

A Simple Method to Obtain a Swollen PVA Gel Crosslinked by Hydrogen Bonds

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ABSTRACT: A simple method to obtain a physically crosslinked poly(vinyl alcohol) (PVA) hydrogel is reported. In this technique, the PVA solution in pure water was simply cast at room temperature without using any additional chemical. The gelation proceeded during the dehydration after casting the PVA solution into a mold. After the completion of gelation, the swelling ratio of the gel in its equilibrium was measured whenever the solvent water was repeatedly exchanged. The weight gradually decreased due to the elution of non-crosslinked polymers into the solvent, and became constant after sufficient

water exchange. The measurements using a Fourier Transform infrared spectroscopy and an X-ray diffraction suggested that the crosslinks due to hydrogen bonds and microcrystals were formed during the dehydration process of the PVA solution. We concluded that the sample obtained by the present method is a physically crosslinked polymer network, insoluble in water, i.e., a swollen gel in water. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 10–16, 2009

Key words: crystallization; FTIR; gelation; hydrogels; XRD

INTRODUCTION

Poly(vinyl alcohol) (PVA) has been widely used for practical applications^{1,2} in a variety of fields, such as the textile industry, the cosmetics industry, and the paper industry. It is widely known that PVA has many advantages due to its low toxicity and high biocompatibility. For these reasons, PVA or PVA-based gels are also used in a variety of pharmaceutical and biomedical applications as biomaterials³ in wound dressing, implants, cell encapsulation, drug-delivery systems, soft contact lenses, and dental applications. For the preparation of PVA gels,² various methods have been reported. For example, chemical PVA gels can be prepared by using chemical crosslinkers like glutaraldehyde^{4,5} or multifunctional reactive compounds.⁶ Chemical gels can be also obtained by crosslinking PVA polymers in the solid state or in solution by radiating a γ -ray⁷ or electron beam.⁸ Physical PVA gels, on the other hand, can be obtained by the freeze-thaw method in water^{9,10} or in a dimethyl sulfoxide (DMSO)/water mixed solvent.^{11–14} These methods are useful to obtain a variety of hydrogels with high performance and high water absorption ability. To the best of our knowledge, however, the preparation of crosslinked PVA hydrogels at room temperature starting from

an aqueous PVA solution without using additional chemical reagents except PVA polymer has never been reported. Although PVA films or thin plates have been prepared using the solvent casting method,¹⁵ no report on the preparation of swollen gels in water using the solvent casting method is available.

In this article, we report, for the first time, a simple method to obtain a physically crosslinked PVA gel from a PVA aqueous solution through dehydration at room temperature without using any special chemical. This article aims to prove that the obtained dehydrated material becomes a swollen gel, which is defined here as a crosslinked polymer network that can absorb enough solvent to swell and insoluble in the solvent water. The static swelling ratio was measured starting from the dehydrated state whenever the solvent water was repeatedly exchanged. The results are discussed in terms of the formation of hydrogen bonds and microcrystal using Fourier transform infrared spectroscopy (FTIR) and X-ray diffraction (XRD) measurements as well as measurements of the swelling ratio under repeated exchanges of the solvent water.

EXPERIMENTAL SECTION

Materials

PVA powder was purchased from Wako Pure Chemical Industries, Ltd., which was of the commercial grade and used without further purification. The

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average degree of polymerization was in the range between 1500 and 1800, and the average degree of hydrolysis was larger than 98 mol %. An aqueous PVA solution was obtained by dissolving 15.0 wt % of the PVA powder into deionized and distilled water at 90°C for more than 2 h. The PVA solution (3.0 g) was poured into a plastic dish of polyethylene with an inner diameter of 33 mm with the lid off and left in air at room temperature (ca. 25°C) in a closed space to prevent the air passing over the sample. The solution was fluid at first, became very viscous in a few days, and became a solid (thin disk) after water content (defined below) decreased less than 20 wt %. The preparation process consisted of this evaporation treatment in an air conditioning room where the temperature and the humidity were kept roughly constant with the accuracies of $\pm 3^\circ\text{C}$ and $\pm 10\%$, respectively. This simple gelation process is named as “cast-drying method.”

