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A Universal Molecular Stent Method to Toughen any Hydrogels Based on Double Network Concept

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Double-network hydrogels (DN gels), despite their high water content, are the strongest and toughest soft and wet materials available. However, in conventional DN gels, which show extraordinarily high mechanical performance comparable to that of industrial rubbers, the first network must be a strong polyelectrolyte and this requirement greatly hinders the widespread application of these gels. A general method involving the use of a "molecular stent" for the synthesis of tough DN gels using any hydrophilic polymer as the first network is reported. This is the first reported method for the synthesis of tough DN gels using various neutral or weak polyelectrolyte hydrogels as the first network. This method helps extend the DN gel concept to various functional polymers and may increase the number of applications of hydrogels in various fields.

1. Introduction

Hydrogels, which are water-swollen polymer networks, have high water content that affords them unique properties such as biocompatibility, responsiveness to various kinds of stimuli, ultralow surface friction, and environment friendliness.[1,2] Because of these properties, hydrogels are considered innovative medical, industrial, and pharmaceutical materials. A main disadvantage of hydrogels is their brittleness resulting from the high water content, which severely restricts their applications. Among the several approaches adopted for strengthening hydrogels,[3–5] development of double-network gels (DN gels), the toughest and strongest hydrogels having both industrial-rubber-like robustness and high water content (ca. 90 wt%),[5] is the most notable. Optimized DN gels possess excellent hardness (elastic modulus: 0.1–1.0 MPa), strength (tensile fracture stress: 1–10 MPa; strain 100–3000%), and toughness (tearing energy: 100–4500 J/m^2)[5–8] and hence have attracted attention as advanced soft and wet materials for various applications, especially tissue engineering.[9,10] Tough DN gels consist of two polymer networks with contrasting physical properties: a densely cross-linked strong polyelectrolyte (rigid and brittle skeleton) network in low concentrations and a sparsely cross-linked neutral polymer (soft and ductile substance) network in high concentrations (henceforth, these two networks are referred to as N1 and N2, respectively).[5,8,11,13] Studies on the toughening mechanism of DN gels have shown that N1 serves as a "sacrificial bond" during fracture.[11] This DN concept is considered universal and applicable to any species of polymeric materials, whenever the abovementioned contrast DN structure is formed.

For widespread application, tough DN gels of various types must be synthesized from a variety of chemical species. However, the candidate materials for the rigid N1 in these "tough" DN gels are limited to polyelectrolyte gels. **Figure 1** shows some examples of the stress-strain curves of neutral-polymer-based DN gels, which have modest strength but poor extensibility, and polyelectrolyte-based DN gels, which have both high strength and extensibility. The difference between the characteristics of these gels can be explained by the difference in the synthesis processes adopted. Conventional DN gels are synthesized via a two-step network formation process. The first gel is synthesized and immersed in a solution of the second monomer, and then the second gel was polymerized within the first gel. If a polyelectrolyte is used as the first gel, it swells to a considerable extent in the monomer solution owing to the high osmotic pressure Π, resulting in a highly extended rigid N1 in the final product, and the N2 content of the final DN gel is much greater than that of N1. In contrast, when neutral gels, which show poorer swelling ability in the second monomer solution, are used to create N1, neither the rigidity of N1 nor the large content of N2 would be achieved, and the resulting DN gel has very low toughness. Hence, a universal approach that allows for the

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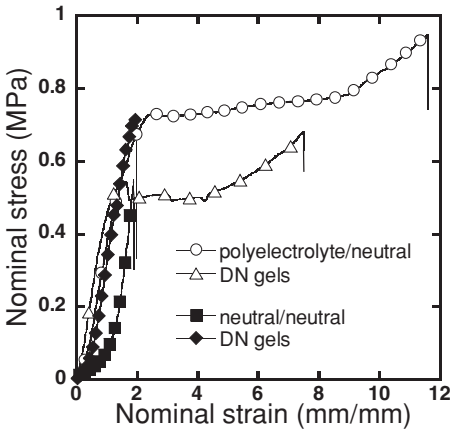

Figure 1. Stress-strain curves of polyelectrolyte/neutral DN gels and neutral/neutral DN gels. ○: PAMPS/PAAm, △: PDMAPAA-Q/PAAm, ■: PHEA/PAAm, and ◆: PAAm/PAAm DN gels (complete definitions for each abbreviation are provided in the Supporting Information). For clarity, only some of the plots are shown.

choice of a wide variety of chemical species affording tough DN gels is required.

