

# Elution of Polymers from Poly(vinyl alcohol) Cast Gels with Different Degrees of Polymerization and Hydrolysis

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Received 9 June 2011; accepted 26 January 2012

DOI 10.1002/app.36919

Published online in Wiley Online Library (wileyonlinelibrary.com).

**ABSTRACT:** Poly(vinyl alcohol) (PVA) gels physically crosslinked by microcrystallites were prepared by a cast-drying method using PVA powders with different degrees of polymerization ( $n_{DP}$ ) between 300 and 2400 and hydrolysis ( $r_{DH}$ ) between 79.5 and 98.5 mol %. Polymer elution of gels in a limited amount of water was investigated by measuring the total carbon in the outer water by a total organic carbon analyzer. As a result, polymer elution was detected for all gels, the total amount of which depended on both  $n_{DP}$  and  $r_{DH}$ . In the cases of lower  $n_{DP}$  and higher  $r_{DH}$ , the gel became

opaque and cracks were observed on the surface during a simple swelling process. On the other hand, polymers dissolved without cracks in the cases of higher  $n_{DP}$  and lower  $r_{DH}$ . These results are discussed on the basis of the network microstructure of the dried states before and after the polymer elution.  
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**Key words:** poly(vinyl alcohol); degree of polymerization; degree of hydrolysis; polymer elution; network microstructure; microcrystallite

## INTRODUCTION

Poly(vinyl alcohol) (PVA) gels are useful biomaterials because of their low toxicity and high biocompatibility, and many reports on their practical applications have been published in a variety of fields.<sup>1–5</sup> Recently, a simple method to obtain a physically crosslinked PVA gel (called a “PVA cast gel”) was successfully developed.<sup>6,7</sup> The materials used in this method were water and PVA powders without using additional chemical reagents, and the gelation proceeded during the drying process after casting the PVA solution into a mold. The formation of hydrogen bonds and microcrystallites was identified during the drying process (gelation process) using an X-ray diffraction (XRD) technique, Fourier-transform infrared (FTIR) spectroscopy, and measurements of the swelling ratio under repeated water exchanges.<sup>7</sup> The dried sample could swell and was insoluble in water after sufficient water exchange. During simple swelling, polymer elution was observed using weight measurements.<sup>6,7</sup> It was suggested<sup>6</sup> that a high degree of polymerization ( $n_{DP}$ ) is required to make an amorphous network strong by distributing the microcrystallites homogeneously, while a high degree of hydrolysis ( $r_{DH}$ ) is required to make large microcrystallites for crosslinking the

amorphous region. Comparing with the conventional PVA gels prepared by a freeze-thawing method, the PVA cast gels are transparent and elastic, while the conventional PVA gels are white-opaque and inelastic, although the network structures in the nanometer level is similar to that of each other.

Recently, it was found<sup>8</sup> that molecular chains in a gellan gel are partially released from the gel when it is immersed in a good solvent. The experimental results indicated that the released chains of gellan were unassociated with the crosslinking domains composed of the associated double helices in the gels. It seems that the amount and rate of polymer release depend on the polymers and experimental conditions. For example, the release of free chains from the gel was suppressed by adding KCl while it was promoted by adding tetramethylammonium chloride to the external solution.<sup>9</sup> More recently, the elution of polymers from physically crosslinked PVA cast gels with high  $n_{DP}$  and high  $r_{DH}$  values was evaluated quantitatively using a total organic carbon (TOC) analyzer.<sup>10</sup> It was found that a PVA cast gel film swelled and released uncrosslinked PVA into the outer water in a limited amount of water, and that this process stopped after the gel reached its equilibrium state. This is the first quantitative observation of the release of PVA chains from PVA gels, which has not received much attention so far, although a change in the water content was observed by washing the gels to remove excess PVA chains.<sup>11</sup> Moreover, polymer elution would restart

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whenever the solvent water was repeatedly exchanged with new fresh water. We are currently examining the quantitative experiments to answer the question whether it will stop after sufficient water exchanges. The results will be published elsewhere.

There are two problems related to the principles of the elution phenomena. The first is that the elution of polymers is an important phenomenon in physically crosslinked gels, one that is completely different from the molecular release from non-organic materials such as mesoporous silica,<sup>12</sup> because the gel can swell as a result of osmotic pressure. We believe that polymer elution into the outer water in a limited amount of water is not restricted to the release of the uncrosslinked PVA introduced at gelation but is attributed to the release induced by the swelling. The swelling-induced destruction of microcrystallites must be taken into account. This complicated nature makes it more difficult to predict the elution rate and possible erosion. The other problem is related to the definition of gels. Generally speaking,<sup>13</sup> a gel prepared by casting polymer solutions can be called a gel as long as it does not flow. In this sense, PVA cast gels with both high  $n_{DP}$  and  $r_{DH}$  values are well-established gels because they do not flow in a limited amount of water.<sup>10</sup>

As a follow-up to our previous works,<sup>6,7,10</sup> it is highly desirable to investigate the elution phenomena of gels with different  $n_{DP}$  and  $r_{DH}$  values during simple swelling processes. If  $n_{DP}$  and  $r_{DH}$  of PVA powders are changed systematically, the network microstructure should be changed, which might affect the elution phenomena. Although there have been some reports on the effects of  $n_{DP}$  and  $r_{DH}$  on the rheological and thermal properties,<sup>14,15</sup> the release of the main constituent has not received much attention. In this study, we measured the dependences of  $n_{DP}$  and  $r_{DH}$  on the elution phenomena of PVA chains from PVA cast gels using a TOC analyzer. We will discuss the effects of  $n_{DP}$  and  $r_{DH}$  on the polymer elution from PVA cast gels during simple swelling on the basis of the changes in the network structure, which can be characterized by the microcrystallites and amorphous networks.

