Reswelling Transition of Poly(sodium acrylate) Gels due to Destruction of Hydrogen Bonds Observed by ATR FTIR Spectroscopy

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ABSTRACT: We report the reswelling transition of a physically crosslinked polyelectrolyte hydrogel in water, which was prepared using poly(sodium acrylate) as the main constituent and Al ions as the crosslinker. The nonmonotonic swelling behavior was observed at room temperature (25°C) under the continuous exchange of water; an as-prepared gel swelled at the first stage (the swelling process) and then shrunk very slowly at the second stage (deswelling process). In the deswelling process, the water exchange was stopped and the diameter of the gel in a limited amount of water was measured as a function of the temperature. The gels reswelled at different transition temperatures in the heating processes, which depended on the initial diameter at 25°C (resulting from the different numbers of water exchange). The reswollen state was stable at 25°C and could shrink again as a result of successive water exchanges at 25°C. In the following temperature increase in the closed system, the reswelling phenomenon was observed again. The destruction of the hydrogen bonds introduced by the water exchange was confirmed by the attenuated total refraction Fourier transform infrared measurements. The reversible transition behavior between the deswollen and the reswollen states is discussed in terms of the formation and destruction of the hydrogen bonds. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 105: 3809–3816, 2007

Key words: polyelectrolyte hydrogels; swelling behavior; hydrogen bond; FTIR

INTRODUCTION

Recently, some interesting swelling properties were reported on polyelectrolyte hydrogels consisting of a chemically or physically crosslinked network of linear polymers that have carboxyl groups.[1–7] As for the chemical gels,[1–4] the swelling ratio and the phase transition behavior of strongly ionized poly(*N*-isopropylacrylamide-*co*-sodium acrylate) gels were extensively investigated under the continuous exchange of solvent water. The size and the transition behavior were easily and precisely controlled by the number of water exchanges. These phenomena have been interpreted in terms of the exchange of counter ions by protons and the formation of the dimeric form of a hydrogen bond between carboxyl and carbonyl groups. As for the physical gels,[5–7] the swelling behavior of poly(sodium acrylate) (PSA) gels crosslinked by Al ions was investigated in detail by the repeated exchange of solvent water. The gel exhibited two relaxation processes in the nonmonotonic swelling behavior by the repeated water exchange; it swelled at the first stage and then shrank at the sec-

ond stage, where the swelling ratio approached the smaller swelling ratio than the initial one of as-prepared gel. The observations were explained using a qualitative model based on the ion exchanges and the creation of a hydrogen bond. These phenomena are believed to be common properties of hydrogels, regardless of whether they are chemically or physically crosslinked when they have the carboxyl groups in their polymer networks.

There are two noteworthy findings of these pioneering works for the practical applications of the polyelectrolyte hydrogels. One is that the swelling ratio of the gel depends on the amount of water at a fixed temperature (room temperature); it is necessary to take care of the amount of water around the gel when the gel is put into a solvent, water, after completion of its gelation. Even after the gel reached the equilibrium state, the swelling ratio can be changed if the gel is put out from the ''old'' water solvent and placed in ''new'' pure water. The other is that the diameter of the gel decreased rapidly at room temperature by the repeated change of water because of the formation of hydrogen bonds. All these observations were obtained at room temperature. In order to follow up our previous work[7] on the formation of the hydrogen bonds at room temperature, it is highly desirable to investigate the recovering process of the gel

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to the initial swollen state because of the destruction of the hydrogen bonds.

In this study, we investigated the temperature dependence of the swelling behavior of PSA hydrogels physically crosslinked by aluminum ions, which have been widely used in the medical field in products such as anti-inflammatory analgesic cataplasm. The changes in diameter of the deswollen gels by the successive water exchanges were measured during the heating process, and the formation and destruction of the hydrogen bond were examined by analyzing the Fourier transform infrared (FTIR) spectra. To investigate the conformation, dissociation and bonding state of the functional groups of the swollen gels in water, an attenuated total refraction (ATR) FTIR was used.[4,7–9] The effects of the hydrogen bond on the swelling behavior were examined in detail. Our interest was focused on how the formation and destruction of the hydrogen bonds can affect the swelling behavior of the present physically crosslinked hydrogels.

EXPERIMENTAL

PSA gels physically crosslinked by Al ions were prepared[5–7] by mixing 50 g of a PSA aqueous solution (for the main constituent, Wako Pure Chemical Industries; 18.1 wt % of PSA (31% of the total Na^+ ions was replaced by protons); average degree of polymerization from 2700 to 7500) with 0.5g of aluminum hydroxide $Al(OH)_3$ (for the crosslinker, Kyowa Chemical Industry, 1 wt % of a PSA solution). After 2.1 g (0.014 mol) of L(+)-tartaric acid (Wako Pure Chemical Industries) was added to the solution to adjust the solution pH in an acidic condition, the mixed solution was stirred with a spatula. By adding tartaric acid, the pH of the solution changed from ~9.5 to ~5. It is noteworthy that the amount of tartaric acid (a dicarboxylic acid) added was small enough not to affect the experiments.