In this study, we developed a general method and applied it for the successful synthesis of tough DN gels by using any neutral hydrogel to create N1. Since the key to the development of such a strong DN gel is making the neutral N1 rigid while maintaining its concentration low and cross-linking density high, we attempted to expand this network, as in the case of polyelectrolyte gels, before incorporating N2. The equilibrium swelling degree of a gel is determined by the balance between Π, which promotes swelling, and the elastic tension in the polymer network, which suppresses swelling.[14,15] Therefore, gel swelling can be promoted by increasing Π. In the case of neutral gels, Π results from the free energy change associated with the polymer-solvent mixing. On the other hand, in polyelectrolyte gels, the dissociated counterions induce an extra osmotic pressure in the network, and the resulting Π is typically 100 times that of neutral gels;[16] consequently, the network is well extended to facilitate a high degree of swelling. Accordingly, we planned to introduce a *linear* polyelectrolyte into a neutral gel and thus increase the overall Π. The linear polyelectrolyte trapped in the neutral gel network behaves like a dangling chain and produces a large ionic osmotic pressure but does not contribute to the elastic tension of the gels. As a result, the swelling degree and rigidity of neutral gels increase to the level of those of polyelectrolyte gels. Such highly swollen neutral gels can also be used to create the *rigid and brittle* N1 of tough DN gels. Since the function of the polyelectrolyte in network expansion is similar to that of a stent (a medical device that dilates stuffed blood vessels), we named these polyelectrolytes "molecular stents" and the neutral gels containing stents "St gels." Furthermore, we named the tough DN gels synthesized by introducing N2 in the St gels "St-DN gels." **Figure 2** shows a schematic of the synthesis of St gels and St-DN gels.

2. Synthesis of St Gels Using a Molecular Stent

First, we show that the polyelectrolyte molecular stent significantly increases the swelling ratio and rigidity of neutral gels. We developed two methods for the introduction of the stent into a neutral gel: 1) pre-addition, in which neutral gels with the stent are synthesized from a monomer solution containing

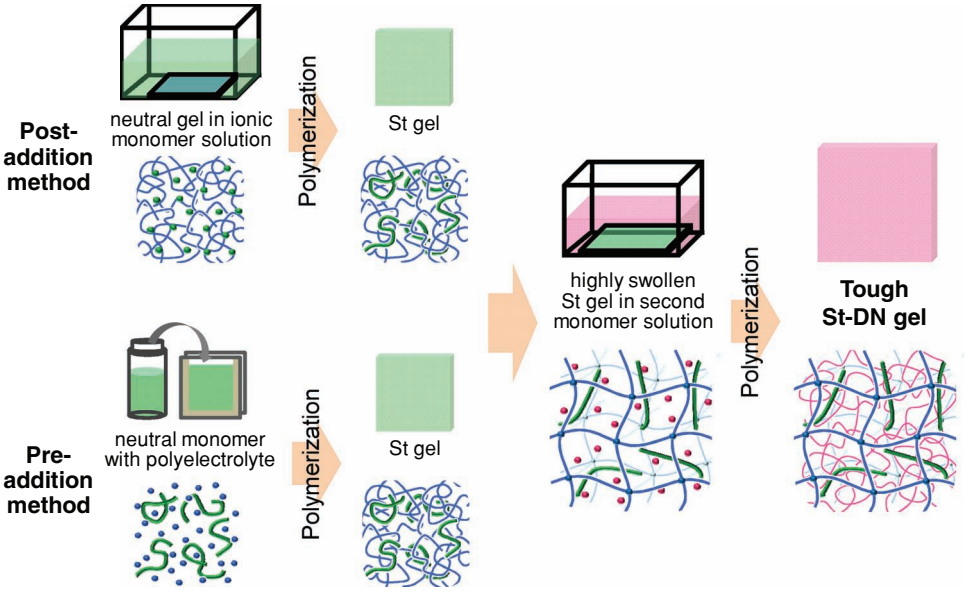

Figure 2. Schematic illustration of the synthesis of tough St-DN gels with a contrast double-network structure using a neutral polymer as the first network. First, a neutral gel containing a linear polyelectrolyte (St gel) is synthesized and immersed in the precursor solution of the second gel. The high ionic osmotic pressure of the polyelectrolyte, which acts as a molecular stent, facilitates substantial expansion of the first network in the solution. The precursor solution is then polymerized to obtain the second network.