## EXPERIMENTAL

### Sample preparation

Samples were prepared using a single process consisting of drying of the PVA aqueous solution at room temperature (cast-drying method).<sup>6</sup> PVA powder was kindly supplied by Kuraray Co., Ltd. (Tokyo, Japan) (see Table I) and used without further purification. The average degrees of polymerization,  $n_{DP}$ , and the average degrees of hydrolysis,  $r_{DH}$ , are summarized in Table I. Aqueous PVA solutions were obtained by

**TABLE I**  
Samples of PVA Cast Gels and their Degrees of Polymerization and Hydrolysis (Manufacturer-Specified)

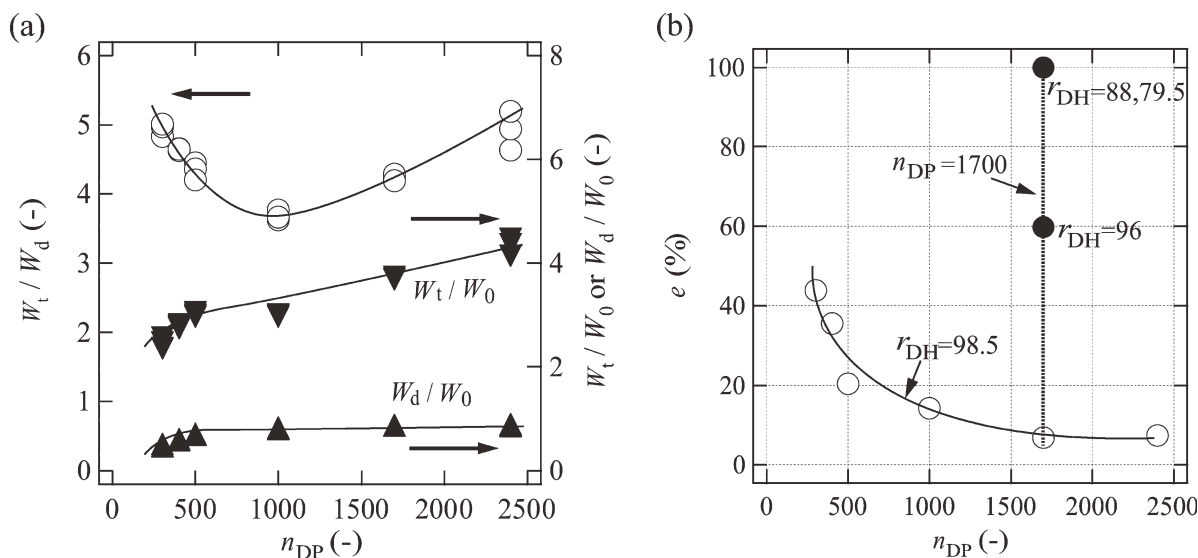
Cat. no.	$n_{DP}^*$	$r_{DH}^*$	Abbreviation
PVA103	300	$98.5 \pm 0.5$	PVA300/98.5
PVA104	400		PVA400/98.5
PVA105	500		PVA500/98.5
PVA110	1000		PVA1000/98.5
PVA117	1700		PVA1700/98.5
PVA124	2400		PVA2400/98.5
PVACST	1700	$96.0 \pm 0.5$	PVA1700/96
PVA217		$88.0 \pm 1.0$	PVA1700/88
PVA417		$79.5 \pm 1.5$	PVA1700/79.5

\* $n_{DP}$  of PVA217 & PVA417 = 1700, and  $r_{DH}$  of PVA104, PVA105, PVA110, PVA117 & PVA124 =  $98.5 \pm 0.5$

dissolving PVA powder in pure water (deionized and distilled water) at 90°C or higher for more than 2 h. The amount of PVA was adjusted to be 6.64 mol % of the concentration of the monomer units of PVA (6.64 mol % corresponded to 15 wt % PVA117 powder in the pre-gel solution). 0.01 mol of PVA solution was poured into a polyethylene dish with an inner diameter of 33 mm and left in air at room temperature of  $(25 \pm 3)^\circ\text{C}$  (0.01 mol corresponded to 3 g of the pre-gel solution of 15 wt % PVA117 powder). After the sample was sufficiently dried at room temperature, the water content became almost constant, and rectangular pieces (5 mm  $\times$  5 mm with a thickness of 0.27–0.39 mm, depending on the  $r_{DH}$  of the PVA powder) were cut from the center of the cast gel film. In our previous reports, the swelling behavior did not depend on the thickness if the film thickness was not too small, i.e., less than 0.2 mm. In addition, a smooth surface could not be obtained during drying at gelation when the film thickness became larger than 1.6 mm. The thickness of the cast gel film used in the present experiment was determined to be in the intermediate range. We used six pieces as one sample, and the total weight of the initial dried sample was defined as  $W_0$ .

### Measurements of swelling ratio and elution ratio

The  $W_0$  to water weight ratio was kept constant at 3 g of sample to 695 g of water for more than 21 h during all of the processes. According to our recent article,<sup>10</sup> this waiting period was sufficient for the gel to reach the equilibrium state, and the swelling ratio reached constant. Although it is possible that elution continued after the gel reached its equilibrium state, the total amount of residual polymers to elute was less than 3% at most, which can be estimated from Figure 1 of Ref. 10. After the sample was taken out of the water, drops of water were wiped off the surface with Kimwipes, and the weight of the swollen sample,  $W_t$ , was measured at room temperature. After this measurement, the



**Figure 1** (a) Swelling ratio ( $W_t/W_d$ ) of PVA cast gels with  $r_{DH} = 98.5$  as a function of  $n_{DP}$ .  $W_t$ ,  $W_d$ , and  $W_0$  indicate the weight of the swollen sample, the weight of the dried sample, and the total weight of the initial dried sample, respectively. (b) Elution ratio ( $e$ ) of PVA cast gels with  $r_{DH} = 98.5$  as a function of  $n_{DP}$ . The  $r_{DH}$ -dependence of PVA cast gels with  $n_{DP} = 1700$  is also shown.

sample was again sufficiently dried at 60°C for more than 24 h, and the dried weight,  $W_d$ , was measured. The swelling ratio,  $W_t/W_d$ , was then calculated.