Two types of thin capillaries (one: inner volume = 50 μL; the other: inner volume = 2 μL) were inserted into the solution to make the gels with a uniform cylindrical shape. The solution was sealed with a parafilm to prevent evaporation and was left in the air at room temperature (around 25°C) for 1 week. After gelation, the cylindrical gels (designated here as ''50 μL-gel'' and ''2 μL-gel'') were removed from the capillaries and dehydrated in air at 45°C for 2 days. The dehydration treatment was necessary for the present weak gel with a small density of crosslinking not to rupture by the successive water exchanges (see Ref. 7). The dehydrated gels were stored in a desiccator. The total monomer concentration of nonprotonated and protonated sodium acrylates in the gels at gelation before the dehydration was around 2.32 mol/L,

and that of Al ions was 0.14 mol/L. It is noteworthy that the maximum amount of $Al(OH)_3$ to contribute to crosslinking is ~5.5 times larger than the present sample when the valence per Al ion is ideal, i.e., 3. Considering the fact that the diffusion of Al ions into solvent by the water exchange (or flow) is about 20% of the nominal amount,[7] one can say that the crosslinking density of the present gel was weak enough to swell and shrink evidently in response to the changes in external conditions. The diameter was measured by an optical microscope apparatus equipped with a calibrated Charge Coupled Device camera and with a video processor. In the present study, the swelling degree of the gel was represented by the swelling ratio, d/d_0, where d_0 was the gelation diameter (the inner diameter of the glass capillary in which the gel was prepared; the diameters of 50 μL-gel and 2 μL-gel were 1.46 and 0.283 mm, respectively) and d is the measured diameter of the gel.

The midinfrared spectra of PSA solutions and PSA–Al gels were measured using an FTIR spectrophotometer (Jasco: FT/IR-610) equipped with an ATR (attenuated total reflectance) attachment with ZnSe crystal. The appropriate amount of the polymer solution or the gel was placed on the ZnSe crystal, and the FTIR spectra were then measured at room temperature. The spectra, which were obtained by subtracting the solvent component measured under the same condition, were normalized based on the C—H bending vibration at 1470–1430 cm^{-1}. The components of the absorption band at 1600–1300 cm^{-1} were deduced from the second-derivative of the spectra. The complex absorption band was then resolved by applying the curve-fitting method using the mixed Gaussian–Lorentzian function. All spectra were found to involve C—H bending vibration consisting of three peaks around 1450 cm^{-1}. The total absorbance of three peaks integrated between 1470 and 1430 cm^{-1} was assumed to be equivalent in the present experimental conditions and the spectra were normalized by the total area.[7]

RESULTS AND DISCUSSION

Reswelling transition

Figure 1 shows the change in the swelling ratio, d/d_0, by the initial treatment of water exchange at room temperature (open system) and the reswelling transition by successive heating in a limited amount of water (closed system). In the case of 50 μL-gel [Fig. 1(a)], the dehydrated gel was put in 100 mL of solvent pure water, which was repeatedly exchanged every 24 h. The diameter of the gel was measured just before the solvent was exchanged. In the case of 2 μL-gel [Fig. 1(b)], on the other hand, the dehydrated gel was placed in a quartz capillary (inner diameter = 6.0 mm)
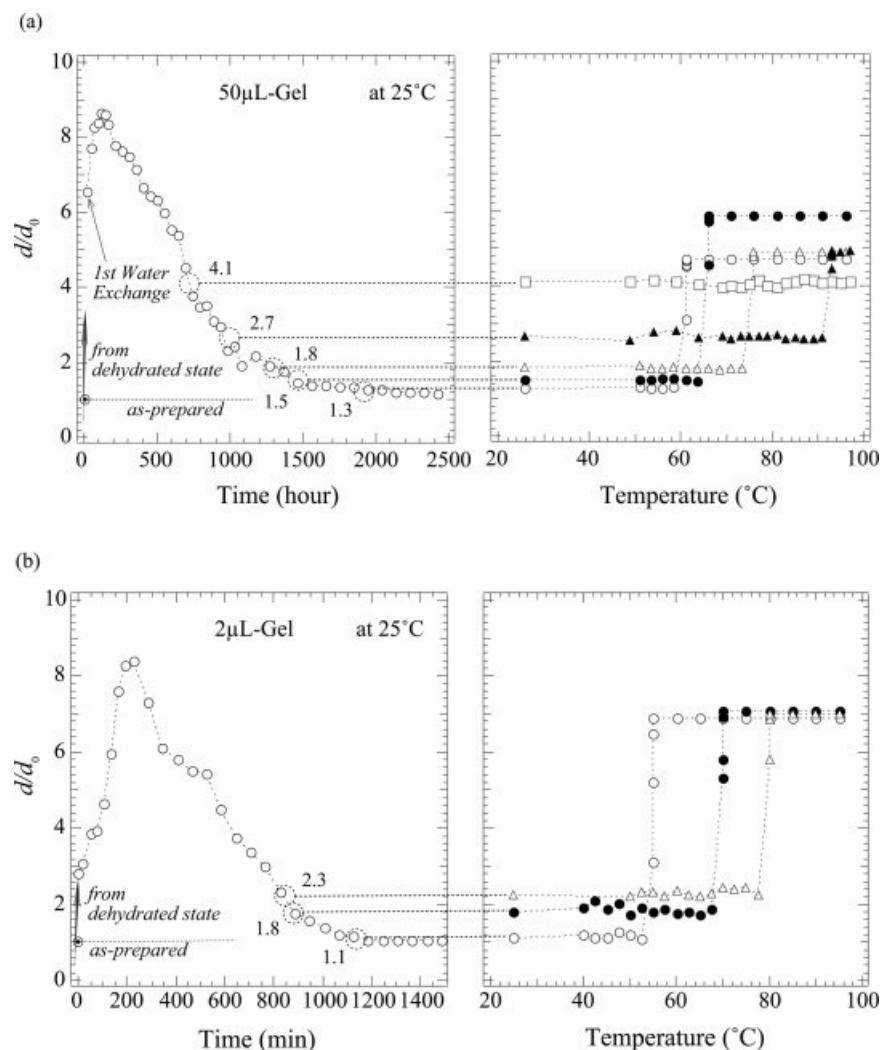
Figure 1 Change in the swelling ratios, d/d_0 of (a) 50 μL-gel and (b) 2 μL-gel. Left figures: the pure water was repeatedly exchanged in a constant interval at room temperature (a), or continuously flowed with a constant speed (b). The initial d/d_0 cannot be determined since the gel was in a dehydrated state (It should be lower than $d/d_0 = 1$). Right figures: the temperature was successively increased where the gel was held in a closed system (limited amount of water). In the case of the water flow (b), $d/d_0 = 2.8$ at time = 0, since the as-prepared gel ($d/d_0 = 1$) rapidly swelled just after the sample set with water. Lines were added to guide the eye.

