ATR-FTIR Spectroscopic Study on Hydrogen Bonding of Poly(*N*-isopropylacrylamide-*co*-sodium acrylate) Gel

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ABSTRACT: Diameter decrement by the repeated exchange of solvent water has been reported in a polyelectrolyte hydrogel ionized by sodium acrylate in its swollen state. This behavior has been attributed to the exchange of counterions of carboxyl groups and the formation of hydrogen bonding. In this paper, the formation and destruction of hydrogen bonding in poly(*N*-isopropylacrylamide-*co*-sodium acrylate) (NIPA/SA) gel were studied using Fourier transform infrared (FTIR) spectroscopy with attenuated total reflection (ATR) at 25 °C. Several swollen samples with different swelling ratios were prepared by changing the number of water exchanges at 25 °C. It was found that the ATR-FTIR spectra evidently depended on the initial swelling ratio. By sufficient water exchanges, new peaks appeared at ca. 1713 cm^{-1} (assigned to the carboxyl dimer) and at ca. 1650 cm^{-1} in the amide I region (assigned to a stretching vibration of the C═O group that forms a hydrogen bonding with the N−H bond of a neighboring amide group), and the amide II band shifted to a smaller wavenumber by ca. 7 cm^{-1}. From the detailed analysis of the IR spectra, the macroscopic polymer network shrinkage was attributed to the formation of three types of hydrogen bonding, that is, between two carboxyl groups of SA, between the carboxyl group of SA and the amide group of NIPA, and between two amide groups of NIPA. Moreover, the IR results indicated experimentally that the reswelling transition of the present system was caused by the destruction of hydrogen bonding on heating. It was concluded that not only the formation by the exchange of water but also the destruction of hydrogen bonding by heating is essentially important to determine the swelling ratio as well as the volume phase transition behavior in this system.

Introduction

Polymer gels exhibit unique properties, such as the phase transition or critical phenomena in response to external stimuli.[1−3] In the experimental studies of the phase transition gels, it is a fundamental technique to observe the phase transition behavior by measuring the changes in volume. This is because the observed volume should be reflected by the average network structure, and macroscopic volume change should be determined by the interactions between the monomers.

Among the phase transition gels, it has been proven that chemically cross-linked poly(*N*-isopropylacrylamide) gel (abbreviated as "NIPA gel" here) and its copolymer gels in water undergo a phase transition in response to very small temperature changes.[3,4] Especially, ionized hydrogel, such as poly(*N*-isopropylacrylamide-*co*-sodium acrylate) gel (abbreviated as "NIPA/SA gel"), has been widely studied for its the physical and chemical properties in various fields, such as materials science, physics, chemistry, biology, and pharmacology.[4−9]

In our previous work, we experimentally investigated the effects of repeated water exchange on the swelling properties and the phase transition behavior of strongly ionized NIPA/SA gels.[10−12] The diameter of the gel, the Na^+ concentration in the solvent around the gel, and the pH of the solvent were measured after the solvent exchanged. To reveal the structural change at the molecular level, NMR measurements were conducted for several dried and swollen gels with different times of water exchange. The gel size at the swollen state depended strongly on the number of water exchanges. The diameter of the gel decreased rapidly at room temperature by the repeated change of water. The macroscopic polymer network shrinkage was discussed in terms of the replacement of counterions Na^+ by H^+ and of the formation of intermolecular hydrogen bonding between the two nonionized groups (−COOH) and/or between the −COOH and −CONH− groups. However, considering the results of NMR experiments, it is difficult to determine the contribution of two types of carbonyl groups to hydrogen bonding.

Moreover, recently, the phase transition of the NIPA/SA gel was investigated after introducing hydrogen bonding by the exchange of solvent water for cylindrical gels with different diameters at gelation. After the water exchange, the diameter of the NIPA/SA gel in a limited amount of water was measured as a function of the temperature. We found that the transition behavior could be controlled by the degree of the water exchange. The volume change of the NIPA/SA gel was classified into three different behaviors: discontinuous, reswelling, and continuous, depending on the initial swelling ratio at 25 °C and not the gelation diameter. It was concluded that the formation of hydrogen bonding, which is controlled by the degree of the water exchange, is essentially important to determine not only the gel size at the swollen state but also the phase transition behavior.

In this paper, we investigated the roles of hydrogen bonding on the swelling behavior of strongly ionized NIPA/SA gels. To obtain a better understanding of the mechanism of the volume phase transition of the NIPA/SA gel, the classification of hydrogen bonding forms in

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the gels was examined in detail. To investigate the conformation, dissociation, and bonding state of functional groups of swollen NIPA/SA gels, an attenuated total reflection (ATR) FTIR was used. IR spectroscopy is one of the most suitable methods for observing changes in the conformation, interaction, and microscopic local environment of individual chemical groups.[13−21] Recently, several groups have studied IR spectroscopy to investigate the coil−globule transition of NIPA polymer aqueous solution[14,16] and the volume phase transition of neutral NIPA gel[22] or interpenetrating polymer network gels composed of poly(*N*-isopropylacrylamide) and poly(acrylic acid)[13] (abbreviated as "NIPA/AA-IPN gel"). The IR absorption peaks of the NIPA/SA gel were assigned on the basis of those of the neutral NIPA gel and the aqueous polymer solutions. The roles of the creation and destruction of hydrogen bonding on the macroscopic swelling behavior (the polymer network shrinkage by the repeated water exchange (or the continuous water flow) and the reswelling transition phenomenon) were discussed on the basis of the microscopic structural changes obtained by the FTIR method.