Table 1. A list of compositions and the properties of the St gels and others shown in Figure 3,4. Abbreviations X(*a*-*b*-*c*) are used for composition of the first gels, where X is the monomer name, *a* is the monomer concentration (M), *b* is the cross-linker concentration (mol%) and *c* is the initiator concentration (mol%) in the precursor solution of the first network. For the post-addition method, abbreviations Y(*d*-*e*) are used for composition of molecular stents, where Y is the monomer name, *d* is the monomer concentration (M) and *e* is the initiator concentration (mol%) in the precursor solution of the stent polymer. For the pre-addition method, see the footnotes for detailed compositions. q_v the volume swelling ratio in relative to the as-prepared state, and E_{bulk} is the elastic modulus of the St gels.

Sample code	First gel X(*a*-*b*-*c*)	Stent Y(*d*-*e*)	q_v [m^3/m^3]	E_{bulk} [MPa]
Single1	HEA (1-4-0.1)	-	1.06	0.0545
Single2	AMPS (1-4-0.1)	-	13.6	0.207
St1	HEA (1-4-0.1)	AMPS (0.3-0.1)	6.74	0.0769
St2	HEA (1-4-0.1)	AMPS (0.5-0.1)	9.41	0.0871
St3	HEA (1-4-0.1)	AMPS (0.7-0.1)	11.8	0.136
St4	HEA (1-4-0.1)	AMPS (1-0.1)	13.6	0.205
St5	HEA (1-4-0.1)	NaSS (1-0.1)	8.93	not measured
St6	HEA (1-4-0.1)	DMAPAA-Q (1-0.1)	10.8	0.229
St7	HEA (1-4-0.1)	DMAEA-Q (1-0.1)	8.86	0.311
St8	HEA (1-4-0.1)	AAm (1-0.1)	2.54	0.0565
St9	HEA (1-4-0.1)	[a]	12.9	not measured
St10	HEA (1-4-0.1)	[b]	9.81	not measured
St11	AAm (1-4-0.1)	AMPS (1-0.1)	13.9	0.146
St12	AAc (1-4-0.1)	AMPS (1-0.1)	16.4	0.0670

[a]0.4 M of PAMPS was pre-added; [b]0.4 M of PNaSS was pre-added.

a pre-added polyelectrolyte; 2) post-addition, wherein the synthesized neutral gel is immersed in an ionic monomer solution, and the polyelectrolyte molecular stent is subsequently polymerized in the presence of the neutral gel. Henceforth, the latter method would be referred to at all instances in this paper, unless specifically indicated otherwise. The sample codes, compositions, and properties of the synthesized St gels are listed in **Table 1**.

Poly(2-hydroxyethylacrylate) (PHEA) gels and poly(2-acrylamido-2-methylpropanesulfonic acid) (PAMPS) were used as N1 and the polyelectrolyte molecular stent, respectively. Polyelectrolyte PAMPS single-network gels were also prepared and used as controls. **Figure 3**a shows the difference in the diameters of the fully swollen PHEA gel (left) and St-PHEA gel (right). As expected, introduction of PAMPS increased the degree of swelling of the PHEA gel, and the volume of the St-PHEA gel became eight times that of the PHEA gel in water. In addition, the PHEA gel was very soft and deformed by gravity (Figure 3b), while the St-PHEA gel was so rigid that it could sustain its original shape, regardless of the substantial swelling (Figure 3c). Figure 3d shows the swelling degree q_v and elastic modulus E_{bulk} of the St-PHEA gels with various stent concentrations. Both q_v and E_{bulk} increased remarkably with an increase in the stent concentration to 0.6 M, eventually becoming comparable to those of the PAMPS gel. Notably, E_{bulk} of the St-PHEA gels increased with the stent concentration, notwithstanding a concurrent increase in q_v, which corresponded to a decrease in the polymer density. This fact implied that upon the introduction of the stent, every partial chain of the St-PHEA gel showed considerable stretching and became so rigid that the effect of chain rigidity surpassed the effect of the polymer chain density. To characterize the rigidity of each individual network chain, the normalized modulus E_n of the St gels, which represents chain rigidity, was calculated as

$$E_n = q_v E_{bulk} / E_{bulk(before)}$$

on the basis of the theory that E_{bulk} is the product of the number density of elastically effective chains and the elastic energy per chain (see Supporting Information for details). $E_{bulk(before)}$ is E_{bulk} of the as-prepared N1 gels. As shown in Figure 3e, E_n of the St-PHEA gels was 50 times that of the PHEA gel at high stent concentrations and comparable to that of the PAMPS gel with the same composition.

The swelling effect induced by the polyelectrolyte molecular stent is universal and independent of the chemical species and synthesis methods used. The upper histograms in **Figure 4** show q_v of the St-PHEA gels synthesized using several chemical species of stents by pre-addition or post-addition. q_v increases significantly when using a strong cationic or anionic polyelectrolyte as the stent but shows only a slight increase when the neutral polyacrylamide (PAAm) is used as the stent. The lower histograms in the figure show the q_v values of several kinds of St gels prepared from neutral or weak polyelectrolyte networks, with PAMPS as the stent. q_v always increases almost independently of the type of chemical species used in N1.