in which the solvent water flowed continuously with a constant speed, 1.2 mL/min, from a reservoir of distilled deionized water. The gel exhibited two relaxation processes in the nonmonotonic swelling behavior by the repeated water exchanges or by the water flow; it swelled at the first stage and shrank at the second stage, where the swelling ratio approached the initial one of as-prepared gel. This nonmonotonic behavior is qualitatively consistent with the reported results on the gels prepared with a much larger amount (4 wt % of a PSA solution) of Al(OH)$_3$.[5–7] This behavior is attributed to the diffusion of Al ions into the solvent, the exchange of Na$^+$ counter ions by protons, and the formation of a hydrogen bond. This characteristic swelling behavior in this system is observed when the gel is repeatedly (or continuously) placed in "new" pure water at the respective treat-

ment. In the respective water exchange (or in the water flow), the osmotic pressure (swelling force) created by the counter ions trapped within the Donnan potential changed to reach the respective "new" equilibrium osmotic pressure. As is shown in Figure 1, the rate of the diameter change depended on the gelation diameter d_0 (1.46 or 0.283 mm). The total amount of the exchanged water for the 50 μL-gel ($d_0 = 1.46$ mm) was 10 L (100 times for 2400 h) and that for the 2 μL-gel ($d_0 = 0.283$ mm) was 1.5 L (1.2 mL/min for 1250 h). The former was $\sim$6.7 times larger than the latter, which did not qualitatively correspond to the ratio of the gel volume (around 25 times). This result is inconsistent with the reported one,[3] which indicated that the ratio of the total amounts between two treatments (the water exchange and the water flow) was approximately proportional to the ratio of the gel volume at
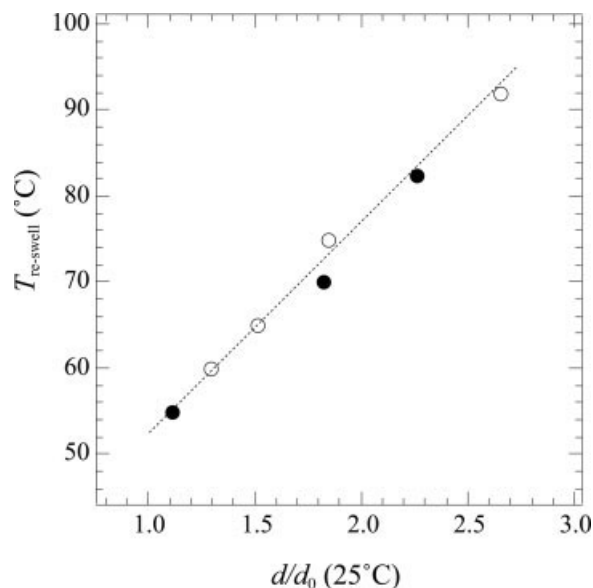
Figure 2 Reswelling transition temperature, T_{reswell}, of a 50 μL-gel (open symbols) and a 2 μL-gel (closed symbols), obtained in Figure 1, as a function of the initial swelling ratio, d/d_0, at 25°C. This initial d/d_0 was obtained when water exchange (or flow) was stopped after an insufficient water exchange (or flow); therefore it depended on the degree of the water exchange (or flow).

gelation. This result indicated that the speed of the water flow was much larger than the time typically required for the gel to reach equilibrium. It is noteworthy that the initial ($\sim$5) increased to reach 5.8 (pure water) step by step during the water exchange.