Experimental Procedures

Materials. Strongly ionized NIPA/SA gels were prepared by free radical copolymerization: 5.63 g of NIPA (500 mM, main constituent, Kohjin), 1.867 g of SA (200 mM, ionizable monomer, Wako), 0.133 g of *N,N′*-methylenebis(acrylamide) (8.6 mM, cross-linker, Wako), and 240 μL of *N,N,N′,N′*-tetramethylethylenediamine (TEMED, accelerator, Wako) were dissolved in 100 g of distilled deionized water.[9−12] Then, nitrogen gas was bubbled through the solution to remove the dissolved oxygen. To initiate the gelation, 40 mg of ammonium persulfate (APS, initiator, Wako) was further added into the pregel solution. Thin and thick capillaries (inner diameter = 0.283 mm, and 1.42 mm) were inserted into the solution to make gels in a uniform cylindrical shape. The gelation reaction was carried out at ca. 0 °C for more than 24 h. After the polymerization was completed, the cylindrical gels were dried gently at room temperature (ca. 25 °C) and then removed from the glass capillaries.

Measurements of Diameter. The experimental setup was similar to that used in ref 12. One piece of the thin dried NIPA/SA gel was placed in a quartz capillary with a diameter ~10 times larger than that of the gel. The capillary was encapsulated in a transparent square glass. Within the cell, water was circulated to control the temperature with an accuracy of ±0.05 °C. The solvent water can continuously flow from a reservoir of pure water (distilled deionized water). The diameter of the thin gel was measured with an optical microscope apparatus equipped with a calibrated charge-coupled device (CCD) camera and a video processor.

For the IR measurements, the thick dried NIPA/SA gels were placed in a container with a constant volume of pure water (usually 100 mL) at room temperature (ca. 25 °C), and the water was repeatedly exchanged at a constant interval (usually 24 h). The diameter of the thick gel was measured by using an optical microscope equipped with a calibrated scale (accuracy, 1 μm).

In this measurement, the swelling degree of the gel was represented by the swelling ratio, d/d_0, where d is the diameter of the gel and d_0 is the original diameter (the inner diameter of the capillary in which the gel was synthesized).

ATR-FTIR Measurements and Analysis. To study the network structure on the molecular level, the measurements of Fourier transform infrared (FTIR) spectroscopy with an attenuated total reflection (ATR) method were carried out. Several swollen samples with different swelling ratios by varying the times of the water exchange were prepared for the FTIR studies. Details of the preparation of samples for FTIR analysis are given in the next section.

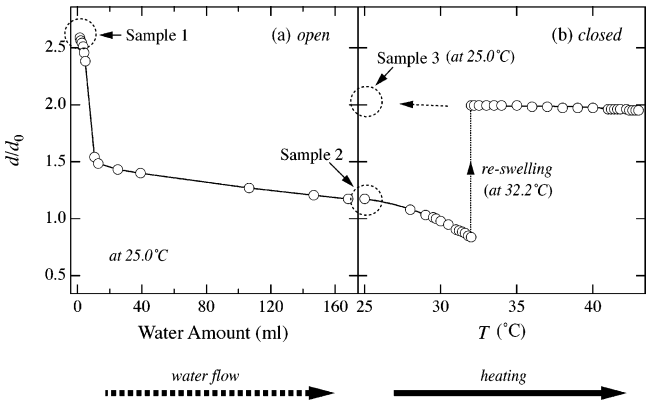

Figure 1. Effects of the continuous water flow and the temperature change on the swelling ratio, d/d_0, of the thin NIPA/SA gel (d_0 = 0.283 mm). (a) d/d_0 as a function of the total amount of exchange water and (b) d/d_0 as a function of temperature measured on heating process. After a sufficient water flow, the gel in a closed system (limited amount of water solvent) reswelled at the phase-transition point by increasing the temperature. The sample numbers in this figure indicate three different states of gels used FTIR measurements (see text).

ATR-FTIR spectra were recorded on an FTIR spectrophotometer (Jasco FTIR-610) equipped with an ATR attachment with a horizontal ZnSe crystal (Jasco PRO400S). The resolution of the spectra was 4 cm^{-1}, and scans were repeated 100 times. The appropriate amount of the gel was placed on the ZnSe crystal, and then the FTIR spectrum was measured. All measurements were performed at ambient temperature (ca. 25 °C).

