Electronic Supplementary Material (ESI) for Soft Matter.

Supplementary information for

Double-network gels as polyelectrolyte gels with salt-insensitive swelling properties

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Derivation of $\Pi_{\mathrm{el}} \cong -G$ for the generalized 8-chain model

We assume the following generalized 8-chain model network for estimation of the single- and double-network gels, which is an expansion of the model proposed by Arruda and Boyce.[S1] This model network is an assemblage of cubic elements containing eight network strands from the centre to eight vertices at its relaxed state. We also assume the following things;

1. affine deformation
2. uniform strand length
3. Helmholtz free energy due to elasticity of the network, F_{el}, is simply sum of that of the network strands, F_{chain}.

Note that we do not assume Gaussian chain statistics. In this section, relaxed ($\lambda = 1$), equilibrium swelling state is set as its reference state. The gel volume at the reference state is V_{ref}. Our purpose is to derive $\Pi_{\mathrm{el}} \cong -G$ of the model gel at its reference state ($V = V_{\mathrm{ref}}$ and $\lambda = 1$).

Stretching ratio of a network strand, Λ , is defined as end-to-end distance of the strand at a state of interest divided by its reference state. Owing to the network configuration and the assumption 2, all the network strands show same stretching ratio, Λ , at any state of deformation. This fact and the assumption 3 lead Eq. S1;

$$F_{\mathrm{el}} = nF_{\mathrm{chain}} \tag{S1}$$

where F_{chain} is elastic free energy of the single network strand and n is number of elastically effective network strands in the network. As F_{chain} should be a function of Λ and n should be constant, F_{el} is also a function of Λ. We also define elastic energy density of the gel, W, as;

$$W = \frac{\Delta F_{\mathrm{el}}}{V_{\mathrm{ref}}} = n\frac{\Delta F_{\mathrm{chain}}}{V_{\mathrm{ref}}} \tag{S2}$$

W is also a function of Λ.

Firstly, we consider free swelling of the network. Elastic pressure, Π_{el}, is calculated by differentiation of ΔF_{el} by gel volume V;

$$\Pi_{\mathrm{el}} = -\frac{\partial \Delta F_{\mathrm{el}}}{\partial V} = -\frac{\partial W}{\partial (V/V_{\mathrm{ref}})} \tag{S3}$$

As W is a function of Λ and Λ should be a function of V/V_{ref}, we can decompose Eq. S3 as;

$$\Pi_{\mathrm{el}} = -\frac{\partial W}{\partial \Lambda}\frac{\partial \Lambda}{\partial (V/V_{\mathrm{ref}})} \tag{S4}$$

$\mathit{\Lambda}$ is proportional to $(V/V_{\mathrm{ref}})^{1/3}$, which leads;

$$\frac{\partial \mathit{\Lambda}}{\partial (V/V_{\mathrm{ref}})} = \frac{1}{3}\left(\frac{V}{V_{\mathrm{ref}}}\right)^{-\frac{2}{3}} \tag{S5a}$$

$$\Pi_{\mathrm{el}} = -\frac{1}{3}\frac{\partial W}{\partial \mathit{\Lambda}}\left(\frac{V}{V_{\mathrm{ref}}}\right)^{-\frac{2}{3}} \tag{S5b}$$

Subsequently, nominal stress, σ, upon uniaxial deformation is calculated by differentiation of W by the macroscopic deformation ratio, λ, as;

$$\sigma = \frac{\partial W}{\partial \lambda} \tag{S6}$$

Eq. S6 can be decomposed like Eq. S3 as

$$\sigma = \frac{\partial W}{\partial \mathit{\Lambda}}\frac{\partial \mathit{\Lambda}}{\partial \lambda} \tag{S7}$$

Considering the network configuration and volume incompressibility, we can derive the relationship between $\mathit{\Lambda}$ and λ upon uniaxial deformation as;

$$\mathit{\Lambda} = \sqrt{\frac{\lambda^2+2\lambda^{-1}}{3}} \tag{S8a}$$

$$\frac{\partial \mathit{\Lambda}}{\partial \lambda} = \frac{\lambda-\lambda^{-2}}{\sqrt{3(\lambda^2+2\lambda^{-1})}} \tag{S8b}$$

