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Formation and destruction of physical crosslinks by mild treatments in chemically crosslinked poly(vinyl alcohol) gels

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Abstract We report the formation, destruction, and re-formation of the microcrystallites in a chemical PVA gel, crosslinked slightly by glutaraldehyde. The dried gel, in which the microcrystallites were formed, was immersed in a poor solvent of a mixture of DMSO and water at 8 °C, where the gel stayed in its collapsed state. The gels swelled on heating to 50 °C, but did not return to the initial state on cooling to 8 °C. After washing the gel completely in water, a drying process caused the microcrystallites to be re-formed and the gel could return to the initial dried state at 8 °C. By using XRD and FT-IR measurements, it was concluded that the formation and destruction of microcrystallites in chemically crosslinked PVA gels could be controlled by the mild treatments of initial drying, temperature change, and washing and drying.

Keywords Poly(vinyl alcohol) gel · Microcrystallite · Swelling ratio · WAXS · SAXS · FT-IR

Introduction

Hydrogels are used for many practical purposes as retainers of water and solutes, and play a vital role in the fields of medicine, foods, chemical, agricultural, and other industries. For these industries, it is crucial to understand the physical and

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chemical principles that govern the degree of swelling or shrinking in the individual environment conditions. Among the experimental studies of hydrogels, it is a fundamental technique to obtain the swelling ratio and its changes in response to external stimuli [1, 2]. 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. Understanding how the nanoscopic structure can determine the macroscopic volume is a fundamental problem in polymer science. It is also important to understand the principles by which polymer gels can take a unique conformation and show a smart function.

Among the hydrogels as retainers of water and solutes, poly(vinyl alcohol) (PVA) gels are useful biomaterials due to its low toxicity and high biocompatibility, and many studies on their practical applications have been reported by researchers in a variety of fields [3, 4]. Although there are many reports on the swelling properties for the practical application, the swelling behavior in pure PVA gels with different degrees of hydrolysis has not been extensively studied. Recently, some interesting swelling properties were reported in chemical PVA gels that were slightly crosslinked by glutaraldehyde (GA) [5]. The swelling behavior of the gels with different degrees of hydrolysis was examined in pure water, several organic solvents, and their mixed solvents. It was suggested that the microcrystallites, which were formed in a chemical PVA gel during a drying process after gelation, were partly destroyed in a good solvent, but the residual hydrogen bonds had an essential role in determining the swelling behavior in a poor solvent. In addition, the ability to form the microcrystallites during the drying process after gelation were examined for the chemical PVA gels with different degrees of chemical crosslinks by GA [6]. Almost all these observations using an X-ray diffraction (XRD) measurement and a Fourier transform infrared (FT-IR) spectroscopy measurement were obtained for the dried gels [6], and not the gels in the swollen state. In order to follow up our previous works [5, 6], it is highly desirable to investigate the changes in the microscopic network structure of the gel in the swollen states due to the formation of the microcrystallites and the destruction of the hydrogen bonds.

In this article, we report the evidence of formation and destruction of the microcrystallites of chemical PVA gels in a poor solvent, and their effects on the swelling behavior. The swelling behavior is discussed in terms of the network microstructure of the swollen gels observed by XRD and FT-IR measurements.

Experimental

Sample preparation

Gels were prepared in two shapes: thin cylindrical gels were prepared in glass microcapillaries with an inner diameter of $d_0 = 1.45$ mm (the inner volume was 50 μL), and thin plate gels were prepared between two glass plates (slide) with a thin spacer (thickness is about 2 mm). The former was used for the measurement of the diameter, and the latter was used for the measurements of the weight, XRD pattern and FT-IR spectrum. PVA powder was kindly supplied by Kuraray Co., Ltd. (Cat. No. PVA117), and was used without further purification. The average degree of polymerization was 1,700, and the average degree of hydrolysis was between 98 and 99 mol%. An aqueous PVA solution was obtained by dissolving PVA powder into deionized and distilled water at 90 °C for more than 2 h. The effects of the degrees of polymerization and hydrolysis of PVA powder on the formation of microcrystallites will be described later. The concentration of the monomer units of PVA was fixed at ca. 2,100 mM, and the mole ratio of GA (Wako Pure Chemical Industries, Ltd., 25% aqueous solution) to the total concentration of the monomer units of PVA plus the monomer of GA was 0.5 mol%. The ratio of main constituent to crosslinks, 2,100:10.5 was larger than that of the popular chemical gels, e.g., 700:8.6 in the case of poly(*N*-isopropylacrylamide) gel [2], which indicated that crosslink density (or chain length) was smaller (or larger) than the usual phase transition gels.