In this study, the IR spectra obtained by the ATR method were corrected to eliminate the dependence of the penetration depth. To distinguish characteristic bands of the sample gels, all spectra in the experiment were obtained by subtracting the solvent component measured under the same conditions. Moreover, since the volume fraction of the polymer network in the present strongly ionized hydrogel was extremely small and the subtracted absorption spectrum of the swollen gel was too weak to be analyzed, the water in the gels was evaporated in part by leaving the gels in air at room temperature to a constant swelling ratio, $d/d_0 = 0.67$. It is noteworthy that the sample gels were still in the swollen states.

The complex absorption bands obtained here were resolved applying a well-established curve-fitting method. The baseline and the band shape (the mixed Gaussian−Lorentzian function) were fixed, and the wavenumber, height, and width of the components were optimized to obtain the best-fit curve. Analysis of the IR spectra, such as the subtraction of a water spectrum, the calculation of a second-derivative spectrum, baseline subtraction, and curve-fitting analysis of complex absorption bands, was performed by using the Spectra Manager software equipped in the spectrophotometer (Jasco).

The IR absorbance spectra of NIPA/SA gels were normalized based on C−H_2 bending vibration that appears at ca. 1470−1430 cm^{-1}. The components of the absorption band at 1550−1380 cm^{-1} were deduced from the second-derivative spectra and were resolved applying the curve-fitting method. All spectra were found to involve C−H_2 bending vibration consisting of two peaks at ca. 1463 cm^{-1} (1464 and 1446 cm^{-1}). The total absorbance areas of the two peaks were assumed to be equivalent in the present experimental conditions, and the spectra were normalized by the total area.

Results and Discussion

Samples for ATR-FTIR Experiments. Figure 1a shows the changes in the swelling ratio, d/d_0, of the thin gel (d_0 = 0.283 mm) when the water around the gel continuously flowed from a reservoir at 25 °C. The gel size at the swollen state strongly depended on the water

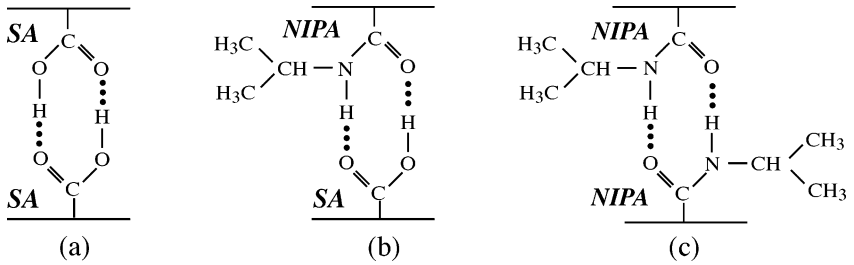

Figure 2. Three possible forms of hydrogen bonding illustrated for the carboxyl group (−COOH) of SA and the amide group (−CONH−) of NIPA in NIPA/SA gel: (a) hydrogen bonding between SA and SA, (b) hydrogen bonding between NIPA and SA, and (c) hydrogen bonding between NIPA and NIPA. The hydrogen-bonded carbonyl is supposed to be a monomeric or dimeric form of hydrogen bonding.

flow;[10−12] the d/d_0 decreased rapidly at first to d/d_0 = 1.5 and, thereafter, gradually below $d/d_0 = 1.5$. After a sufficient (but not complete) water flow ($d/d_0 = 1.25$), the water flow was stopped, and the diameter of the gel in the limited amount of water was measured as a function of the temperature. As shown in Figure 1b, the gel exhibited a discontinuous reswelling transition on heating at 32.2 °C. According to the previous work,[11] neither the swelling ratio at the swollen state nor the phase transition behavior depended on the d_0. They only depended on the exchanged amount of water. Therefore, the thick gel (d_0 = 1.42 mm) was expected to exhibit a similar swelling behavior if the initial swelling ratio was the same as that of the thin gel used in Figure 1 (d/d_0 = 1.25).

The effects of a repeated water exchange on the conformational change of the NIPA/SA gel were investigated through an ATR-FTIR study. In the measurements, the thick gel was used for a technical reason. For the FTIR experiments, several swollen samples with different d/d_0s at 25 °C were prepared. Sample 1 was the one in which the water had been exchanged slightly with $d/d_0 = 2.76$ (dipped in a small amount of water for a short time), and sample 2 was the one in which the water had been exchanged with $d/d_0 = 1.25$. In addition, sample 3 was prepared for the FTIR measurements to confirm the destruction of hydrogen bonding by the reswelling transition; the d/d_0 of this sample, which was cooled to 25 °C after the reswelling transition on heating, was 1.92. The sample numbers in Figure 1 indicate three different states of gels used in the FTIR experiments, that is, the states before a successive water exchange, after a sufficient (but not complete) water exchange, and after the reswelling transition.

Figure 2 shows three possible forms of hydrogen bonding illustrated for the carboxyl group of SA and the amide group of the neutral NIPA in the NIPA/SA gel. It is possible that there are monomeric or dimeric forms of hydrogen bonding.