3. Synthesis of Neutral-Gel-Based Tough St-DN Gels

This section discusses the high mechanical performance of St-DN gels. The second PAAm gel was introduced into the

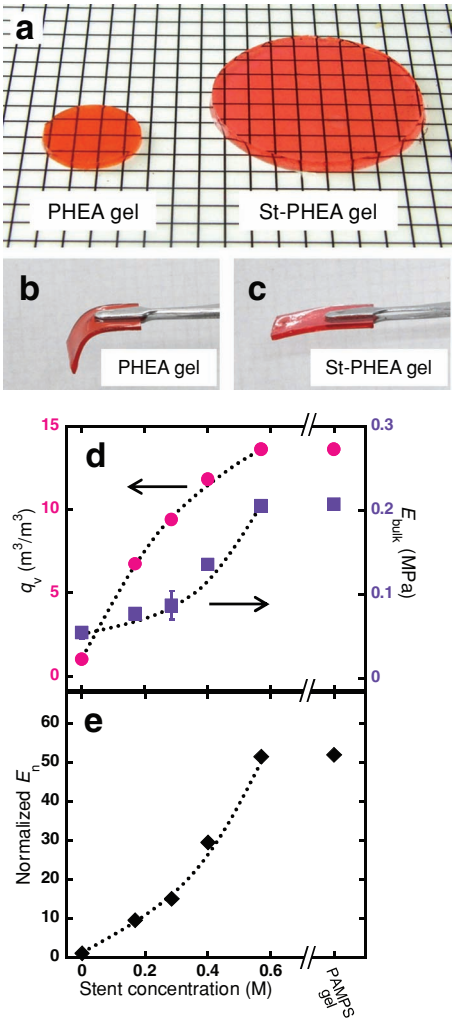

Figure 3. Swelling behavior of the St gels. a) Diameter difference between the PHEA gel (left, Single1) and the St-PHEA gel (right, St4) in the swollen state. These gels have the same diameters (20 mm) in the as-prepared state. The grid size is 5 mm. Rigidity difference between b) the soft PHEA gel (Single1) and c) the rigid St-PHEA gel (St4) in the swollen state. The gels are colored by methyl orange. d) The swelling degree q_v, elastic modulus E_{bulk}, and e) normalized elastic modulus E_n of the swollen St-PHEA gels with various stent concentrations in the feed. For comparison, the results obtained for a single PAMPS gel are also shown (Single1–Single2, St1–St4).

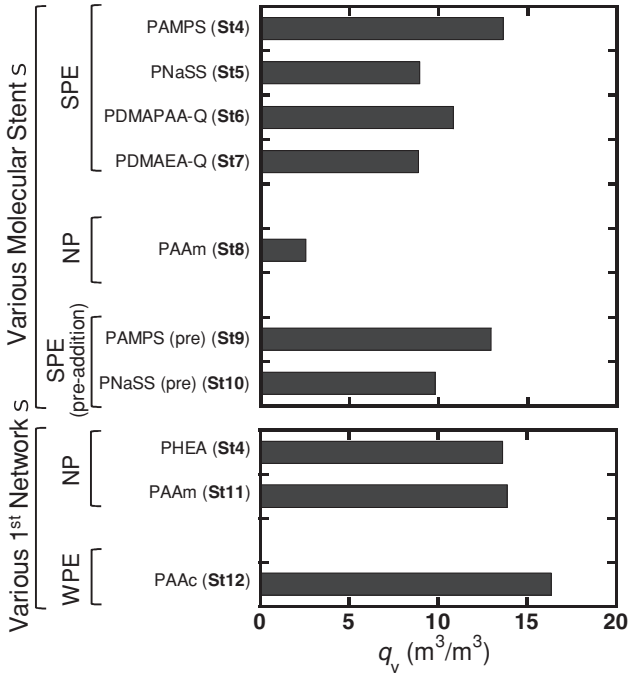

Figure 4. q_v values of various kinds of St gels (St4–St12). SPE, NP, and WPE denote strong polyelectrolyte, neutral polymer, and weak polyelectrolyte, respectively.

