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Title	Double-network gels as polyelectrolyte gels with salt-insensitive swelling properties
Author(s)	Nakajima, Tasuku; Chida, Takaharu; Mito, Kei et al.
Citation	Soft matter, 16(23), 5487-5496 https://doi.org/10.1039/d0sm00605j
Issue Date	2020-06-21
Doc URL	https://hdl.handle.net/2115/81939
Type	journal article
File Information	chida_submission3_nohighlight.pdf

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ARTICLE

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

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

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Polyelectrolyte gels exhibit intrinsic salt-sensitive swelling behaviour, which causes size instability in ionic environments. Thus, polyelectrolyte gels that show salt-insensitive swelling have been anticipated for the applications in ionic environments, such as medical materials used *in vivo*. We found that double-network (DN) gels consisting of both a polyelectrolyte network and a non-ionic network are resistant to the salt-sensitive swelling. This resistance is attributed to their lower osmotic pressure originating from mobile ions relative to the osmotic pressure of mixing at swelling equilibrium. Our investigation indicated that the two contrasting network structures within DN gels are vital for achieving these properties, where the structures include a highly prestretched and sparse polyelectrolyte network and a coiled and dense non-ionic network. The salt-insensitivity of the DN gels has led to their unique applications in ionic environments.

Introduction

Swelling is a complex properties of polymer gels, where gels can swell to different extents in a solvent or solution depending on the several factors, such as affinity between polymer and solvent or ionic strength of the solution.[1,2] One may take advantage of this environmentally dependent swelling when developing stimuli-responsive gels, where applications include sensors,[3] drug delivery systems,[1,4,5] and actuators.[6] However, these properties are associated with unfavourable environmental stability.

The extent of swelling at equilibrium is determined by the balance of osmotic pressure and elastic pressure.[7] Swelling in non-ionic polymer (NP) gels is promoted by the osmotic pressure that originates from the polymer-solvent mixing and is suppressed by the elastic pressure of the network. Polyelectrolyte (PE) gels contain fixed charges on polymer chains with corresponding counterions; thus, the osmotic pressure originating from the mobile ions should also be considered as a factor.[7] A gel reaches equilibrium swelling when these pressures are balanced. PE gels typically exhibit a significantly larger swelling ratio than NP gels in a pure water or polar solvent due to higher osmotic pressure caused by the increased ionicity. At the same time, PE gels exhibit ionic strength-sensitive swelling behaviour. The swelling ratio of the PE gel decreases substantially with an increase in environmental ionic strength because of a decrease in the concentration difference of mobile ions between gels in their environment.[8–11] Not only homo-PE gels but also copolymer gels consisting of PE and NP, and interpenetrating network (IPN) gels containing PE component exhibit salt-sensitive swelling behaviour.[12–14] This can lead to unfavourable dimensional and mechanical instability of PE gels in ionic environments, including in the human body. Managing these changes in size and mechanical properties is required to allow for wider application of PE gels and their derivatives.

Double-network (DN) hydrogels have become popular due to their extreme toughness despite a high water content (ca. 90 wt.%).[15,16] Chemically cross-linked DN gels typically comprise of a PE first network and a non-ionic second network, and are referred to as PE/NP DN gels in this paper. PE/NP DN gels are usually synthesised as shown in Figure 1a. A densely cross-linked PE gel is prepared and immersed in a NP gel precursor solution. The PE gel becomes very swollen in the precursor solution due to its polyelectrolyte nature, leading to pre-stretching of the PE gel network strands. A sparsely cross-linked NP network forms within the swollen PE network to produce a PE/NP DN gel. These two networks have contrasting characteristics, where the PE network is rigid and brittle due to pre-stretching of the network strands and dense cross-linking, while the NP network is soft and stretchable due to its coiled network strands and sparse cross-linking. Optimised PE/NP DN gels can exhibit extreme fracture energies ranging 1,000 to 4,000 J m^{-2}, while single PE and NP gels usually range 1 to 100 J m^{-2}.[16,17] This high toughness of DN gels has been attributed to the contrasting double-network structure.[18,19]

Although the swelling properties of PE gels are typically sensitive to ionic strength of the environment, previous studies have indicated that the swelling behaviour of PE/NP DN gels is not sensitive to the ionic strength.[20–22] Thus, despite having PE as the first network, PE/NP DN gels do not behave like regular

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Electronic Supplementary Information (ESI) available: [The stress-deformation ratio curves of the PAMPS gels and the PAAm gels after swelling in the NaCl solutions]. See DOI: 10.1039/x0xx00000x

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PE gels. This is a great advantage that allows for various unique applications of PE/NP DN gels in ionic environments. PE/NP DN gels have been used as a substrate for *in vivo* cartilage regeneration, where the DN gel embedded at the cartilage defect induced spontaneous cartilage regeneration. This success was attributed to the salt-insensitive polyelectrolyte nature of the DN gel. The PE component in the PE/NP DN gels played a vital role in activating the cartilage regeneration signalling pathway,[23] while the ionic strength-insensitive swelling led to size stability of the gels embedded *in vivo*.[22] PE/NP DN gels have also been used as a template for biomineralization, which involves the synthesis of minerals in/on materials under mild conditions to develop functional hybrid materials.[24,25] PE gels show potential for use as a biomineralisation template because the ionic groups in the PE gels can serve as nucleation sites for crystal growth.[26] However, PE gels shrink substantially when immersed in biomineralisation precursor salt solutions, which leads to high internal stress and macroscopic failure of the gel. PE/NP DN gels are a viable alternative for biomineralisation that offer nucleation sites due to the PE component and do not shrink significantly in salt solutions due to their salt-insensitive swelling ability.[20,21] Furthermore, PE/NP DN gels may be used in marine environments, especially as an anti-fouling material against barnacles.[27]

This study aimed to investigate the basis of the ionic strength-insensitive swelling properties of PE/NP DN gels. The swelling behaviour of PE/NP DN gels in ionic environments were evaluated experimentally and theoretically. DN gel and its components were subjected to a swelling test in aqueous sodium chloride (NaCl) solutions (monovalent ions) and multivalent salt solutions. The experimental data and established theoretical knowledge were used to discuss the origin of PE/NP DN gel's salt-insensitive swelling behaviour. A model system was developed based on a typical DN gel consisting of poly(2-acrylamido-2-methylpropanesulfonic acid) (PAMPS) as the PE first network and polyacrylamide (PAAm) as the NP second network. This DN gel has been used widely in previous studies.[16]

The following symbols, superscripts and subscripts are used throughout this paper to describe the parameters of each gel component in different swelling states:

Symbols:
m: mass
w: weight fraction
ϕ: volume fraction
ρ: density
Superscripts: state of gels
p: as-prepared state (before swelling)
w: equilibrium swelling state in water
s: equilibrium swelling state in salt solutions
d: dried state
No subscript: general case
Subscripts: components
1: PAMPS
2: PAAm
s: solvent
No subscript: total polymer (general case)

For example, w_1^s is the weight fraction of the PAMPS component at swelling equilibrium in a salt solution and ϕ_2^d is the volume fraction of the PAAm component at the dried state. Schematic illustrations of the PAMPS. PAAm and DN gels at their as-prepared state and at equilibrium swelling in pure water are given in Figure 1b.

