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The Influence of Salt-Linkages on the Adhesion and Hardness Variance of Hydrogels

Hirohisa Tamagawa,* Fumio Nogata, Susumu Umemoto,† Norimasa Okui,† Suzana Popovic,†† and Minoru Taya††

Department of Mechanical and Systems Engineering, Faculty of Engineering, Gifu University,
1-1 Yanagido, Gifu-shi, Gifu 501-1193

†Department of Organic and Polymeric Materials, Tokyo Institute of Technology,
2-12-1 Ookayama, Meguro-ku, Tokyo 152-8552

††Department of Mechanical Engineering, University of Washington, Box 352600, Seattle, WA 98195-2600 U.S.A.

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Adhesion between anionic and cationic gels was observed. This adhesion force varied according to the pH and the ionic strength of solutions bathing the gels. A quite strong adhesion was observed in neutral and the ionic-strength solutions. The cause of this phenomenon was suggested to be due to electrostatic interaction between the anionic and cationic fixed groups on the respective gel surfaces, that is, the formation of salt-linkages between the dissociated –COOH and $-NH_2$ groups, $-COO^- \cdots {}^+H_3N-$. They were also found in an amphoteric gel body, thus suggesting a great influence on the degree of hardness. Salt-linkages serve as crosslinkings in amphoteric gel in addition to the permanently formed chemical crosslinkings of *N*,*N*-methylenediacrylamide. The degree of amphoteric gel hardness can be controlled reversibly by their formation and disruption. Since a reversible hardness change was also observed in real human muscle, the use of salt-linkages is a new principle used to design practical artificial gel muscles.

Electrically responsive gels have attracted the attention of many researchers as future artificial-muscle materials, owing to their similar properties to real muscles.[1–5] For example, Shiga et al. developed electrically driven poly(vinyl alcohol)–poly(acrylic acid) gel fingers, and demonstrated the ability to grab an egg with them.[3] Hirai et al. demonstrated an extraordinarily fast bending of a dimethyl sulfoxide swollen PVA gel strip.[4] However, as artificial muscle materials, most of the gels have exactly the same serious drawback: their mechanical weakness. For example, acrylamide-based gels are the most well-investigated gels to date, but their mechanical strength is quite low, and they are easily torn apart. This is a main cause of stagnation in the development of artificial gel muscles. Although there exists a gel with high mechanical strength, such as polyacryronitrile gel,[6] it has not been successfully designed into a practical artificial gel muscle.

Needless to say, real human muscles have highly sophisticated functions, and exhibit reversible hardening and softening in accordance with the aims of their movement. Such a large reversible hardness variance is preferable as a property of an artificial muscle.

This paper is addressed an investigation of the hardness variance of acrylamide-based amphoteric gels in accordance with their environment. This hardness variance is suggested to have an intimate correlation with the cause of adhesion[7] observed between anionic and cationic gels which have $-COO^-$ and $-NH_3^+$, respectively.

Experimental

Specimen Preparation. The preparation procedure of gel specimens for investigating adhesion phenomena between anionic and cationic gels is explained.

Specimens for Investigation Gel Adhesion. Anionic Gel: A pregel solution of an anionic gel consisted of acrylamide and acrylic acid monomers, *N*,*N*-methylendiacrylamide crosslinker, *N*,*N*,*N′*,*N′*-tetramethylethylendiamine polymerization accelerator, and a deionized water solvent. In order to prepare this gel through radical polymerization, ammonium peroxodisulfate polymerization initiator was added to it. This mixture was poured into a mold and heated up at 65 °C for 30 min, resulting in a plate-shaped anionic gel. This gel was designated as **G-Aad** (**G**el-**A**nionic for the **ad**hesion force measurement).