Measurements of the water content

The change in the weight of the PVA solution, W_s , during the dehydration was measured, and the water content, w , was calculated against time, t days. In this article, w is defined as the ratio of the weight of water to the weight of PVA powder (the manufacturing product without any pretreatment), W_p : $w = (W_s - W_p) / W_p \times 100$ (%). W_p contained the weight of bound water despite definition of “the weight of PVA powder.” To obtain the real water content, it is necessary to determine the real dry (water free) weight, which requires some complicated treatments of the PVA powder. However, in the present cast-drying method, we especially focused on the simple method, where the approximate (but reproducible) weight of polymer is adequate to discuss the qualitative discussion of the preparation process. Therefore, in the case of the dehydration of the PVA solution, the initial W_s , which was the weight of the PVA solution (=3.0 g), was the sum of W_p ($=3.0 \times 0.15 = 0.45$ g) and the weight of pure water (=2.55 g).

After the first dehydration process, the dehydrated sample (thin disk) was removed from the dish and put in pure water, the amount of which was the same as that of the evaporated water during the dehydration. The dehydrated thin disk swelled and did not appear to dissolve in pure water. After the sample reached the equilibrium state, this swollen sample was taken out from the solvent water, the drops of water were wiped off the surface with a type of cleaning tissue (Kimwipes, Nippon Paper Crexia Co., Ltd.), and the change in the weight of the swollen sample (W_s in the above equation) was measured at room temperature. In the calculation of w in this second dehydration process, the original

nominal weight ($W_p = 0.45$ g) could not be used because of elution during the swelling process. To compensate for the elution effect, W_p was used by subtracting the weight of the eluted polymer into the solvent water from 0.45 g. The weight of the eluted polymer was obtained as follows; after the gel reached the equilibrium state, the swollen gel was carefully removed from the solvent water. After the solvent water was dehydrated, the weight of the leftover was measured, which was assumed to be the weight of the eluted polymer.

Measurements of the swelling ratio

The dehydrated thin disk was put into 1000 g of pure water for 24 h or more to reach the equilibrium state. After the sample was taken out from the solvent water, the drops of water were wiped off the surface with Kimwipes, and the weight of the sample, W_t , was measured at room temperature. Immediately after the measurement, the sample was again put in the new solvent (1000 g of pure water), where it was left for 24 h or more. This process of water exchange and measurement was repeated many times in the course of 60 days. After 60 days (the number of water exchanges was 47 times for this period, and W_t was measured 23 times), the sample was dehydrated at room temperature for more than 5 days. Then, the dehydrated weight, W_d , was measured, and the swelling ratio, W_t / W_d , was calculated. The elution ratio of the polymer, defined as $(1 - W_d / W_p) \times 100$ (%), was also calculated.

ATR FTIR and XRD measurements

To study the change in molecular structures (e.g., the formation of hydrogen bonds) of the PVA solution during the dehydration process at preparation, the measurements of FTIR with an Attenuated Total Reflection (ATR) method were carried out at room temperature. The ATR FTIR spectra were recorded on an FTIR spectrophotometer (Jasco FTIR610) 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 spectra were normalized on the basis of the C—H bending vibration at 1427 cm^{-1} ¹⁶, which was obtained by deconvoluting the spectra. The measurements were conducted on samples with different degrees of dehydration (waiting periods) from 0 to 7 days after pouring the PVA solution into the plastic dish.

To confirm the structural details in the different length scale, XRD measurements were performed at room temperature using a SAXSess camera (Anton Paar, PANalytical) with $K\alpha$ wavelength of 0.1542 nm operated at 40 kV and 50 mA. This apparatus

