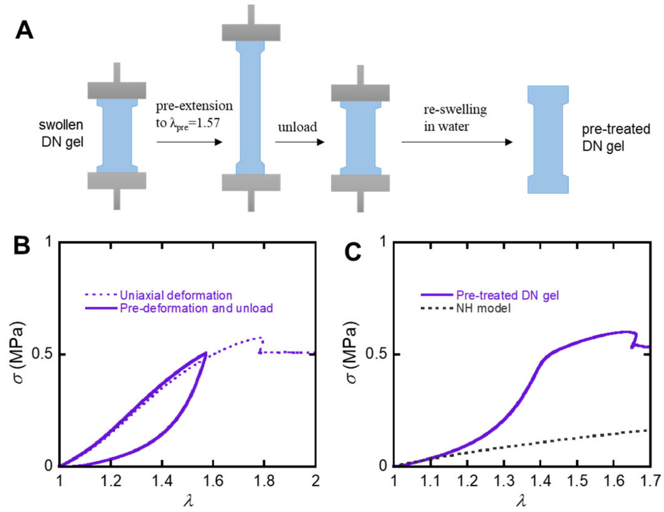

Fig. S1. Pre-treatment of the PNaAMPS/PAAm DN gel.

(**A**) Pretreatment process of the PNaAMPS/PAAm DN gel. The PNaAMPS/PAAm DN gel was subjected to uniaxial pre-extension to λ_{pre} = 1.57 for cutting the short primary network strands, and thereafter, unloaded and swollen in pure water to achieve another swelling equilibrium. (**B**) Pre-extension cyclic curve of PNaAMPS/PAAm DN gel during the pretreatment. The irreversible mechanical hysteresis during the loading–unloading process corresponds to the partial rupture of the primary network strands. After the pretreatment, the DN gel slightly swelled (1.14 times) along the stretching axis but negligibly swelled (1.00 times) along the remaining two axes owing to the anisotropic mechanical damage. (**C**) Uniaxial σ–λ curve of the pretreated PNaAMPS/PAAm DN gel. Dashed lines denote predictions of NH model. The uniaxial σ–λ curve could not be fitted using the NH model. The σ–λ curve possesses obvious flection at λ = 1.40, corresponding to the maximum elongation at the pre-deformation. Note that the observed λ = 1.40 was slightly smaller than the applied deformation ratio λ_{pre} = 1.57 at the pre-extension owing to the further swelling of the DN gel after the pretreatment, as discussed earlier (1.57/1.40 = 1.12 ≈ 1.14).

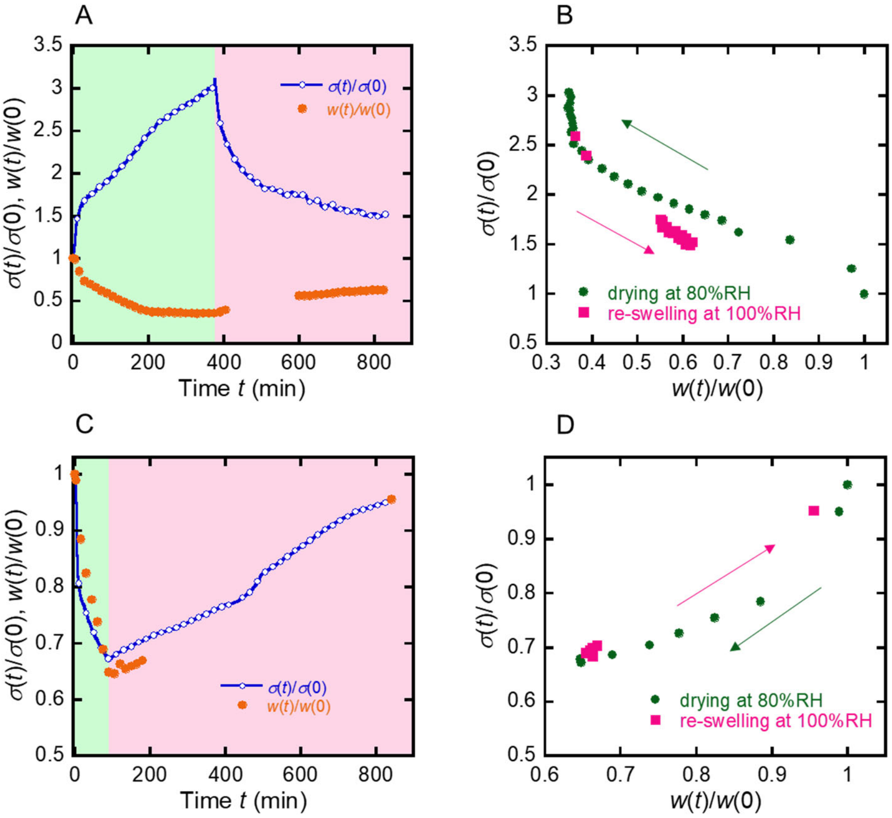

Fig. S2. Reversibility of the stress-width relationship.