Cationic Gel: A pregel solution of a cationic gel consisted of acrylamide and allylamine hydrochloride monomers, *N*,*N*-methylendiacrylamide crosslinker, *N*,*N*,*N′*,*N′*-tetramethylethylendiamine polymerization accelerator, and a deionized water solvent. In order to prepare this gel through radical polymerization, ammonium peroxodisulfate polymerization initiator was added to it. The rest of the processing procedure was the same as that of anionic gels. This gel was designated as **G-Cad** (**G**el-**C**ationic for the **ad**hesion force measurement). The chemical compositions of **G-Aad** and **G-Cad** are summarized in Table 1. All chemicals, except allylamine hydrochloride, which was purchased from TCI (Tokyo, Japan), were obtained from Aldrich (Milwaukee, WI). All gel specimens were stored in pH solutions ranging from pH = 1 to 13, where they were prepared by diluting 1 M HCl and 1 M NaOH aqueous solutions with deionized water. Since the gels released ions in the pH solution, the solution pH deviated from the initial value with the storage time. Therefore, the exchange of the pH solution with a new one was carried out until its pH value was established close enough to its initial pH value.

Specimens for the Investigation on the Amphoteric Gel Hardness. We have prepared anionic, cationic, and amphoteric gels primarily for investigating their hardness. For the convenience of conducting the experiments, the compositions of anionic and cationic gels were made differently from those prepared for investigating the adhesion phenomenon described above.

Anionic Gel: A pregel solution of an anionic gel consisted of acrylamide, acrylic acid, *N*,*N*-methylendiacrylamide, *N*,*N*,*N*′,*N*′-tetramethylethylendiamine, and deionized water. An initiator of ammonium peroxodisulfate was added to the pregel solution. The solution was then poured into a mold and heated up at 65 °C for 30 min, resulting in a 1.90 mm-thick plate-shaped gel. This gel was designated as **G-Ah** (**G**el-**A**nionic for the **h**ardness measurement).

Cationic Gel: A pregel solution of a cationic gel consisted of acrylamide, allylamine hydrochloride, *N*,*N*-methylendiacrylamide, *N*,*N*,*N*′,*N*′-tetramethylethylendiamine, and deionized water. An initiator of ammonium peroxodisulfate was added to this solution. The rest of the processing procedure was the same as that for **G-Ah**. This cationic gel was designated as **G-Ch** (**G**el-**C**ationic for a **h**ardness measurement).

Amphoteric Gel: Exactly the same gel as **G-Ch** was prepared and immersed in a NaOH solution (pH = 13) for a given time. Due to the hydrolysis of –$CONH_2$ groups contained in **G-Ch**, the anionic –COOH groups were created, which converted the cationic gel, **G-Ch**, into an amphoteric one.[8] Three amphoteric gels were prepared by employing three different hydrolysis times (1.0, 5.0 and 48.0 h). They are designated as **A-sh** (**A**mphoteric gel-**s**hort hydrolysis time for the **h**ardness measurement), **A-mh** (**A**mphoteric gel-**m**edium hydrolysis time for the **h**ardness measurement), and **A-lh** (**A**mphoteric gel-**l**ong hydrolysis time for the **h**ardness measurement).

The chemical compositions of **G-Ah**, **G-Ch**, **A-sh**, **A-mh**, and **A-lh** are summarized in Table 1.

The preparation method of an amphoteric gel may have one drawback. This method may cause a serious matrix inhomogeneity, since the hydrolysis proceeds gradually from the surface to the core due to the permeation direction of NaOH. Particularly, **A-sh** gel that underwent the shortest hydrolysis time might have significantly different properties between at its surface and at its core. However, a small thickness of **A-sh** gel is assumed so as to allow complete permeation of the NaOH solution throughout the gel body over time, thus minimizing the effect of inhomogeneity in the structures. To confirm this speculation, the following experiment was performed.

Table 1. Composition of Gels

Gel	**G-Aad**[†1]	**G-Cad**[†1]	**G-Ah**[†2]	**G-Ch**[†2]
AAm[†3]	5.98	5.98	8.52	8.52
AA[†4]	4.04	0.00	2.87	0.00
Al[†5]	0.00	5.24	0.00	3.72

[†1] Both of **G-Aad** and **G-Cad** contain *N*,*N*-methylendiacrylamide (0.267 g), *N*,*N*,*N*,′*N*′-tetramethylethylendiamine (a few drops), ammonium peroxodisulfate (0.08 g), and deionized water (100 g).