After mixing GA into the dissolved PVA solution, 0.3 mL of 1 M-HCl was added to the mixture as a catalyst. The solution was placed in an oven at 30 °C for 48 h. After gelation, the cylindrical and plate gels were removed from the microcapillaries or moulds, and subsequently washed in distilled de-ionized pure water (the water volume was 1,000 times larger than the gel volume) for 48 h to wash away any residual chemicals and the uncrosslinked polymers from the polymer networks. Then the gels were again placed in an oven at 30 °C for 48 h to dry sufficiently.

Measurements of swelling ratio, XRD, and FT-IR

The swelling ratio was examined by two kinds of measurements after the dried gels were put into a large amount of a poor solvent of the 60/40 vol% dimethyl sulfoxide (DMSO)–water mixture. The equilibrium diameter of a cylindrical gel, d, was measured and the swelling ratio, d/d_0, was calculated. The equilibrium weight of the thin plate gel, W_t (the dried weight: W_0 and its size: 5 × 5 mm) was measured and the swelling ratio, W_t/W_0, was calculated.

To characterize the microstructure of polymer networks, XRD measurements were performed at room temperature using two methods: one is a small-angle scattering (SAXS) using a SAXS apparatus installed at BL10C of the Photon Factory at the Institute of Materials Structure Science, High Energy Accelerator Research Organization (KEK), Tsukuba, Japan, and the other is a wide-angle X-ray scattering (WAXS) techniques using an X-ray diffractometer (40 kV, 200 mA; RINT-2000, Rigaku).

The mid-infrared spectra of the plate gels were measured at room temperature using an FT-IR spectrophotometer (Jasco: FT/IR-610) equipped with an ATR (attenuated total reflectance) attachment with ZnSe crystal in order to investigate the conformation, dissociation, and bonding state of the functional groups of the swollen gels in the solvent. The FT-IR spectra were normalized based on the C–H bending vibration at 1,427 cm^{-1}, the peak area of which was assumed to be equivalent.

Results and discussion

Re-swelling behavior in response to the temperature change

The equilibrium diameter, d, of the cylindrical gel in a 60/40 vol% DMSO–water mixture was measured after changing the temperature. The results are shown in Fig. 1a. First, the dried gel (S1) was immersed in the mixed solvent at 8 °C (S2). In our recent study, the swelling ratio, d/d_0, in the mixed solvent increased with increasing temperature [5]. If the dried gel was put into a 60/40 vol% DMSO–water mixture at room temperature, d/d_0 became ca. 0.6, while the gel did not swell and kept $d/d_0 =$ ca. 0.4 of the collapsed state when it was put into the solvent at 8 °C. Therefore, the measurement was started at 8 °C, so as to observe