rigidified St gel by immersing the latter in AAm monomer solution and polymerizing it. The sample codes, compositions, and properties of all the St-DN gels are listed in **Table 2**. **Figure 5**a shows the stress-strain curves of two kinds of St-DN gels obtained from the St-PAAm and St-poly(dimethylacrylamide) gels (St-PAAm/PAAm and St-PDMAAm/PAAm DN gels, respectively), with PAMPS as the stent. The single-network PAAm gel was so brittle that its fracture strain was as low as 2. The conventional PAAm/PAAm DN gel, in which the second PAAm network was introduced into the PAAm gel without any stent, not only showed much higher fracture stress than did the single-network PAAm gel but also suffered brittle fracture. In contrast, the St-PAAm/PAAm DN gel (water content: 90 wt%) had excellent strength and toughness (high fracture stress σ_f (0.9 MPa) and fracture strain ε_f (10)) and showed yielding-like behavior, which is generally observed in tough DN gels.[17] Moreover, the St-PDMAAm/PAAm DN gel (water content: 87 wt%), which is the optimized St-DN gel, showed higher fracture stress and strain than did the conventional tough PAMPS/PAAm DN gel (water content: 92 wt%). Subsequently, we synthesized a series of St-DN gels from various types of St gels and evaluated their strength and toughness. The tensile fracture stress σ_f was used as the index of the strength. The work of extension W, which is the total work required for the fracture of a unit volume of a material and defined as the area under the tensile stress-strain curves, was used as the index of toughness.[18] Figure 5b shows the σ_f and W values of various St-DN gels and other conventional gels. σ_f and W of the single-network gels were always extremely low. The conventional neutral/neutral DN gels showed moderate σ_f and W; however, W of these gels was one order of magnitude lower than that of the PAMPS/PAAm DN gel. In contrast, the St-DN gels showed high σ_f and W comparable to those of the PAMPS/PAAm DN gel. W of the St-DN gels was always much larger than that of the neutral/neutral DN gel (without the stent). The results for the St-DN gels were so well reproducible that the error bars were hidden by the plots in some cases. These results demonstrated that neutral gels obtained from any chemical species could be significantly toughened by DN formation using a molecular stent to increase their volume and rigidity.

The developed method provides a simple means of fabricating tough cartilage-like hydrogels containing biopolymers that have

Table 2. A list of compositions and the mechanical properties of the St-DN gels and others shown in Figure 5. X(*a-b-c*) and Y(*d-e*) have the same meaning with those in Table 1. Abbreviations Z(*f-g-h*) was used for the composition of second networks, where Z is the monomer name, *f* is the monomer concentration (M), *g* is the cross-linker concentration (mol%), and *h* is the initiator concentration (mol%) in the precursor solution of the second network. For the pre-addition method, see the footnotes for detailed compositions.

Sample code	First gel X(*a-b-c*)	Stent Y(*d-e*)	Second gel Z(*f-g-h*)	σ_f [MPa]	W [MJ/m^3]
Single1	HEA (1-4-0.1)	-	-	0.0370	0.0229
Single3	AAm (1-4-0.1)	-	-	0.0312	0.0222
DN1	AMPS (1-4-3)	-	AAm (2-0.02-0.01)	1.07	11.0
DN2	HEA (1-4-0.1)	-	AAm (2-0.02-0.01)	0.646	0.415
DN3	AAm (1-4-0.1)	-	AAm (2-0.02-0.01)	0.569	0.517
StDN1	AAm (1.2-4-0.1)	AMPS (1-0.1)	AAm (2-0.02-0.01)	0.829	5.466
StDN2	DMAAm (0.7-3-0.1)	AMPS (1-0.1)	AAm (2-0.02-0.01)	1.95	19.5
StDN3	DMAAm (0.7-2-0.1)	AMPS (1-0.1)	AAm (2-0.02-0.01)	1.01	9.52
StDN4	DMAAm (1-2-0.1)	AMPS (1-0.1)	AAm (2-0.02-0.01)	1.57	15.7
StDN5	DMAAm (1-3-0.1)	AMPS (1-0.1)	AAm (2-0.02-0.01)	1.05	7.78
StDN6	NIPAAm (0.7-2-0.5)	AMPS (1-0.1)	AAm (2-0.02-0.01)	1.02	9.28
StDN7	AAc (1-4-0.1)	AMPS (0.7-0.1)	AAm (2-0.02-0.01)	0.703	8.31
StDN8	AAm (1-4-0.1)	AMPS (0.7-0.1)	AAm (2-0.02-0.01)	0.694	4.36
StDN9	HEA (1-4-0.1)	AMPS (0.7-0.1)	AAm (2-0.02-0.01)	0.819	4.53
StDN10	HEA (1-4-0.1)	NaSS (1-0.1)	AAm (2-0.02-0.01)	0.344	1.78
StDN11	HEA (1-4-0.1)	DMAPAA-Q (1-0.1)	AAm (2-0.02-0.01)	0.468	4.19
StDN12	HEA (1-4-0.1)	DMAEA-Q (1-0.1)	AAm (2-0.02-0.01)	0.469	3.46
StDN13	AAm (1-2-0.1)	[a]	AAm (4-0.02-0.01)	0.690	2.68
StDN14	AAm (1-2-0.1)	[b]	AAm (4-0.02-0.01)	0.729	2.68
StDN15	DMAAm (1-4-0.1)	[b]	DMAAm (4-0.02-0.01)	0.930	3.35

