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# Structural changes of water in poly(vinyl alcohol) hydrogel during dehydration

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To investigate the mechanism of structural changes of water and polymer networks with drying and swelling, we measured the Raman spectra of a physically cross-linked poly(vinyl alcohol) (PVA) hydrogel synthesized using the freezing–thawing method. The results show that the vibrational frequencies of the O–H and C–H stretching modes decrease with dehydration. The frequency shifts observed are attributed to reduction of free water inside the polymer network. The C–H bonds elongate as the water density decreases, and the average length of the O–H bonds increases with increasing proportion of bound water to the total amount of water. On the basis of the dependence of the frequency shifts on the PVA concentration of the original solution, it was found that the structure of the polymer network in the reswollen hydrogel becomes inhomogeneous due to shrinkage of the polymer network with drying. Furthermore, to investigate the effects of the cross-linking structure on the drying process, these results were compared with those of a chemically cross-linked PVA hydrogel synthesized using glutaraldehyde as a cross-linker. The result shows that the vibrational frequency of the O–H stretching mode for the chemically cross-linked hydrogel increases with dehydration, whereas that of the C–H stretching mode decreases. The opposite trend observed in the O–H stretching mode between the physically and chemically cross-linked hydrogels is due to the difference in the shrinkage rate of the polymer network. Because the rate of shrinking is slow compared with that of dehydration in the chemically cross-linked hydrogel, water density in the polymer network decreases. For the physically cross-linked hydrogel, the polymer network structure can be easily shrunken, and the average strength of hydrogen bonds increases with dehydration. The results show that the structures of the polymer network and water change with the gel preparation process, cross-linking method, and drying and reswelling processes. The structure of the polymer network and the behavior of water accommodated in the network are important factors governing the chemical and physical properties of gel materials.  
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## I. INTRODUCTION

Hydrogels are unique materials consisting of large amounts of water in polymer networks. Because of its characteristic properties, hydrogels are used in various fields such as medicine, agriculture, and daily life.<sup>1–4</sup> Poly(vinyl alcohol) (PVA) is a typical water soluble polymer, and its hydrogel is widely used in biomaterials, medicinal products, life articles, and so on.<sup>5,6</sup> Figure 1 shows the chemical structure of PVA.

A hydrogel is generated by the formation of a physically or chemically cross-linked structure between polymer chains in an aqueous solution. Chemically cross-linked gels are formed using a cross-linker such as glutaraldehyde (GA),  $\gamma$  irradiation, or electricity.<sup>7–9</sup> For physically cross-linked gels, gelation occurs without a cross-linker, and microcrystals, ionic bonds, or hydrogen bonds formed between the polymer chains become the cross-linking points.<sup>10</sup> The freezing–thawing method is recognized as a typical genera-

tion method for physically cross-linked PVA hydrogels.<sup>11</sup> The PVA hydrogel synthesized using this method has characteristics such as high dynamic strength, porous structure, and higher water content.<sup>12–14</sup> The PVA hydrogel has a spherical porous structure with an average diameter of about 30 nm, and micro crystals of about 3–8 nm in diameter in the mesh structure.<sup>13</sup>

The mechanical strength of physically cross-linked PVA hydrogels synthesized using the freezing–thawing method depends on freezing and thawing temperatures and the number of times they are frozen and thawed.<sup>4,15</sup> From tensile tests, Nakajima *et al.*<sup>15</sup> showed that the fracture stress and elastic modulus of PVA hydrogel increase with the number of times they are frozen and thawed and reach their maxima when this process is repeated 5 times. Hatakeyama *et al.*<sup>16</sup> observed the scanning electron microscopy (SEM) images of a PVA hydrogel and showed that the thickness of porous wall from aggregation of PVA chains and pore size increase with the freezing–thawing time. Because of the volumetric expansion of water during the freezing process, the pore size increases and the PVA chains are compressed. While the hydrogel becomes fragile with an increase in the pore size, the formation of new inter- and intra-molecular hydrogen bonds

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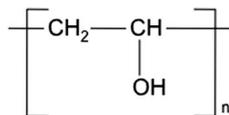


FIG. 1. Chemical structure of PVA.

between the adjacent PVA chains cause an increase in mechanical strength. From X-ray diffraction (XRD) and nuclear magnetic resonance (NMR) results, Ricciardi *et al.*<sup>14</sup> showed that the volumetric ratio of PVA crystalline phase in three phases of PVA hydrogel (i.e., water, PVA amorphous, and PVA crystal) increases with the freezing–thawing time. The microcrystals act as cross-linking points and have the effect of increasing the mechanical strength of the hydrogel.

Water in hydrated polymer systems has been classified into three types: free water, intermediate water, and bound water.<sup>17–19</sup> Free water consists of water molecules with a structure similar to that of bulk water, and the interaction of their molecules with polymer chains is negligible. Bound water is usually associated with water molecules that form hydrogen bonds with polar polymers or that strongly interact with polymer chains. Intermediate water exists between free and bound water and interacts weakly with polymer chains.