In the deswelling process, the water exchange or flow was stopped when d/d_0 dropped below $\sim$5. After the gel reached equilibrium in a closed system (when the gel was in a limited amount of water) at 25°C, the temperature was gradually increased. Here, this equilibrium swelling ratio at 25°C was denoted as the initial swelling ratio, d/d_0 (25°C). As is shown in Figure 1, the reswelling transition was observed regardless of d_0. When the temperature was increased, d/d_0 did not change in the lower range and the gel discontinuously swelled at the transition point. After the reswelling transition, d/d_0 did not change in the swollen state with further increasing the temperature.

Figure 2 shows the reswelling transition temperature, T_{reswell}, as a function of d/d_0 (at 25°C). It is evident that T_{reswell} increased with d/d_0 (25°C) and that T_{reswell} could be traced on a line regardless of d_0. This observation is inconsistent with the conventional prediction. According to the conventional swelling theory based on the Flory-type free energy,[10–12] it is expected in the case of the swelling transition with increasing temperature that the temperature should be increased higher when the osmotic shrinking pressure in the collapsed state becomes stronger. Although we do not have a decisive picture to

describe the relation between the reswelling transition temperature and d/d_0 (25°C), it could be related to the cooperative destruction of the hydrogen bonds by the temperature increase. It is noteworthy that the present swelling transition is not reversible by a temperature change, and, in that sense, it is not a phase transition.[11] Therefore, the conventional swelling theory might not be applicable to this phenomenon in its conventional form. We believe that it is necessary to modify by taking into consideration the chemical aspects of the molecular level, such as an orientational coordination, of the two monomers (see later discussion).

ATR FTIR measurements and analysis

Figure 3 shows the ATR FTIR spectra with different numbers of water exchange, as indicated in the inset figure, states A, B, and C on the swelling process (the first stage) and states C, D, E, F, and G on the deswelling process (the second stage). Two strong absorption peaks were observed at around 1560 and 1410 cm^{-1} in the spectra of state A (before the water exchange) and state B (after the first water exchange). According to our preliminary study of the gels prepared with 4 wt % aluminum hydroxide Al(OH)$_3$ of a PSA solution,[5–7] these two peaks were expected to correspond to the dissociated carboxyl groups ($-COO^-$). The overall shapes of the spectra of the present gels (1 wt %) are similar to that of the reported one (4 wt %), which indicates that most carboxyl groups in the gel were dissociated and did not form a hydrogen bond immediately after the water exchange was started. In the spectrum of state C, in addition to the two peaks, a peak was evident at
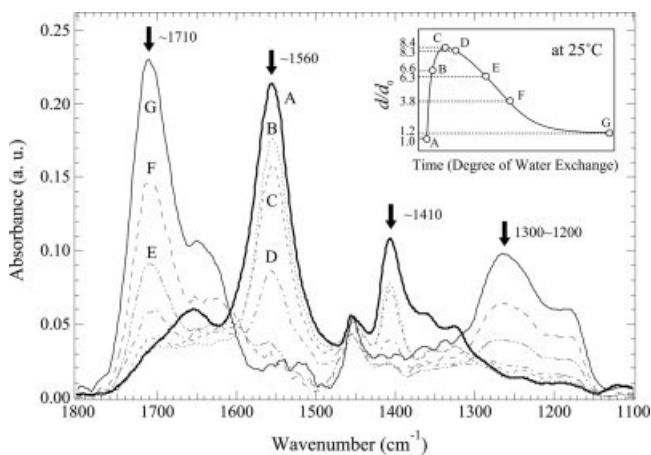

Figure 3 ATR FTIR spectra of gels in the swelling processes (from State A ($d/d_0 = 1$), via B ($d/d_0 = 6.55$) to C($d/d_0 = 8.39$)) and in the deswelling process (from State C, via D ($d/d_0 = 8.34$), E ($d/d_0 = 6.33$), and F ($d/d_0 = 3.79$) to G ($d/d_0 = 1.16$)). The schematic of swelling behavior is shown in the inset.

around 1710 cm^{-1}, which corresponds to the associated carboxyl groups[7]; the relative broad peak at 1710 cm^{-1} indicates the coexistence of a hydrogen bonded (in a monomeric or dimeric form) and nonhydrogen bonded carboxyl groups, and the present peak at 1710 cm^{-1} should correspond to the hydrogen bonded carboxyl group. In the course of this swelling process (from state A via B, to C), the two peaks gradually decreased, which suggests that the Al ions diffused into the solvent and the Na$^+$ counter ions were exchanged by protons because of the relatively low pH (around 5.8) of solvent water at the point where the hydrogen bond was accelerated and formed at the end of the swelling process. On the other hand, in the IR spectra on the deswelling process (state C via D, E, and F, to G), the absorption peaks at around 1560 and 1410 cm^{-1} slightly decreased, whereas the absorption peaks at around 1710 and 1300–1200 cm^{-1} clearly increased with increasing the number of repeated water exchanges. This observation indicates that the dimeric carboxyl groups were formed through the hydrogen bond. In addition, a strong absorption peak appeared at around 1640–1650 cm^{-1} in the highly deswollen states (F and G).