[a]3 wt% of sodium hyaluronate was pre-added; [b]5 wt% of proteoglycan was pre-added.

specific biofunctions. Most biopolymers, for example, chondroitin sulfate proteoglycan (CSPG) and sodium hyaluronate (HA), in the cartilage matrix, are strong polyelectrolytes that can serve as both bioactive moieties and effective stents for toughening neutral gels.[19] We synthesized St-PDMAAm/PDMAAm DN gel by the pre-addition method using CSPG as the stent (StDN15). Since PDMAAm has better biocompatibility than does PAAm,[20] the gel was as robust as the other St-DN gels, as shown in Figure 5b.

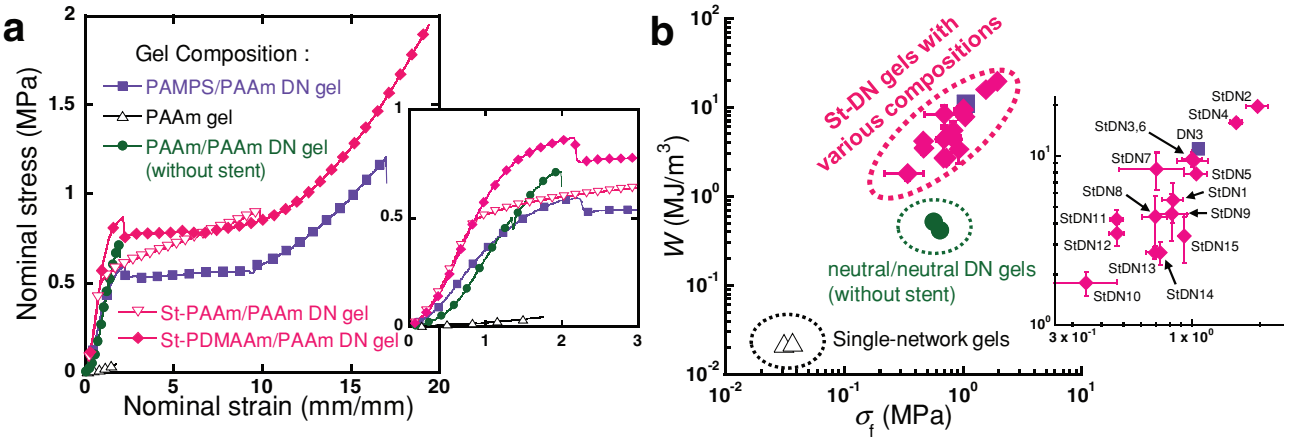

Figure 5. Mechanical performance of the St-DN gels. a) Tensile stress-strain curves of PAMPS/PAAm DN (DN1), PAAm (Single3), PAAm/PAAm DN (DN3), St-PAAm/PAAm DN (StDN1), and St-PDMAAm/PAAm DN (StDN2) gels. For clarity, only some of the data are shown. b) The tensile fracture stress σ_f and work of extension W of Single1, Single3, DN1–DN3, and StDN1–StDN15. No error bars are shown for single-network gels and neutral/neutral DN gels.

4. Synthesis of St-DN Gels with Removable Molecular Stent

We assume that the polyelectrolyte stent plays a role only in the formation of the contrast DN structure but does not affect the mechanical properties of the resulting St-DN gels since it does not bear any stress under deformation. To confirm this, we need to remove the molecular stent from the St-DN gels. Furthermore, true neutral/neutral DN gels without the polyelectrolyte stent may be required for many applications. However, the molecular stent could not be removed from the synthesized St-DN gel by simple methods such as prolonged washing or electrophoresis, because of entanglement of the polyelectrolyte long chains with the gel network or chemical bonding between the stent and the DN network via the residual double bonds in N1.[8] Thus, we used an ionic surfactant instead of a polyelectrolyte to prepare an easily removable stent. Ionic surfactants form large micelles in water, and their counterions produce a large osmotic pressure, as in the case of a polyelectrolyte. As the diffusion coefficient is inversely proportional to the radius of the substance, the diffusion coefficient of micelles ($\approx 10^{-7}$ (cm/s) for sodium dodecyl sulfate) is much smaller than those of single molecules ($\approx 10^{-5}$ (cm/s)). Taking this advantage, micelles are temporally trapped in gels and can also serve as molecular stents.[21] Further, micelles are in thermodynamic equilibrium with single surfactant molecules, and no covalent bonds would be formed between the surfactants and DN networks because surfactants generally do not have polymerizable groups. Thus, micelles can be removed easily from the gels by washing with water.