The relative amount of the three types of water varies according to the water content.<sup>20,21</sup> Because of the difference in dehydration rate among these three types of water, three stages exist in the dehydration process of hydrogel.<sup>18,22,23</sup> The structure of water and polymer network change with water content. Sekine and Ikeda-Fukazawa<sup>18</sup> analyzed the changes in the Raman scattering of poly-*N,N*-dimethylacrylamide (PDMAA) hydrogel with natural drying and showed the process of structural changes of water and polymer network with dehydration.

The composition of the three types of water also depends on the structure of the polymer network. Hatakeyama *et al.*<sup>16</sup> measured the differential scanning calorimetry (DSC) of PVA hydrogels and found that the amounts of free and intermediate water decrease with increase in the cross-linking density. From the observation of swelling process of a chemically cross-linked PVA hydrogel using montmorillonite (MOM) as the cross-linker, Paranhos *et al.*<sup>24</sup> showed that the swelling rate decreases as the MOM concentration increases. For a physically cross-linked PVA hydrogel, the cross-linking density depends on the PVA concentration of its original solution. Nakaoki and Yamashita<sup>25</sup> measured DSC of a physically cross-linked PVA hydrogel and found that the relative amount of bound water increases with PVA concentration. Using SEM and XRD, Gupta<sup>26</sup> showed that the pore size decreases with increasing PVA concentration. From the results, it was concluded that the number density of a microcrystal, which acts as a cross-linking point in a physically cross-linked hydrogel, increases with the PVA concentration increases because the polymer chains can adhere more easily due to the micro-Brownian motion in the PVA solution.

Previous studies suggest that the structures of water and polymer network in hydrogels depend on various factors such as cross-linking method, polymer concentration, and water content. To investigate the mechanism of structural changes

with water content and PVA concentration, we measured the Raman scattering of physically cross-linked PVA hydrogels synthesized using the freezing–thawing method during drying and swelling. Furthermore, the effect of the cross-linking method was investigated by comparing our results with those of the chemically cross-linked PVA hydrogel using GA as a cross-linker. The Raman spectra provide direct information about the molecular structure of PVA and the molecular arrangement of the surrounding water.

## II. EXPERIMENT

Samples of physically cross-linked PVA hydrogels were prepared by the following procedure. PVA powder with an average molecular weight of  $M_w = 220\,000$  (Nippon Synthetic Chemical Industry Co., Ltd.) was dissolved in distilled water, and the solution was obtained after the mixture at 363 K for 2 h. The PVA concentration (i.e., the weight ratio of PVA to water) of the solutions was controlled and maintained at 4.95–16.29 wt.%. After cooling the solution to room temperature, it was poured into a cylindrical sample cup with 12.2 mm in diameter and 22.0 mm in height. The sample was frozen at  $253 \pm 2$  K in a freezer and kept for 23 h, and thereafter, the sample was maintained at room temperature ( $293 \pm 5$  K) for 5 h. This process was repeated twice to promote gelation. After this process, a cylindrical gel sample with 12 mm diameter and 10 mm thickness was prepared. After gel formation, the gel samples were soaked in distilled water for 24 h to achieve equilibrium water contents in the maximum swollen state.

For the samples of chemically cross-linked PVA hydrogels, GA was used as a cross-linker.<sup>10</sup> After cooling the PVA solutions to room temperature, GA and 1 N hydrochloric acid were added in the solutions, and the solutions were kept at room temperature for 72 h. The GA/PVA ratio and pH of the solutions were adjusted to 0.66 and  $2 \pm 0.1$ , respectively. The PVA concentrations were 5.63–15.06 wt.%.

The gel samples were dried in a desiccator at  $293 \pm 5$  K and  $45 \pm 15\%$  humidity for 300 h. The Raman spectra and the weights of the samples were measured every 20 h during the drying process. The Raman spectra were measured using a spectrometer (JASCO, NRS-3300). The excitation radiation for the Raman emission was produced using a YAG laser that had single-mode operation at 532 nm with an output power of 100 mW. The spectra were measured in the frequency range  $100\text{--}4000\text{ cm}^{-1}$ . The laser beam was focused using an optical system on the surface of the gel at a spot with  $5\text{ }\mu\text{m}$  diameter. During the Raman measurements, the temperature of the gel samples was kept at room temperature ( $298 \pm 2$  K).