Substitution of Eq. S8b to Eq. S7 gives;

$$\sigma = \frac{\partial W}{\partial \mathit{\Lambda}}\frac{\lambda-\lambda^{-2}}{\sqrt{3(\lambda^2+2\lambda^{-1})}} \tag{S9}$$

Here, we define shear modulus, G, as follows;

$$G = \frac{\sigma}{\lambda-\lambda^{-2}} \tag{S10a}$$

$$\sigma = G(\lambda-\lambda^{-2}) \tag{S10b}$$

In general cases, G may depend on λ. Since the first order Taylor series for $\lambda-\lambda^{-2}$ at $\lambda = 1$ is $3(\lambda-1)$, Eq. S10b is approximated near $\lambda = 1$ as

$$\sigma = 3G(\lambda-1) = E(\lambda-1) \tag{S11}$$

where $E = 3G$ is Young's modulus and what we measured by the mechanical tests.

Substitution of Eq. S10b into S9 gives;

$$G(\lambda-\lambda^{-2}) = \frac{\partial W}{\partial \mathit{\Lambda}}\frac{\lambda-\lambda^{-2}}{\sqrt{3(\lambda^2+2\lambda^{-1})}} \tag{S12a}$$

$$G = \frac{\partial W}{\partial \Lambda}\frac{1}{\sqrt{3(\lambda^2+2\lambda^{-1})}} \tag{S12b}$$

Finally, Eqs. S5b and S12b are calculated under the conditions of the reference state ($V = V_{\mathrm{ref}}$ and $\lambda = 1$);

$$\Pi_{\mathrm{el}}|_{V=V_{\mathrm{ref}}} = -\frac{1}{3}\frac{\partial W}{\partial \Lambda} \tag{S13a}$$

$$G|_{\lambda=1} = \frac{1}{3}\frac{\partial W}{\partial \Lambda} \tag{S13b}$$

Thus, we obtain the desired relationship;

$$\Pi_{\mathrm{el}}|_{V=V_{\mathrm{ref}}} = -G|_{\lambda=1} \tag{S14}$$

By the way, it is well known that G is independent of λ for neo-Hookean solids assuming Gaussian chain model. Let us derive this relationship as a verification of the calculation. According to the Gaussian chain model, elastic energy per a single strand is given as;[S2]

$$\Delta F_{\mathrm{chain}} = \frac{3kT}{2}\Lambda^2 \tag{S15}$$

and the corresponding W and $\frac{\partial W}{\partial \Lambda}$ are;

$$W = \frac{3nkT}{2V_{\mathrm{ref}}}\Lambda^2 \tag{S16a}$$

$$\frac{\partial W}{\partial \Gamma} = \frac{3nkT}{V_{\mathrm{ref}}}\Lambda \tag{S16b}$$

Substitution of Eqs. S16b and S8a into Eq. S12 gives;

$$G = \frac{3nkT}{V_{\mathrm{ref}}}\frac{\Lambda}{\sqrt{3(\lambda^2+2\lambda^{-1})}} = \frac{nkT}{V_{\mathrm{ref}}} \tag{S17}$$

The obtained G is independent of λ and has well-known form, suggesting validity of our calculation.