[†2] Both of **G-Ah** and **G-Ch** contain *N*,*N*-methylendiacrylamide (0.154 g), *N*,*N*,*N*,′*N*′-tetramethylethylendiamine (a few drops), ammonium peroxodisulfate (0.08 g), and deionized water (100 g). **A-sh**, **A-mh,** and **A-lh** were prepared from the hydrolysis of **G-Ch**.

[†3] AAm: acrylamide

[†4] AA: acrylic acid

[†5] Al: allylamine hydrochloride

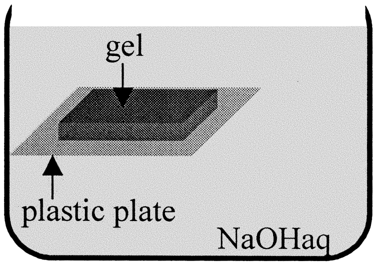

Fig. 1. Hydrolysis of cationic gel, **G-Ch**, in NaOH aqueous solution. Since this **G-Ch** is attached on a plastic plate, NaOH permeates from its free top surface to the bottom surface. Therefore the degree of hydrolysis of **G-Ch** is expected to decrease with the distance from top surface.

A plate-shaped cationic gel specimen (1.9mm thick) was prepared on a plastic plate by the same method as that for preparing **G-Ch**. It was immersed in a NaOH solution (pH = 13) for 1 h in order to be converted into an amphoteric gel. Although this preparation procedure is the same as that for **A-sh** gel, its structure might be different from **A-sh** gel. In the case of this gel, NaOH could permeate into its body only from the free top surface (Fig. 1), while in the case of **A-sh** gel it proceeds from both, top and bottom sides. After the completion of hydrolysis, this gel was stored in acetone until it reached a fully shrunken state; after that, the plastic plate was detached from the gel. It was then transferred into deionized water. If there existed a significant gradient of the degree of hydrolysis in the gel from its top surface to bottom surface, the gel must have exhibited a significantly curved shape in the swollen state. However, merely a slightly curved shape was observed. Therefore, it is concluded that the amphoteric gels (**A-sh**, **A-mh**, and **A-lh**) have almost a homogeneous structure.

Adhesion Force Measurement. Specimens of **G-Aad** and **G-Cad** gels with a 7 mm × 7 mm cross-sectional area were prepared. They were swollen in solutions of the same pH value. Both gel pieces were attached to the arms of an adhesion force measurement apparatus with a super glue, as shown in Fig. 2, and their adhesion force was measured at 20 °C while being immersed in the pH solution. First, the gel pieces were completely in contact with each other; they were then slowly separated by micro-displacing the arms. The force just before their detachment was measured as the adhesion force.

Gel Hardness Measurement. We have investigated the effect of temperature and the ionic strength on the swelling ratio and hardness of gels. First, their swelling ratio at a given temperature is discussed.

Swelling Ratio: The specimens (**G-Ah**, **G-Ch**, **A-sh**, **A-mh**, and **A-lh**) were swollen in three different kinds of solutions (H_2O, 0.1 M KCl, and 0.1 M NaCl aqueous solutions) until they reached the equilibrium state at a given temperature. Their thickness in the fully swollen state (d) was measured. The swelling ratio (SR) was calculated by $SR = (d/d_o)^3$, where d_o is the thickness of the gel immediately after the synthesis. Since the ionic gels release mobile ions into the solution, the condition of the bathing solutions

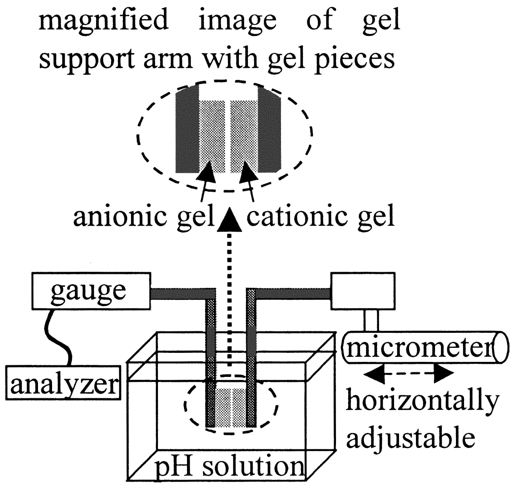

Fig. 2. Gel adhesion force measurement apparatus.