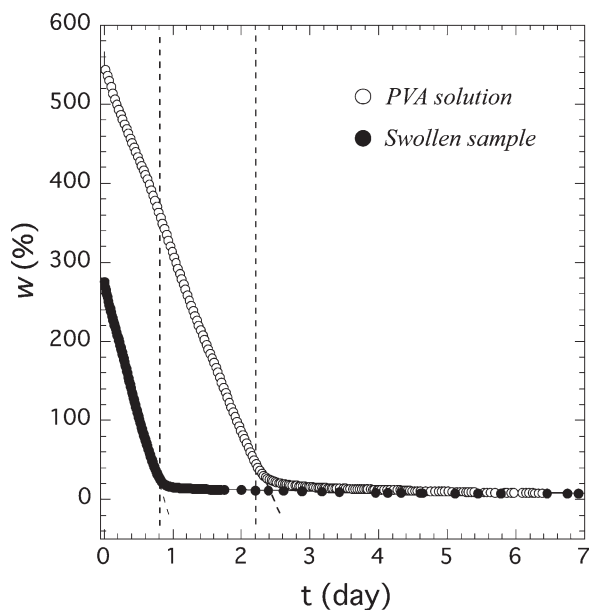


Figure 1 Time evolutions of water content of PVA solution and swollen sample during two dehydration processes at room temperature.

combines both small-angle scattering (SAXS) and wide-angle X-ray scattering (WAXS) techniques, which allows the measurements of structures with scattering features down to 0.25 nm in a single scan.

RESULTS AND DISCUSSION

Waiting period and changes in w

Figure 1 shows two evolution curves of w over time. One is the first dehydration process of the PVA aqueous solution, which was dehydrated at room temperature for 7 days. The dehydrated sample was removed from the plastic dish [Fig. 2(a)] and put into pure water for 24 h where it swelled to reach the equilibrium state. The other curve is the second dehydration process of the swollen sample, which was taken out from the solvent water. The drops of water were wiped off the surface with Kimwipes, and the change in the weight after the first dehydration process was successively measured at room temperature.

In the case of the first dehydration process, w decreased rapidly and linearly with time, deviated from the line at $t = 2.2$, and continued to decrease very slowly. During this process, the sample changed from a liquid to a solid. In the case of the second dehydration process, w at $t = 0$ was approximately half of w of the first dehydration process and decreased rapidly and linearly with time. It deviated from the line at $t = 0.8$ and continued to decrease very slowly. According to the literature,^{17,18} the initial rapid decreases in both w 's of the first and second dehydration processes correspond to the

evaporation of free water molecules. The second slow decrements after $t = 2.2$ or 0.8 resulted from the evaporation of bound water molecules to polymers. The initial slope of the swollen sample seems steeper than that of the PVA solution. This is attributed to the fact that the contact area of the swollen sample to air was apparently larger than that of the PVA solution.

Change in the weight

Figure 2(a) shows the dehydrated sample after the first dehydration process. The dehydration period was 7 days and $w = 5.5\%$. The sample was transparent, and firm like a soft plastic. The diameter was 32 mm (slightly shrunk from the size of a mold), and the thickness was about 0.5 mm in the center and about 1 mm in the edge; the edge became thicker due to the surface tension between the PVA solution and the inside wall of the dish. Figure 3 shows W_t against time during the repeated water exchanges. Two swelling ratios, W_t/W_d , are added in this figure. One is calculated using $W_d = 0.457$ g, which was measured after the first dehydration (first water exchange), and the other was calculated using $W_d = 0.410$ g, which was measured after 60 days (47 water exchanges). Therefore, the total elution ratio of the polymer, $(1 - W_d (=0.410))/W_p) \times 100$, amounted to 8.9%. In the present experiment, the sample was not dehydrated between the initial and final dehydrations, but water was repeatedly exchanged to maintain the gel in a swollen state. Therefore, the actual W_d between the initial and final dehydrations could not be obtained (W_t/W_d could not be determined). However, it is evident that the final W_t/W_d is larger than the initial one, which indicated that the swelling ratio increased by polymer elution during the repeated water exchanges.¹⁹ As shown in this figure, W_t decreased and became constant after 20 days, which indicated that the elution almost stopped after 20 days. Therefore, it is reasonable to consider that the actual swelling ratio became constant after 20 days (broken curve in Fig. 3).