We synthesized St-poly(*N*-isopropylacrylamide)/PAAm DN gel using sodium dodecyl sulfate (SDS) as the stent and then tried to remove SDS by immersing the gel in pure water, as shown in **Figure 6**a. Elemental analysis showed that the sulfur content of the as-prepared gel was 0.83 wt% and that of the gel immersed in water after 4 d was zero, indicating complete removal of the surfactant and formation of a true neutral/neutral St-DN gel.

Normalization (details shown in the Supporting Information) was carried out to nullify the effect of size change (swelling) after immersion in water. Figure 6b shows the normalized stress-strain curves of the micelle-based St-DN gels in the as-prepared state and after removal of the surfactant stent (the stress-strain curves before normalization are shown in the Supporting Information). The normalized curves almost overlapped with each other, confirming that the stent does not have any effect on the mechanical properties of the St-DN gel once the contrast DN structure is formed.

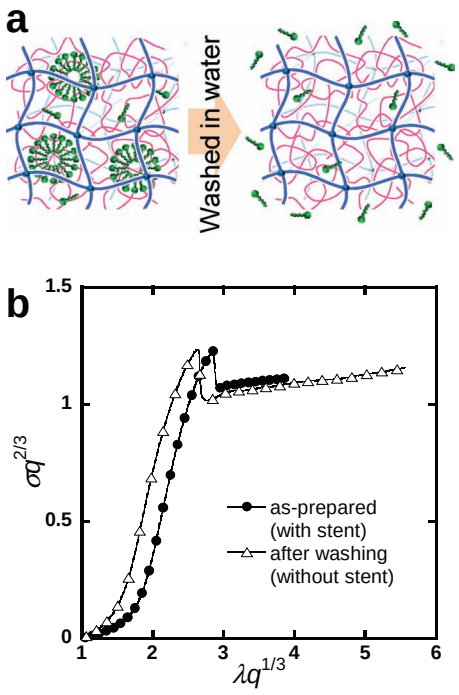

Figure 6. a) Schematic illustration of stent removal from micelle-based St-DN gels. b) Normalized tensile stress-strain curves of St-PNIPAAm/PAAm DN gels with a micelle as the stent, in the as-prepared state and after immersion for 4 d in pure water. $\sigma q_v^{2/3}$ is used for *y*-axis and $\lambda q_v^{1/3}$ is used for *x*-axis in order to remove the swelling effect, where σ is the nominal stress and λ is the deformation ratio ($\lambda = \varepsilon + 1$). For clarity, only some of the data are shown.

5. Conclusions

We developed a universal approach based on the DN concept and use of a molecular stent to toughen neutral gels and successfully synthesized tough St-DN gels from various hydrophilic polymers. The strength and toughness of these gels were comparable to those of conventional DN gels. Moreover, ionic micelles were used as stents so that they could be easily removed from the St-DN gels. The DN concept is universal and independent of specific interactions between the two networks (any combination of polymers with the contrast DN structure would afford a tough gel), and the proposed method is an effective means of toughening any kind of functional hydrogel, which was previously considered difficult. Hence, our study is expected to be a milestone in soft-wet materials science. Some high-toughness functional gels developed by the proposed approach will be reported in near future.

6. Experimental Section

Materials: The materials used in this study are shown in the Supporting Information and Figure S1.

Synthesis of St-DN Gels by Post-Addition: In the first step, the neutral gels, which would form N1, were synthesized. 1 M HEA, 4 mol% cross-linker (*N*,*N*′-methylenebis(acrylamide); MBAA), and 0.1 mol% photoinitiator (2-oxoglutaric acid) were dissolved in pure water (the molar percentages are presented respective to the monomer). Neutral hydrogels were then synthesized via irradiation by 365-nm UV light for 8 h in an argon blanket. In the second step, the molecular stent was polymerized. The neutral gels were immersed for at least 3 d in the precursor stent solution containing 0.3–1.0 M AMPS monomer and 0.1 mol% 2-oxoglutaric acid, and then, polymerization was carried out in the presence of the N1 gel by irradiation for 8 h using 365-nm UV light to obtain St gels. Several kinds of ionic monomers were used as stent precursors. The amount of molecular stent incorporated in St gels was determined by elemental analysis. In the final step, N2 was synthesized. The St gels were soaked for at least 2 d in an aqueous solution of 2 M AAm, 0.02 mol% MBAA, and 0.01 mol% 2-oxoglutaric acid. The