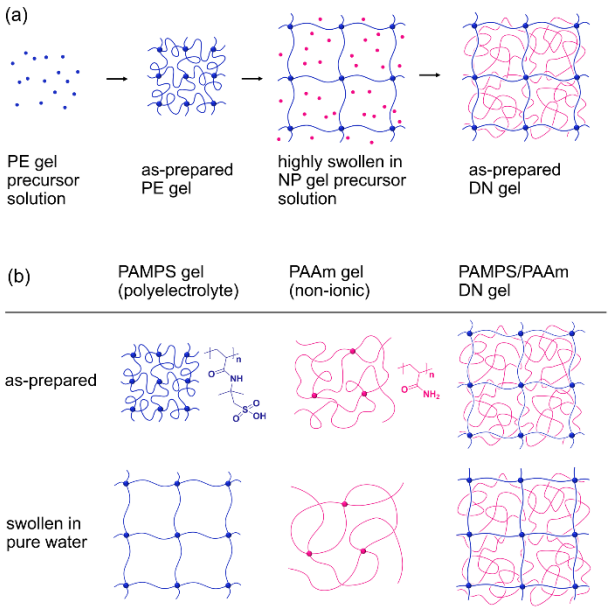

Figure 1. (a) Preparation of PE/NP DN gels consisting of a prestretched polyelectrolyte first network and a dense non-ionic second network. (b) The PAMPS, PAAm and PAMPS/PAAm DN gels at their as-prepared state and equilibrium swelling state in pure water, where the DN gels consist of a prestretched PAMPS network and the coiled PAAm network.

Theory

A DN gel consists of three components, namely the first network, the second network and solvent. According to the Flory-Rehner-like swelling theories, swelling equilibrium of a gel is determined by a balance of three independent contributions: Π_{el}, Π_{mix} and Π_{ion}.[7] Π_{el} is the elastic pressure of the network that suppresses swelling. Π_{mix} and Π_{ion} are the osmotic pressure differences between a gel and its environment, that basically promote swelling, originating from the mixing of polymer and solvent and from mobile ions, respectively. At the swelling equilibrium, the osmotic pressure difference of a gel is balanced by its elastic pressure, giving Eq. 1:

$$\Pi_{el} = \Pi_{mix} + \Pi_{ion} \quad (1)$$

For simplicity, in this paper, Π_{el}, Π_{mix} and Π_{ion} are termed elastic, mixing and ionic contributions, respectively.

Π_{mix} is often estimated using the Flory-Huggins lattice model.[7] Assuming that no volume change occurs upon mixing the polymer networks and solvent, the change in Helmholtz's

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free energy during the formation of the ternary system by mixing two polymers and one solvent is given in Eq. 2:[28]

$$\frac{\Delta F_{\mathrm{mix}}}{nkT} = \frac{\phi_1}{N_1}\ln\phi_1 + \frac{\phi_2}{N_2}\ln\phi_2 + \phi_s\ln\phi_s + \chi_{12}\phi_1\phi_2 + \chi_{1s}\phi_1\phi_s + \chi_{2s}\phi_2\phi_s \quad (2)$$

The volume of each lattice (v_{s}) was based on one solvent molecule, namely water. v_{s} = 3 x 10^{-29} m^3 was estimated from the density of liquid water.[29] n is total number of lattices in the gel, where the total volume of the gel (V) = nv_{s}. ϕ_i is the volume fraction of the component i in a gel, N_i is number of lattices occupied by a single molecule of i, and χ_{ij} is Flory interaction parameter between the components i and j, where i and j = 1, 2 or s indicate the first network, second network, and solvent, respectively. Polymer networks have a quasi-infinite polymerisation degree ($N \gg 1$), and the first two terms in Eq. 2 may be ignored for full-IPN gels, including DN gels, giving Eq. 3:

$$\frac{\Delta F_{\mathrm{mix}}}{nkT} \cong \phi_s\ln\phi_s + \chi_{12}\phi_1\phi_2 + \chi_{1s}\phi_1\phi_s + \chi_{2s}\phi_2\phi_s \quad (3)$$

Π_{mix} can be calculated by differentiating F_{mix} with respect to V. The change in V upon swelling of gels is caused by solvent migration, thus

$$\mathrm{d}V = v_s\mathrm{d}n_s \quad (4)$$

where n_{s} is number of lattices occupied by the solvent. Eq. 5 is based on this relationship:

$$\Pi_{\mathrm{mix}} = -\frac{1}{v_s}\frac{\delta F_{\mathrm{mix}}}{\delta n_s} \cong -\frac{kT}{V_s}\left(\ln\phi_s + \phi_1 + \phi_2 - \chi_{12}\phi_1\phi_2 + \chi_{1s}\phi_1(1-\phi_s) + \chi_{2s}\phi_2(1-\phi_s)\right) \quad (5)$$

For Π_{el}, we adopt the generalized 8-chain model network that shows affine deformation and has isotropic network strands. We also assume that elastic energy of the network is simply a sum of that of its network strands. Under these assumptions, Π_{el} can be estimated directly from the measured moduli of the gel without assuming Gaussian chain model:

$$\Pi_{\mathrm{el}} \cong -G = -\frac{E}{3} \quad (6)$$

where G is the shear modulus and E is the Young's modulus.[7] Detailed derivation process of Eq. 6 is shown in Supplementary information. Note that many previous papers have estimated Π_{el} based on the classical rubber elasticity theory, which assumes Gaussian end-to-end distance distribution of the network strands.[30] This estimation is valid for moderately swollen gels but is not applicable in highly swollen gels, including the PAMPS network used in this study. The actual elastic contribution of highly swollen gels is significantly larger than the classical estimation due to non-linear elasticity of the highly-prestretched network strands.[31,32]

For Π_{ion}, several factors that are related to charges contribute to the osmotic pressure of PE gels, including concentration differences of mobile ions between the gels and their environment and electrostatic repulsion between fixed changes on the network.[33] Following the previous theoretical studies about swelling of PE gels,[34,35] we only considered the concentration difference of mobile ions, although the other factors may affect slightly. When PAMPS is immersed in a NaCl solution, three mobile ion species should be present in the system, namely Na^+ and Cl^- (from NaCl) and H^+ (from PAMPS). Thus, Π_{ion} of the gel in this study was:

$$\Pi_{\mathrm{ion}} = kT\left(\left(c^g_{H^+} + c^g_{Na^+} + c^g_{Cl^-}\right) - \left(c^{env}_{H^+} + c^{env}_{Na^+} + c^{env}_{Cl^-}\right)\right) \quad (7)$$

where c^g_k and c^{env}_k are the concentration of mobile k ions in the gel and environment, respectively.[34] At swelling equilibrium, the system reaches Donnan equilibrium, where:

$$\left(c^g_{H^+} + c^g_{Na^+}\right)c^g_{Cl^-} = \left(c^{env}_{H^+} + c^{env}_{Na^+}\right)c^{env}_{Cl^-} \quad (8)$$