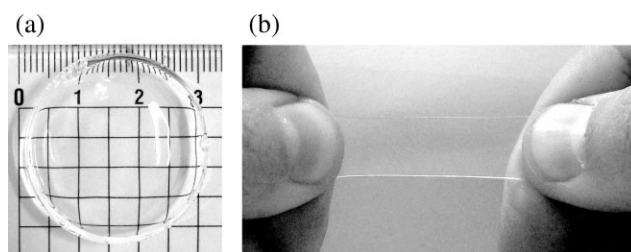


Figure 2 Pictures of the dehydrated sample with $w = 5.5\%$ (a) and the stretched swollen gel cut in a rectangle shape after repeated water exchange (b).

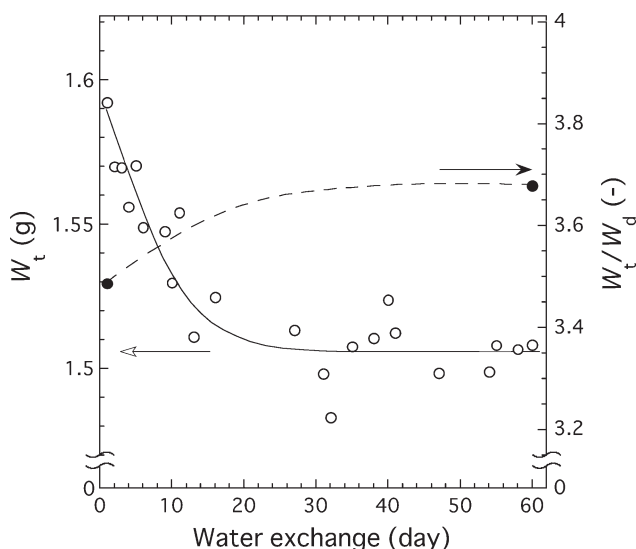


Figure 3 Weight of the swollen sample during repeated water exchange. Two swelling ratio at the initial and final dehydrated sample are added.

Figure 2(b) shows the stretched swollen gel cut in a rectangle after 60 days of water exchange. The sample remained transparent and it was hard to break. From a macroscopic point of view and on the basis of these results, we confirmed that the cast-drying method could be used to make firm swollen gels without dissolution.

FTIR studies

Figure 4 shows the ATR FTIR spectra of the PVA solution for the gels with different waiting periods during the first dehydration process ($t = 0 \sim 4$). After $t = 4$, the spectra did not change, and those of $t = 5, 6$, and 7 were almost the same as that of $t = 4$. Four characteristic regions with strong absorption peaks were observed at around $3300, 1640, 1240$, and 1100 cm^{-1} . With increasing t from 0 to 4, the O—H stretching vibration region due to the hydrogen bonds at $3378\text{--}3281 \text{ cm}^{-1}$ ²⁰ decreased, which indicated that the hydrogen bonds due to free water molecules decreased during the initial dehydration process. The peak position clearly shifted to the lower range. In fact, the peak around 3300 cm^{-1} consists of two components, and the peak at 3378 cm^{-1} is assigned to the O—H bands of the free and hydrogen-bonded groups.²⁰ The peak located at 3281 cm^{-1} observed after the evaporation of free water can be related with the formation of hydrogen bonds between PVA polymers.²⁰ The peak located at 1643 cm^{-1} can be assigned to the O—H bending vibration between free water molecules, which is confirmed by the observation that the peak intensity decreased with increasing t and disappeared at $t = 3$. This evi-

dence corresponded to the result of the water content (Fig. 1); the free water completely evaporated before $t = 2.2$. The C—H deformation of PVA at 1236 cm^{-1} ²¹ decreased with increasing t , and the peak almost disappeared at $t = 3$ by the completion of the evaporation of the free water. The C—O stretching of PVA at 1090 cm^{-1} ²¹ also decreased with increasing t . However, the main peak still remained at $t = 3$, and a small peak at 1142 cm^{-1} and a shoulder around 1050 cm^{-1} appeared. The small absorption peak was evident at around 1142 cm^{-1} after the highly dehydrated state at $t = 2$, and the shape of this peak did not change after $t = 3$ (the inset of Fig. 4). This peak can be assigned to C—O stretching²¹ due to the formation of the microcrystal of hydrogen bonds, which is also related with the decrement of the free water in Figure 1. At the same time, a shoulder appeared at 1050 cm^{-1} after $t = 2$, which is also assigned to C—O stretching.²¹ Since this peak coincided with the appearance of the peak at 1142 cm^{-1} , it might be related with the formation of microcrystals. These results may indicate that the decrement of free water, resulting in the decrement of the average polymer-polymer distance, assisted in the formation of hydrogen bonds between O—H groups of the PVA and microcrystal.