ATR-FTIR Spectra of the NIPA/SA Gels. Figure 3 shows the ATR-FTIR spectra of a NIPA gel (Figure 3a), NIPA/SA gels before and after a sufficient water exchange (Figure 3b), and NIPA/SA gels before and after the reswelling transition (Figure 3c). Each set of two peaks in Figure 3b,c was normalized by the peak area of the C−H_2 bending vibration at ca. 1463 cm^{-1}, which should not be affected by the water exchange (or the reswelling transition). Details of the normalization are reported in the Experimental Procedures section.

All spectra of the neutral NIPA gel and the ionized NIPA/SA gels are characterized by several peaks in three regions with wavenumbers 1680−1500, 1420−1350, and 1300−1100 cm^{-1}. On the other hand, the

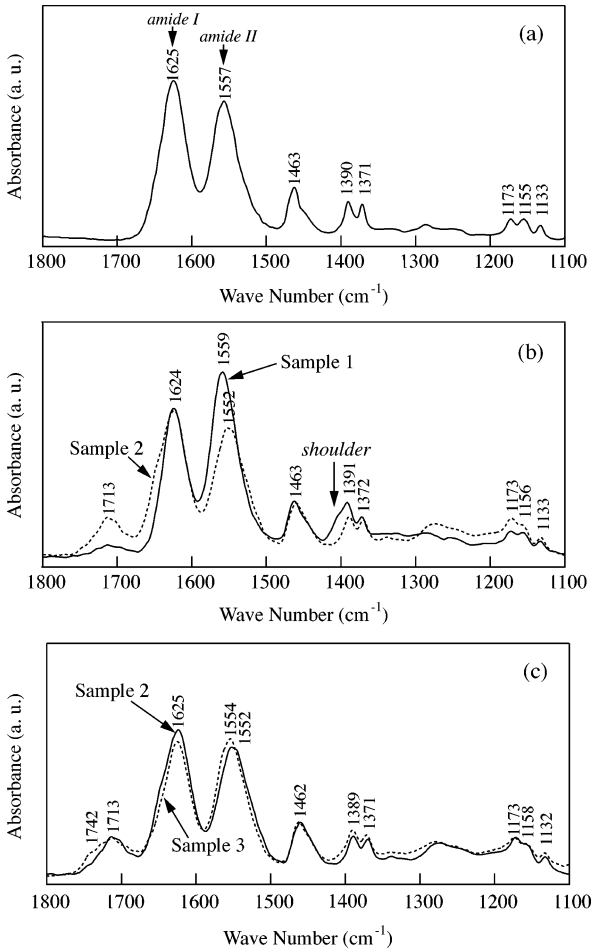

Figure 3. ATR-FTIR absorption spectra of gels at room temperature (ca. 25 °C): (a) NIPA gel, (b) NIPA/SA gels [sample 1: initial, $d/d_0 = 2.76$ (solid line); sample 2: water exchanged, $d/d_0 = 1.25$ (broken line)], and (c) NIPA/SA gel [sample 2: water exchanged, $d/d_0 = 1.25$ (solid line); sample 3: reswollen by heating, $d/d_0 = 1.92$ (broken line)].

specific wavenumbers at 1750−1700 cm^{-1} were observed only in the spectra of ionized NIPA/SA gels.

Effects of Ionization. First of all, we will discuss the effects of ionization. In a comparison of the spectra of the neutral NIPA gel with that of the ionized one (sample 1), it is evident that the amide II band became larger than the amide I band as a result of the ionization, and a shoulder was visible in the peak located at ca. 1391 cm^{-1}. According to the literature,[17,18,23] the peak of the C=O stretching vibration of the ionized carboxyl group ($-COO^-$) appears at ca. 1540 and 1410 cm^{-1}. Therefore, changes in the spectra resulting from ionization can be attributed to the signals

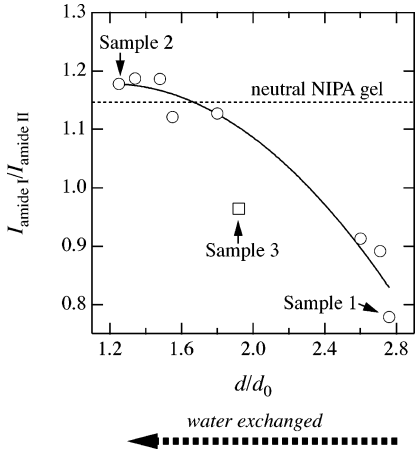

Figure 4. Relationship between the swelling ratio, d/d_0 (at 25 °C), of NIPA/SA gels and the peak intensity ratio of the amide I band and the amide II band, $I_{amide\ I}/I_{amide\ II}$. Open box symbol denotes the data of sample 3. The solid line guides the eye.

of ionized carbonyl groups (−COO⁻) that are expected to appear at ca. 1540 cm^{-1} (involved in the amide II region) and 1410 cm^{-1} (located in the vicinity of the main peak at ca. 1391 cm^{-1}).