At the same time, the concentration of total carbon (TC) was measured using a TOC analyzer (TOC-VCSN, Shimadzu Corp., Kyoto, Japan), which had an accuracy of 50  $\mu\text{g/L}$ , and the weight of the eluted polymer,  $W_e$ , was calculated from the TOC;  $W_e$  was obtained by subtracting the total inorganic carbon (TIC), which came from the carbon dioxide, from the TC. The reference pure water for the measurement of TIC was also kept in the same vial container under the same conditions as the sample container.

For the calculation of  $W_e$ , the TIC in pure water was measured in advance, and a calibration curve was obtained by taking into account the aging effects in air and in the glass bottle. The elution rate,  $e$ , was defined as follows;

$$e = \frac{W_e}{W_0} \times 100(\%) \quad (1)$$

### Measurement of microstructure

To characterize the microstructure of polymer networks, the mid-infrared spectra of the plate gels were measured at room temperature using an FTIR spectrophotometer (FT/IR-610, Jasco Corp., Tokyo, Japan) equipped with an attenuated total reflectance (ATR) attachment with a ZnSe crystal in order to investigate the conformation, dissociation, and bonding state of the functional groups of the swollen gels in the solvent. The FTIR spectra were normalized based on the  $\text{CH}_2$  bending (rocking) vibration at  $853 \text{ cm}^{-1}$ ,<sup>16</sup> the peak area of which was assumed to be equivalent.

In addition, XRD measurements were performed at ambient temperature [ $(25 \pm 3)^\circ\text{C}$ ] using three methods: a wide-angle X-ray scattering (WAXS) technique using an X-ray diffractometer (40 kV, 200 mA; RINT-2000, Rigaku Corp., Tokyo, Japan); a small- and wide-angle X-ray scattering (SWAXS) measurement, which was performed using a SAXSess camera (Anton Paar, GmbH Graz, Austria PANalytical) with a  $\text{K}\alpha$  wavelength of 0.1542 nm and operated at 40 kV and 50 mA; and a small-angle X-ray scattering (SAXS) measurement using an SAXS apparatus installed at BL10C of the Photon Factory at the Institute of Materials Structure Science, the High Energy Accelerator Research Organization (KEK), Tsukuba, Japan. An X-ray beam from a synchrotron orbital radiation facility (1.488 Å in wavelength) was used as the light source, and the magnitude of the observed scattering vectors ranged from 0.01 to 0.15  $\text{\AA}^{-1}$ . To confirm the peak position obtained by SWAXS measurements, we performed the synchrotron SAXS measurement, which has the advantages of a high wavelength resolution, higher X-ray flux, faster measurements, and a tightly focused, collimated beam.

## RESULTS AND DISCUSSION

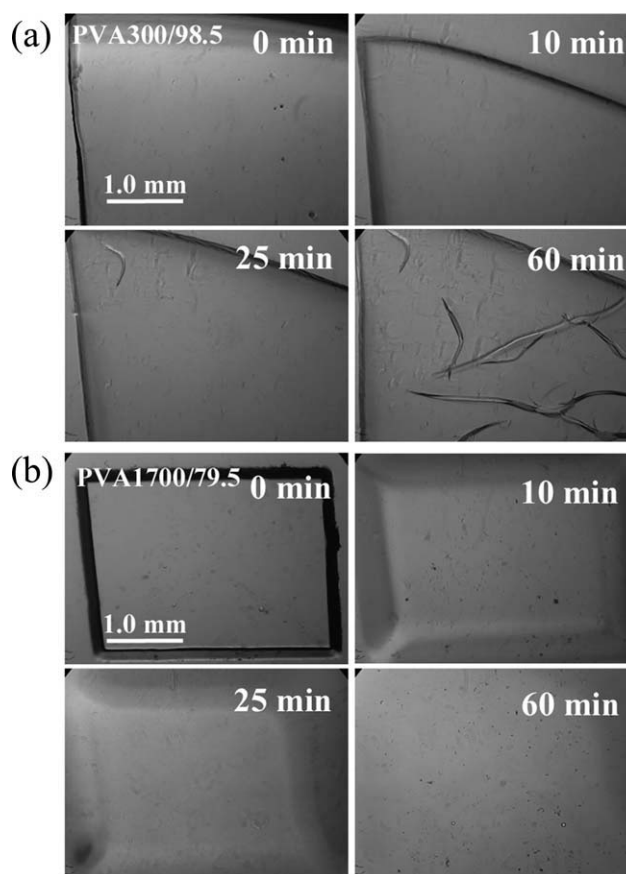
### Swelling ratio

Figure 1 shows the  $W_t/W_d$  and  $e$  values of PVA cast gels with  $r_{DH} = 98.5$  as a function of  $n_{DP}$ . With an increase in  $n_{DP}$ ,  $W_t/W_d$  exhibited a decrease and an increase, respectively, below and above  $n_{DP} = 1000$  [Fig. 1(a)]. To understand the non-monotonic change in  $W_t/W_d$ , we should first take into account the