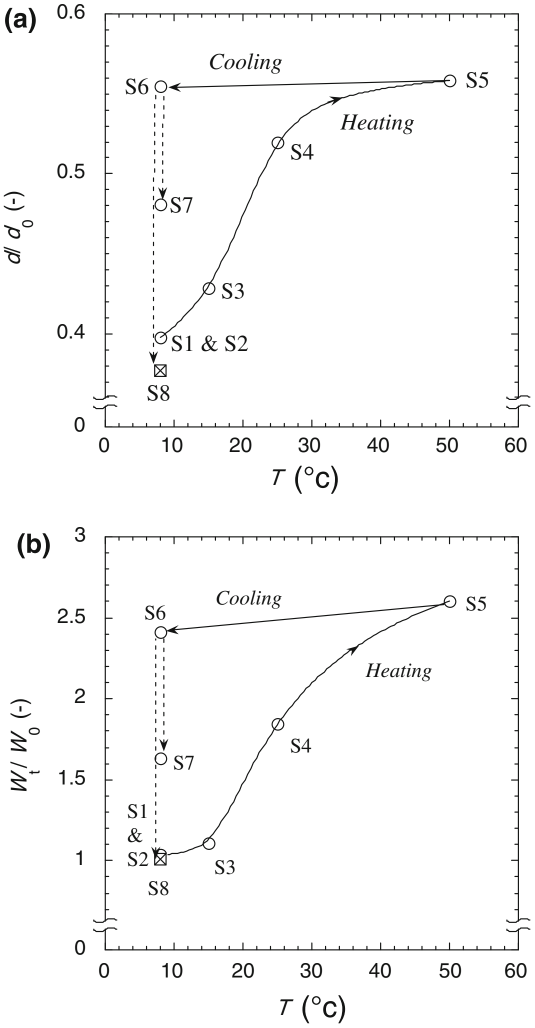

Fig. 1 Change in the swelling ratio, **a** d/d_0 and **b** W_t/W_0 of PVA gel in the 60/40 vol% DMSO–water mixture in response to the temperature change. The dried gel (S1) was immersed in the mixed solvent at 8 °C (S2), and the temperature was increased up to 50 °C (from S2 to S5) and decreased to 8 °C (S6). After drying in air at 60 °C for 48 h, the dried gel was immersed again in the mixed solvent at 8 °C (S7). Then, the gel was immersed in pure water to completely replace the solvent by pure water. After drying in air at 60 °C for 48 h, the dried gel was immersed in the mixed solvent at 8 °C (S8)

the destruction of hydrogen bonds and microcrystallites in the heating process. Then, the temperature was increased up to 50 °C (from S2 to S5). At the different temperatures, d was measured after the gel reached the equilibrium state. As shown in Fig. 1a, d/d_0 increased with an increase in temperature. After the measurement at 50 °C, the temperature was decreased to 8 °C (S6). We found that d/d_0 slightly decreased but did not return to the initial d/d_0 (= ca. 0.4 at 8 °C (S2)). Although it is possible that the hydrogen bonds could be formed gradually at 8 °C if the gel had been kept in the mixed solvent for an extremely long period, the system seemed to have reached equilibrium within the usual period of the experiment, i.e., a month at the longest. The irreversible behavior could be attributed to the irreversible change in the network structure during the heating and cooling processes, i.e., the microcrystallites were destroyed on heating, and were not reversibly formed on cooling.

In order to return to the initial state (S2), i.e., to re-form the hydrogen bonds, the gel ($d/d_0 =$ ca. 0.55 (S6)) was dried in air at 60 °C for 48 h, and immersed again in the mixed solvent at 8 °C (S7). Although d/d_0 decreased slightly (to ca. 0.48), it did not return to its initial value (ca. 0.4). This is because the DMSO could not be removed (evaporated) completely by this simple drying, which was confirmed by the IR spectrum, as shown in Fig. 4 (see later “Results and Discussion” section). Therefore, we put the gel in pure water and completely replaced the solvent by pure water. After drying at 60 °C for 48 h, the gel was immersed again in the 60/40 vol% DMSO-water mixture at 8 °C (S8). Due to this treatment, d/d_0 decreased to ca. 0.38 at 8 °C, which is similar to the initial value (ca. 0.4 (S2)). These results proved that the network structure could be controlled by the mild treatments of drying, temperature change, and solvent exchange (washing in pure water).

The results of W_t/W_0 of the thin plate gel in a 60/40 vol% DMSO–water mixture versus temperature are shown in Fig. 1b, which are qualitatively consistent with the results of d/d_0. The measurements were conducted on two different samples for each of thin cylindrical and thin plate gels, which were prepared by the same method at the same time. The differences of the absolute values between two samples were less than 8 and 3% for thin cylindrical and thin plate gels, respectively. Although we could not present a statistical analysis, the present results were qualitatively reproducible for the following discussions.