XRD measurements

Figure 5 shows the XRD spectra of the PVA solution ($t = 0 \sim 7$). In the cases of $t = 0$ and 1 , a kapton (polyimide) film was used as a mold for the liquid samples. After $t = 2$, the sample became firm enough to keep its shape by itself, and it was set in the sample holder without the kapton mold. In the area of large q , a broad peak centered at $q = 18.6 \text{ nm}^{-1}$ ($d = 3.38 \text{ \AA}$) was observed at $t = 0$ and 1 , which possibly corresponded to the average distance between the centers of mass of water molecules.²² In $t = 2$, the peak at $q =$

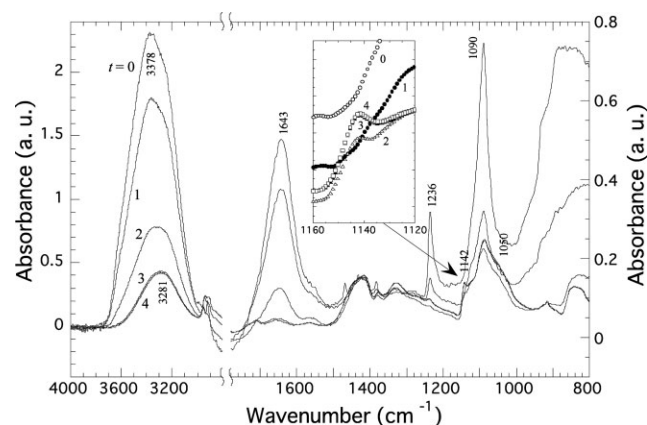


Figure 4 ATR FTIR spectra of the PVA solution with different waiting periods in the first dehydration process.

18.6 nm⁻¹ was not observed, and a broad peak with two subpeaks at $q = 16.6$ nm⁻¹ ($d = 3.79$ Å) and at $q = 13.9$ nm⁻¹ ($d = 4.59$ Å) appeared. The appearance of small subpeak at $q = 16.6$ nm⁻¹ might be related with the decrement of the distance among polymers at $t = 2$ after the evaporation of free water. After $t = 3$, a peak at $q = 13.9$ nm⁻¹ became sharp, which indicated that the PVA formed the crystalline regions in the amorphous regions.²³

The XRD measurement of the PVA gel prepared in a DMSO/water solvent^{23–26} was cited because the gelation process was similar to our sample, which was started from polymer and the microcrystals were formed in a poor solvent using DMSO/water (60/40) mixed solvent; the mixed solvent enhanced the aggregation of polymers, which results in the formation of the microcrystals by hydrogen bonds. The degrees of polymerization and hydrolysis used in the literature were, respectively, 1700 and fully hydrolysis (almost 100 mol %), which were almost same as the PVA powder used in the above experiment.

The WANS measurement of the PVA gel prepared in a DMSO/water solvent strongly suggests that the peak at around $q = 13.9$ nm⁻¹ corresponds to the physical crosslinks by the microcrystal introduced at gelation.²⁴ To compare the size with that of the microcrystal (the crosslinked region) in the present sample, the average crystallite size, D , was estimated from the half-width of the diffraction peak in Figure 3 using Scherrer's formula,²⁵ $D = k\lambda/(\beta \cos \theta)$; here, $k = 1$ is a constant and is related to several aspects, including the shape of the crystal, the Miller index of the reflecting crystallographic planes, and the crystallite shape, β is the width at half maximum intensity of the reflection in radians, θ is Bragg's angle, and $\lambda = 1.54$ Å is the wavelength of the X-ray radiation. Using the peak at $q = 13.9$ nm⁻¹ of the XRD spectrum at $t = 3$, D was estimated 2.6 nm, which is close to the value of the PVA gel prepared in the DMSO/water mixed solvent.²⁴ After $t = 3$, D was almost constant. In the area of small q , on the other hand, a broad peak was observed at around $q = 0.3$ nm⁻¹ after $t = 2$, which shifted to the higher region at $q = 0.61$ nm⁻¹ with time. The peak-top position of this broad peak after $t = 3$ corresponded to the average distance ($L = 10.3$ nm), which was shorter than the case of the PVA gel with a DMSO/water mixed solvent.²⁶ This smaller L might be related with the evaporation of water more than 80% in the present sample. As is schematically summarized in Figure 6, the above results confirmed that the decrement of free water in Figure 1 formed the crosslinked point of hydrogen bonds with an average distance of $d = 4.59$ Å, which formed a microcrystal with $D = 2.6$ nm size. One possible interpretation of the structural modulation of $L = 10.3$ nm might be the average distance between the microcrystals.