The volume of the environmental solution (containing NaCl) is assumed to be infinite, thus:

$$c^{env}_{H^+} \ll c^{env}_{Na^+} \quad (9a)$$

and

$$c^{env}_{H^+} + c^{env}_{Na^+} = c^{env}_{Cl^-} \cong c_{NaCl} \quad (9b)$$

where c_{NaCl} is the concentration of NaCl in the environment. Due to the electroneutrality of the gels:

$$c^g_{H^+} + c^g_{Na^+} = c^g_{Cl^-} + \frac{\alpha\phi_1}{v_1} \quad (10)$$

where v_1 is the volume of a monomeric unit of PAMPS, estimated as 2 x 10^{-28} m^3.[29] α is the ratio of the mobile counterions to the total counterions in the PAMPS network, while other immobile counterions may be bound to the network (counterion condensation).[36] Combining Eqs. 7, 8b and 9 gives Eq. 11:

$$\left(c^g_{H^+} + c^g_{Na^+} + c^g_{Cl^-}\right)^2 \cong \frac{\alpha^2{\phi_1}^2}{{v_1}^2} + 4{c_{\mathrm{NaCl}}}^2 \quad (11)$$

Π_{ion} can be calculated by substituting Eqs. 9b and 11 in Eq. 7, giving Eq. 12:

$$\Pi_{\mathrm{ion}} \cong kT\left(\sqrt{\frac{\alpha^2{\phi_1}^2}{{v_1}^2} + 4{c_{\mathrm{NaCl}}}^2} - 2c_{\mathrm{NaCl}}\right) \quad (12)$$

Substituting Eqs. 5, 6 and 12 in Eq. 1 gives the equation of state of the PE/NP DN gels at swelling equilibrium (Eq. 13):

$$\frac{E}{3} \cong -\frac{kT}{v_s}\left(\ln\phi_s + \phi_1 + \phi_2 - \chi_{12}\phi_1\phi_2 + \chi_{1s}\phi_1(1-\phi_s) + \chi_{2s}\phi_2(1-\phi_s)\right) + kT\left(\sqrt{\frac{\alpha^2{\phi_1}^2}{{v_1}^2} + 4{c_{\mathrm{NaCl}}}^2} - 2c_{\mathrm{NaCl}}\right) \quad (13)$$

Experimental

Materials

Acrylamide (AAm, Junsei Chemical Co., Ltd.) was recrystallised from chloroform. *N*,*N*'-Methylenebisacrylamide (MBAA, Wako Pure Chemical Industries, Ltd.) was recrystallised from ethanol. 2-Acrylamido-2-methylpropanesulfonic acid (AMPS) was acquired from Toa Gosei Co., Ltd. 2-oxoglutaric acid, sodium chloride, calcium chloride, barium chloride, magnesium chloride, cobalt(II) chloride, nickel(II) chloride, iron(III) chloride

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were acquired from Wako Pure Chemical Industries, Ltd. and used as received.

Preparation of gels

Synthesis of PAMPS gels. 1 M AMPS, 40 mM MBAA and 10 mM 2-oxogultaric acid were dissolved in pure water. The solution was transferred to an argon atmosphere and poured into a glass mould consisting of two soda-lime glass plates (thickness = 3 mm) separated by a U-shaped silicone rubber sheet. The mould was exposed to UV radiation (365 nm; 4 mW cm^{-2}) for 6 h.

Synthesis of PAAm gels. 2 M AAm, 2 mM MBAA and 2 mM 2-oxogultaric acid were dissolved in pure water. The solution was transferred to a glass mould in argon atmosphere as described above. The mould was irradiated under the same UV conditions for 8 h.

Synthesis of DN gels. The PAMPS gel was immersed in an aqueous solution of 2 M AAm, 0.4 mM MBAA and 0.2 mM 2-oxogultaric acid (PAAm precursor) for a minimum of 2 days. The PAMPS gel swelled significantly and was sandwiched by two glass plates and covered by a plastic wrap in an argon atmosphere. The gels were irradiated under the same UV conditions for 8 h to synthesise the PAAm network within the PAMPS gel.

Swelling test

Swelling test in water. The PAMPS gel, PAAm gel and DN gel were soaked in pure water at 297 K until swelling equilibrium was reached. The initial volume swelling ratio of the gels was defined as $\boldsymbol{V^{w}/V^{p}}$, where $\boldsymbol{V^{w}}$ is volume of the swollen gel in water and $\boldsymbol{V^{p}}$ is volume of the as-prepared gel.

Swelling test in salt solutions. After swelling in pure water, the PAMPS gel, PAAm gel and DN gel were transferred to two series of aqueous salt solutions at 297 K. The first was a NaCl series with varied concentrations ($\boldsymbol{c_{NaCl}}$) ranging 0 to 4 M, including the physiological concentration of 0.14 M. The second was a variety of chloride and multivalent counter-cation solutions, namely $CaCl_2$, $MgCl_2$, $BaCl_2$, $CoCl_2$, $NiCl_2$ and $FeCl_3$. The concentration of these multivalent salts was 1 M, regardless of cation valency. The volume de-swelling ratio of the gels was based on equilibrium swelling in water and is defined as $\boldsymbol{V^{s}/V^{w}}$, where $\boldsymbol{V^{s}}$ is the volume of the swollen gel in the salt solution.

Estimation of polymer volume fraction

Polymer volume fractions of the gel before swelling was estimated based on the weight fraction and density of each component. Polymer weight fraction of the gel was calculated based on its masses at the as-prepared state and the dried state:

$$w^{\mathrm{p}} = \frac{m^{\mathrm{d}}}{m^{\mathrm{p}}} \tag{14}$$

The weight ratio of the PAMPS and PAAm components in DN gels has been reported as 1:7.[37] Thus, weight fraction of the PAMPS and PAAm components in the DN gels at the as-prepared state can be calculated separately:

$$w_1^{\mathrm{p}} = \frac{1}{8} w^{\mathrm{p}} \tag{15a}$$

$$w_2^{\mathrm{p}} = w^{\mathrm{p}} - w_1^{\mathrm{p}} = \frac{7}{8} w^{\mathrm{p}} \tag{15b}$$

The corresponding polymer volume fraction of the gels at the as-prepared state (ϕ^{p}) was estimated as:

$$\phi^{\mathrm{p}} = \frac{\frac{w^{\mathrm{p}}}{\rho}}{\frac{w^{\mathrm{p}}}{\rho} + \frac{1-w^{\mathrm{p}}}{\rho_s}} \tag{16}$$

where ρ is the average density of the dried polymer and ρ_{s} is density of the solvent (water). It was assumed that no volume change occurred while mixing the polymers and solvent. The estimated ρ values of PAMPS and PAAm were 1.739±0.3 and 1.437±0.2 g cm^{-3}, respectively,[37,38] and the volume fraction of PAMPS (ϕ_1^{p}) and PAAm (ϕ_2^{p}) in the as-prepared DN gel were estimated separately based on these density values:

$$\phi_1^{\mathrm{p}} = \frac{\frac{w_1^{\mathrm{p}}}{\rho_1}}{\frac{w_1^{\mathrm{p}}}{\rho_1} + \frac{w_2^{\mathrm{p}}}{\rho_2} + \frac{1-w^{\mathrm{p}}}{\rho_s}} \tag{17a}$$

$$\phi_2^{\mathrm{p}} = \frac{\frac{w_2^{\mathrm{p}}}{\rho_2}}{\frac{w_1^{\mathrm{p}}}{\rho_1} + \frac{w_2^{\mathrm{p}}}{\rho_2} + \frac{1-w^{\mathrm{p}}}{\rho_s}} \tag{17b}$$

where ϕ^{p} of the DN gel is the sum of ϕ_1^{p} and ϕ_2^{p}.