The origin of the peaks and the changes that occur as a result of the water exchange and reswelling transition are discussed here. Comparing the spectra of sample 1 (slight water exchange) and sample 2 (sufficient water exchange), the intensity of the amide II band decreased, and the shoulder at ca. 1391 cm^{-1} disappeared. These changes can be attributed to the ionization. Figure 4 displays a plot of the peak-intensity ratio of the amide I band to the amide II band, $I_{amide\ I}/I_{amide\ II}$, as a function of the d/d_0 at 25 °C. An obvious relationship exists between $I_{amide\ I}/I_{amide\ II}$ and d/d_0. Because the peak position of the C=O stretching vibration of the ionized carboxyl groups (−COO⁻) of SA is involved in the amide II region, it is evident that $I_{amide\ I}/I_{amide\ II}$ is small in the case of sample 1. In the process of the water exchange, the original counterions Na^+ could be replaced by H^+, and the pH of the water decreased to ca. 5.7, which resulted in the increment of nonionized carboxyl groups (−COOH).[10] Therefore, as shown in Figure 4, the intensity of the signal of the ionized carboxyl groups (−COO⁻) in the amide II region decreased, and $I_{amide\ I}/I_{amide\ II}$ became larger after a sufficient water exchange.

Analysis of the Nonionized Carboxyl Region (ca. 1750−1700 cm^{-1} and ca. 1300−1200 cm^{-1}). In the spectra of the NIPA/SA gels, a peak was obvious at ca. 1713 cm^{-1}. This peak does not exist in the spectrum of the neutral NIPA gel (Figure 3a). This is because the signal of the C=O stretching vibration of nonionized carboxyl groups (−COOH) of SA appeared. Thus, the broad peak at ca. 1713 cm^{-1} indicated the coexistence of hydrogen-bonded and non-hydrogen-bonded carboxyl groups. As shown in Figure 3b, with increasing the number of repeated water exchanges, the absorption of this peak obviously increased.

This complex band at ca. 1713 cm^{-1} was deconvoluted by a curve-fitting program. Figure 5 shows an IR spectrum and the results of the best curve fitting. Here, the intensity of this peak at ca. 1713 cm^{-1} of sample 1 (initial, $d/d_0 = 2.76$) is not large enough to analyze; therefore, another sample in which the water had been exchanged slightly with $d/d_0 = 2.71$ was analyzed to investigate the effect of repeated water exchanges. As shown in this figure, there are four major peaks (1745, 1731, 1715, and 1695 cm^{-1}) in this region. According to the literature,[17,18,23] the peak of the C=O stretching vibration of the non-hydrogen-bonded carboxyl group appears at ca. 1740 cm^{-1}, and that of the C=O stretching vibration of the hydrogen-bonded group (dimeric form) appears at a rather low wavenumber (ca. 1710 cm^{-1}). Therefore, the peak located at the higher wavenumber region (at ca. 1745 and 1731 cm^{-1}) can be assigned to the C=O stretching vibration of the non-hydrogen-bonded carboxyl groups of SA ("free" C=O), and the peak located at the lower wavenumber region (at ca. 1715 and 1695 cm^{-1}) can be assigned to the C=O stretching vibration of the hydrogen-bonded carboxyl groups of SA (C=O···H−O hydrogen bond).

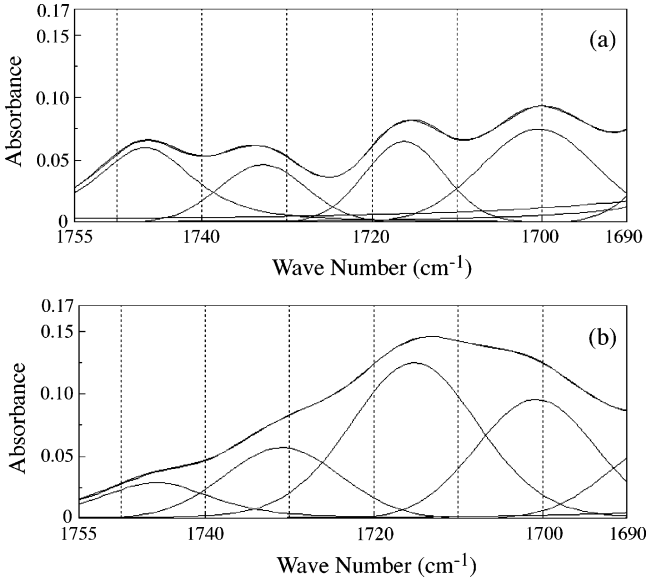

Figure 5. Curve-fitting results of the nonionized carboxyl region (1755−1690 cm^{-1}) of NIPA/SA gels: (a) the slightly water exchanged one with $d/d_0 = 2.71$ and (b) sample 2 (water exchanged, $d/d_0 = 1.25$). Here, the intensity of this peak at ca. 1713 cm^{-1} of sample 1 (initial, $d/d_0 = 2.76$) is not large enough to analyze; therefore, another sample in which a slight water exchange had taken place with $d/d_0 = 2.71$ was analyzed to investigate the effect of repeated water exchanges.

Figure 6 shows a plot of the peak area ratio (percentage of total peak area) in this complex band at ca. 1713 cm^{-1}, $\alpha_{carboxyl}$, as a function of the swelling ratio for the NIPA/SA gels. The data presented in Figure 6 show that the hydrogen bonding between two carboxyl groups of SA formed as a result of the repeated water exchanges and that it accelerated below $d/d_0 = 1.55$. It is noteworthy that this value was consistent with that of the bend point in Figure 1a.