To make clear the effects of Al ions on the IR spectrum, the peak positions of the interaction between the polymer and Al ions should be assigned from the spectra of high accuracy with superb S/N ratio. At this moment, it is difficult to distinguish them from the present data because the band overlaps with a single broad band and cannot be distinguished from the present data.[7] The following discussion, however, might be reasonable since the diffusion of Al ions into the solvent was expected to be completed in the first stage (the swelling process) and did not strongly affect the diffusion of Al ions into the solvent.[7]

After the reswelling transition, the temperature slowly decreased and the gel was left at 25°C for a long time (2 months at most). The results showed that d/d_0 maintained the reswollen value and did not return to the initial d/d_0 (at 25°C). Therefore, the ATR FTIR spectra of the deswollen and reswollen states of gels can be measured at room temperature (called the P and Q states, respectively). Figure 4 shows a comparison of the IR spectra between the deswollen state (at 25°C, $d/d_0 = 2.7$; $P_{2.7}$) after an insufficient water exchange [from Fig. 1(a)] and its reswollen state (at 25°C after the reswelling transition to $d/d_0 = 4.9$; $Q_{4.9}$ (see the inset)). As is shown in this figure, the absorption peaks at around 1710 and 1300–1200 cm^{-1} clearly decreased as a result of the reswelling transition, which indicates that the dimeric carboxyl groups through the hydrogen bond were destroyed. In addition, the absorption peak observed at around 1640–1650 cm^{-1} in Figure 4 was suppressed in the spectrum of the reswollen gel. Although we do not have a decisive picture to explain the peak in this range, the
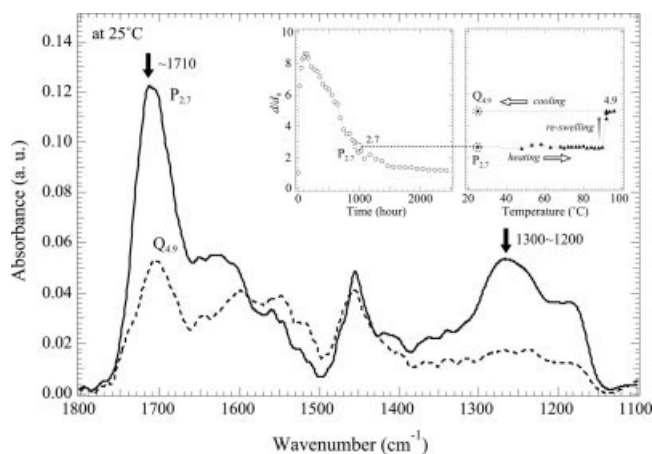

Figure 4 An example of ATR FTIR spectra of gels before and after the reswelling transition. In this transition, the initial state before the reswelling transition was obtained by insufficient water exchanges with d/d_0 (25°C) = 2.7. The details of the swelling behavior are shown in the inset.

apparent change might be related to the formation and destruction of a hydrogen bond.

Reproducibility of the reswelling transition

To explore the swelling behavior after the reswelling transition, the gel was successively placed again under a second water exchange (100 mL, every 24 h) at 25°C. After shrinking to d/d_0 from which the first heating had started, the temperature was gradually increased again. Figure 5 shows an example of the successive temperature increases used in the first and second water exchange processes [the first one is also shown in Fig. 1(a)]. It is evident that the swelling behavior in the second water exchange was identical to that in the first one. In the second treatment, the water exchange was again stopped at $P_{1.3\ (2nd)}$ (d/d_0 of 1.3 was reached again after about 70 more daily replacements, compared with the first deswelling process, counting from $d/d_0 = 4.7$), and the temperature increased. The gel then exhibited a reswelling transition similar to the first one once again; however, the transition temperature was slightly larger and the reswollen gel took a slightly larger d/d_0 because of the slight difference of d/d_0 (at 25°C). The slight increment of the transition temperature might have resulted from the fact that $P_{1.3\ (2nd)}$ was slightly larger than that of $P_{1.3}$.