## III. RESULTS AND DISCUSSION

### A. Structural changes during drying and swelling processes

Figure 2 shows the temporal variation of water content in a physically cross-linked PVA hydrogel from the original solution with 5.6 wt.% of PVA concentration during dehydration. The water content of the sample at time  $t$ ,  $W(t)$ , is

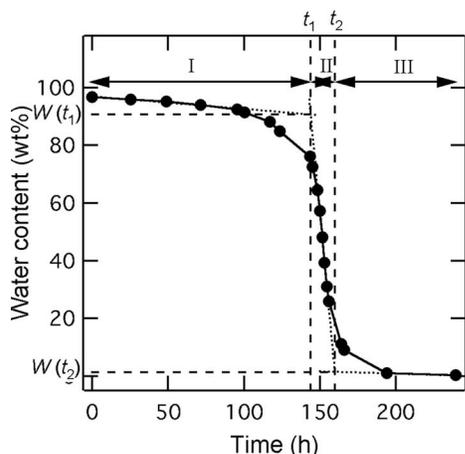


FIG. 2. Time dependence of water content in a physically cross-linked PVA hydrogel from the original solution with 5.6 wt.% of PVA during dehydration.

given by

$$W(t) = \frac{M(t) - M_d}{M(t)} \times 100, \quad (1)$$

where  $M(t)$  is the weight of the sample at  $t$  and  $M_d$  is the weight of the dried sample after dehydration. As shown in Fig. 2, the water content decreases toward zero with time. From the reduction rate, the dehydration process can be classified into three stages (i.e., stages I, II, and III, as shown in Fig. 2). The boundaries between stages I and II and stages II and III are  $t_1 = 144$  h and  $t_2 = 160$  h, respectively. The  $W(t)$  values at  $t_1$  and  $t_2$  are 90.6 and 1.4 wt.%, respectively. The water content slowly decreases in stage I and the reduction rate increases in stage II. In stage III, the water content becomes almost constant. This tendency is consistent with the result for the PDMAA hydrogel.<sup>18</sup> The change in reduction rate is attributed to the evaporation of the different types of water.<sup>21</sup> From the DSC results, Ikeda-Fukazawa *et al.*<sup>21</sup> showed the change in the relative amount of the three types of water with water content. The result indicates that the observed change in reduction rate arises from the change in the relative amount of the three types of water. Free water primarily evaporates from hydrogel in stage I. In stage II, the intermediate water starts to evaporate and the hydrogel becomes an intermediate state of gel and glass. In stage III, the hydrogel transforms into glassy state and the remaining bound water slowly evaporates.

Figure 3(a) shows the variation of Raman spectra in the frequency region of the O–H and C–H stretching modes for a physically cross-linked PVA hydrogel from the original solution with 5.6 wt.% of PVA during dehydration. The intensity of the broad band at around  $3400\text{ cm}^{-1}$  decreases with dehydration because the band is associated with the vibration of water molecules.

Several peaks exist in the broad band of the frequency region of Fig. 3(a). The arrows in Fig. 3(a) show the observed peak positions. These peaks are assigned to three C–H stretching modes of the polymer chain and four O–H stretching modes of the water molecules.<sup>27,28</sup> To analyze the frequencies of the O–H and C–H stretching modes, the band was

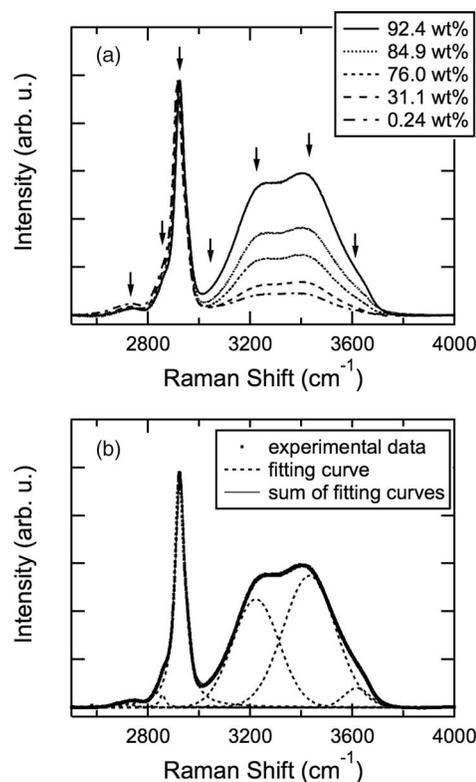


FIG. 3. (a) Variation in Raman spectrum of a physically cross-linked PVA hydrogel from the original solution with 5.6 wt.% of PVA during dehydration. (b) Deconvoluted spectrum of the O–H and C–H stretching modes in a physically cross-linked PVA hydrogel with 92.4 wt.% of water content. The dot marks, dotted lines, and solid line in (b) represent the experimental data, fitting curves, and sum of the fitting curves, respectively.

decomposed into seven modes by fitting the data. Lorentzian functions were used for the three C–H stretching modes, and Gaussian functions were used for the four O–H stretching modes. We used these functions according to previous studies on hydrogels and aqueous solutions,<sup>18,31,32</sup> and obtained better fits than with pure Gaussian (or Lorentzian) deconvolutions. The dot marks, dotted lines, and solid line in Fig. 3(b) are the experimental data, fitted curves, and sum of the fitted curves, respectively.