Based on ϕ^{p}, the polymer volume fraction of the gel at any swelling states (ϕ) was estimated as:

$$\phi = \phi^{\mathrm{p}} \frac{V^{\mathrm{p}}}{V} \tag{18a}$$

Volume fraction of the PAMPS (ϕ_1) and PAAm (ϕ_2) in the DN gels was estimated similarly as:

$$\phi_1 = \phi_1^{\mathrm{p}} \frac{V^{\mathrm{p}}}{V} \tag{18b}$$

$$\phi_2 = \phi_2^{\mathrm{p}} \frac{V^{\mathrm{p}}}{V} \tag{18c}$$

The symbol ϕ_1 will be also used for the volume fraction of PAMPS in the PAMPS gel, thus $\phi = \phi_1$ for the PAMPS gel.

Mechanical characterizations.

Uniaxial tensile and compression testing of the gels were performed at 297 K. Nominal stress (σ) is defined as the force divided by initial cross-sectional area of the sample. Deformation ratio (λ) is defined as the length of the deformed sample divided by the undeformed length. Tensile tests were performed on DN gel and PAAm gel samples cut into dumbbell shapes (gauge length = 12 mm) at a stretching rate of 0.14 s^{-1}. The Young's modulus (E) was estimated based on the initial slope of the stress-deformation ratio curve ($1< \lambda <1.1$). Compression tests were performed on cylindrical PAMPS gel samples (diameter = 15 mm; thickness = 2.3–3.8 mm) using a TENSILON RTC-1310A compressive tester (Orientec Co.) at a

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compression rate of 0.1 min^{-1}. E was estimated based on the initial slope of the stress-deformation ratio curve ($0.9<\lambda<1$). Note that λ = 1 in the relaxed state and decreases with increasing compression.

Results and Discussion

Swelling in water

The initial volume swelling ratio of the PAMPS gel, PAAm gel and PAMPS/PAAm DN gel is given in Figure 2a. The PAMPS gel swelled significantly in pure water due to its ionic characteristics. The structure of the PAAm network in the PAAm and DN gels was very similar at their as-prepared states, while the DN gel included the additional prestretched PAMPS network (Figure 1b). The initial volume swelling ratio of the PAMPS/PAAm DN gel was smaller than the PAAm gel, despite containing the PAMPS network that exhibited a tendency toward substantial swelling.

The Young's modulus of the PAMPS gel and PAMPS/PAAm DN gel after swelling in pure water were similar, ranging 0.2 to 0.3 MPa, while that of the PAAm gel was much smaller (ca. 0.01 MPa) (Figure 2b). The swollen PAMPS network was densely cross-linked and extremely prestretched. Thus, its elastic modulus was quite large despite its low polymer fraction. The swollen PAAm network was sparsely cross-linked and coiled. Thus, despite its high density, the PAAm gel was less stiff than the PAMPS gel.

The smaller initial volume swelling ratio of the DN gel than the PAAm gel is because their Young's modulus directly correlated to the elastic pressure (Eq. 6). The large Young's modulus of the DN gel indicated that the highly prestretched PAMPS network within the DN gel contributed to a large elastic pressure. This high elasticity counteracted the large mixing contribution, and the swelling of the DN gel was effectively suppressed by the stiff, highly prestretched PAMPS component.

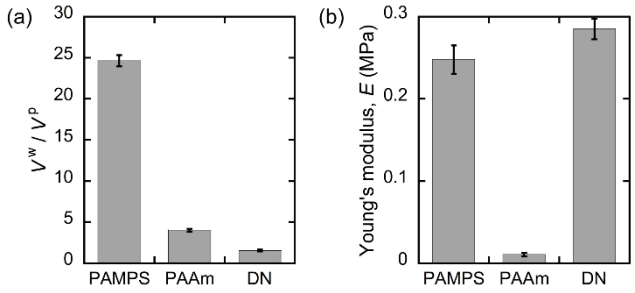

Figure 2. (a) Initial volume swelling ratios (V^w/V^p) of the PAMPS, PAAm and PAMPS/PAAm DN gels, where V^p and V^w denote volume of a gel at as-prepared state and at equilibrium swelling state in pure water, respectively. (b) Young's modulus of the PAMPS, PAAm and PAMPS/PAAm DN gels after swelling in pure water.

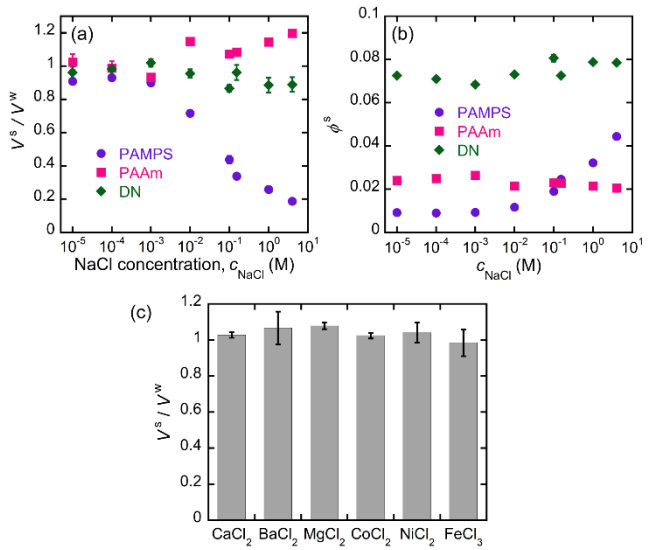

Figure 3. (a) De-swelling ratios (V^s/V^w) of the PAMPS, PAAm and PAMPS/PAAm DN gels in aqueous NaCl solutions of various concentrations (c_{NaCl}), where V^s denotes volume of a gel at equilibrium swelling in the salt solution. (b) Polymer volume fraction at equilibrium swelling (ϕ^s) of the gels in the NaCl aqueous solutions. (c) V^s/V^w of the PAMPS/PAAm DN gel in various 1 M multivalent salt aqueous solutions.

Swelling in salt solutions

The volume de-swelling ratio and corresponding polymer volume fraction of the PAMPS gels, PAAm gels and PAMPS/PAAm DN gels were evaluated in NaCl aqueous solutions of various concentrations (Figures 3a and 3b). The PAMPS gels shrank dramatically with increasing NaCl concentration, which is typical in a PE gel because the penetration of ions from the environment decreased the ionic contribution (Eq. 12). The PAAm gel did not shrink due to its non-ionic nature, while the DN gel similarly exhibited a swelling ratio that was not dependent on NaCl concentration. Even at the highest NaCl concentration of 4 M, the DN gel did not shrink significantly despite comprising a polyelectrolyte first network.

The de-swelling ratio of the PAMPS/PAAm DN gel immersed in various multivalent ion solutions demonstrated that the DN gel was resistant to changes in size in divalent or trivalent cation solutions (Figure 3c). This salt-insensitive swelling provides strong evidence that the mixing contribution of the DN gel was much larger than the ionic contribution because the salt-sensitive swelling characteristics of a PE gel is attributed to the ionic one. The positive osmotic pressure of the DN gel was dominated by the dense non-ionic PAAm.