Moreover, as shown in Figure 3b, the broad peak at 1300−1200 cm^{-1} appeared in the spectrum of sample 2. This broad peak can be assigned to the coupled peaks of the C=O stretching vibration and the O−H bending vibration in the hydrogen bonding between two carboxyl groups of SA.[23] Therefore, in the process of repeated water exchanges, the original counterions Na^+ could be replaced by H^+, the number of the nonionized carboxyl groups (−COOH) increased, and two nonionized carboxyl groups were formed through hydrogen bonding.

Figure 3c shows a comparison of sample 2 (after a sufficient water exchange) and sample 3 (after the reswelling transition). As shown in this figure, a peak at ca. 1742 cm^{-1} located in the vicinity of the main peak

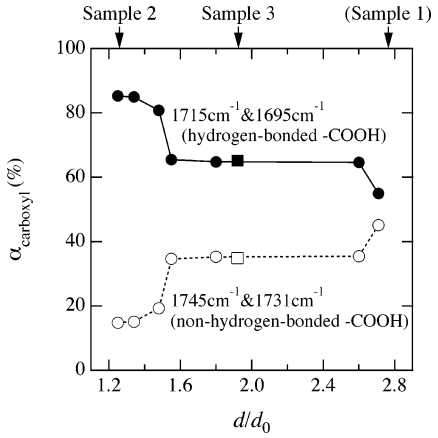

Figure 6. Relationship between the swelling ratio, d/d_0 (at 25 °C), of NIPA/SA gels and the peak area ratio in the complex band at ca. 1713 cm^{-1}, $\alpha_{carboxyl}$, of the four components of carboxyl region of SA. Box symbol denotes the data of sample 3. The data of sample 1 (initial, $d/d_0 = 2.76$) is not presented here. The lines guide the eye.

at 1713 cm^{-1} in the nonionized carboxyl (−COOH) region was clearly observed after the reswelling transition. Moreover, as shown in Figure 6, the peak area ratio of the hydrogen-bonded carboxyl groups of SA decreased and that of the non-hydrogen-bonded carboxyl groups of SA increased. The data presented in Figure 6 suggest that the hydrogen bonding between two carboxyl groups of SA is destroyed during the reswelling transition. The experimental results can be summarized as follows: the hydrogen bonding between the carboxyl groups of SA was destroyed, and the number of non-hydrogen bonded carboxyl groups (−COOH) increased during the heating process.

Analysis of the Amide Region (ca. 1680−1500 cm^{-1}). Finally, two major bands, the amide I and II bands observed in 1680−1500 cm^{-1}, are discussed. It has been established that the amide I band (between ca. 1680 and 1580 cm^{-1}) is mainly associated with the C=O stretching vibration of the amide group of NIPA.[13,14,16,23] On the other hand, the amide II band (between ca. 1580 and 1500 cm^{-1}) mainly resulted from the N−H bending vibration of the amide group of NIPA.[13,14,16,23]

In recent years, several groups have studied IR spectroscopy to investigate the coil−globule transition of the NIPA polymer solution and the volume phase transition of the NIPA/AA-IPN gel. Furthermore, the band assignments of NIPA have been discussed in the amide I and II regions, and more specifically, the influences of the hydrogen bonds between the amide groups of NIPA on the transition have been investigated.[14,16] It is well-known that ATR-FTIR has been used as a probe for hydrogen bonding, especially to help substantiate interpolymer interaction by hydrogen bonding.[24] The C=O stretching vibration can be markedly influenced by the formation and destruction of hydrogen bonding, and the exact band position is determined by the backbone conformation and the hydrogen-bonded pattern. Like the amide I band, the amide II band is sensitive to the strength of hydrogen bonding. Therefore, the analysis of the amide region is effective to investigate the microenvironment around the amide groups of NIPA in the ionized NIPA/SA gels. Details of the curve-fitting results of the amide I region will be discussed in the following.

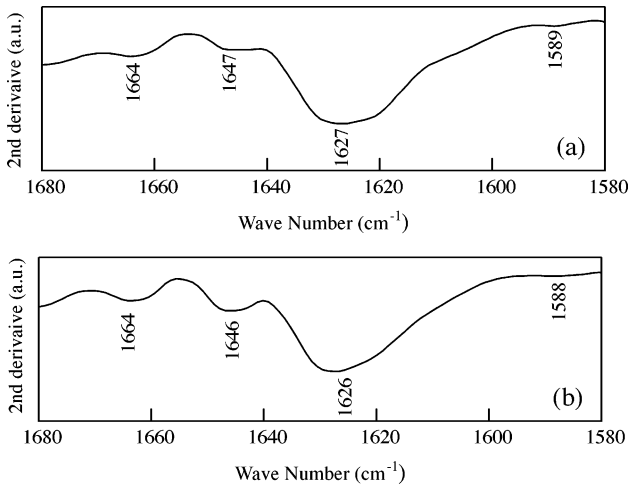

Figure 7. Second-derivative spectra in the 1680−1580 cm^{-1} region of NIPA/SA gels: (a) sample 1 (initial, $d/d_0 = 2.76$) and (b) sample 2 (water exchanged, $d/d_0 = 1.25$).