Temperature dependence of network microstructure

XRD measurements and analysis

Figure 2 shows the WAXS profiles obtained at different temperatures using the same thermal history as indicated in Fig. 1. In the case of the dried gel (S1), a sharp peak located at $q = 13.7\ \text{nm}^{-1}$ could be seen, which corresponds to the average distance between polymers of $d = 4.59$ Å in the microcrystallites due to hydrogen bonds [7, 8]. Figure 3 shows the schematic illustration of the formation of the hydrogen bonds and microcrystallite between polymer chains in drying process at sample preparation. With a gradual evaporation of free water the hydrogen bonds were formed between polymers with an average distance of $d = 4.59$ Å as a result

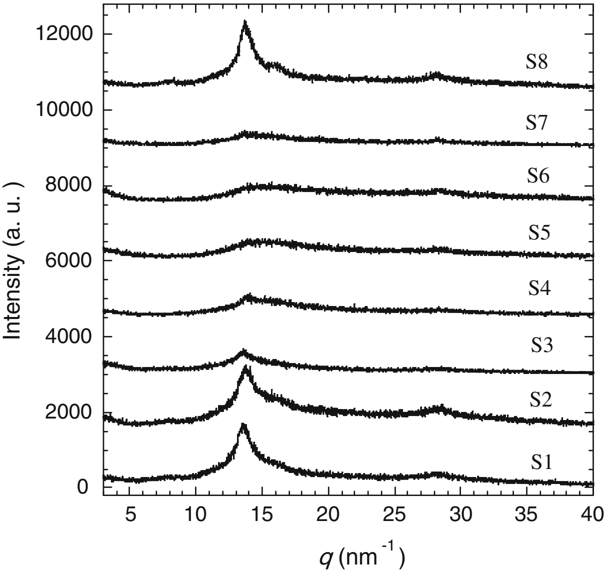

Fig. 2 WAXS profiles of PVA gel in the 60/40 vol% DMSO–water mixture in response to the temperature change. Each spectrum is shifted vertically from S1 to S8, which denotes the respective state of gels described in Fig. 1

of possible combination of different types of hydrogen bonds. The microcrystallite was formed by the aggregation of hydrogen bonds. As these results, the unique PVA gels were obtained, which were chemically crosslinked by glutaraldehyde and physically crosslinked by the microcrystallites due to hydrogen bonds.

In the cases of the gels in the 60/40 vol% DMSO–water mixture, the peak gradually became broad with an increase in temperature (from S2 to S5), suggesting that the hydrogen bonds and microcrystallites were gradually destroyed, corresponding to an increase in the swelling ratio. When the temperature was decreased from 50 °C to the initial 8 °C (S6), the WAXS profile did not apparently change. It was also unchanged after the sample was simply dried in air at 60 °C for 48 h (S7). Then, the sample was dried again after it was immersed in pure water and the solvent was fully exchanged by pure water. Thereafter, the dried gel was again immersed in the mixed solvent at 8 °C (S8), and the WAXS profiles were obtained. As a result, the WAXS profile became almost the same as the initial one (S2). In order to determine the size of the microcrystallites (crosslinked region), the average crystallite size, D, was roughly estimated from Fig. 2 using Scherrer's equation [9]: $D = k\lambda/(\beta\cos\theta))$ where $k = 1$ (the shape of the crystal is assumed to be a sphere); β is the width at half maximum intensity of the reflection; q is the Bragg's angle; and $\lambda = 1.54$ Å is the wavelength of the X-ray radiation. As a result, the D of the dried gel (S1) was ca. 3.63 nm, and it was unchanged evidently, i.e., ca. 3.56 nm after the gel was immersed in the mixed solvent at 8 °C (S2). With increasing the temperature, the D value started to decrease; at 15 °C (S3), D was ca. 2.22 nm and rapidly decreased above 25 °C (S4). After the thermal history, the exchange of pure