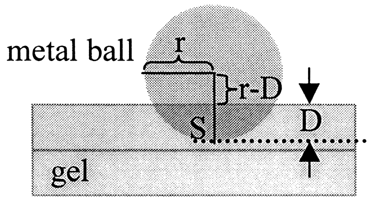

Fig. 3. Side view of the layered plate shaped gels on which a metal ball is placed for harness measurement.

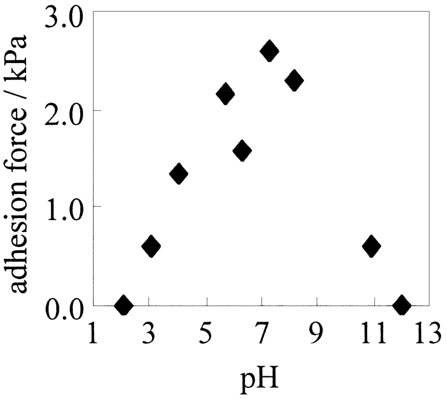

Fig. 4. pH dependence of adhesion force between the anionic and the cationic gels.

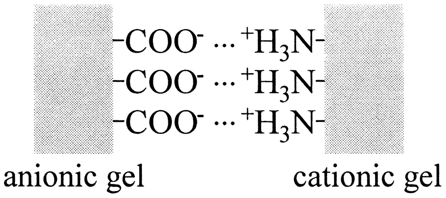

Fig. 5. Salt-linkages formed at the interface between the anionic and the cationic gels.

gradually changes, which in turn changes the gel volume. Therefore, the bathing solutions were replaced with new ones repeatedly until a stable solution condition was achieved.

Hardness: We performed hardness tests on gel specimens (**G-Ah**, **G-Ch**, **A-sh**, **A-mh**, and **A-lh**) at 20, 50 and 80 °C. The specimens were swollen with given solutions, which were periodically replaced by new ones for the same reason as explained above concerning the **Swelling ratio**. A plate-shaped gel was placed on a flat acrylic plate, and a metal ball (diameter = 12.50 mm, weight = 9.29 g) was placed on its surface. The depth of the hollow created in the gel (D) shown in Fig. 3, was measured, where a few pieces of gels were piled up in order to realize a sufficient height of the gel. Otherwise, due to the small thickness and the inherent softness of the gels, the metal ball would fully subside through the thickness of the gels. From $\sigma = (w\ g)/S = (w\ g)/[2\pi r^2\{1\text{-}(r\text{-}D)/r\}]$, the stress ($\sigma$) induced on the contacting area between the metal ball and the gel surface was calculated, where w, r, S, and g are the weight of the metal ball, its radius, the contacting area between the metal ball and the gel surface, and the gravitational acceleration, respectively. A larger stress suggests a harder gel matrix.

Results and Discussion

Adhesion Force Measurement. Figure 4 shows the pH dependence of the adhesion force between the anionic and cationic gels. In neutral environment at pH = 7, the adhesion force is the highest, and it decays with the pH value being away from 7. The strongest adhesion at pH = 7 is speculated to be due to an effective electrostatic interaction between –COO^- and –NH_3^+ on the respective anionic and cationic gel surfaces. Namely, adhesion exists due to the formation of salt-linkages at the interface of anionic and cationic gels, as shown in Fig. 5.[8–11] In an acidic environment, –COOH does not dissociate well, while –NH_2 is easily converted into –NH_3^+. Therefore –NH_3^+ of the cationic gel cannot have a counterpart, –COO^-, for the formation of salt-linkages, resulting in the adhesion force lowering with a decrease in the pH from pH = 7. Similarly, in a basic environment, a sufficiently large number of –NH_3^+ groups will not be created for salt-linkage formation while, easily, a large number of –COO^- are created. Namely, –COO^- groups cannot have the counterpart, the –NH_3^+ group, for the formation of salt-linkages at high pH, resulting in a lowering of the adhesion force along with an increase in the pH from pH = 7. Furthermore, the same experiment was conducted in pH solutions containing 0.1 M NaCl, where their pH ranges from 1 to 13. In this case, we have observed no adhesion, even at pH = 7. This result is additional supporting evidence of salt-linkages being a cause of adhesion in a pH solution containing no NaCl. Namely, this result is interpreted as meaning that the mobile ions, Na^+ and Cl^-, cluster around –COO^- and –NH_3^+, respectively, and shield the electrostatic interaction parlayed for the formation of the salt-linkages, resulting in a lowering of the adhesion force.[12] An aqueous solution with a high ionic strength hinders gel adhesion. However, another question may arise, which is that a lowering of adhesion force in lower and higher pH solutions than in a pH = 7 solution containing no NaCl (shown in Fig. 4) could also be attributed to the shield of electrostatic interaction by the high ionic strength of acidic and basic pH solutions, and not due to the creation of a smaller amount of –COO^- and –NH_3^+ in acidic and basic solutions, respectively. To elucidate this point, an additional experiment was performed.