To compare the two deswollen states, $P_{1.3}$ and $P_{1.3\ (2nd)}$, in Figure 5, the ATR FTIR spectra were obtained. The overall features of two spectra were determined to be the same, and the absorption peaks at around 1710 and 1300–1200 cm^{-1}, which decreased by the reswelling transition (similar to the change in Fig. 4), were recovered by the second repeated water
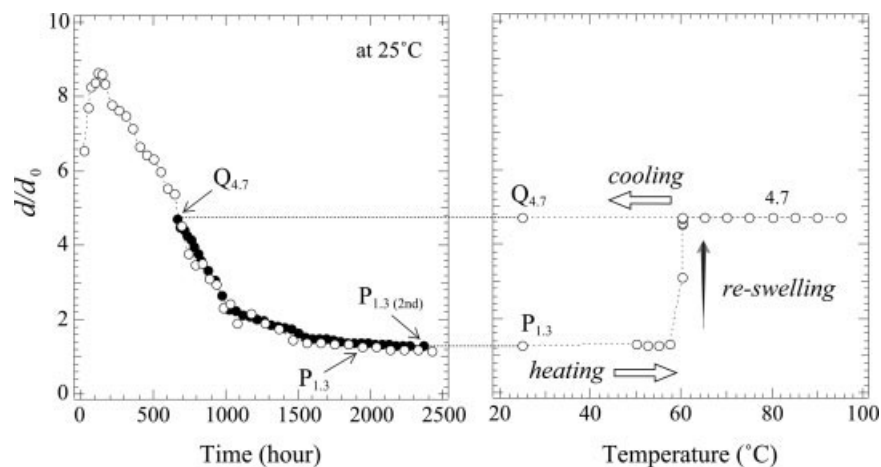
Figure 5 Changes in d/d_0 by the two sets of the water exchanges and successive temperature increases. The gel in the first deswollen state, $P_{1.3}$, exhibited the reswelling transition by the increasing temperature and changed to the reswollen state, $Q_{4.7}$, after the gel was left at 25°C for more than 1 month (open circles). The gel was successively placed again under a second water exchange and changed to the second deswollen state, $P_{1.3(2nd)}$, (closed circles).

exchange. This evidence indicates that the hydrogen bonds between the two dimeric carboxyl groups, which were broken during the reswelling transition, could be recovered by the second water exchange.

The experimental results are summarized as follows: the hydrogen bond between the carboxyl groups was destroyed by the temperature increase, and the number of hydrogen bonded carboxyl groups (—COOH) increased during the water exchange.

Analysis of the nonionized carboxyl region of the spectra

To investigate the formation of the hydrogen bond in detail, a curve-fitting analysis of the nonionized carboxyl region (1800–1500 cm^{-1}) was performed by deconvoluting the spectra. The results of the second derivative spectra determined that there were four peaks (~1748, 1738, 1716, and 1700 cm^{-1}) reproducible in this region. The existence of four components would be expected to contribute to the C=O band of nonionized carboxyl groups. According to literature,[4,7,13,14] the peak of the C=O stretching vibration of the free (nonhydrogen-bonded) —COOH group appears at ~1740 cm^{-1}, and that of the C=O stretching vibration of the cyclic hydrogen-bonded —COOH group in the dimeric form appears at a rather low wave number (~1710 cm^{-1}). Therefore, the peak located at ~1748 cm^{-1} can be assigned to the C=O stretching vibration of the free carboxyl groups (free C=O), and the peak located at ~1716 cm^{-1} can be assigned to the C=O stretching vibration of the cyclic hydrogen-bonded carboxyl groups of SA in the dimeric form (C=O···H—O hydrogen bond). The peaks located at ~1738 and 1700 cm^{-1} might correspond to some combinations of side chains that are not clear at

the present time. A recent report[15] suggested that the peaks of the C=O stretching vibration of the hydrogen-bonded —COOH group in a lateral fashion and in a face-on fashion appear in this region. Moreover, the wave number of the free C=O band might depend upon whether or not its O—H group is hydrogen-bonded or free. Because of the lack of further experimental observations, it is difficult to make a precise assignment on the basis of the present data. The observed peaks located at ~1738 and 1700 cm^{-1}, however, might be assigned to the C=O stretching vibration of the hydrogen-bonded carboxyl groups in a lateral fashion and a face-on fashion that are related with the main peaks at 1748 and 1716 cm^{-1}. We now believe that the peaks located at ~1738 and 1700 cm^{-1} could have similar roles in determining the macroscopic conformations of gels with main peaks at 1748 and 1716 cm^{-1}, respectively. On the basis of this assumption, the percentage of the sum of the peak areas of two components at 1716 and 1700 cm^{-1} (and that of two components at 1748 and 1738 cm^{-1}) to the total area was calculated in Figure 6 for the states obtained for the different stages in the deswelling process by water exchange and for the successive re- and deswollen states. The data presented in this figure show that the cyclic hydrogen bond between the two carboxyl groups was formed as a result of the repeated water exchanges and was destroyed by the temperature increase. The formation and destruction of the hydrogen bond was found to be reversible by the treatment of water exchanges and successive temperature increases [Fig. 6(b)].