The three peaks observed at  $2731$ ,  $2856$ , and  $2923\text{ cm}^{-1}$  (i.e., the dotted lines in the lower frequency region of Fig. 3(b)) are assigned to the C–H stretching mode of CH, the symmetric, and asymmetric stretching modes of  $\text{CH}_2$ , respectively.<sup>27,28</sup> The peak at  $3045\text{ cm}^{-1}$  arises from the Fermi resonance between the overtone of the bending mode (a component near  $1640\text{ cm}^{-1}$ ) and the O–H stretching mode.<sup>18,29</sup> The peaks at  $3240$  and  $3411\text{ cm}^{-1}$  are associated respectively with the in-phase and out-of-phase modes of the O–H stretching vibration of water molecules with four hydrogen bonds (i.e., hydrogen bonds that involve two protons and two lone electron pairs).<sup>18,29–32</sup> The peak at  $3612\text{ cm}^{-1}$  corresponds to the O–H stretching mode of weakly or non-hydrogen-bonded water molecules, in which the hydrogen bonds of water molecules are partially or entirely broken.<sup>18,29–32</sup> In previous studies on hydrogels and aqueous solutions, the band around  $3600\text{ cm}^{-1}$  has been fitted to two modes (i.e., the symmetric and asymmetric stretching modes)

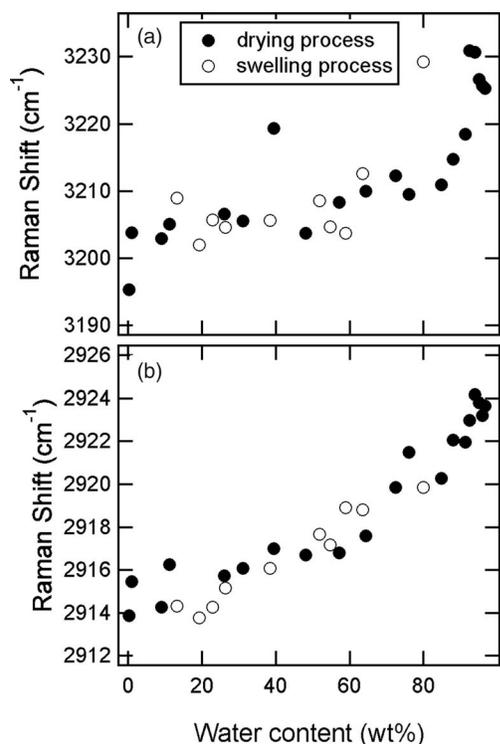


FIG. 4. Dependence on water content of vibrational frequencies of (a) in-phase mode of O–H stretching vibration of water molecules with four hydrogen bonds and (b) C–H asymmetric stretching mode of CH<sub>2</sub> for a physically cross-linked PVA hydrogel from the original solution with 5.6 wt.% of PVA. The solid and open circles show the values for the drying and swelling processes, respectively.

of unbounded or weakly bonded water molecules.<sup>18,31,32</sup> For the PVA hydrogel, however, we fitted the band to one peak, because better fits were obtained than the case of the fittings to two peaks. Although the O–H stretching mode of PVA also exists in the frequency region, this mode was not used in the analysis, because the peak is negligible compared to the intensities of the seven modes.

Figure 4 shows the dependence on water content of the vibrational frequencies for the in-phase mode of the O–H stretching vibration of water molecules with four hydrogen bonds and C–H asymmetric stretching mode of CH<sub>2</sub> for a physically cross-linked PVA hydrogel from the original solution with 5.6 wt.% of PVA. The vibrational frequencies of the O–H and C–H stretching modes decrease as the water content decreases. The frequencies of the dried state for the O–H and C–H stretching modes are approximately 30 and 8 cm<sup>-1</sup> lower than those of the maximum swollen state, respectively. A similar tendency was observed for other O–H and C–H stretching modes. Figure 5(a) shows the out-of-phase mode of the O–H stretching vibration of water molecules with four hydrogen bonds. The frequency of the dried state for the out-of-phase mode is approximately 40 cm<sup>-1</sup> lower than that of the maximum swollen state.

The low frequency shifts observed in the O–H and C–H stretching modes are attributed to an elongation of the O–H and C–H bonds. The C–H bonds are elongated by the reduction of free water from the inside of the polymer network because the C–H bonds are released from repulsion with sur-