The Young's modulus of the PAMPS, PAAm and DN gels after swelling in NaCl solutions of various concentrations indicated that mechanical properties of the PAMPS gel was strongly influenced by NaCl concentration, while those of the PAAm and DN gels were minimally affected (Figure 4a). The Young's modulus and overall stress-deformation curves of the DN gels at the various NaCl concentrations almost identical (Figures 4a and 4b), indicating mechanical stability of the DN gels in ionic environments. The stress-deformation ratio curves of the PAMPS gels and the PAAm gels in the NaCl solution of various concentrations are shown in Figure S1 of Supplementary Information. The changes in mechanical behaviour of the gels in the presence of NaCl were directly related to the swelling behaviour under these conditions. Mechanical properties of an elastic gel are determined by its network structure. The significant shrinkage of the PAMPS gel in the NaCl solutions indicated that its mechanical properties were dependent on NaCl concentration, while the minimal effects on swelling of the

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PAAm and DN gels indicated that their mechanical properties were independent of NaCl.

The relationship between swelling and the elastic properties of the gels was then investigated. The Young's modulus vs. the polymer volume fraction at equilibrium swelling (E-ϕ^s) plots of the gels after swelling in the aqueous NaCl solutions are given in Figure 4c. The PAMPS gels exhibited a negative correlation between when ϕ^s<0.02, while the E-ϕ^s relationships of the PAAm gel exhibited no clear trend due to the narrow polymer volume fraction range. The trends shown by the DN gels are also not clear because of the narrow ϕ^s range, but a negative E-ϕ^s correlation could be found like the PAMPS gels. As the Young's modulus of the PAMPS/PAAm DN gel was mainly dominated by the fully stretched PAMPS, the E of the PAMPS and DN gels should be both dependent on the volume fraction of PAMPS component in the PAMPS or DN gel (ϕ_1). Thus, the E-ϕ_1^s relationship of the PAMPS and the DN gels was investigated (Figure 4d). As expected, data of both samples exhibited the single empirical power-law relationship $E \propto \phi_1^{-1.2}$, suggesting that the E of the both gels was dominated by ϕ_1.

Negative E-ϕ correlation ($E \propto \phi_1^{-1.2}$) is uncommon in gels. The modulus of an elastic gel is determined by its network strand density (ν) and elastic energy per a network strand (U) based on the relationship $E \sim \nu U$. Swelling (volume increase) of a gel results in a decreased ϕ, causing a decrease in ν ($\nu \propto \phi^1$) and increase in U. Network strands characterised as Gaussian chains will behave like Hookean springs ($U \propto \phi^{-2/3}$). These two relationships lead to a positive E-ϕ correlation, i.e. $E \propto \phi^{1/3}$, which has been widely reported. The exponent of a real system may not be exactly 1/3 and can vary slightly due to the condition of a gel.[39,40] Conversely, highly stretched network strands exhibit non-linear strain hardening and an abrupt increase in elastic energy upon swelling, which is typically described by the inverse-Langevin function or the worm-like chain model.[41] This strong nonlinearity leads to large increases in U with a decrease in ϕ, and thus negative E-ϕ correlation. This behaviour has been observed in highly swollen PE gels.[34] Thus, the negative E-ϕ^s correlation of the PAMPS and DN gels means that the PAMPS network strands were highly stretched and possess a large elastic energy.[32]

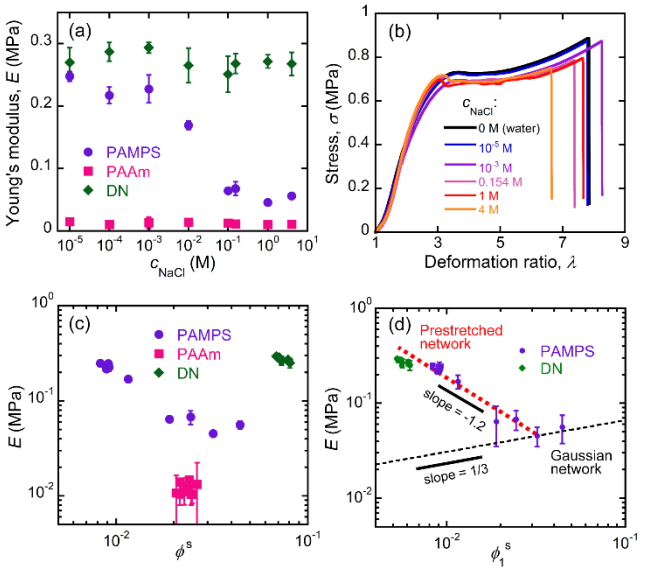

Figure 4. (a) Young's modulus (E) of the PAMPS, PAAm and PAMPS/PAAm DN gels in aqueous NaCl solutions with varying environmental NaCl concentration (c_{NaCl}). (b) Nominal tensile stress-deformation ratio curves of the DN gels after swelling in the NaCl solutions. (c) Relationship between E and polymer volume fraction at equilibrium swelling (ϕ^s) of the PAMPS, PAAm and DN gels. (d) Relationship between E and ϕ_1^s in the PAMPS and DN gels, where the empirical power-law relationship $E \propto \phi_1^{-1.2}$ is applicable at small ϕ_1^s values in a large swelling regime. The relationship of these gels deviated strongly from the typical $E \propto \phi^{1/3}$ based on a gel with Gaussian network strands.

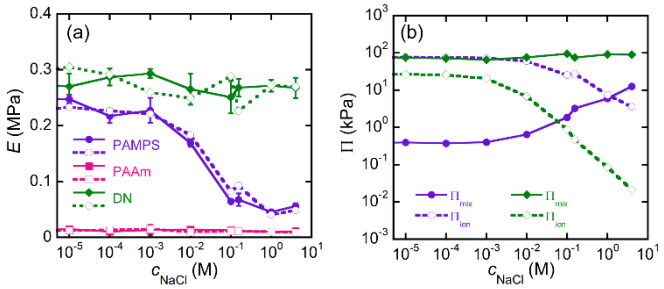

Figure 5. (a) Theoretical calculation of the relationship between NaCl concentration and Young's modulus (E) of the PAMPS, PAAm and PAMPS/PAAm DN gels. The filled points denote the experimental values and the open points denote the calculated values (Eq. 13). The parameters best fit for the calculation are given in Table 1. (b) Π_{mix} and Π_{ion} of the PAMPS (purple circle) and the DN (green diamond) gels calculated based on Eqs. 5 and 12.

Discussion

The experimental data confirmed that the PAMPS/PAAm DN gels exhibit salt-insensitive swelling and mechanical properties even at extremely high ionic strength. The salt-insensitivity of the PE/NP DN gels were then characterised using the theoretical estimations of the mixing and ionic contributions to the total swelling pressure of the gels. These estimations were based on the equation of state of the PE/NP DN gels (Eq. 13). The equation considers various parameters, where T (297 K) and c_{NaCl} were experimental conditions and ϕ_1^s and ϕ_2^s were experimentally determined. The remaining parameters χ_{12}, χ_{1s}, χ_{2s}, and α were based on fitting parameters that were assumed to be independent of other parameters such as NaCl concentration. These experimental and fitted values were used to calculate the Young's modulus.