effects of polymer elution on the network structure. As shown in Figure 1(a),  $W_d/W_0$  increased rapidly below  $n_{DP} = 1000$  and gradually above  $n_{DP} = 1000$ , which corresponded to the monotonic decrease in  $e$  [Fig. 1(b)] In the case of the lower range of  $n_{DP}$  below 1000, therefore, the increase in  $W_d$  is the essential reason for the decrease in  $W_t/W_d$ , although  $W_t/W_0$  increased slightly. In the case of the higher range of  $n_{DP}$  above 1000, on the other hand, the increase in  $W_t/W_d$  could not be explained by the slight increase in  $W_d/W_0$  but could be attributed to the increase in  $W_t$ . It is important to consider the reason for  $W_t$  continuing to increase even when the elution was suppressed, and it became constant in the high-molecular weight samples with  $n_{DP} = 1700$  and 2400. Because  $e$  was not smaller (8% or larger up to 40%) than the initial  $W_0$ , it was reasonable to assume that the polymer elution was not limited to the release of the uncrosslinked polymers introduced at gelation, but that the release of polymer chains (in the backbone network) was induced by the swelling force. In the lower range of  $n_{DP}$  below 1000, the average polymer length was short, and the connectivity between microcrystallites should be weak, which resulted in the release of uncrosslinked polymers and the large increase in  $e$ . Therefore, the decrement in the number of crosslinks could increase  $W_t/W_d$  as well as  $e$ . By increasing  $n_{DP}$  above 1000, however, the connectivity between microcrystallites became strong, which suppressed the release of polymer chains, and the release of uncrosslinked polymers in the amorphous region could be relatively enhanced. The decreases in the dangling bonds and the hydrogen bonds and other intermolecular forces by elution above  $n_{DP} = 1000$  were possibly the reasons for the increase in  $W_t/W_d$ . As a result of these different mechanisms, it can be concluded that the changes in  $W_t/W_d$  overlapped at around  $n_{DP} = 1000$ .

### Cracks in gel surfaces during simple swellings

The surfaces of as-prepared PVA cast films were macroscopically smooth, without cracks, scratches, or other signs of damage. According to our original study,<sup>6</sup> it is necessary to use PVA powder with relatively high  $n_{DP}$  and  $r_{DH}$  values to obtain firm gels with a strong amorphous network crosslinked by large microcrystallites. During simple swelling, the PVA cast gels maintained smooth surfaces in the cases of both high  $n_{DP}$  and high  $r_{DH}$ . On the other hand, the gels became weak and they were broken into pieces or dissolved when either  $n_{DP}$  or  $r_{DH}$  was low. Typical examples of the time evolution for PVA300/98.5 and PVA1700/79.5 gels are shown in Figure 2. In the case of PVA300/98.5 (low  $n_{DP}$  and high  $r_{DH}$ ), the gels gradually became opaque, many



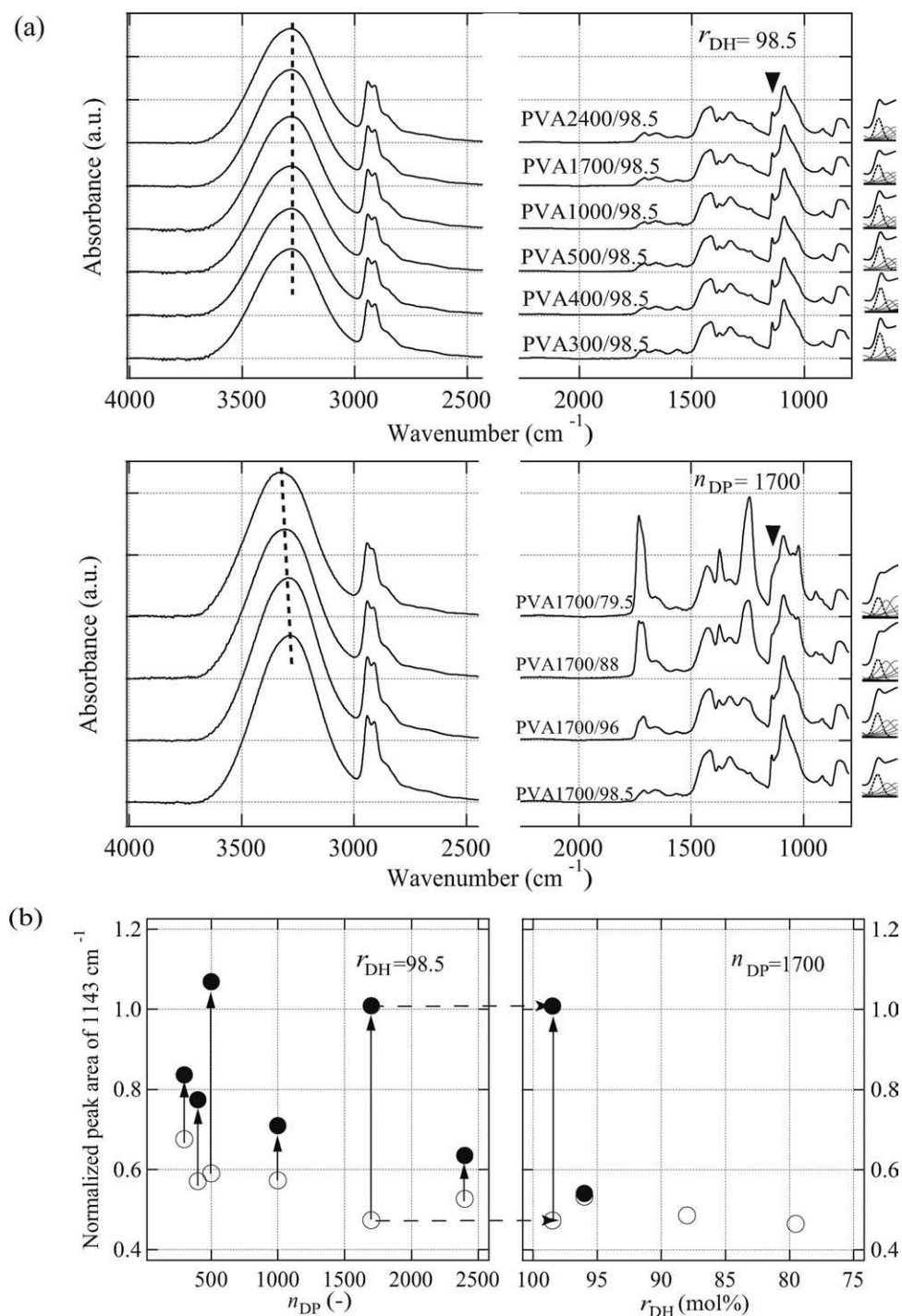
**Figure 2** Time evolution of swelling behavior of (a) PVA300/98.5 and (b) PVA1700/79.5 gels observed by optical microscopy. In the case of a low  $n_{DP}$  (a), the surface was smooth by 10 min, a sharp crack and shallow cracks appeared on the upper left surface at 25 min, and cracks appeared on the whole surface at 60 min. In the case of a low  $r_{DH}$  (b), on the other hand, no cracks could be observed, and the edges of the square sample, which were cut with slopes that appeared black at 0 min, became blurred at 10 min, extended inwardly at 25 min, and finally disappeared.