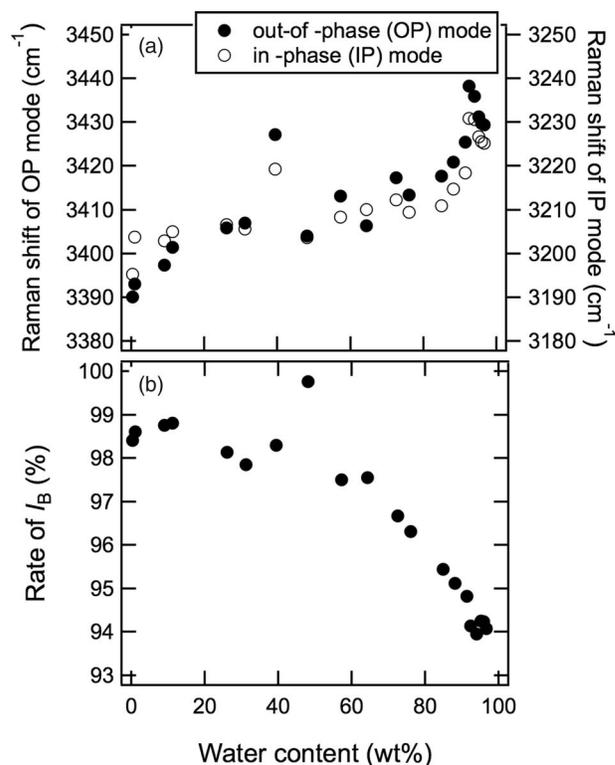


FIG. 5. Dependence on water content of (a) vibrational frequencies for out-of-phase mode of O–H stretching vibration of water molecules with four hydrogen bonds (the solid circles) and (b) rate of integrated intensity of vibrational modes of water with four hydrogen bonds ( $I_B$ ) in the total integrated intensity of four peaks O–H stretching modes (i.e.,  $I_B + I_{UB}$ ) for a physically cross-linked PVA hydrogel from the original solution with 5.6 wt.% of PVA. The open circles in (a) show the values for the in-phase mode.

rounding water. The continuous decrease observed in the C–H stretching mode in the region of low water content, in which only bound water remains, is due to the evaporation of bound water. The low frequency shift in the O–H stretching mode is attributed to the increase in average length of the O–H bonds. Because the hydrogen bonds of bound water with the hydroxyl group of PVA are stronger than those between free water, the O–H bond length of bound water is longer than that of free water. Thus, the average length of the O–H bonds increases as the proportion of bound water to the total amount of water increases. This suggests that most of the bound water molecules form hydrogen bonds with the hydroxyl group of PVA, and the hydrogen bonds are stronger than those between the water molecules.

The structural change of water due to interaction with the surrounding water and PVA can be analyzed from the integrated intensities of the four peaks of the O–H stretching modes.<sup>18,29–32</sup> The four peaks are classified to two types of water structures: (1) the water molecules with four hydrogen bonds (i.e., the peaks at 3045, 3240, and 3411 cm<sup>-1</sup> of Fig. 3(b)) and (2) the unbounded or weakly bonded water molecules (i.e., the peak at 3612 cm<sup>-1</sup> of Fig. 3(b)). The sum of the integrated intensities of three peaks from the water molecules with four hydrogen bonds is designated as  $I_B$ . The integrated intensity of the peak from the unbounded or

weakly bonded molecules is designated as  $I_{UB}$ . Figure 5(b) shows the rate of  $I_B$  in the total area of four peaks (i.e.,  $I_B + I_{UB}$ ) for a physically cross-linked PVA hydrogel from the original solution with 5.6 wt.% of PVA.

As shown in Fig. 5(b), the  $I_B$  rate increases as the water content decreases. This indicates that the number density of tetragonal structure consisting of four hydrogen bonds in bound water increases. The result is consistent with the conclusion from the frequency shifts for the O–H stretching modes. Because the most of the bound water molecules forms strong hydrogen bonds with the hydroxyl group of PVA, the number density of tetragonal structure and the average strength of hydrogen bonds increases as the water content decreases.

Furthermore, Raman spectral analyses were performed during the reswelling process after the drying of the hydrogels. After the water content reached 0.24 wt.% by drying, distilled water was added to the sample to be reswollen. The frequencies of the reswelling process for the O–H and C–H stretching modes (the open circles in Fig. 4) were approximately consistent with those of the drying process (the solid circles in Fig. 4). This result suggests that the water structures are independent of the process and depend only on the water content. The achieved water content in the maximum swollen state after the reswelling is slightly lower than that before drying. This decrease in the swelling rate indicates that the polymer network structure distorts with drying and is not completely reconstructed by reswelling.

## B. Effects of PVA concentration in original solution on structures

For the freezing–thawing method, cross-linking networks are formed by the volume expansion of ice crystals with decreasing temperature.<sup>16</sup> Thus, the network structure in a physically cross-linked hydrogel is expected to depend on the PVA concentration of its original solution. Figure 6(a) shows the dependence of  $W(t_1)$  and  $W(t_2)$  on PVA concentration of the original PVA solution. The  $W(t_1)$  and  $W(t_2)$  values include errors of a few wt.% caused during the determination process of the boundaries between stages I and II and between stages II and III. The boundaries are determined by fitting the data for temporal variation of water content (for instance, Fig. 2) to three lines. Although the  $W(t_1)$  and  $W(t_2)$  values are distributed due to the errors, a systematic change is observed. The  $W(t_1)$  value decreases as the PVA concentration increases, whereas the  $W(t_2)$  value increases with the concentration. This indicates that the relative amount of bound water increases with the PVA concentration. The tendency is consistent with the DSC result.<sup>25</sup> Because the water content in the maximum swollen state decreases as the PVA concentration increases, as shown in Figure 6(b), the relative amounts of the three types of water change.