Table 1. The best fitting parameters for each gel.

	PAMPS gel		PAAm gel		DN gel	
Parameter	this work	literature	this work	literature	this work	literature
χ_{12}	-	-	-	-	0.0160	0.015[18]
χ_{1s}	0.469	0.48[28]	-	-	0.299	0.3[18]
χ_{2s}	-	-	0.456	0.48–0.51[29]	0.433	0.45[18]
α	0.413	0.35[30]	-	-	0.232	-

The relationship between E and NaCl concentration of the PAMPS, PAAm and DN gels based on Eq. 13 and the best fit parameters is shown in Figure 5a, where the fitting parameters are given in Table 1. The experimental and calculated results were very similar, although the calculated E values exhibited slight deviates attributed to experimental errors in determining ϕ_1^s and ϕ_2^s. The best fit values were closely related to the literature values. The χ_{12}, χ_{1s} and χ_{2s} values of the

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PAMPS/PAAm DN gels in water were determined experimentally in a previous study as 0.3, 0.45 and 0.015, respectively, using the neutron scattering technique,[29] and closely reflect the best fit values of 0.299, 0.433 and 0.0160, respectively. The χ_{1s} and χ_{2s} values of the PAMPS and PAAm gel in water were estimated to be 0.48 and 0.48–0.51, respectively, based on the swelling test.[12,42] These experimental values were close to the best fit values of 0.469 and 0.456, respectively. The best fit ratio of the mobile counterions among total counterions (α) of the PAMPS gel was 0.413, which is consistent with a reported value of 0.35.[30] The best fit α of the DN gel was 0.232, only 56% of the PAMPS gel value. This implies that counterion condensation was more obvious in the DN gel than the PAMPS gel. This phenomenon was attributed to the difference in relative permittivity between the PAMPS and the DN gels. According the condensation theory by Manning, the minimum charge spacing allowed of a polyelectrolyte chain is the Bjerrum length, l_B, which is defined as:

$$l_{\mathrm{B}} = \frac{e^2}{\varepsilon kT} \qquad (19)$$

where e is the charge of an electron and ε is the relative permittivity.[36] Counterion condensation occurs when the distance between two adjacent ionic groups (l_0) is closer than (l_B). Thus, α can be determined as

$$\alpha = \frac{l_0}{l_{\mathrm{B}}} \qquad (20)$$

Eqs. 19 and 20 indicate that α is positively dependent on relative permittivity ($\alpha \propto \varepsilon$). The dense PAAm component of the DN gel should result in a difference in relative permittivity (ε) compared to the PAMPS gel. The best fit α value for the DN gel was 56% the PAMPS gel value, thus the ε value of the DN gel was expected to be 56% of the PAMPS gel value. Assuming the ε of the PAMPS gel was almost equal to that of pure water, namely 78, the ε of the DN gel was 44 (56% of 78). Ishida et al. reported that the ε value of poly(N-isopropylacrylamide) hydrogels at room temperature was 46.[44] Poly(N-isopropylacrylamide) is a derivative of PAAm, indicating that an ε value of 44 for the PAMPS/PAAm DN gels was reasonable.

As all of the best fit values were validated, the Π_{mix} and Π_{ion} of the gels were calculated based on Eqs. 5 and 12. The calculated Π_{mix} and Π_{ion} values of the PAMPS and DN gels were dependent on NaCl concentration and there was a clear difference between the two gels at a low NaCl concentration (Figure 5b). The Π_{ion} value of the PAMPS gel was two or three orders of magnitude higher than Π_{mix}, while the Π_{ion} value of the DN gels was significantly smaller than Π_{mix}. Thus, at low NaCl concentration, the swelling of the PAMPS gels was Π_{ion}-dominant while the swelling of the DN gels was Π_{mix}-dominant. The large Π_{mix} component in the DN gels was attributed to the dense PAAm. The Π_{ion} value of both gels decreased with increasing NaCl concentration, as predicted by Eq. 12. The PAMPS gel exhibited Π_{ion} -dominant swelling and thus the swelling ratio decreased with increasing NaCl concentration, whereas the Π_{mix}-dominant swelling with negligible effect of

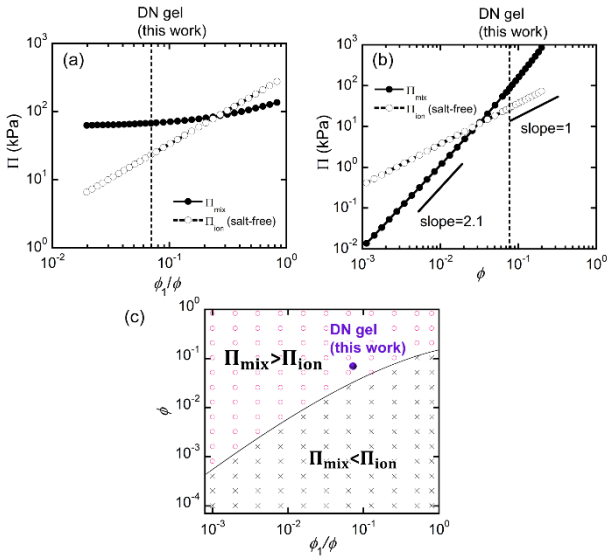

Figure 6. Magnitude correlation of calculated Π_{mix} and Π_{ion} of the PAMPS/PAAm DN gel. (a) Dependence of the Π_{mix} and Π_{ion} on ϕ_1/ϕ with fixed ϕ = 0.070; (b) dependence of the Π_{mix} and Π_{ion} on ϕ with fixed ϕ_1/ϕ = 0.077. (c) A phase diagram for the magnitude correlation of Π_{mix} and Π_{ion} against ϕ_1/ϕ and ϕ. Circle magenta symbols denote $\Pi_{\mathrm{mix}}>\Pi_{\mathrm{ion}}$, while cross black symbols denote $\Pi_{\mathrm{mix}}<\Pi_{\mathrm{ion}}$. The data of the DN gel swollen in water, denoted as a purple filled circle, is in the former regime, corresponding to its salt-insensitive swelling property.

Π_{ion} of the DN gel allowed for a swelling ratio independent of NaCl concentration.