The adhesion force was measured in a solution of pH = 7 containing 0.001 M NaCl; its ionic strength was almost the same as those of aqueous solutions with pH = 3 and 11 containing no NaCl. The measured adhesion force in pH = 3 and 11 solutions containing no NaCl was around 0.6 kPa according to Fig. 4; yet, that in a pH = 7 solution containing 0.001 M NaCl was found to be 1.8 kPa. If the strength of the adhesion force is dominated solely by the ionic strength, the adhesion force should be identical, regardless of the pH. Therefore, this result is interpreted as meaning that all three solutions must have had a shielding effect against an electrostatic interaction between –COO^- and –NH_3^+ to some extent. Yet among them, a solution of pH = 7 containing 0.001 M NaCl can provide the most appropriate number of –COO^- and –NH_3^+ on the respective gel surfaces for an effective formation of salt-linkages, owing to the lower concentration of H^+ and OH^- than in two other solutions, respectively. Thus, the low ionic strength and its variance cannot be a main cause of this adhesion phenomenon, nor of the adhesion-force variance. The variance in the number of –COO^- and $-NH_3^+$ due to an environmental pH change as the main cause of both the adhesion phenomenon and the adhesion-force variance can explain this observation quite consistently.

The formation of hydrogen bonds at the interface between the anionic and cationic gels may also have an influence on this adhesion. In order to determine whether hydrogen bonds were involved in this adhesion phenomenon, the anionic and the cationic gels which were adhered to each other in deionized water were then transferred into a saturated urea aqueous solution. Urea is known for its function to disrupt hydrogen bonding, such as observed in the case of denaturation of protein.[13–15] However the adhesion force did not decay in this urea aqueous solution. Therefore, hydrogen bonding is ruled out as a cause of adhesion, and it is concluded that the adhesion is dominated by the formation of salt-linkages.

Amphoteric Gel Hardness Measurement. Swelling Ratio: The swelling ratio data are summarized in Table 2. The swelling ratios of **G-Ah** and **G-Ch** at 20 °C are compared first. At 20 °C, **G-Ah** and **G-Ch** in 0.1 M KCl and 0.1 M NaCl solutions exhibit abrupt drops of their swelling ratios compared with their swelling ratios in H_2O. This is attributed to the neutralization of fixed ions on the gel network with mobile ions, K^+&Cl^-, or Na^+&Cl^-. Namely, **G-Ah** and **G-Ch** gels lose the ability to absorb water molecules.

At temperatures, 50 and 80 °C, **G-Ah** exhibits swelling, while **G-Ch** exhibits shrinking. This is attributed to the higher dissociation and association of fixed functional groups contained in them, respectively. Usually, the degree of functional group dissociation and association depends heavily on the environmental temperature. An increase in the swelling ratio of **G-Ah** strongly suggests an enhancement of the conversion of neutral –COOH into the –COO^- group, which attracts water molecules. On the other hand, a decrease in the swelling ratio of **G-Ch** suggests the expulsion of water molecules absorbed in its body due to an enhancement of the conversion of –NH_3^+ into the neutral –NH_2 group. To verify this argument, another experiment was performed.