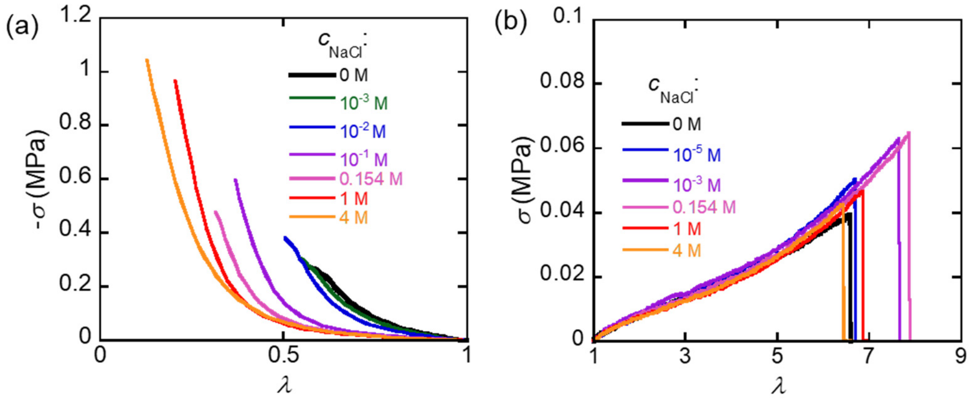

Figure S1. (a) Compressional stress-deformation ratio curves of the PAMPS gels after swelling in the NaCl solutions. (b) Tensile stress-deformation ratio curves of the PAAm gels after swelling in the NaCl solutions. The curves of the PAMPS gels are c_{NaCl}-dependent, whereas the curves of the PAAm gels are c_{NaCl}-independent.

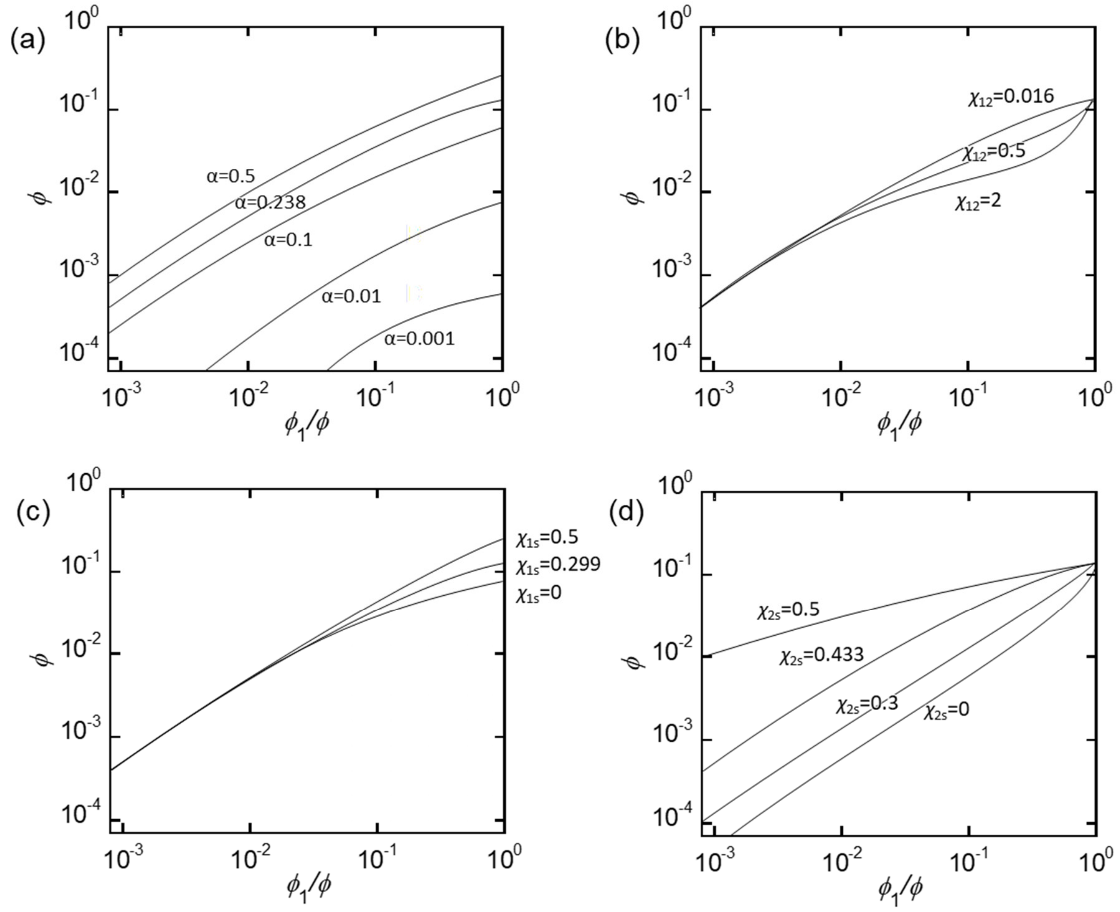

Figure S2. Effect of the parameter on the phase diagram shown in Figure 6(c); (a) α, (b) χ_{12}, (c) χ_{1s}, and (d) χ_{2s}. Unless mentioned in the figures, α, χ_{12}, χ_{1s}, χ_{2s} are set as 0.238, 0.016, 0.299 and 0.433, respectively. The solid lines denote $\pi_{\mathrm{mix}} = \pi_{\mathrm{ion}}$.