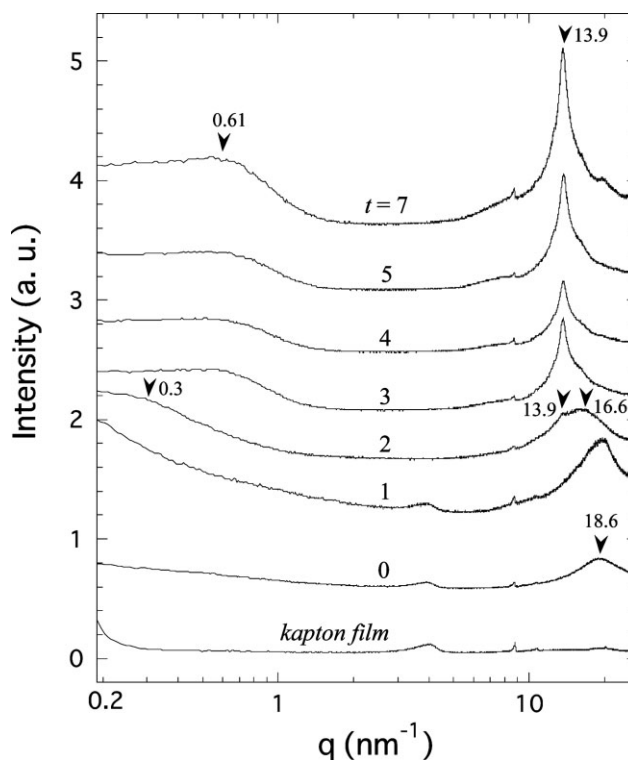


Figure 5 XRD spectra of the PVA solution with different waiting periods in the first dehydration process.

Conditions to form a swollen PVA hydrogel

We have presented a simple technique to prepare a swollen PVA hydrogel with a cast-drying technique. The three experiments explained above, i.e., swelling ratio, ATR FTIR, and XRD, suggested that the cast-dried PVA solution forms a swollen PVA hydrogel, i.e., a crosslinked network of gel. In the above preparation, PVA powder with relatively high degrees of polymerization as well as hydrolysis was used, as is described in section of the sample preparation and shown in Table I (Powder A). To understand the effects of the degrees of polymerization and hydrolysis on the gelation ability, the preparation technique was tested using two different kinds of PVA powder, which were kindly provided by Kuraray Co., Ltd. (Powders B and C in Table I); the degree of polymerization of Powder B is much smaller than that of Powder A, whereas the degree of hydrolysis of Powder C is much smaller than that of Powder A. The dehydrated disk samples (Samples A, B, and C) were prepared using Powders A, B, and C as a starting material by the cast-drying method under the same condition described in section of the sample preparation; each 15.0 wt % PVA solution (3.0 g) was poured into a plastic dish (inner diameter of 33 mm) and left in air at room temperature until w reached 5.5%.