As discussed above, the salt-insensitive swelling behaviour of the PAMPS/PAAm DN gels was attributed to a larger Π_{mix} than Π_{ion}. The structural requirements of these properties were subsequently investigated by calculating Π_{mix} and Π_{ion} of the PAMPS/PAAm DN gels in salt-free conditions by changing two variables in Eqs. 5 and 12, namely ϕ_1/ϕ (volume ratio of the PE among the total polymer in the gel) and ϕ (absolute polymer volume fraction in the gel). The Π_{mix} and Π_{ion} values of the DN gels were dependent on ϕ_1/ϕ (Figure 6a). The Π_{ion} value of the DN gel increased with increasing ϕ_1/ϕ, while the Π_{mix} value remained constant. According to Eqs. 5 and 12, the volume fraction of the PAMPS (ϕ_1) contributed to both Π_{mix} and Π_{ion}, while the volume fraction of the PAAm (ϕ_2) only contributed to Π_{mix}. Thus, the ϕ_1/ϕ ratio needs to be small enough to achieve a Π_{mix} value larger than Π_{ion}. The Π_{mix} and Π_{ion} values of the DN gels were also dependent on ϕ (Figure 6b). Both Π_{mix} and Π_{ion} increased with increasing ϕ but exhibited significantly different scaling relationships of $\Pi_{\mathrm{mix}} \propto \phi^{2.1}$ and $\Pi_{\mathrm{ion}} \propto \phi^{1}$. Note that $\Pi_{\mathrm{mix}} \propto \phi^{2.1}$ is in good agreement with the well-known scaling relationship of $\Pi_{\mathrm{mix}} \propto \phi^{9/4}$ for polymers in their good solvent.[41] Since Π_{mix} is more sensitive to ϕ than Π_{ion}, it can be imagined that enough large ϕ is required to achieve $\Pi_{\mathrm{mix}}>\Pi_{\mathrm{ion}}$. For example, if ϕ_1/ϕ =0.07, the lower limit of ϕ for $\Pi_{\mathrm{mix}}>\Pi_{\mathrm{ion}}$ is 0.03. The phase diagram for $\Pi_{\mathrm{mix}}>\Pi_{\mathrm{ion}}$ shown in Figure 6c exhibits that both of small ϕ_1/ϕ and large ϕ are necessary to achieve $\Pi_{\mathrm{mix}}>\Pi_{\mathrm{ion}}$ and salt-insensitive swelling of the gels. Effect of the gel parameters (such as α) on the phase diagram is shown in Figure S2 of Supplementary information. Also, the relationship between the

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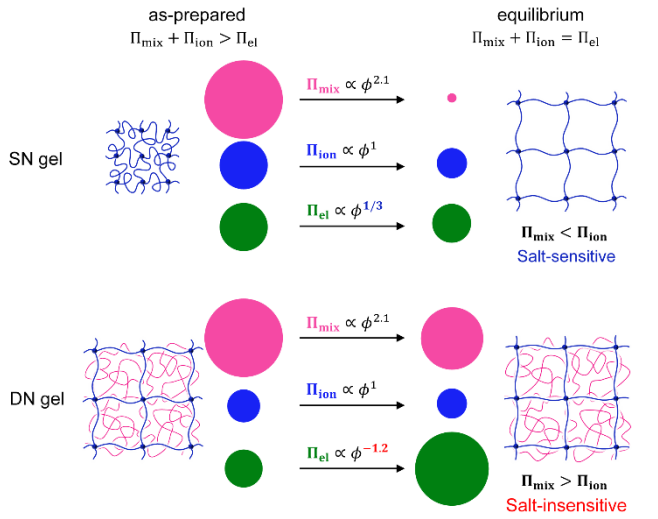

Figure 7. Schematic illustrations of change of the three contributions to the total swelling pressure of a polyelectrolyte SN gel and a DN gel upon swelling. Area of circles denote relative magnitude of the three contributions of the gels at each state.

toughening condition of DN gels and the phase diagram is discussed in Figure S3 of Supplementary information.

However, we should emphasize that it is quite difficult for a PE gel to achieve large ϕ *at its equilibrium swelling state* for which contrasting double-network structure is a requirement. Let us compare an as-prepared PE/NP DN gel and a single-network (SN) PE gel whose polymer volume fractions at as-prepared state, ϕ^{p}, are sufficiently large. As illustrated in Figure 7, the as-prepared DN gel has the prestretched PE first network, while the as-prepared SN gel has a coiled PE network. They can satisfy Π_{mix}>Π_{ion} at their as-prepared state with enough large ϕ^{p} (Figure 6c). Since these as-prepared gels should show $\Pi_{\mathrm{el}} \ll \Pi_{\mathrm{mix}} + \Pi_{\mathrm{ion}}$ due to their large ϕ^{p}, the gels swell when immersed in water. In the case of the DN gel, because the prestretched first network shows negative E-ϕ relationship as shown in Figure 4d (empirically $E \propto \phi^{-1.2}$ in this work) and sustains large elastic energy, swelling greatly increases their elastic contribution Π_{el}. As a consequence, the large osmotic pressure $\Pi_{\mathrm{mix}} + \Pi_{\mathrm{ion}}$ of the DN gel can be balanced by Π_{el} just by a little swelling, and the DN gel can maintain large polymer fraction ϕ^{w} even at its equilibrium swelling state in water. Thus, the DN gel still satisfy Π_{mix}>Π_{ion} at their equilibrium swelling state, and the DN gel shows salt-insensitive swelling property. In the case of the SN gel, because its network strand is coiled at its as-prepared state, the gel initially shows positive E - ϕ relationship (typically $E \propto \phi^{1/3}$). It means swelling of the gel network leads to a decrease in its elastic contribution Π_{el}. Thus, at the initial swelling stage, the elastic pressure of the network cannot suppress the its swelling. With proceeding of the swelling, all three contributions, Π_{el}, Π_{mix}, and Π_{ion}, decrease with decrease of ϕ roughly as $\Pi_{\mathrm{el}} \propto \phi^{1/3}$, $\Pi_{\mathrm{mix}} \propto \phi^{2.1}$, and $\Pi_{\mathrm{ion}} \propto \phi^{1}$. Because decays of Π_{mix} and Π_{ion} with decrease of ϕ are faster than Π_{el} and the E-ϕ relationship may become positive at low ϕ, finally the three contributions are balanced at certain ϕ^{w} after significant swelling. As a consequence, the resulting ϕ^{w} of the SN gel is much smaller than the threshold ϕ for Π_{mix}>Π_{ion}, so that the obtained SN gel swollen in water shows salt-sensitive swelling property.

Conclusions

In conclusion, we confirmed that swelling and mechanical properties of the PAMPS/PAAm DN gels are certainly insensitive to concentration and valency of ions in the environment although the DN gels contain polyelectrolyte components. In the case of the DN gels, the mixing contribution Π_{mix} is superior to the ionic contribution Π_{ion}, which is the direct reason of salt-insensitive swelling behaviour of the DN gels. The highly-prestretched first network of the DN gels the key to achieve Π_{mix}>Π_{ion} at their swelling equilibrium. This study has clarified that the contrasting double-network structure in DN gels not only works to improve mechanical properties of the gels but also brings unique salt-insensitive swelling ability. The combination of high toughness and salt insensitivity of the DN gels can lead various applications as already described in the introduction part, such as tough and stable polyelectrolyte gels that work in biological and marine environments, template for biomineralisation, and tough gels with large conductivity (by immersion in a salt solution) for electronics applications.

In addition, this work proposes a novel idea: the liberation of the swelling ratio of a gel from its characters. The swelling ratio of a polymer gel in a solvent is generally determined by characters of the polymer-solvent pair, including affinity between polymer and solvent and charges of the polymer; thus, they have been considered inseparable. However, once the contrasting PE/NP DN gel is formed, the swelling ratio of the first PE network in the DN gel is no longer controlled by characters of the PE network-solvent pair, but by those of the NP network-solvent pair. The independency of the swelling ratio from its characters may cause some unexpected phenomena, such as large swelling of the first network in its poor solvent. This can be realized by the immersion of a DN gel into the solvent that is poor solvent for the first target network but the good solvent for the second network.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This research was supported by JSPS KAKENHI grant numbers 17H04891 and 17H06144. The Institute for Chemical Reaction Design and Discovery (WPI-ICReDD) was established by World Premier International Research Initiative (WPI), MEXT, Japan. T. N. thanks Ryuji Kiyama (Hokkaido University) for his useful comments on this manuscript.