We prepared three specimens of neutral acrylamide gels. They were immersed in a NaOH solution (pH = 13) for 1, 5, and 48 h to be hydrolyzed, and converted into the anionic gels having –COOH groups. They are referred to as **Anionic-1**, **Anionic-5**, and **Anionic-48**, respectively. The amount of –COOH created in them through this process increased in the order **Anionic-1** < **Anionic-5** < **Anionic-48**. They were transferred into deionized water, and their swelling ratio in the equilibrium state at 20 °C was obtained. Their swelling ratios were found to be larger in the order **Anionic-1** < **Anionic-5** < **Anionic-48**, having values of 26.23, 31.53 and 73.10, respectively. This order is identical to that of the amount of –COOH contained in them. Thus, it is strongly suggested that an increase in the amount of the dissociable group enhances the gel swelling ratio. Therefore, we conclude that the increase in the swelling ratio of **G-Ah** and the decrease in the swelling ratio of **G-Ch** with an increase in the temperature suggest the creation of more –COO^- and diminishing the amount of –NH_3^+ groups.

Amphoteric gels (**A-sh**, **A-mh**, and **A-lh**) were produced from **G-Ch** through its hydrolysis; that is, they contain anionic groups in addition to cationic groups. Thus, each of them has a larger amount of fixed functional groups totally than **G-Ch** does, and thus are expected to exhibit a higher swelling ratio than **G-Ch**. However, a different behavior was observed. No amphoteric gels exhibited a larger swelling ratio than **G-Ch** in H_2O at 20 °C (Table 2). This is speculated to be because of the formation of intramolecular salt-linkages, –$COO^- \cdots {}^+H_3N$–, in all amphoteric gels,[8] and which play a role in intramolecular crosslinkings among their molecular chains, as shown in Fig. 6, thus preventing any further swelling of the gels.

Mostly, amphoteric gels have a tendency to decrease the swelling ratio with an increase in temperature in H_2O. Howev-

Table 2. The Swelling Ratio of Gels, SR

Gel	G-Ah	G-Ch	A-sh	A-mh	A-lh
at 20 °C					
in H_2O	14.94	23.73	9.19	12.68	11.11
in KCl[†]	4.39	2.59	2.22	3.56	3.59
in NaCl[†]	4.39	2.39	1.80	3.94	4.18
at 50 °C					
in H_2O	21.46	8.72	7.38	14.19	9.69
at 80 °C					
in H_2O	27.00	2.39	3.17	3.86	5.38

[†] Concentration is 0.1 M.

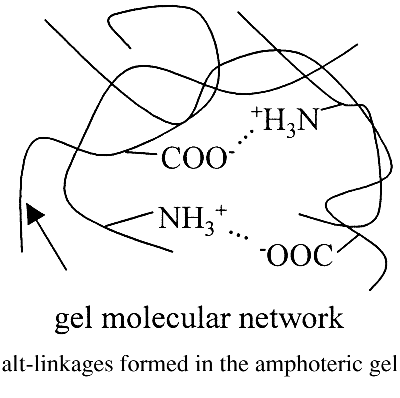

Fig. 6. Salt-linkages formed in the amphoteric gel.

Table 3. The Hardness of Gels[†1]

Gel	G-Ah	G-Ch	A-sh	A-mh	A-lh
at 20 °C					
in H_2O	1.55	0.95	1.50	2.70	6.10
in KCl[†2]	2.03	1.21	1.62	2.49	1.36
in NaCl[†2]	1.81	1.55	1.80	2.32	1.16
at 50 °C					
in H_2O	0.93	1.33	1.41	4.22	2.39
at 80 °C					
in H_2O	0.98	1.66	2.97	2.17	4.46

[†1] Stress exerted on the gel surface by placing a metal ball (diameter = 12.50 mm, weight = 9.29 g) Unit is kPa.
[†2] The concentration is 0.1 M.

er, **A-mh** exhibited an increase in the swelling ratio along with an increase in the temperature from 20 °C to 50 °C. Amphoteric gels contain both –COOH and $–NH_2$ groups, whose dissociations are promoted and hobbled with an increase in temperature, respectively, as described above. The promotion of –COOH dissociation plays both roles of swelling and shrinking of amphoteric gels. Some $–COO^-$ groups enhance the absorption of H_2O (swelling) and, at the same time, some create salt-linkages (shrinking) with $–NH_3^+$. Similarly, some $–NH_3^+$ groups have a dual effect on the gel swelling behavior. A reduction in the amount of $–NH_3^+$ expels H_2O from the gel, thus causing shrinking; at the same time, it disrupts the salt-linkages, thus promoting swelling. The swelling behavior of amphoteric gels depends on the balance between the dissociation of functional groups, –COOH and $–NH_2$. A further discussion is detailed later along with the hardness behavior.