First, each center region of the dehydrated samples was cut in a rectangular shape (6 × 4 mm) and

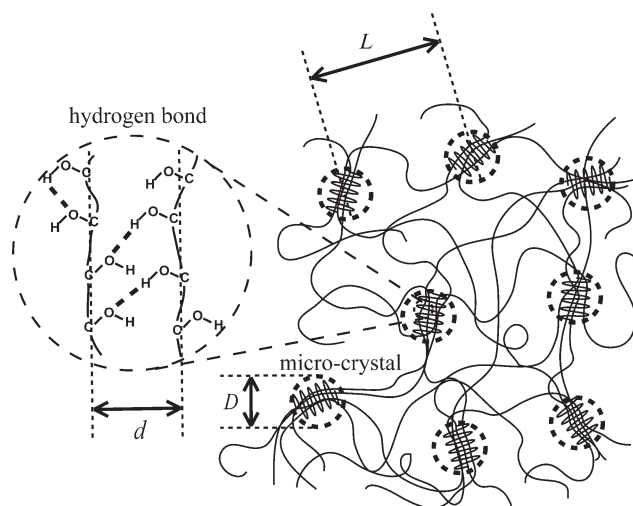


Figure 6 Schematic representation of the network structure of PVA gels crosslinked by microcrystals; three characteristic lengths, d , D , and L were deduced from the diffraction peaks of XRD spectra.

put in 100 g of water for 24 h. After the sample reached the equilibrium state, Samples A and B swelled and kept their form in appearance, but Sample C dissolved completely into the solvent water. However, Sample B was too fragile to be picked up from water using tweezers. These results confirm that the cast-drying method could yield a firm swollen gel using PVA powder with high degrees of polymerization and hydrolysis.

Figure 7 shows the ATR FTIR spectra of as-prepared Samples A, B, and C with $w = 5.5\%$. There was no difference between the spectra of Samples A and B, and the spectrum of Sample C was quite different from them. The peak of O—H stretching at around 3300 cm^{-1} is observed at 3309 cm^{-1} , which is slightly larger than that of Samples A and B at 3281 cm^{-1} . This evidence indicated that the 19 ~ 22% acetic acid group in Sample C prevented O—H groups from forming hydrogen bonds. As is shown in Figure 7, the acetic acid group in Sample

TABLE I
PVA powders as Starting Materials with Different Combinations of the Degrees of Polymerization and Hydrolysis

Powder	Average degree of polymerization	Average degree of hydrolysis (mol %)
A	1500 ~ 1800	98 ~ 100
B	500	98 ~ 99
C	2000	78 ~ 81

Note) The average degrees of polymerization and hydrolysis were commercial grades. The approximate values or ranges were evaluated experimentally by the product companies.

C also increased C=O stretching at 1733 cm^{-1} ,²⁷ C—H stretching at 1373 cm^{-1} , and C—H deformation at 1239 cm^{-1} . Moreover, C—O stretching at 1142 cm^{-1} due to the formation of microcrystal was not clearly observed in the spectrum of Sample C, whereas the peak at 1021 cm^{-1} was evidently observed. Although the assignment of this peak at 1021 cm^{-1} is not clear at the present time, we believe that the appearance of this peak could cooperate with the absence of the peak at 1142 cm^{-1} , which originated from the existence of acetic acid groups.

Figure 8 shows the XRD spectra of as-prepared Samples A, B, and C with $w = 5.5\%$. Although the peak at $q = 13.9\text{ nm}^{-1}$ ($d = 4.59\text{ \AA}$) due to the hydrogen bonds between polymers was observed in all samples, the peak height of Sample C was small, and D of Samples A, B, and C was, respectively, 2.6, 3.5, and 1.3 nm, which indicated that the acetic acid group in Sample C prevented O—H groups from enhanced the crystal growth. On the other hand, the peak intensity at around $q = 0.61\text{ nm}^{-1}$ ($d = 10.3\text{ nm}$) of Sample B was the broadest as well as the smallest of the three samples, which suggested that the microcrystals were more randomly distributed without a specific structural modulation of L and the network structure in the amorphous region was inhomogeneous. Moreover, its peak position shifted slightly to larger q , which indicated that L was slightly smaller than those in the other two samples. This may be possibly related to the difference in the number and/or the size of microcrystals (D) or that in the number of dangling bonds due to the different numbers of polymers. In addition, the small peak at $q = 20.0\text{ nm}^{-1}$ ($d = 3.14\text{ \AA}$) was not exclusively observed in Sample C, which may be attributed to the high degree of hydrolysis in Powder C.