cracks were found to arise on the surface during simple swelling, and the gel could not keep its shape and broke into pieces because of the destruction of the crosslinks. This phenomenon was not observed for the PVA1700/79.5 gel (high  $n_{DP}$  and low  $r_{DH}$ ), which dissolved from the surface while remaining transparent and finally disappeared [ $e = 100\%$ , see Fig. 1(b)]. These differences could be attributed to the differences in the microstructures of the backbone networks.

### Network microstructure of PVA cast gels

#### Degree of crystallinity

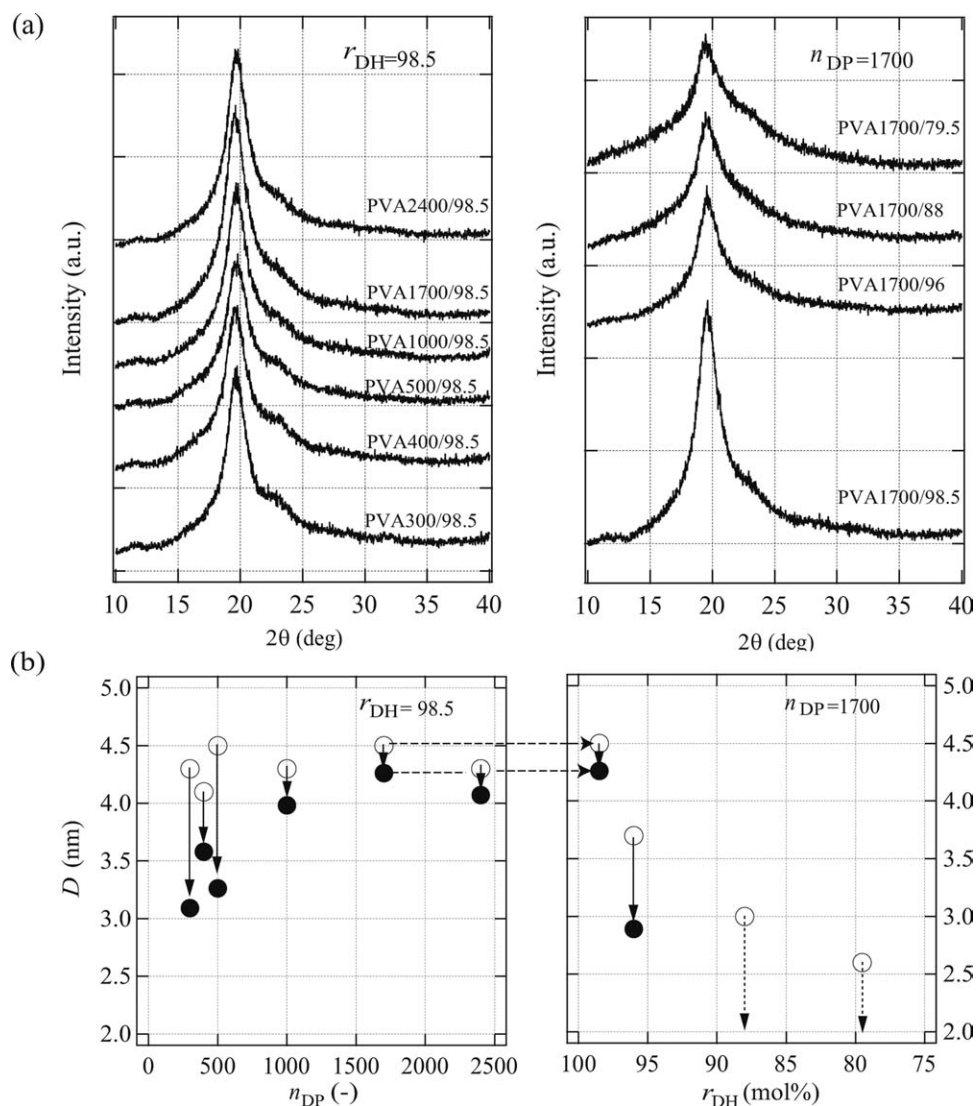
Figure 3(a) shows the ATR FTIR spectra of PVA cast films before elution with different  $n_{DP}$  ( $r_{DH} = 98.5$ ) and different  $r_{DH}$  ( $n_{DP} = 1700$ ). The large and broad peak at around  $3300\text{ cm}^{-1}$  consisted of two peaks