A-lh gels shattered into small pieces or became irregularly shaped during swelling at 20 °C. The cause of these phenomena are also detailed below.

Hardness: The hardness data (stress value σ) are summarized in Table 3, where a larger stress value (σ) suggests a harder gel matrix, as can be intuitively understood. All ionic gels exhibited a strong dependence of their hardness on the environmental temperature and the solution ionic strength.

The hardness of **G-Ah** decreases along with an increase in the temperature in H_2O. As explained in the previous section, the swelling ratio of **G-Ah** increases at higher temperatures, leading to a low gel network density. Such a low gel network density causes a deterioration of the gel hardness. On the other hand, its hardness increases with the ionic strength of the bathing solution. This is also explained in terms of the gel network density. The swelling ratio of **G-Ah** was found to decrease with an increase of the solution ionic strength, resulting in a higher gel network density. Consequently, hardening of the gel matrix occurs. Similarly, **G-Ch**'s hardness behavior can also be explained by considering the gel's swelling ratio. As the temperature increases, the swelling ratio decreases, leading to a higher gel network density. Higher gel network density strengthens the gel matrix. In KCl and NaCl aqueous solutions, **G-Ch**'s hardness increases by the same mechanism as in the case of **G-Ah**.

The hardness behavior of amphoteric gels cannot be explained solely in terms of the gel network density. Especially, the hardness behavior of **A-lh** is very different from that of others. Its hardness in H_2O at any temperature is much higher than those in KCl and NaCl aqueous solutions, although its swelling ratio in H_2O is by far larger than that in KCl and NaCl aqueous solutions. Namely, **A-lh** will not harden in ionic solutions, although its gel network density in these ionic solutions increases due to the occurrence of shrinking. This phenomenon is explained by the existence of a larger number of salt-linkages in gel in the swollen state in H_2O. In H_2O, **A-lh** contains a large number of $–COO^-$ owing to the longer hydrolysis time, which results in forming a larger number of salt-linkages. Therefore, hardening of its matrix occurs in non-ionic solutions (deionized water) at any temperature. On the other hand, in 0.1 M KCl and 0.1 M NaCl ionic solutions, the salt-linkages are disrupted by K^+&Cl^-, and Na^+&Cl^-. Thus, even though the gel network density of **A-lh** is initially increased, the following disruption of the salt-linkages causes a deterioration of the gel's hardness. This explanation is in good agreement with the phenomenon of **A-lh** shattering, mentioned in the previous section, **Swelling ratio**. Since **A-lh** has a larger number of $–COO^-$, it can absorb more H_2O, resulting in large swelling. At the same time, a larger number of $–COO^-$ promotes the formation of a large number of salt-linkages, resulting in the prevention of swelling. These conflicting effects induce a non-uniform internal stress state that causes **A-lh** to shatter.

It is known that the salt-linkage can be disrupted in the presence of NaOH.[10] Once **A-lh** in the middle of its swelling in H_2O is transferred into NaOH, it further swells uniformly without shattering. This observation indirectly indicates the existence of salt-linkages in H_2O-swollen amphoteric gels. In addition, the observation of gel's softening in NaOH is also supportive evidence toward the salt-linkage formation in H_2O. Namely, the disruption of salt-linkages leads to gel matrix softening.