gels were sandwiched between two glass plates in an argon blanket. Then, the second PAAm network was synthesized in the presence of the St gels by irradiation using 365-nm UV light for 8 h. The synthesized St-DN gels were immersed in pure water for at least 5 d for the removal of unreacted reagents. St-DN gels using other monomers as N1 and N2 and different stents were synthesized in a similar manner. The compositions of the synthesized St and St-DN gels are shown in Table 1 and 2, respectively.

Synthesis of Linear Polyelectrolyte for Pre-Addition: 0.5 M electrolyte monomer and 0.1–0.6 mol% 2-oxogultaric acid were dissolved in pure water in an argon blanket. Photopolymerization was carried out by 365-nm UV irradiation for 5 h. After the synthesis, the polyelectrolyte chains (molecular stent) were dialyzed in pure water for 5 d to remove any unreacted reagents and then freeze-dried.

Synthesis of St-DN Gels by Pre-Addition: First, neutral gels initially containing a polyelectrolyte molecular stent (St gels) were synthesized. 1 M neutral monomer, 4 mol% MBAA, 0.1 mol% 2-oxogultaric acid, and 0.4 M polyelectrolyte were dissolved in water. The monomer solutions were then placed in an argon blanket and poured into glass molds made of two glass plates separated by silicone rubber. Photopolymerization was carried out by irradiation using 365-nm UV light for 8 h. The St gels were then soaked for 3 h in an aqueous solution of 2 M AAm, 0.02 mol% MBAA, and 0.01 mol% 2-oxoglutaric acid for 3 h. The gels were then sandwiched between two glass plates in an argon blanket. Photopolymerization of the PAAm gels was carried out in the presence of St gels by irradiation using 365-nm UV light for 8 h. The St-DN gels were immersed in pure water for at least 5 d for the removal of unreacted reagents. The compositions of various St and St-DN gels are shown in Table 1 and 2, respectively.

Synthesis of St-DN Gels by Use of Micelles: 1 M *N*-isopropylacrylamide (NIPAAm), 1.8 mol% MBAA, 0.1 mol% 2-oxogultaric acid, and 1 M SDS were dissolved in water. The St-PNIPAAm gel was polymerized by irradiation with 365-nm UV light for 8 h at 4 °C. Subsequently, an aqueous solution of the second monomer was prepared using 2 M AAm, 0.02 mol% MBAA, and 0.01 mol% 2-oxoglutaric acid and dropped slowly (1.5 ml/10 min) onto the as-prepared St-PNIPAAm gel to induce slow swelling. It should be mentioned that if the gel was directly immersed in a large amount of second monomer solution, micelles gradually escaped from the gel and as the result swelling ratio of the gel did not increase large enough. After the equilibrium swelling state was reached, the St-PNIPAAm gel was sandwiched between two glass plates, and then, photo-polymerization of the second PAAm gel was carried out by irradiation with 365-nm UV light for 8 h. The St-PNIPAAm/PAAm gel was immersed for 4 d in pure water for the removal of SDS, which was confirmed by elemental analysis of sulfur.

Swelling Degree Measurements: The swelling degree q_v (v/v) of the St gels was calculated by using the expression $q_v = (d_{swell}/d_0)^3$, where d_{swell} and d_0 denote the thickness of the swollen St gels and the as-prepared N1 gels (without the stent), respectively. d_{swell} and d_0 were measured by using a caliper.

Mechanical Strength Measurements: A tensile-compressive tester (Tensilon RTC-1310A, Orientic Co.) was used for the measurement of mechanical properties of the St gels and the St-DN gels. Compression tests were performed on cylindrical (thickness: 4 mm; diameter: 9 mm) gel samples.[6] The compression rate was 10%/min. The elastic modulus E_{bulk} (MPa) was the slope of the compressive stress-strain curves over the strain range $0 < \varepsilon < 0.1$. Tensile tests were performed on dumbbell-shaped St-DN gels standardized as per the JIS-K6251-7 size.[8] The tensile velocity was 100 mm/min. The tensile fracture stress σ_f (MPa) was determined as the nominal stress at the breaking point. The work of extension W (MJ/m^3) was determined as the area under tensile stress-strain curves.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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