A broad peak at 1300–1200 cm^{-1} was clearly observed in the spectrum of states E, F, and G. This broad peak can be assigned to the coupled peaks of the C=O stretching vibration and the O—H bending
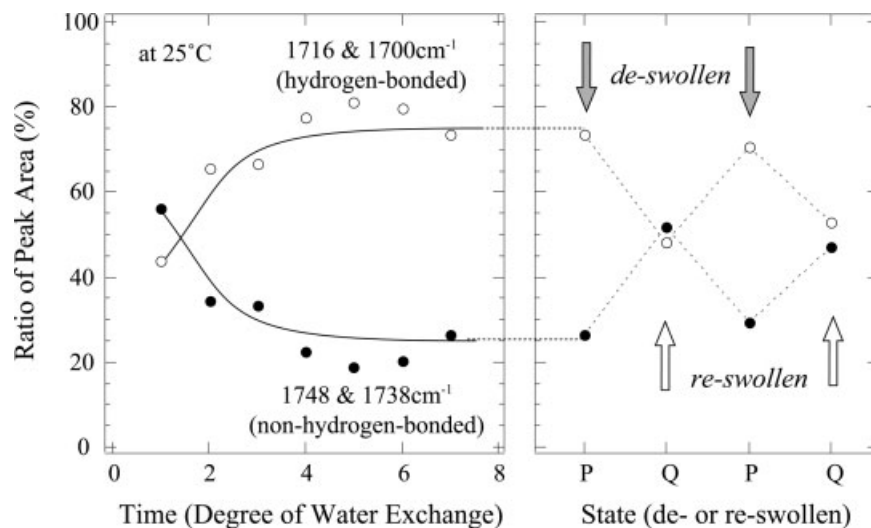
Figure 6 Relationship between the states of gels and the peak area ratio of the two components of the main peaks at 1748 and 1716 cm^{-1}, $[A_I]/[A_T]$ (open circles) and $[A_{II}]/[A_T]$ (closed circles). $[A_I]$, $[A_{II}]$, and $[A_T]$ denote the sum of the peak areas of two components at 1716 and 1700 cm^{-1}, the sum of those at 1748 and 1738 cm^{-1}, and the sum of $[A_I]$ and $[A_{II}]$, respectively. The lines guide the eye.

vibration in the cyclic hydrogen bond between two carboxyl groups.[13] Therefore, in the process of repeated water exchanges, the original counter ions Na$^+$ could be replaced by protons, the number of the nonionized carboxyl groups (—COOH) increased, and pairs of nonionized carboxyl groups were formed through hydrogen bond; it is possible that there are not only monomeric or dimeric forms of hydrogen bonds between carboxyl groups and/or amide groups in lateral fashions and face-on fashions,[15,16] but also hydrogen bonds between a side chain of carboxyl or amide group and a water molecule (Fig. 7).

Effects of the formation and destruction of a hydrogen bond on the swelling behavior

In the present experiments, the reswelling transition of the physically crosslinked hydrogels was, for the first time, observed using weakly crosslinked PSA gels. Repeated experiments of deswelling by water exchanges and reswelling by temperature increases proved that the formation and destruction of hydrogen bonds were qualitatively but reproducibly detected, which indicates that this is a universal property in a system in which the hydrogen bond is dominant among the intermolecular forces to create attractive forces in the system. As noted above, the present transition is not a phase transition that has been reported in other systems in response to temperature changes, such as those used with IPN gels,[17] random copolymer gels with multiple phases,[18] and random copolymer gels with hydrogen bond.[19] These phase transition gels are all chemical gels. The reason that the present system did not recover to the initial dia-

meter before the reswelling transition could be the weak crosslinked network. Once the hydrogen bond was destroyed, it could not be formed in the polymer system. It is believed that each of the four fundamental interactions, hydrogen bond, hydrophobic interaction, the van der Waals interaction, and electrostatic interaction induces a phase transition between two different phases in water at near body temperature. The present observation of the irreversible transitions indicated that the hydrogen bond in the physical gel system of PSA is strong enough to induce deswelling by water exchange but too weak to induce a shrinking
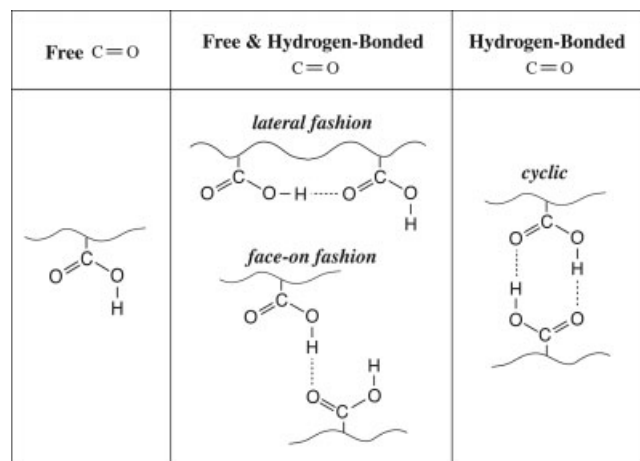

Figure 7 Possible forms of free C=O and/or hydrogen-bonded C=O illustrated for the carboxyl group (—COOH): free C=O without hydrogen-bond, free C=O, and hydrogen-bonded C=O between two monomers in a lateral fashion and a face-on fashion, and two hydrogen-bonded C=O between two monomers.