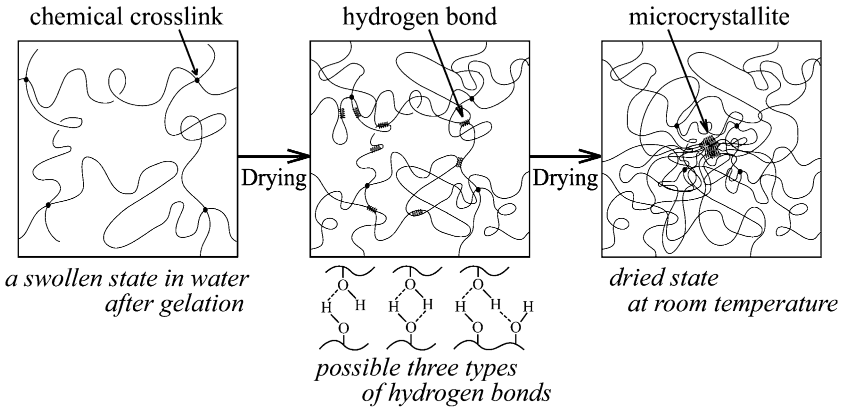

Fig. 3 Schematic illustration of the formation of the hydrogen bonds and microcrystallites between polymer chains in drying process at sample preparation. Possible three types of hydrogen bonds were presented, a hydrogen bond between two O–H groups, two hydrogen bonds between two O–H groups, and two hydrogen bonds between three O–H groups

water, and the successive second drying (S8), *D* became 3.99 nm, which was slightly larger than its initial value (ca. 3.6 nm).

Figure 4a shows the SAXS profiles of the gels in the poor solvent of the 60/40 vol% DMSO–water mixture during the above thermal history. A small peak can be seen in each diffraction pattern in the small angle region, which corresponds to the average distance between the microcrystallites, *L*. With an increase in temperature (from S2 to S5), the peak gradually became broad and the peak position shifted to a lower wavelength, which suggested that *L* increased (Fig. 4b) and the scattering of data became larger with weaker structural modulation. The SAXS profile in the mixed solvent at 8 °C (S2) was almost the same as that of the dried PVA cast gel (S1). However, the value of *L* at 50 °C (S5) was approximately twice larger than that of the *L* at 8 °C (S2). Although this increase in *L* resulted partly from an increase in the volume of the gel, the ratio of the increase (approximately double) was apparently larger than the change in the swelling ratio, ca. 1.4 times (Fig. 1). One possible origin of this relatively large change in *L* might be related to the destruction (disappearance) of the microcrystallites. When the temperature was decreased to the initial 8 °C (S2) from 50 °C (S6), the peak position shifted slightly to the larger range of wavenumber, but the characteristics of the diffraction pattern, its width and broadness, did not change greatly. This irreversible change was consistent with the above results for the swelling ratio.

ATR FT-IR measurements and analysis

Figure 5a shows the ATR FT-IR spectra found using the same thermal history as the above measurements, normalized by the peak area at ca. 1,427 $\mathrm{cm^{-1}}$ [10]. We supposed that the effects of the peaks due to DMSO on the normalization were negligibly small since 1,427 $\mathrm{cm^{-1}}$ was far from the typical peak positions of DMSO at 1,043 $\mathrm{cm^{-1}}$ (assigned to S=O stretching and C–S stretching [11]) and at