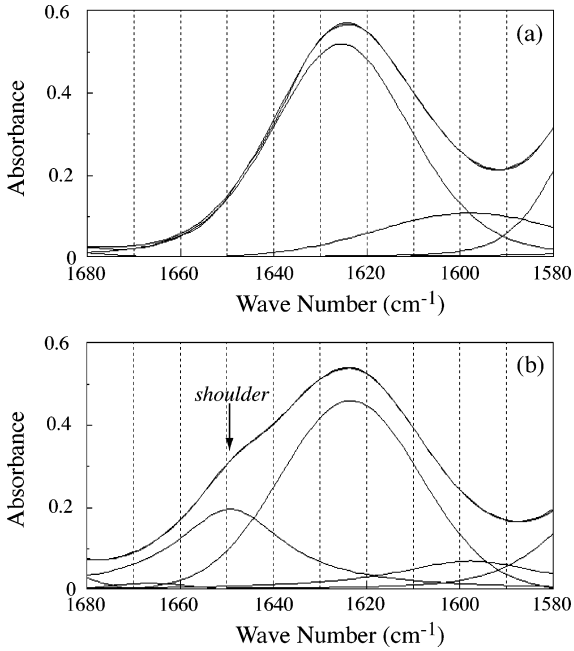

Figure 8. IR spectrum and curve-fitting results of the amide region (amide I band, 1680−1580 cm^{-1}) of NIPA/SA gels: (a) sample 1 (initial, $d/d_0 = 2.76$) and (b) sample 2 (water exchanged, $d/d_0 = 1.25$).

To investigate the formation of hydrogen bonding in detail, a curve-fitting analysis of the amide I region was performed. For the logical approach to curve fitting, some reasonable assumptions were made. The baseline (1800−1100 cm^{-1}) and the band shape (the mixed Gaussian−Lorentzian function) were fixed. The curve fitting was limited from 1800 to 1500 cm^{-1} for the initial wavenumber, height, and width of the components. An iterative procedure was employed to obtain a best-fit curve. Figure 7 shows the second-derivative spectra of the NIPA/SA gels, samples 1 and 2. Judging from the results of the second-derivative spectra, the initial wavenumbers of the components were determined. Figure 8 shows the IR spectra and the results of the best curve-fitting analysis for samples 1 and 2 by a peak separation method. The wavenumbers of the amide I and II bands correlate to the electron density on the C=O bond and N−H bond of NIPA and the strength of the hydrogen bonding. Thus, the wavenumber of the hy-

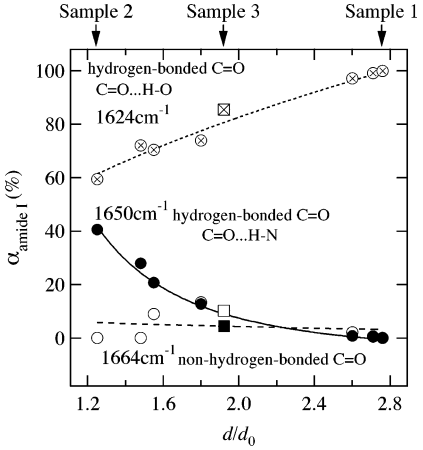

Figure 9. Relationship between the swelling ratio, d/d_0 (at 25 °C), of NIPA/SA gels and the peak area ratio, $\alpha_{\text{amide I}}$, of the three components of the amide I band of NIPA. Box symbol denotes the data of sample 3. The lines guide the eye.

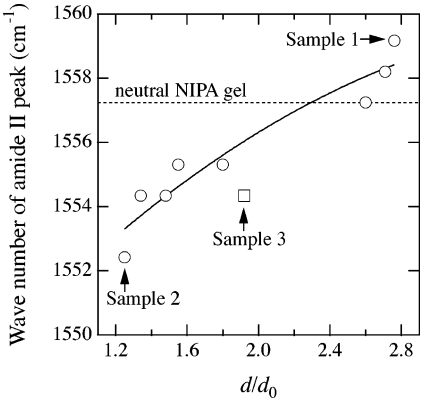

Figure 10. Relationship between the swelling ratio, d/d_0 (at 25 °C), of NIPA/SA gels and the wavenumber of amide II peak. Open box symbol denotes the data of sample 3. The solid line guides the eye.

drogen-bonded C=O bond of NIPA was smaller than that of the "free" C=O bond of NIPA; on the other hand, the wavenumber of the hydrogen-bonded N−H bond of NIPA was larger than that of the "free" N−H bond of NIPA. Here, a "free" C=O and a "free" N−H are a non-hydrogen-bonded C=O and a non-hydrogen-bonded N−H, respectively.

