Electronic Supplementary Material (ESI) for Soft Matter.

Supplementary Information for

Network elasticity of a model hydrogel as a function of swelling ratio; from shrinking to extreme swelling states

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Amount of elution of molecular stent from gels

Following the synthesis of the molecular stent (PNaAMPS) in the presence of the tetra-PEG gels, the St-tetra-PEG gels were immersed in pure water of 50 ml for two days. The amount of elution of the molecular stent from the gels was then investigated using the conductivity of the surrounding water.

First, the standard aqueous solutions of PNaAMPS in different concentrations, C_{PNaAMPS}, were prepared by dissolving PNaAMPS into pure water. Then the electrical conductivities, ρ, of the standard solutions were measured. We obtained the calibration curve for ρ (mS/cm) vs C_{PNaAMPS} (M) as $C_{\mathrm{PNaAMPS}} = 26.1 \times \rho^{0.87}$ from the experiment (Figure S1(a)). Subsequently, molar concentration of the eluted PNaAMPS in the surrounding water, C_{leak}, was determined based on their conductivity and the calibration curve (Figure S1(b)). Finally, the ratio of eluted PNaAMPS from the St-tetra-PEG gels, ϕ_{leak}, was estimated by the following equation,

$$\phi_{leak} \cong \frac{C_{leak} \times 50(ml)}{C_{stent} V_0} \quad \text{(S1)},$$

where V_0 is the volume of the St-tetra-PEG gels before immersion in pure water. The calculated ϕ_{leak} was in the order of several %, suggesting no significant oozing of molecular stent from the gels.

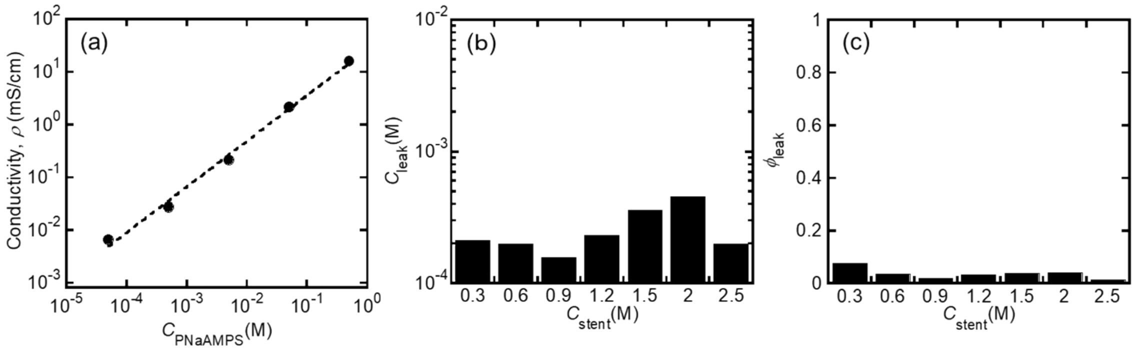

Figure S1. (a) Electrical conductivity, ρ, of the standard PNaAMPS aqueous solutions as a function of their molar concentration, $C_{PNaAMPS}$. The calibration curve for ρ (mS/cm) vs $C_{PNaAMPS}$ (M) was given as $C_{PNaAMPS} = 26.1 \times \rho^{0.87}$ from the experiment. (b) Concentration of the PNaAMPS in the surrounding water, C_{leak}, dependence on C_{stent}. C_{leak} was calculated based on the conductivity ρ of the surrounding water and the calibration curve. (c) The ratio of eluted PNaAMPS from the St-tetra-PEG gels, ϕ_{leak}, dependence on C_{stent}.

Determination of moduli by the indentation test

Hertz's contact theory was formulated for relatively hard materials but is applicable to soft materials such as gels. Figure S2(a) shows the raw indentation force (*f*) versus displacement (*l*) curves of the tetra-PEG gel (*Q*=1). The thickness values of the gel were 2, 3, and 5 mm. The power law relationship $f=Al^{2/3}$ (A is constant) at small values of l corresponded to Hertz's theory (Eq. (1)), suggesting the validity of the theory for soft materials. By using Eq. (1b) in the main text, Young's modulus is determined from coefficient A at $0<l<0.1$ (mm) as $E = 3A\left(1-{\nu_P}^2\right)/\left(4R^{\frac{1}{2}}\right)$. We did not observe the adsorption of gels into the indenter during the test, suggesting a negligible effect of friction between the gels and the indenter on the experimental results.

We confirmed no significant difference between the E of the polyacrylamide (PAAm) gels measured by the indentation test and that by the uniaxial tensile test, as shown in Figure S2(b).

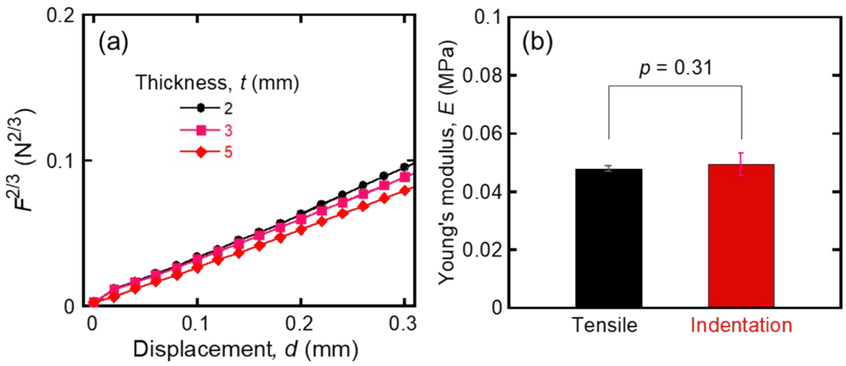

Figure S2. (a) The raw force$^{2/3}$-displacement curves of the indentation test for the tetra-PEG gel (Q=1) with varied thickness, t. Young's moduli were calculated using the slopes between $0<l<0.1$. (b) Comparison of Young's modulus of the PAAm gel determined by the indentation test with that of the uniaxial tensile test. The data were averaged over 8 measurements. The Student's unpaired *t*-test revealed a p value of 0.31, suggesting no significant difference between the mean moduli.

Effect of molecular stent presence on the gel moduli

The as-prepared St-tetra-PEG gels containing various concentration of molecular stent PNaAMPS were prepared in 5 mm thickness. Young's moduli of these as-prepared St-tetra-PEG gels were measured as shown in Figure S3. No tendency between E and C_{stent} could be found, suggesting presence of molecular stent itself does not affect Young's modulus of the St-tetra-PEG gels. It suggests that the molecular stent is either only trapped in the network owing to entanglements or is grafted to the network backbone.

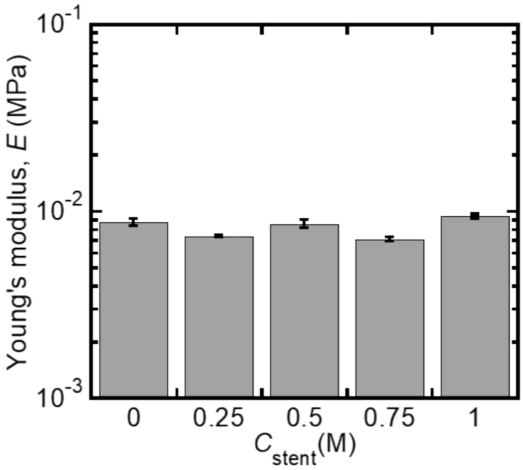

Figure S3. Young's modulus of the as-prepared St-tetra-PEG gels containing various concentration of molecular stent PNaAMPS. The data are average of 4 measurements.