transition by cooling back to around room temperature. From the stand point of the molecular level, a plausible explanation is as follows: the hydrogen bond requires an orientational coordination of two monomers, which is more difficult to form than another physical bonds such as hydrophobic, the van der Waals, and electrostatic interactions. It might be very difficult for the present system in its swollen state to arrange many orientations for the formation hydrogen bonds to induce the shrinking transition. It will be interesting to study the phase behavior of physical gels, in which combinations of hydrogen bonds and each of the four fundamental interactions are introduced and their balance is varied by changing the variables, such as temperature, solvent composition, and pH. We believe that such a study will reveal a fascinating new aspect in the phase behavior of hydrogels in general, and, in particular, of physically crosslinked hydrogels.

CONCLUSION

PSA gels physically crosslinked by Al ions were prepared, and the nonmonotonic swelling behavior (swelling and deswelling) was observed by the repeated exchange of solvent water at room temperature. The formation of a hydrogen bond was confirmed by the measurements of ATR FTIR spectroscopy on gels with different swelling ratios. The carboxyl groups were gradually protonated on the swelling process and on the deswelling process the carboxyl dimers through the hydrogen bond were gradually formed by long-term water exchange that resulted in the shrinkage of the gel in open systems.

The changes in the swelling ratio of the deswollen gels with different swelling ratios at 25°C were measured as a function of the temperature. The reswelling transition was dependent on the heating process in closed systems. The reswelling transition temperature depended on the initial swelling ratio at 25°C, and the larger the swelling ratio, the larger the transition temperature. In the cooling process, on the other hand, the reswollen state did not recover to the deswollen gels and it was stable at 25°C for a long period (more than one month). However, the reswollen state could shrink as a result of successive water exchanges at 25°C. The swelling behavior (the deswelling by repeated water exchanges and the reswelling transition by the temperature increases) was qualitatively

but reproducibly observed in the successive second treatment. These unique behaviors could be attributed to the conformational changes of polymer networks related to the formation and destruction of hydrogen bonds, which were confirmed by measurements using ATR FTIR spectroscopy. The macroscopic swelling behavior completely corresponded to the microscopic structural changes in all successive treatments conducted here (the water exchanges in open systems and temperature changes in closed systems).

The present observations, we believe, are of crucial importance not only for understanding the phase transition related of polyelectrolyte hydrogels but also for developing the future practical applications of hydrogels as functional elements. The technique presented here can be used to control the reversible formation and destruction of hydrogen bonds just by changing the amount of solvent water and the temperature without the use of chemicals.

References

1. Bai, G.; Suzuki, A. Eur Phys J E 2004, 14, 107.
2. Hirashima, Y.; Tamanishi, H.; Sato, H.; Saito, K.; Naito, A.; Suzuki, A. J Polym Sci Part B: Polym Phys 2004, 42, 1090.
3. Hirashima, Y.; Suzuki, A. J Phys Soc Jpn 2004, 73, 404.
4. Hirashima, Y.; Sato, H.; Suzuki, A. Macromolecules 2005, 38, 9280.
5. Harada, T.; Sato, H.; Hirashima, Y.; Igarashi, K.; Suzuki, A.; Goto, M.; Kawamura, N.; Tokita, M. Colloids Surf B 2004, 38, 209.
6. Harada, T.; Hirashima, Y.; Suzuki, A.; Goto, M.; Kawamura, N.; Tokita, M. Euro Polym J 2005, 41, 2189.
7. Sato, H.; Hirashima, Y.; Suzuki, A.; Goto, M.; Tokita, M. J Polym Sci Part B: Polym Phys 2005, 43, 753.
8. Ottenhof, M.; MacNaughtan, W.; Farhat, I. Carbohydrate Res 2003, 338, 2195.
9. Ferri, D.; Frauchiger, S.; Burgi, T.; Baiker, A. J Catal 2003, 219, 425.
10. Flory, P. J. Principles of Polymer Chemistry; Cornell University Press: New York, 1953.
11. Tanaka, T. Sci Am 1981, 1244, 124.
12. Hirotsu, S. Phase Transitions 1994, 47, 183.
13. Maeda, M.; Yamamoto, H.; Ikeda, I. Langmuir 2000, 16, 7503.
14. Maeda, M.; Higuchi, T.; Ikeda, I. Langumuir 2001, 17, 7535.
15. Dong, J.; Ozaki, Y.; Nakashima, K. Macromolecules 1997, 30, 1111.
16. Hirashima, Y.; Suzuki, A. J Colloid Interface Sci 2007, 312, 8.
17. Ilmain, F.; Tanaka, T.; Kokufuta, E. Nature 1991, 349, 400.
18. Mafé, S.; Manzanares, J. A.; English, A. E.; Tanaka, T. Phys Rev Lett 1997, 79, 3086.
19. Tanaka, K. Ph.D. Thesis, Massachusetts Institute of Technology, 2000.