**Figure 3** (a) FTIR spectra of PVA cast gels before elution with different  $n_{DP}$  values ( $r_{DH} = 98.5$ ) and with different  $r_{DH}$  values ( $n_{DP} = 1700$ ), which were normalized based on the C=C bending vibration at  $853 \text{ cm}^{-1}$ . The dotted lines indicate the links of the peaks. The deconvoluted peaks at  $1143 \text{ cm}^{-1}$  are shown in the right margin of the respective spectrum. (b) Peak area at  $1143 \text{ cm}^{-1}$  before (open symbol) and after (closed symbol) elution with different  $n_{DP}$  values ( $r_{DH} = 98.5$ ) and different  $r_{DH}$  values ( $n_{DP} = 1700$ ).

caused by the O—H stretching of the non-hydrogen-bonded (at  $3409 \text{ cm}^{-1}$ ) and hydrogen-bonded O—H groups (at  $3295 \text{ cm}^{-1}$ ).<sup>17</sup> The peak height and peak position did not depend on  $n_{DP}$ , while the peak position shifted slightly but apparently to a higher wavenumber with decreasing  $r_{DH}$ , resulting from

the increase in the free —OH groups. A slight change in C—O stretching at  $1143 \text{ cm}^{-1}$  caused by the formation of microcrallites<sup>16</sup> was observed in the spectra with changing  $n_{DP}$ , while the peak apparently decreased with decreasing  $r_{DH}$  and could not be identified for PVA1700/88 and PVA1700/79.5.



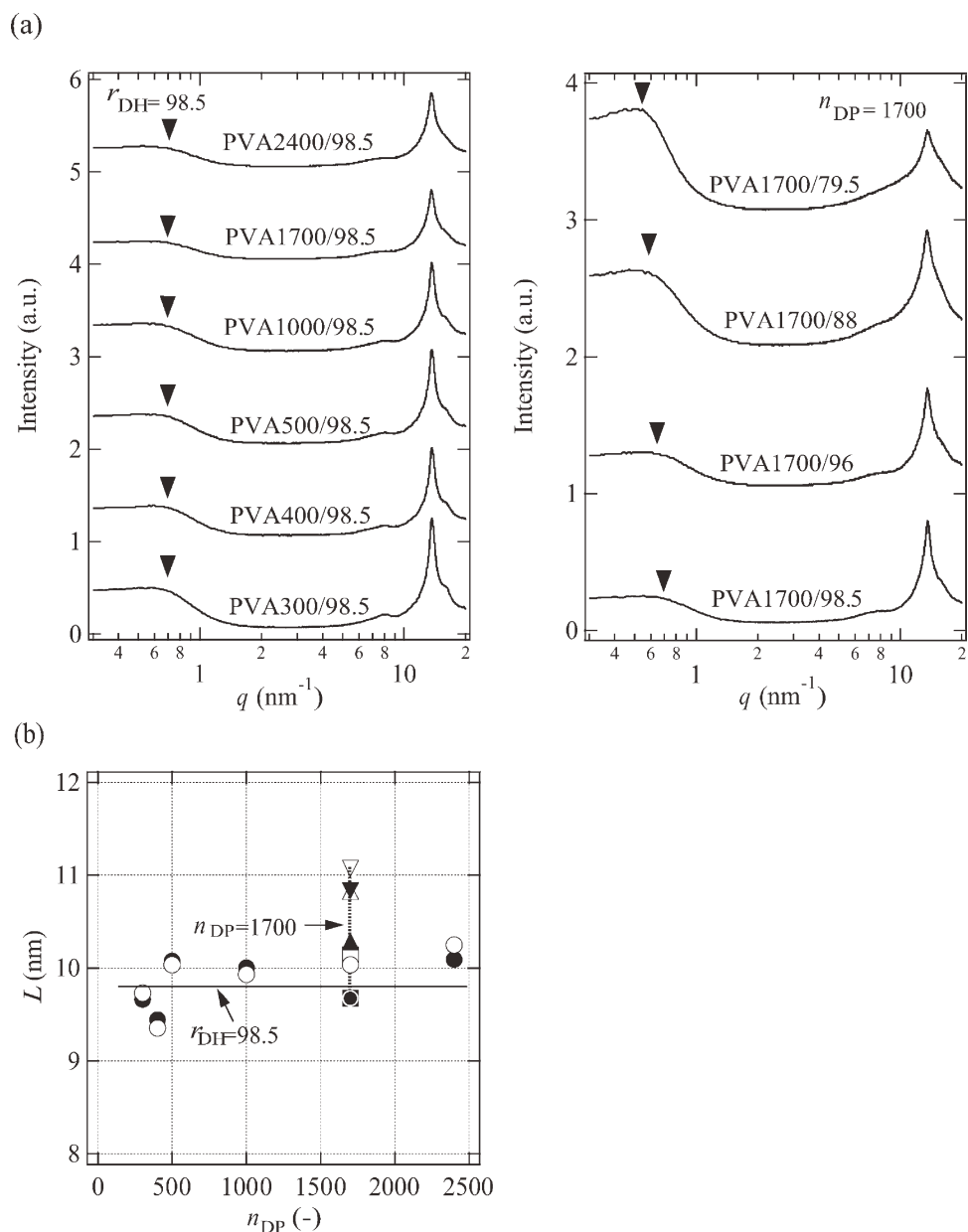
**Figure 4** (a) WAXS profiles of the PVA cast films before elution with different  $n_{DP}$  values ( $r_{DH} = 98.5$ ) and with different  $r_{DH}$  values ( $n_{DP} = 1700$ ). (b) Characteristic size of the microcrystallites ( $D$ ) before (open symbol) and after (closed symbol) elution estimated by the WAXS profiles.