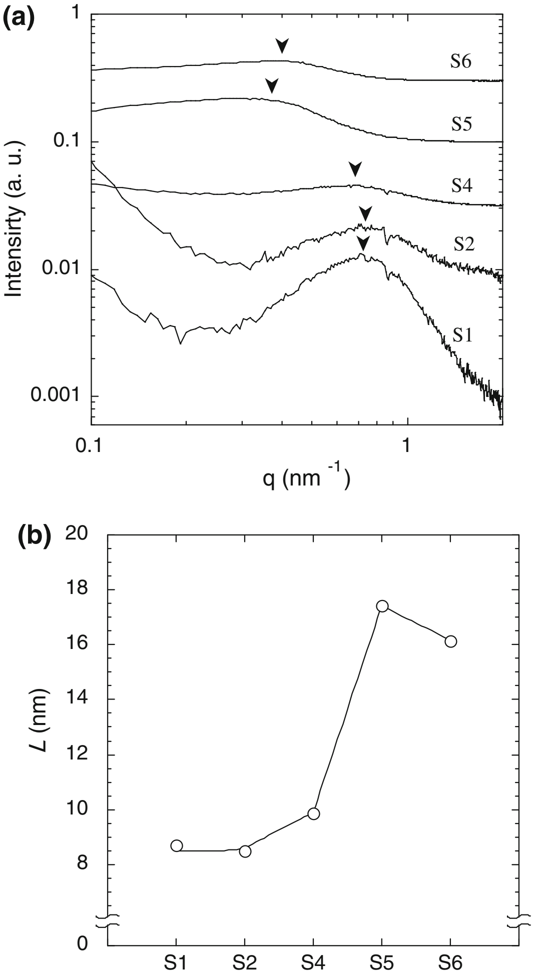

Fig. 4 **a** SAXS profiles of PVA gel in the 60/40 vol% DMSO-water mixture in response to the temperature change. The spectra are shifted vertically and the symbols, S1 to S6 denote the states of gels described in Fig. 1. **b** Average distance between the microcrystallites, *L*, estimated using the peak-top position of SAXS profiles from S1 to S6

953 cm^{-1} (assigned to CH_3 vibration [11]) (see below). The IR spectra changed slightly when the dried gel (S1) was immersed in the mixed solvent at 8 °C (S2), which apparently changed with an increase in temperature. After the temperature was decreased to 8 °C (S6), the IR spectrum did not return to the initial one at 8 °C (S2), but was almost the same as that at 50 °C (S5). After sufficient water exchange by replacing the mixed solvent with pure water and successive drying, the IR spectrum of the mixed solvent at 8 °C (S8) became almost the same as the initial one (S2). The detailed changes in the spectra are as follows.

Five peaks located at 1,437, 1,407, 1,309, 1,043, and 953 cm^{-1}, originated in the presence of DMSO [11], could be seen in the spectra of the gel in the mixed solvent (Fig. 5a). In addition, a small peak located at 1,643 cm^{-1}, originated in the presence of water [12], could be also observed. Their peak areas increased with an increase in temperature due to the change in the solubility with PVA. It is noteworthy that these