References

1 N. A. Peppas and A. R. Khare, *Adv. Drug Deliv. Rev.*, 1993, **11**, 1–35.

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2 M. Quesada-Pérez, J. A. Maroto-Centeno, J. Forcada and R. Hidalgo-Alvarez, *Soft Matter*, 2011, **7**, 10536–10547.
3 I. Tokarev and S. Minko, *Soft Matter*, 2009, **5**, 511–524.
4 Y. Qiu and K. Park, *Adv. Drug Deliv. Rev.*, 2001, **53**, 321–339.
5 T. R. Hoare and D. S. Kohane, *Polymer*, 2008, **49**, 1993–2007.
6 L. Ionov, *Adv. Funct. Mater.*, 2013, **23**, 4555–4570.
7 P. J. Flory, *Principles of Polymer Chemistry*, Cornell University Press, Ithaca, NY, 1953.
8 A. Katchalsky, S. Lifson and H. Exsenberg, *J. Polym. Sci.*, 1951, **7**, 571–574.
9 A. Katchalsky and I. Michaeli, *J. Polym. Sci.*, 1955, **15**, 69–86.
10 R. Skouri, F. Schosseler, J. P. Munch and S. J. Candau, *Macromolecules*, 1995, **28**, 197–210.
11 M. Rubinstein, R. H. Colby, A. V. Dobrynin and J.-F. Joanny, *Macromolecules*, 1996, **29**, 398–406.
12 S. Durmaz and O. Okay, *Polymer*, 2000, **41**, 3693–3704.
13 S. J. Kim, S. U. R. Shin, N. G. Kim and S. I. Kim, *J. Macromol. Sci. - Pure Appl. Chem.*, 2005, **42 A**, 1073–1083.
14 Q. Tang, J. Wu, J. Lin, Q. Li and S. Fan, *J. Mater. Sci.*, 2008, **43**, 5884–5890.
15 J. P. Gong, Y. Katsuyama, T. Kurokawa and Y. Osada, *Adv. Mater.*, 2003, **15**, 1155–1158.
16 J. P. Gong, *Soft Matter*, 2010, **6**, 2583–2590.
17 Y. Tanaka, R. Kuwabara, Y. H. Na, T. Kurokawa, J. P. Gong and Y. Osada, *J. Phys. Chem. B*, 2005, **109**, 11559–11562.
18 H. R. Brown, *Macromolecules*, 2007, **40**, 3815–3818.
19 Y. Tanaka, *Europhys. Lett.*, 2007, **78**, 56005.
20 T. Nonoyama, S. Wada, R. Kiyama, N. Kitamura, M. T. I. Mredha, X. Zhang, T. Kurokawa, T. Nakajima, Y. Takagi, K. Yasuda and J. P. Gong, *Adv. Mater.*, 2016, **28**, 6740–6745.
21 R. Kiyama, T. Nonoyama, S. Wada, S. Semba, N. Kitamura, T. Nakajima, T. Kurokawa, K. Yasuda, S. Tanaka and J. P. Gong, *Acta Biomater.*, 2018, **81**, 60–69.
22 C. Azuma, K. Yasuda, Y. Tanabe, H. Taniguro, F. Kanaya, A. Nakayama, Y. M. Chen, J. P. Gong and Y. Osada, *J. Biomed. Mater. Res. A*, 2007, **81A**, 373–380.
23 K. Goto, T. Kimura, N. Kitamura, S. Semba, Y. Ohmiya, S. Aburatani, S. Matsukura, M. Tsuda, T. Kurokawa, J. P. Gong, S. Tanaka and K. Yasuda, *J. Biomed. Mater. Res. A*, 2016, **104**, 734–746.
24 F. Nudelman and N. A. J. M. Sommerdijk, *Angew. Chem. Int. Ed.*, 2012, **51**, 6582–6596.
25 A. Arakaki, K. Shimizu, M. Oda, T. Sakamoto, T. Nishimura and T. Kato, *Org. Biomol. Chem.*, 2015, **13**, 974–989.
26 T. Iwatsubo, R. Kishi, T. Miura, T. Ohzono and T. Yamaguchi, *J. Phys. Chem. B*, 2015, **119**, 8793–8799.
27 T. Murosaki, T. Noguchi, K. Hashimoto, A. Kakugo, T. Kurokawa, J. Saito, Y. M. Chen, H. Furukawa and J. P. Gong, *Biofouling*, 2009, **25**, 657–666.
28 C. C. Hsu and J. M. Prausnitz, *Macromolecules*, 1974, **7**, 320–324.
29 T. Tominaga, V. R. Tirumala, S. Lee, E. K. Lin, J. P. Gong and W.-L. Wu, *J. Phys. Chem. B*, 2008, **112**, 3903–3909.
30 H. M. James and E. Guth, *J. Chem. Phys.*, 1943, **11**, 455–481.
31 M. M. Ozmen and O. Okay, *Polym. Bull.*, 2004, **52**, 83–90.
32 K.-I. Hoshino, T. Nakajima, T. Matsuda, T. Sakai and J. P. Gong, *Soft Matter*, 2018, **14**, 9693–9701.
33 M. Muthukumar, *Macromolecules*, 2017, **50**, 9528–9560.
34 F. Horkay, I. Tasaki and P. J. Basser, *Biomacromolecules*, 2001, **2**, 195–199.
35 T. Tanaka, D. Fillmore, S.-T. Sun, I. Nishio, G. Swislow and A. Shah, *Phys. Rev. Lett.*, 1980, **45**, 1636–1639.
36 G. S. Manning, *J. Chem. Phys.*, 1969, **51**, 924–933.
37 T. Tominaga, V. R. Tirumala, E. K. Lin, J. P. Gong, H. Furukawa, Y. Osada and W.-L Wu, *Polymer*, 2007, **48**, 7449–7454.
38 H. Itagaki, T. Kurokawa, H. Furukawa, T. Nakajima, Y. Katsumoto and J. P. Gong, *Macromolecules*, 2010, **43**, 9495–9500.
39 S. P. Obukhov, M. Rubinstein and R. H. Colby, *Macromolecules*, 1994, **27**, 3191–3198.
40 T. Sakai, M. Kurakazu, Y. Akagi, M. Shibayama and U. Chung, *Soft Matter*, 2012, **8**, 2730–2736.
41 M. Rubinstein and R. H. Colby, *Polymer Physics*, Oxford University Press, New York, 2003.
42 J. Li, Y. Hu, J. J. Vlassak and Z. Suo, *Soft Matter*, 2012, **8**, 8121–8128.
43 H. Guo, T. Kurokawa, M. Takahata, W. Hong, Y. Katsuyama, F. Luo, J. Ahmed, T. Nakajima, T. Nonoyama and J. P. Gong, *Macromolecules*, 2016, **49**, 3100–3108.
44 Y. S. Kim, M. Liu, Y. Ishida, Y. Ebina, M. Osada, T. Sasaki, T. Hikima, M. Takata and T. Aida, *Nat. Mater.*, 2015, **14**, 1002–1007.

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