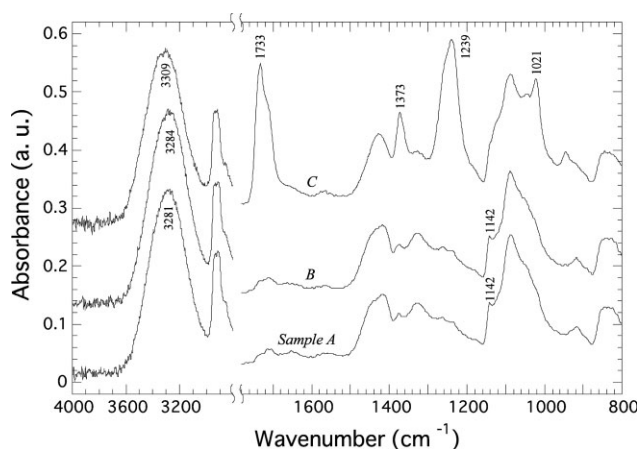


Figure 7 ATR FTIR spectra of as-prepared sample after the first dehydration process with different combinations of the degrees of polymerization and hydrolysis.

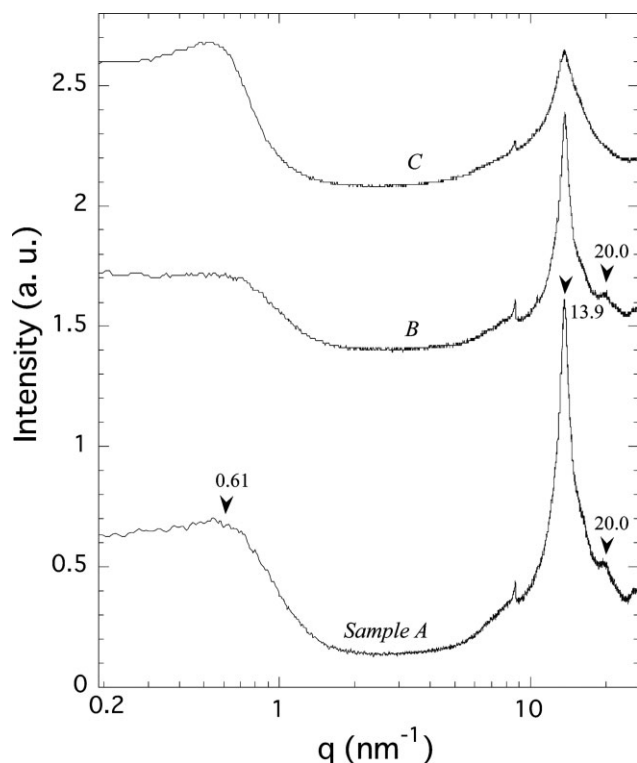


Figure 8 XRD spectra of as-prepared sample after the first dehydration process with different combinations of the degrees of polymerization and hydrolysis.

From these results, a high degree of polymerization is required to make an amorphous network strong by distributing the microcrystal homogeneously, while a high degree of hydrolysis is required to make the large microcrystal for crosslinking the amorphous region. Therefore, it is important to use a starting material (PVA powder) with high degrees of polymerization and hydrolysis to obtain a swollen gel using the present cast-drying method.

CONCLUSIONS

We successfully developed a simple method to obtain a physically crosslinked PVA gel (named as "PVA cast gel") at room temperature without using any special chemical. The materials used here are water and PVA powders, and the method is dehydration. The formation of hydrogen bonds and microcrystals was identified during the dehydration process using ATR FTIR and XRD techniques as well as measurements of the swelling ratio under repeated water exchanges. The dehydrated sample can swell and is insoluble in water even after sufficient water exchange. We conclude that the obtained

sample prepared by the present simple method is a physically crosslinked polymer network, that is, a swollen gel in water.

This method is simple, safe, and inexpensive to obtain physical PVA gels that are completely transparent and absorb a lot of water. The present findings, we believe, are of crucial importance for the understanding of the gelation mechanism of physical gels, and useful for developing PVA-based materials that can be used in biomedical and agricultural fields.

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