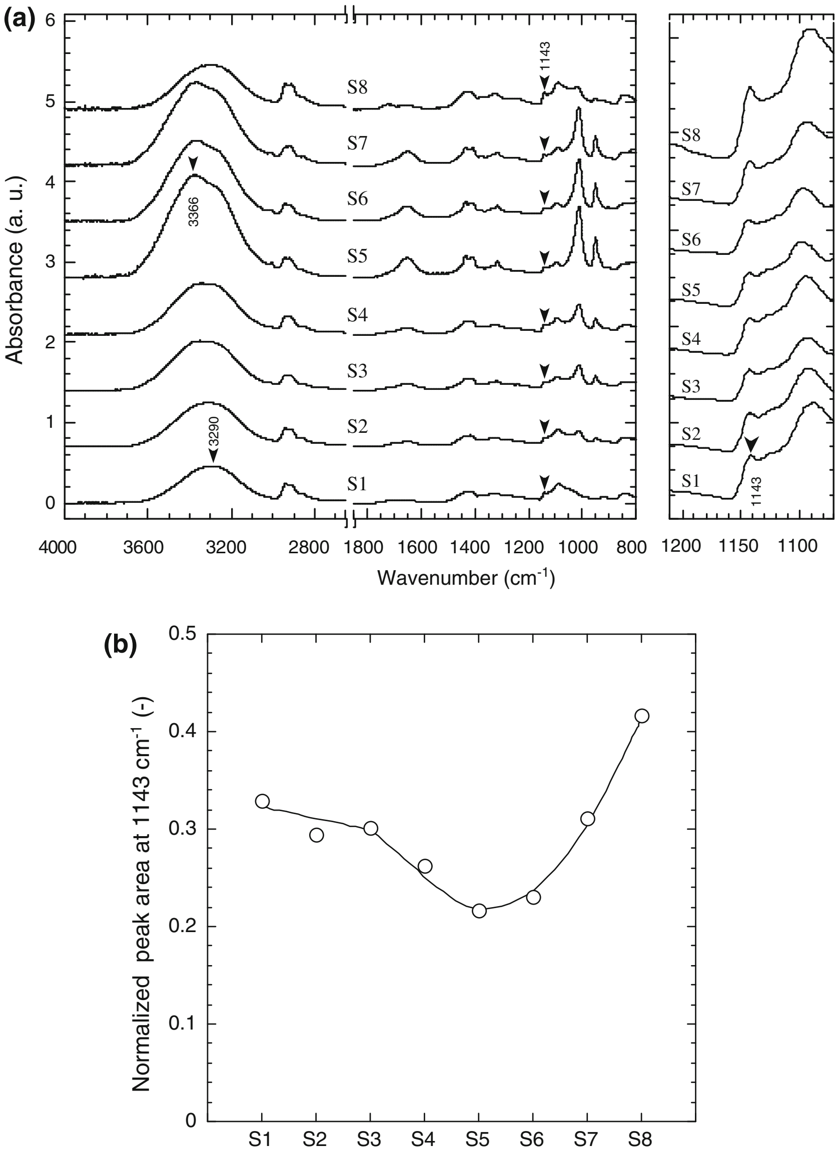

Fig. 5 **a** ATR FT-IR spectra and **b** the peak area at 1,143 cm^{-1} of PVA gel in the 60/40 vol% DMSO-water mixture from S1 to S8. Each spectrum is shifted vertically from S1 to S8, which denotes the respective state of gels described in Fig. 1

peaks were not changed before and after the simple drying (S6 and S7). This evidence confirmed, as mentioned above ("Re-swelling behavior in response to the temperature change" section), that the DMSO could not be removed by the simple drying.

With increasing in temperature, the broad peak at around 3,300 cm^{-1}, which was assigned to the O–H stretching vibration region, became large and its top position shifted to a larger wavenumber (from S2 to S5). This broad peak consisted of two components: the peak located at 3,366 cm^{-1} assigned to the free O–H bands [13] and the peak located at 3,290 cm^{-1} assigned to the hydrogen bonds between polymer chains [13]. The increase in the overall peak area might have resulted from an increase in the total number of O–H groups due to the swelling by the temperature increase. On the other hand, the increase in the peak at a larger wavenumber compared with the peak at a lower wavenumber resulted from the destruction of the hydrogen bonds. In other words, the shift in the top of the peak to a larger wavenumber indicated that the ratio of the numbers of free to hydrogen bonded O–H groups increased since the hydrogen bonds between polymer chains were destroyed by the temperature increase.

The absorption peak that appeared apparently at around 1,143 and 1,090 cm^{-1} in all of the spectra could be assigned to C–O stretching [14, 15]. And the peak located at 1,143 cm^{-1} was due to the formation of microcrystallites of hydrogen bonds between the O–H groups of PVA [14, 16]. Figure 5b shows the peak area at ca. 1,143 cm^{-1} normalized by the peak area at ca. 1,427 cm^{-1} from S1 to S8. The former peak at ca. 1,143 cm^{-1} was obtained by deconvoluting the spectra to remove the effects of the peaks due to DMSO on the peak area at 1,143 cm^{-1}, since 1,143 cm^{-1} was close to the typical peak positions of DMSO (see above). The components of the absorption band at 1,300–950 cm^{-1} were deduced from the second-derivative of the spectra. As shown in Fig. 5b, the peak area decreased with an increase in temperature to 50 °C (from S2 to S5), slightly increased by cooling to 8 °C (S6), and finally increased largely. The increase in this peak could be attributed to the re-formation of the microcrystallites by drying. The apparent larger peak area at S8 should result from the larger drying temperature. It is expected that the formation of microcrystallites could be enhanced by the higher drying temperature.

In our recent study, the normalized peak area at ca. 1,143 cm^{-1} disappeared completely when the dried gel was immersed in the mixed solvent at 90 °C [6]. This result indicates the destruction of the microcrystallites. However, the identification of the critical temperature of microcrystallites in each swollen gel is difficult because the fact that the critical temperature depends not only on the temperature but also on the swelling force due to the osmotic pressure. The temperature dependence of the ability to form the microcrystallites is an important subject for future investigations.

Although it is difficult to assign the evident changes in the shape of the peak at around 2,900 cm^{-1}, which was assigned to the C–H stretching of CH_2 groups [10], the multiple components of this peak might be related to the result of the formation of hydrogen bonds. The peaks in this range also changed by the thermal history and recovered by the re-drying after the replacement of the mixed solvent with pure water.