The equilibrium water content (i.e., the solid circles in Fig. 6(b)) decreases with increasing PVA concentration of the original solution. This result shows that the cross-linking density increases with the PVA concentration. For the physically cross-linked PVA hydrogel, microcrystal of PVA acts as a cross-linking point.<sup>26</sup> Because the close polymer network,

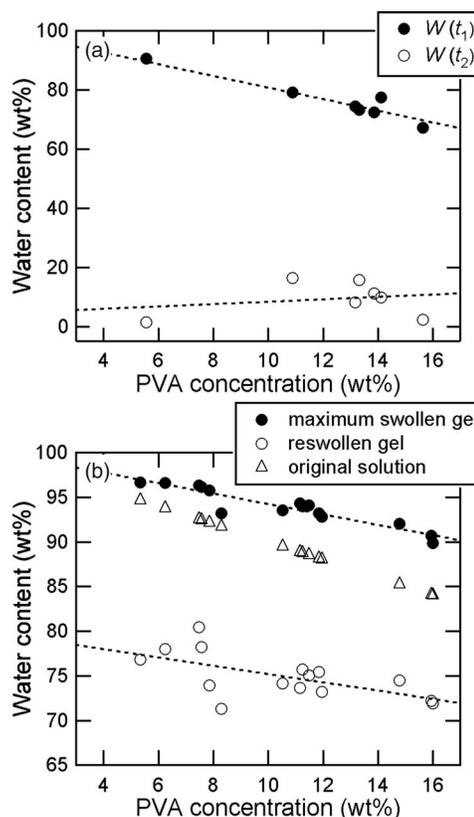


FIG. 6. Dependence on PVA concentration of the original PVA solution of (a)  $W(t_1)$  and  $W(t_2)$  and (b) water content in maximum swollen and reswollen gels. The solid and open circles in (a) show the  $W(t_1)$  and  $W(t_2)$  values, respectively. The solid circles, open circles, and open triangles in (b) represent the data of the maximum swollen gel, reswollen gel, and original solution, respectively. The dotted lines are fitting lines to show the trends.

which is cross-linked with the microcrystals, restricts the volume expansion of hydrogel, the equilibrium water content decreases.

Figure 7 shows the PVA concentration dependence of vibrational frequencies for the in-phase mode of the O–H stretching vibration of water molecules with four hydrogen bonds and C–H asymmetric stretching modes. For the maximum swollen state before drying, the vibrational frequency of the C–H stretching mode decreases with increasing PVA concentration, whereas that of the O–H stretching mode is almost constant. The low frequency shift observed in the C–H stretching mode is attributed to the decrease in water content. The C–H bonds of PVA are elongated as the relative amount of surrounding free water decreases. For the O–H stretching mode, the variation is negligible because the dependence of vibration frequency on water content is small at higher water content. As shown in the open circles in Fig. 7(b), the PVA concentration dependence of the C–H stretching mode drastically reduces by drying and reswelling. This results from the PVA concentration dependence on the dried state (i.e., the solid triangles in Fig. 7(b)). For the dried state, the vibrational frequency of the C–H stretching mode increases as the PVA concentration decreases because the volume shrinking rate of the hydrogel decreases as the cross-linking density increases. The present results suggest that the cross-linking

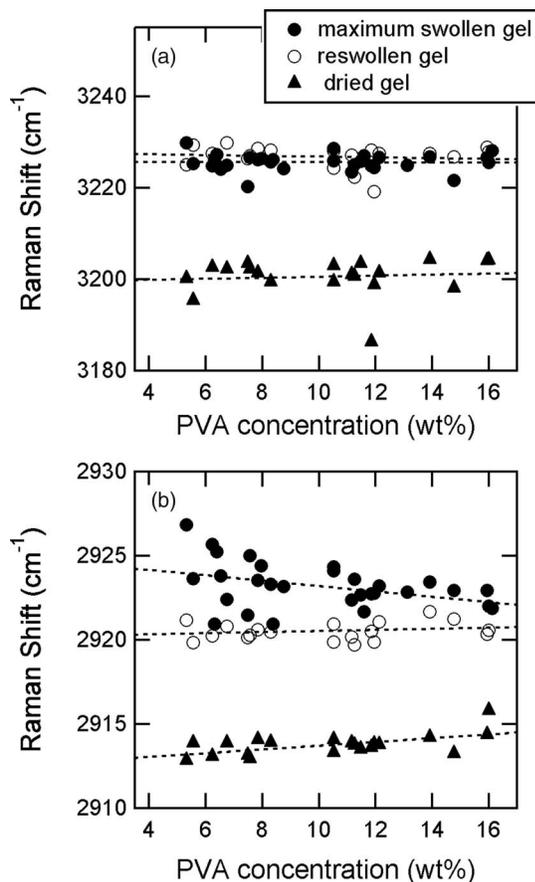


FIG. 7. Dependence on PVA concentration of the original solution of vibrational frequencies of (a) in-phase mode of O–H stretching vibration of water molecules with four hydrogen bonds and (b) C–H asymmetric stretching mode of CH<sub>2</sub> for a physically cross-linked PVA hydrogel. The solid circles, triangles, and open circles are the data of the maximum swollen, dried, and reswollen gels, respectively. The dotted lines are fitting lines to show the trends.

structure formed with the freezing–thawing process depends on the PVA concentration of the original solution.