Moreover, the effectiveness of gel hardening through the formation of salt-linkages was studied in the case of porous gels having a soft matrix. Plate-shaped porous amphoteric gels were prepared as follows[16,17] A pregel solution consisting of acrylamide (8.52 g), allylamine hydrochloride (3.72 g), *N*,*N*-methylenediacrylamide (0.154 g), *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (a few drops), and deionized water (100 g) was prepared. It was heated at 75 °C for 30 min followed by the addition of ammonium peroxodisulfate (0.012 g), resulting in the formation of porous cationic gels. When this cationic gel was swollen in deionized water, its matrix became soft due to the existence of many pores in its body — a low polymer network density. Three different types of porous amphoteric gels were prepared by immersing cationic gels in a pH = 13 NaOH solution for 1, 5 and 48 h. They were designated **PA-s** (**P**orous **A**mphoteric gel-**s**hort hydrolysis time), **PA-m** (**P**orous **A**mphoteric gel-**m**edium hydrolysis time), and **PA-l** (**P**orous **A**mphoteric gel-**l**ong hydrolysis time), respectively.

They were swollen in deionized water at 20 °C, and their hardness was investigated following the method described in the **Hardness** section. The results are summarized in Table 4. Their swelling ratios increase in the order **PA-s** < **PA-m** < **PA-l**, suggesting that the gel molecular network density decreases in that order. However, their hardness did not follow

Table 4. Swelling Ratio and Hardness of Porous Amphoteric Gels

Gel	**PA-s**	**PA-m**	**PA-1**
SR[†]	6.69	8.19	10.50
σ[††]	1.74	1.74	2.04

[†] Swelling ratio.

[††] Stress value. The unit is kPa.

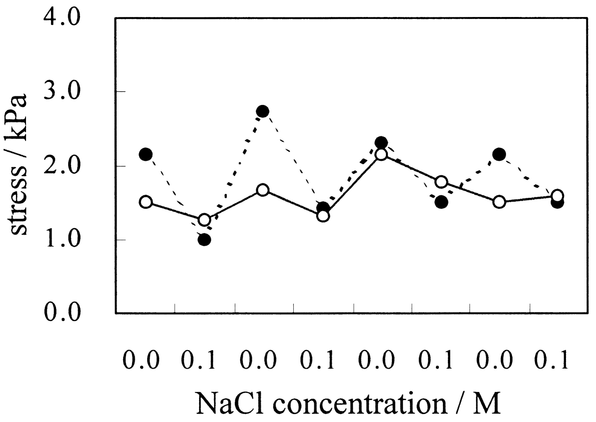

Fig. 7. The hardness change against the NaCl concentration of solution surrounding amphoteric gels. Solid line and dashed line correspond to the hardness variance of **A-sh** and **A-mH** in accordance with the ion concentration of their bathing solutions, respectively.

this rank order, and **PA-l**, having the largest swelling ratio, had the hardest matrix. Hence, the large contribution of salt-linkage to a hardening of gel matrix is strongly suggested here. Next, the possibility of reversible hardness change of gels was investigated by performing the formation and disruption of intramolecular salt-linkages. **A-sh** and **A-mh** were alternately transferred into deionized water and a 0.1 M NaCl aqueous solution at 20 °C; their hardness was measured by the method described in **Hardness** of **Gel Hardness Measurement** in the Experimental section, Fig. 7. Here, **A-lh** was not used because of its matrix shattering. Apparently, their reversible hardening and softening were induced.

It is shown that the formation and disruption of salt-linkages converts the soft acrylamide-based gel into the hard one, and vice versa. Since this bond formation occurs purely due to the electrostatic interaction, unlike in the case of crosslinikings of *N*,*N*-methylenediacrylamide (covalent bonds), salt linkages can be reversibly formed. Namely, without any permanent destruction of the gel matrix, we can control its hardness from low to high and high to low reversibly, which is a key property for an artificial muscle material.

Conclusions

Promoting salt-linkages is a promising way to improve the mechanical strength of amphoteric gels. Salt-linkages can be created and disrupted reversibly without permanently changing the molecular structure of amphoteric gels.

Electrostatic interactions are not commonly used to form or disrupt the crosslinkings in the gels. However, they can convert even a soft acrylamide-based gel into a very hard one, and it is easy to convert it back to the soft state. Importing both positive and negative charges on a gel network in addition to permanently formed chemical crosslinkings is a new principle which can be used to design gel artificial muscle with variable hardness.

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