Figure 3(b) shows the normalized peak areas at  $1143\text{ cm}^{-1}$  before and after elution, which were obtained by deconvoluting the spectra to remove the effects of the other peaks. The peak area at  $1143\text{ cm}^{-1}$  before elution decreased slightly with increasing  $n_{DP}$  ( $r_{DH} = 98.5$ ), which is consistent with the literature,<sup>18</sup> while it became almost constant with decreasing  $r_{DH}$  ( $n_{DP} = 1700$ ). These results indicated that the ability to form microcrystallites at gelation depends only on  $n_{DP}$  and not on  $r_{DH}$ , and it increases with decreasing  $n_{DP}$ . The peak area after elution, on the other hand, tended to decrease with increasing  $n_{DP}$  ( $r_{DH} = 98.5$ ) in spite of the relatively larger scattering in the data points, and rapidly decreased with decreasing  $r_{DH}$  ( $n_{DP} = 1700$ ). The increase in the peak area at  $1143\text{ cm}^{-1}$  after elution could be attributed to the polymer elution from the amorphous region. In the case of PVA1700/96, however, the peak area did not change

before and after elution, although  $e$  [ca., 60%, see Fig. 1(a)] was large, which indicated that the destruction and/or elution of microcrystallites are enhanced by decreasing  $r_{DH}$  ( $n_{DP} = 1700$ ).

#### Size of microcrystallites

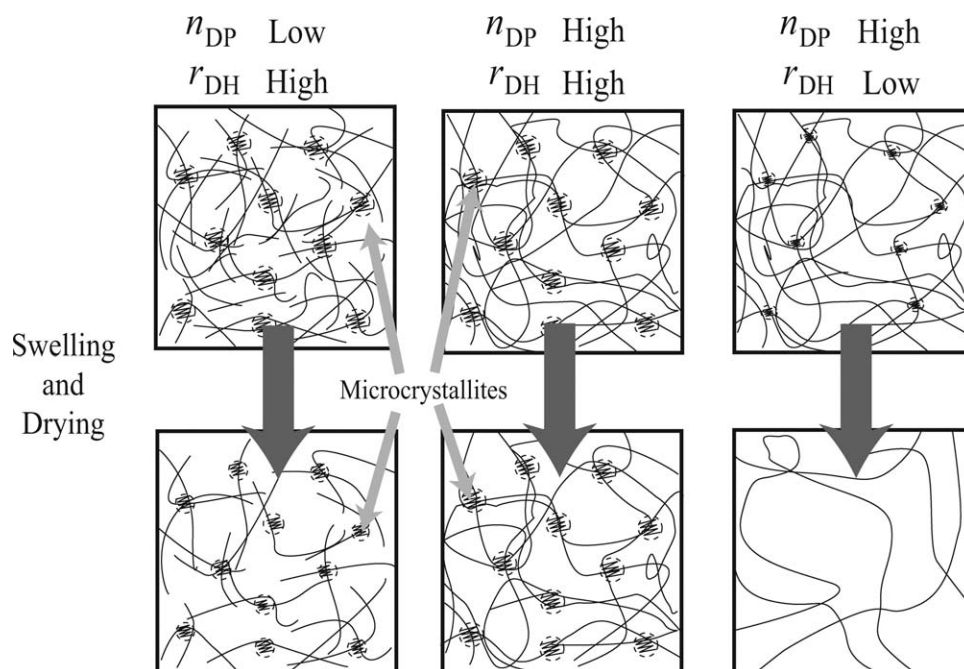
Figure 4(a) shows the WAXS profiles of the PVA cast films before elution with different  $n_{DP}$  ( $r_{DH} = 98.5$ ) and with different  $r_{DH}$  ( $n_{DP} = 1700$ ). The sharp peak at  $2\theta = \text{ca. } 19.7^\circ$ , which corresponded to the reflection<sup>19</sup> ( $d = 4.59\text{ \AA}$ ) caused by the hydrogen bonds between polymers, did not depend on  $n_{DP}$  ( $r_{DH} = 98.5$ ), but it became broader with decreasing  $r_{DH}$  ( $n_{DP} = 1700$ ), indicating that the size of the microcrystallites decreased. To determine the characteristic size of the microcrystallites (crosslinked region),  $D$  was roughly estimated from Figure 4(a)



**Figure 5** (a) SWAXS profiles of the PVA cast films before elution with different  $n_{DP}$  values ( $r_{DH} = 98.5$ ) and with different  $r_{DH}$  values ( $n_{DP} = 1700$ ). (b) Characteristic distance between the microcrystallites ( $L$ ) estimated by the SWAXS profiles (open symbols) and by the SAXS profiles (closed symbols); circle,  $r_{DH} = 98.5$ ; square,  $r_{DH} = 96$ ; triangle,  $r_{DH} = 88$ ; inverted triangle,  $r_{DH} = 79.5$ .