The swelling rate decreases by reswelling after drying. The open circles in Fig. 6(b) show the equilibrium water content of reswollen hydrogels. This suggests that the polymer network structure distorts with the drying and is not reconstructed by the reswelling. This result is consistent with the Raman result. As shown in Fig. 7(b), the C–H stretching mode shifts to a lower frequency with reswelling. Because the ability to contain water in hydrogel decreases with the distortion of the PVA polymer network, the repulsion from surrounding water molecules decreases.

### C. Effects of cross-linking structure on drying process

To confirm the effect of the cross-linking structure on the structural changes of water and polymer network during drying, the Raman spectra of a chemically cross-linked PVA hydrogel were measured. The solid circles in Figure 8 shows the dependence on water content of vibrational frequencies of the in-phase mode of the O–H stretching vibration of water molecules with four hydrogen bonds and C–H asymmetric

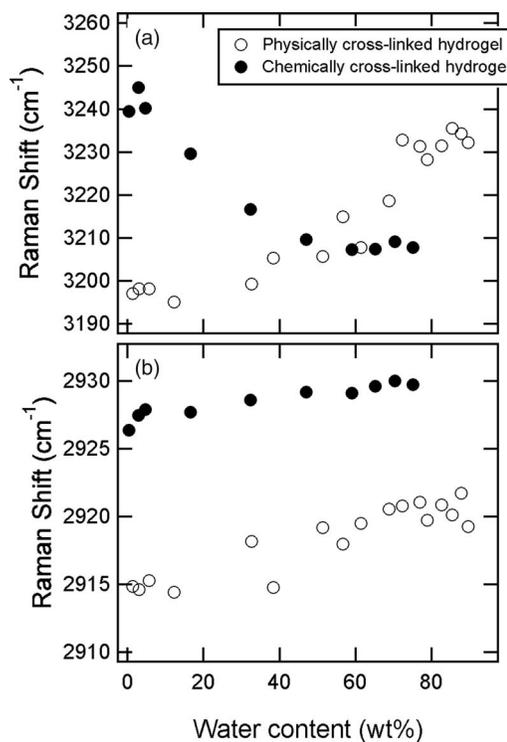


FIG. 8. Dependence on water content of vibrational frequencies of (a) in-phase mode of O–H stretching vibration of water molecules with four hydrogen bonds and (b) C–H asymmetric stretching mode for a chemically cross-linked PVA hydrogel during dehydration. The solid and open circles show the values for the chemically cross-linked hydrogel from the original solution with 12.2 wt.% of PVA and for the physically cross-linked hydrogel from the original solution with 13.2 wt.% of PVA, respectively.

stretching mode of CH<sub>2</sub> for a chemically cross-linked PVA hydrogel. For the chemically cross-linked PVA hydrogel, the vibrational frequency of the O–H stretching mode increases with dehydration, while that of the C–H stretching mode decreases as same as that for the physically cross-linked PVA hydrogel. This tendency is consistent with the result for the chemically cross-linked PDMAA hydrogel.<sup>18</sup>

The opposite trend observed in the O–H stretching mode between the physically and chemically cross-linked hydrogels is due to the difference in the shrinkage rate of the polymer network. As shown in Fig. 9, the chemically cross-linked PVA hydrogel is strongly cross-linked with covalent bonds. Thus, the shrinkage of the polymer network of the chemically cross-linked hydrogel with dehydration is restricted. Because the rate of shrinking is slow compared with that of dehydration, water density in the polymer network decreases. The hydrogen bonds between water molecules become weak as the water density decreases, and the average length of the O–H bonds decreases. Thus, the vibrational frequency of the O–H stretching mode for the chemically cross-linked hydrogel increases. For the physically cross-linked hydrogel, the polymer network structure can be easily shrunken. Thus, the average strength of the hydrogen bonds increases with dehydration, because water density increases due to shrinkage of the polymer network.

The vibrational frequency of the C–H stretching mode decreases with dehydration because of the elongation of the

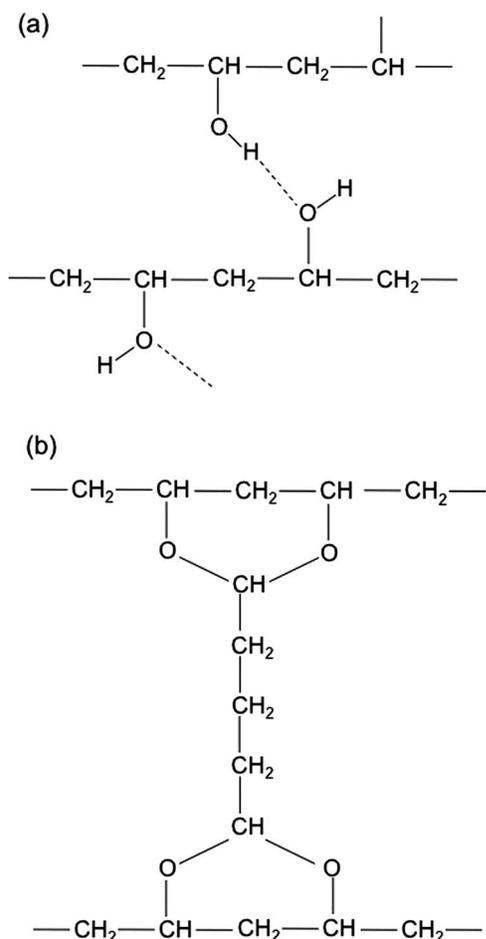


FIG. 9. Cross-linking structures of (a) physically and (b) chemically cross-linked PVA hydrogels.