As a result, the amide I region of NIPA is mainly composed of three distinct bands: a free C=O band at ca. 1664 cm^{-1} (C=O), an intramolecular hydrogen-bonded C=O band at ca. 1650 cm^{-1} (C=O···H−N), and an intermolecular hydrogen-bonded C=O band at ca. 1624 cm^{-1} (C=O···H−O). As shown in Figure 8 a, in the case of sample 1, a single peak was clearly observed at ca. 1624 cm^{-1} in the amide I region. This composition was assigned to the C=O stretching vibration of the amide group (−CONH−) of NIPA that forms an intermolecular hydrogen bonded with water and/or the O−H bond of the neighboring carboxyl group (−COOH) of SA. As shown in Figure 8b, in the case of sample 2, a shoulder can be seen in the main peak located at ca. 1624 cm^{-1}. New peaks at ca. 1650 cm^{-1} appeared in the amide I region. The peak at ca. 1650 cm^{-1} was assigned to the stretching vibration of the C=O bond that forms an intramolecular hydrogen bonded with the N−H bond of the neighboring amide group of NIPA. The results indicate that the hydrogen bonding formed between two amide groups of NIPA during the repeated water exchanges. The peak at ca. 1664 cm^{-1} was assigned to the stretching vibration of the free C=O bond of NIPA, and this peak was very weak.[13]

The peak area ratios of the three components of the amide I band of NIPA, $\alpha_{\text{amide I}}$, were calculated. The calculated results are shown in Figure 9. An obvious relationship exists between the peak area ratio of the three components (at ca. 1624, 1650, and 1664 cm^{-1}) and the d/d_0 at 25 °C. In the process of the water exchange, the peak area ratio of the intermolecular hydrogen-bonded C=O (C=O···H−O) decreased, while that of the intramolecular hydrogen-bonded C=O (C=O···H−N) increased. On the other hand, in the case of sample 3 (after the reswelling transition), the peak area of the intramolecular hydrogen-bonded C=O (C=O···H−N) decreased. Accordingly, it is considered that the number of intramolecular hydrogen bonds with the N−H bond of the neighboring amide group (−CONH−) of NIPA increased, while that of the intermolecular hydrogen bonds with water and/or the O−H bond of the neighboring carboxyl group (−COOH) of SA decreased by the repeated water exchanges. On the other hand, the hydrogen bonding between the amide groups (−CONH−) of NIPA was destroyed during the reswelling transition.

Moreover, it is well-known that hydrogen bonding of the N−H bond causes an upward shift of the amide II band. The wavenumber of the amide II band as a function of the swelling ratio at 25 °C is shown in Figure 10. As shown in this figure, the amide II band shifts to a lower wavenumber by ca. 7 cm^{-1} in the process of repeated water exchanges. On the other hand, in the case of sample 3, the amide II band shifts to a higher wavenumber.

As a result, as with the carboxyl groups of SA, the amide groups of NIPA were formed through hydrogen bonding by continuous water exchanges. Therefore, the analysis of the carboxyl and amide regions suggested that three types of hydrogen bonding, as shown in Figure 2a−c, were formed in the NIPA/SA gel with increasing the number of repeated water exchanges and that these hydrogen bonds were destroyed during the heating process.

Conclusion

This paper discusses the roles of the creation and destruction of hydrogen bonding as they relate to the macroscopic swelling behavior (the polymer network shrinkage by the continuous exchange of water and the reswelling transition phenomenon) and the microscopic structural changes obtained by the ATR-FTIR method.

To clarify the evidence of the formation of hydrogen bonding, ATR-FTIR spectroscopy was applied to a gel with various swelling ratios, which was controlled by the degree of the water exchange. The ATR-FTIR study on the NIPA/SA gel revealed that the microscopic local environment around individual chemical groups (the carboxyl group of SA and the amide group of NIPA) is evidently changed by the continuous exchange of water. With an increasing number of water exchanges, new peaks appeared at ca. 1713 cm^{-1} (in the nonionized carboxyl region) and at ca. 1650 cm^{-1} (in the amide I region), and the amide II band shifted to a lower wavenumber by ca. 7 cm^{-1}. Considering the ATR-FTIR experimental results, it has been suggested that the carboxyl groups of SA were gradually protonated, and the formation of hydrogen bonding was confirmed by

the repeated water exchanges. Judging from the analysis of the IR spectrum, the formation of hydrogen bonding in the NIPA/SA gels was classified into three different forms. The macroscopic polymer network by a repeated water exchange was attributed to the formation of hydrogen bonding between two carboxyl groups of SA (C═O···H−O hydrogen bond), between the carboxyl group of SA and the amide group of NIPA (C═O···H−O hydrogen bond and C═O···H−N hydrogen bond), and between two amide groups of NIPA (C═O···H−N hydrogen bond). Moreover, the ATR-FTIR experimental results indicated that the reswelling transition of the present system was caused by the destruction of hydrogen bonding on heating.

Accordingly, we believe that the formation of hydrogen bonding, which is controlled by the degree of the water exchange, is essential to determine not only the swelling ratio but also the volume phase transition behavior of NIPA/SA gels.

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