From these observations, we can summarize the changes in the network structure as follows. The hydrogen bonds in the dried gel (S1) were slightly destroyed at 8 °C (S2), and the microcrystallites became smaller and were partly destroyed with an increase in temperature, but still remained even after the temperature was increased to 50 °C (S5). The destroyed microcrystallites could be re-formed partly by the

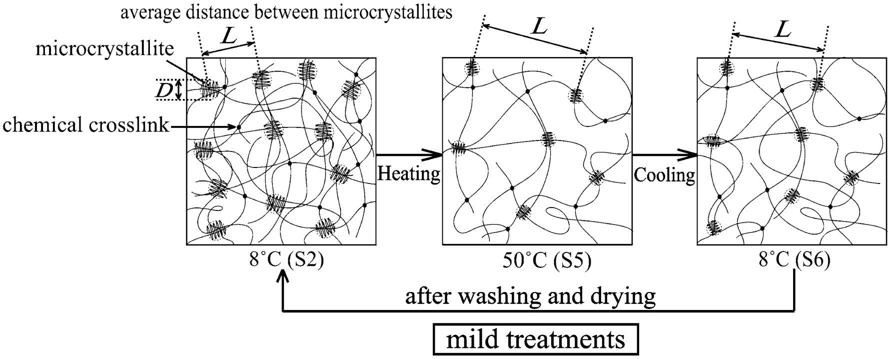

Fig. 6 Schematic illustration of the changes in network structure of PVA gel by mild treatments, resulting from the formation and destruction of the microcrystallites

simple cooling process (S6) or simple drying (S7). However, they were re-formed largely, and the IR spectrum changed similar to the initial 8 °C by the water exchange treatment (S8). In this treatment, the gel was put in pure water, and the solvent in the gel was replaced completely by the pure water, after which the gel was dried and again immersed in the mixed solvent. This irreversible behavior was consistent with the results of the swelling ratio (Fig. 1). Based on these observations, schematic illustrations of the microcrystallites are shown in Fig. 6. In summary, the hydrogen bonds could be destroyed and formed reversibly by mild treatments, involving temperature change, solvent exchange, and drying.

Finally, it should be notified that the appearance of the present findings should depend on the degrees of polymerization and hydrolysis of PVA. According to our report [8], a PVA powder with higher degrees of polymerization and hydrolysis is required to obtain a PVA gel physically crosslinked by microcrystallites; a higher degree of polymerization is required to make an amorphous network stronger, while a higher degree of hydrolysis is required to make the larger microcrystallite for crosslinking the amorphous region. It is, therefore, reasonable to conclude that the use of a PVA powder with a higher degree of hydrolysis is a necessary condition to have the additional crosslinks by microcrystallites. However, it is necessary to examine whether the higher degree of polymerization is necessary or not, which is an important subject for future investigation.

Conclusion

Chemical PVA gels, slightly crosslinked by GA, were prepared, and an irreversible swelling behavior (swelling and de-swelling) was observed with a temperature change in a mixed solvent of DMSO and water; the dried gel gradually swelled when heated from 8 to 50 °C, but it did not shrink when cooled. The initial de-swelling state at 8 °C was recovered by drying after swelling fully in pure water. The formation of a hydrogen bond and microcrystallites during the drying after gelation was confirmed by XRD and ATR FT-IR measurements, which suggested that the irreversible swelling behavior was attributed to the destruction of the microcrystallites introduced by the drying process. The hydrogen bond was destroyed during the temperature increase that resulted in the swelling of the gel, and it re-formed by drying after immersing in a large volume of pure water. Therefore, the formation and destruction of hydrogen bonds was reversible under mild treatments of temperature change, solvent exchange, and drying. The macroscopic swelling behavior corresponded qualitatively, but reproducibly, to the microscopic changes in the network structure due to the formation and destruction of physical crosslinks in the chemical PVA gels.

We believe that the present observations are of crucial importance, not only for understanding the molecular interactions in hydrogels, but also for developing future practical applications of hydrogels as functional elements. The technique observed in this study can be used to control the reversible formation and destruction of hydrogen bonds just by drying and by changing temperature, i.e., by using mild treatments that do not involve the use of chemicals.

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