C–H bonds with decrease in the density of surrounding free water. Although the tendency of the chemically cross-linked hydrogel is consistent with the results of the physically cross-linked hydrogel, the frequency is approximately  $10\text{ cm}^{-1}$  higher. This frequency shift is attributed to the difference in the water density inside the polymer network. For the chemically cross-linked hydrogel, water density is low compared with that for the physically cross-linked hydrogel because of higher number of hydrophobic groups (i.e., methylene and methane groups) as shown in Fig. 9(b).

The increase in the vibrational frequency of the O–H stretching mode with dehydration for the chemically cross-linked hydrogel indicates that the hydrogen bonds of bound water are weaker than that of free water. This suggests that most of the bound water molecules, which exist in the dried chemically cross-linked hydrogel, form hydrogen bonds with surrounding water molecules (Fig. 10(b)) and the strength of the hydrogen bonds are weaker than that with hydroxyl group of PVA. This contrasts with the dried physically cross-linked hydrate, in which the most of the bound water molecules forms hydrogen bonds with the hydroxyl group of PVA (Fig. 10(a)). These results indicate that the structures of the polymer network and water depend on the cross-linking method.

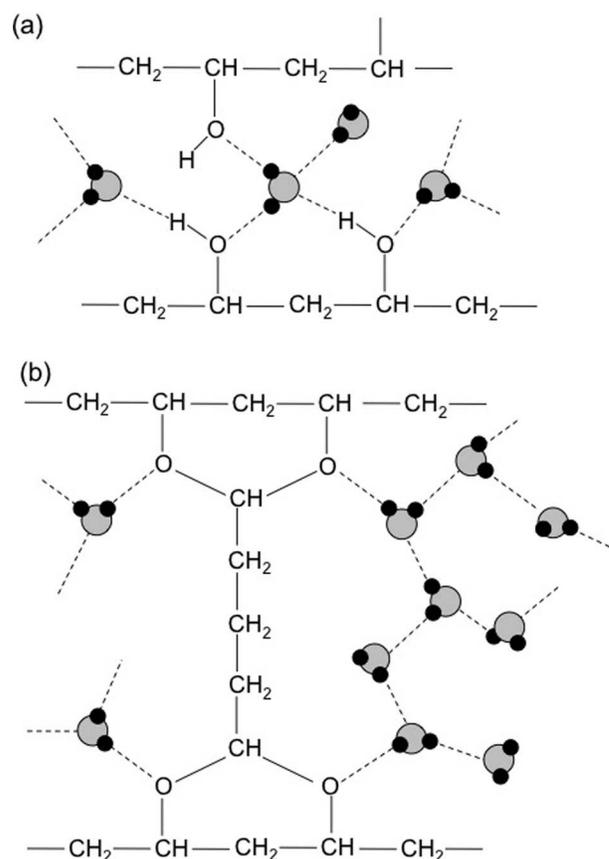


FIG. 10. Schematics of bound water in dried (a) physically and (b) chemically cross-linked PVA hydrogels.

#### IV. CONCLUSIONS

To investigate the mechanism of structural changes of water and polymer networks, we measured the Raman spectra of the physically and chemically cross-linked PVA hydrogels during drying and swelling. From the results of the physically cross-linked hydrogel, it was found that the vibrational frequencies of the C–H stretching mode of PVA and the O–H stretching mode of water decrease with dehydration. This suggests that most of bound water molecules in the physically cross-linked hydrogel form hydrogen bonds with the hydroxyl group of PVA, and the hydrogen bonds are stronger than those between the water molecules. In contrast, an opposite trend was observed in the O–H stretching mode for the chemically cross-linked hydrogel. The vibrational frequency of the O–H stretching mode increases with dehydration for the chemically cross-linked hydrogel because most of the bound water molecules form weak hydrogen bonds with the surrounding water molecules. Because the hydrogen bonds between bound water in the chemically cross-linked hydrogel are weaker than those between free water, the vibrational frequency of the O–H stretching mode increases with dehydration. The difference in the molecular-level structure causes the opposite trends in the vibrational frequency of the O–H stretching mode between the physically and chemically cross-linked hydrogels. Furthermore, a difference in the cross-linked structure causes the difference in the shrinkage rate of the polymer network. These results suggest that the

structures of polymer network and water depend on the gel preparation process, cross-linking methods, and drying and reswelling processes. The water structure is one of the dominant factors governing the chemical and physical properties of a hydrogel. To develop a better hydrogel material, it is essential to understand the water structure and to consider the control method for the structure.

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