Relationship between the toughening condition and the salt-insensitive condition of DN gels

Previously we reported that the mechanical balance of the first and second networks is the key factor for toughening of the PAMPS/PAAm DN gels.[S3] Briefly, the DN gels become ductile (tough) when strength of the second network exceeds that of the first network, which are basically determined by number concentrations of the elastically-effective strands of the two networks. This toughening condition of the DN gels (key factor: concentrations of the strands) is similar to their salt-insensitive condition shown in this paper (key factor: concentrations of the polymers). To discuss the relationship between these two conditions, we plotted the data of the DN gels with various first and second network concentrations on the phase diagram about salt-sensitivity, as shown in Figure S3. These DN gels are classified into brittle and ductile groups based on their mechanical response, as shown in ref. S3. Interestingly, most of data of the brittle DN gels are in the salt-sensitive regime due to insufficient second network concentration, while data of the ductile DN gels are mainly in the salt-insensitive regime due to high second network concentration relative to the first network. However, the boundary for the brittle and ductile DN gels is not same as that for the salt-sensitive and salt-insensitive regimes. It means there is some relationship between the toughening and salt-sensitivity conditions, but there is no strong correlation between them. It is explained as follows. Salt-sensitivity of the DN gels is determined by concentration of the *polymers*. On the other hand, toughening condition is determined by number concentrations of the *strands*, not directly by concentration of the *polymers*.

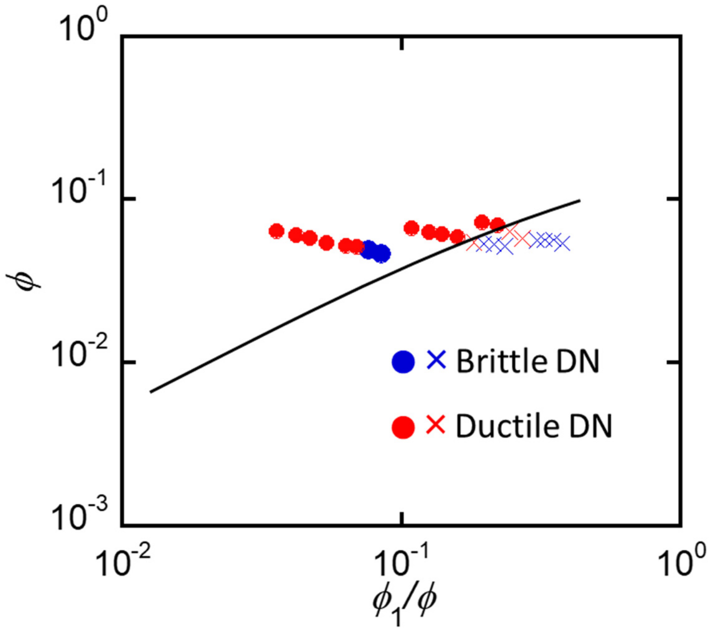

Figure S3. The relationship between the brittle-ductile transition condition of the DN gels and the salt sensitivity. The solid line denotes $\pi_{\mathrm{mix}} = \pi_{\mathrm{ion}}$. The data for brittle and ductile DNs are from ref. S3. Circle symbols denote $\pi_{\mathrm{mix}} > \pi_{\mathrm{ion}}$ and cross symbols denote $\pi_{\mathrm{mix}} < \pi_{\mathrm{ion}}$.

References

S1 E. M. Arruda and M. C. Boyce, *J. Mech. Phys. Solids*, 1993, **41**, 389–412.

S2 M. Rubinstein and R. H. Colby, *Polymer Physics*, Oxford University Press, New York, 2003.

S3 S. Ahmed, T. Nakajima, T. Kurokawa, M. A. Haque and J. P. Gong, *Polymer*, 2014, **55**, 914–923.