The sequential stress relaxation results of the pre-treated DN gels in a humidity-controlled chamber. The relative humidity in the chamber was first set to 80%RH (green background in the graph) then changed to 100%RH (light red background in the graph) during the stress relaxation test. The gel de-swelled at 80%RH and re-swelled at 100%RH. (**A, B**) λ=1.08 where the DN gel shows the normal coupling. The engineering stress first increases with deswelling at 80%RH but decreases with re-swelling at 100%RH. (**C, D**) λ=1.38 where the DN gel shows the inverse coupling. The engineering stress first decreases with deswelling at 80%RH but increases with re-swelling at 100%RH. Note that most of the data of w(t)/w(0) at 100%RH are missing because of the cloudy observation window of the chamber due to the saturation of humidity.

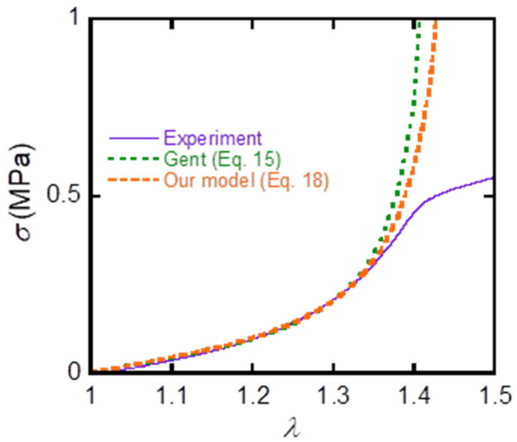

Fig. S3. Model prediction of the uniaxial stress-deformation ratio curve.

The stress-deformation ratio curve of the pre-treated PNaAMPS/PAAm DN gel fitted by the Gent model (Eq. 15) with c_{10}=27 kPa and J_{m}=13.8 and our model (Eq. 18) with c_{10}=38 kPa, c_{20}=−1.8 kPa and J_{m}=14.1.

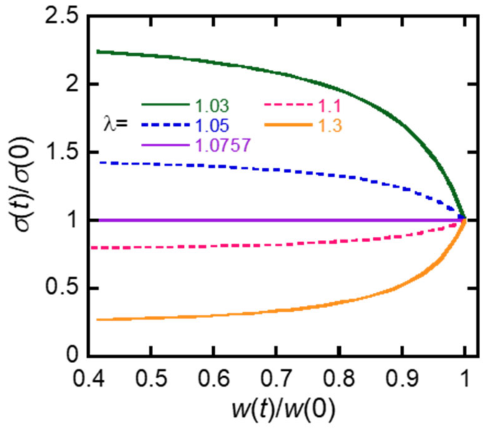

Fig. S4. Gent model prediction of the stress-width relationship.

The theoretical $\sigma(t)/\sigma(0)$ of the Gent model network (Eq. 15) as a function of $w(t)/w(0)$ upon the stress relaxation at various imposed λ with c_{10}=27 kPa and J_{m}=13.8. The Gent model always predicts monotonical stress-width relationship, which does not match the experimental data of the DN gels shown in Figure 7.

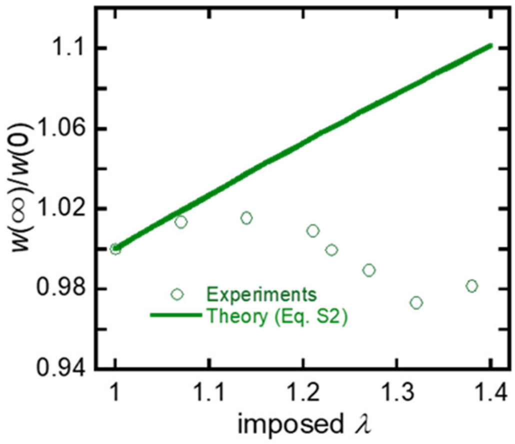

Fig. S5. Neo-Hookean model-based prediction of the equilibrium swelling state.

$w(\infty)/w(0)$ of the PNaAMPS/PAAm DN gel as a function of imposed λ upon the stress relaxation experiment under water estimated by the swelling model based on the Neo-Hookean hyperelastic model (Equation S2) with c_{10}=205 kPa,. The model always predicts extension-induced swelling.

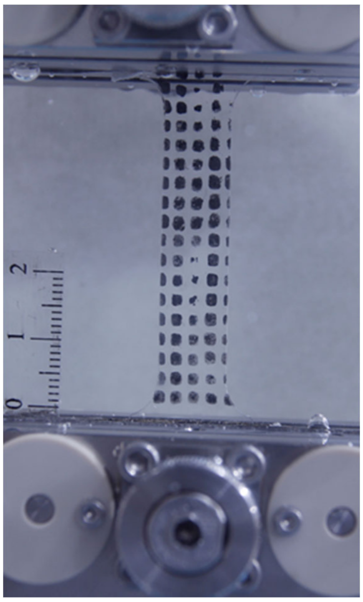

Fig. S6. A picture of a gel specimen for the stress relaxation experiments.
Black dots are periodically stamped on the specimen to determine its deformation ratio and normalized width.