using Scherrer's equation<sup>20</sup>:  $D = k\lambda/(\beta\cos\theta)$ , where  $k = 1$  (the shape of the crystal is assumed to be a sphere);  $\beta$  is the width at the half-maximum intensity of the reflection;  $\theta$  is the Bragg's angle; and  $\lambda = 1.54 \text{ \AA}$  is the wavelength of the X-ray radiation. As is shown in the results [Fig. 4(b)]  $D$  was constant before elution in spite of a different  $n_{DP}$  ( $r_{DH} = 98.5$ ) and decreased with decreasing  $r_{DH}$  ( $n_{DP} = 1700$ ). On the other hand, the  $D$  of the microcrystallites after elution decreased with decreasing  $n_{DP}$ . The change in  $D$  was evident when  $n_{DP} = 300\text{--}500$  ( $r_{DH} = 98.5$ ), corresponding to a rapid increase in the polymer elution [Fig. 1(b)] As described earlier, a shorter

polymer length was associated with a smaller connectivity between the microcrystallites, which resulted in an increase in  $e$  and a decrease in  $D$ . It is noteworthy that the  $D$  of the microcrystallites after elution was larger than 3 nm for the gels with the lowest  $n_{DP}$  in the present experiment (PVA300/98.5). On the other hand, the  $D$  of the microcrystallites after elution was smaller than 3 nm in PVA1700/96 and disappeared in the gels with smaller  $r_{DH}$  (= 88 and 79.5). These observations suggested that the  $D$  of microcrystallites at gelation depended on  $r_{DH}$  and not on  $n_{DP}$ . The growth of the microcrystallites was suppressed much more effectively by a decrease in



**Figure 6** Schematic illustrations of PVA cast gels before and after elution (a) as-prepared dried state and (b) dried state after swelling. Three characteristic types of gels are presented: those with high  $n_{DP}$  and high  $r_{DH}$  values, high  $n_{DP}$  and low  $r_{DH}$  values, and low  $n_{DP}$  and high  $r_{DH}$  values.

$r_{DH}$ . It can also be inferred that the minimum  $D$  needed to maintain the shape of gels during simple swelling is around 3 nm.

It is noteworthy that the  $D$  decreased rapidly with decreasing  $r_{DH}$ . Nevertheless, the normalized peak area at  $1143\text{ cm}^{-1}$  tended to slightly decrease or seems almost constant with decreasing  $r_{DH}$  [Fig. 3(b)] These results indicated that the number of microcrystallites increased rapidly with decreasing  $r_{DH}$ .

#### Distribution of microcrystallites

Figure 5(a) shows the SWAXS profiles of the PVA cast films before elution for different  $n_{DP}$  values ( $r_{DH} = 98.5$ ) and with different  $r_{DH}$  values ( $n_{DP} = 1700$ ). A broad peak was observed in each profile at around  $q = 0.6\text{ nm}^{-1}$ , which corresponded to the characteristic distance between the microcrystallites,  $L$ .<sup>21</sup> The peak top wavenumber was determined by the intersection of two extrapolations of lines before and after the peak top. When  $n_{DP}$  ( $r_{DH} = 98.5$ ) changed, the peak top position did not systematically change, but it shifted to a lower wavenumber with decreasing  $r_{DH}$  ( $n_{DP} = 1700$ ). The  $L$  calculated from the SWAXS profiles is presented in Figure 5(b), where the  $L$  obtained by SAXS measurements is also shown. There is not much difference between the results obtained by two methods. Therefore, the above analysis of the SWAXS profiles was considered reasonable and proper in the present samples. It is clear that  $L$  did not depend on  $n_{DP}$  between 500 and 2400, and increased with decreasing  $r_{DH}$  ( $n_{DP} = 1700$ ).

This evidence indicated that the ability to form the microcrystallites depended on  $r_{DH}$  and not on  $n_{DP}$ : the formation of microcrystallites was suppressed by a decrease in  $r_{DH}$  since the acetoxy groups should disturb the nucleation and growth of microcrystallites. In addition, the water content of the dried gel increased with an increase in  $r_{DH}$  from about 4 to 10%, which was also the reason for the increment in  $L$ .

#### Effects of polymer elution on swelling ratio and microstructure

For the gels with a higher  $r_{DH}$  value ( $=98.5$ ), the microcrystallites were sufficiently strong to persist against the swelling force during simple swelling if  $n_{DP}$  was higher than 1000. With a decrease in  $n_{DP}$  below 1000, the gel weakened, and the swelling ratio increased. Nevertheless, the size of the microcrystallites after elution remained larger than 3 nm, which is, as seen in Figure 4(b), the minimum  $D$  needed to maintain the shape of the gels. The competition between the swelling force of the osmotic pressure and the hydrogen bonds in the microcrystallites induced a local break in the amorphous polymer network between microcrystallites, which resulted in a decrease in transparency, allowing the gel to become opaque over time. An accumulation of local breaks induced cracks on the surface during the swelling process for the PVA300/98.5 gel.

For the gels with a higher  $n_{DP}$  ( $=1700$ ), the  $D$  obtained before elution decreased with decreasing  $r_{DH}$  and became smaller than 3 nm for the



PVA1700/88 and PVA1700/79.5 gels. The microcrystallites were too weak to withstand the swelling force and were destroyed. The destruction of the microcrystallites produced uncrosslinked polymers, which resulted in the dissolutions of polymers from the surface. In this process, the conformational change was on the nanometer scale and the gel remained transparent.

These results indicated that the amorphous region was too weak to maintain the network structure against the swelling force in the case of gels with low  $n_{DP}$  and high  $r_{DH}$  values. This suggested that the effective connections between microcrystallites decreased with decreasing  $n_{DP}$  because the polymer length decreased and became comparable to  $L$ , i.e., the characteristic distance between the microcrystallites. In the case of gels with a higher  $n_{DP}$  ( $= 1700$ ), the nucleation and growth of microcrystallites depended strongly on  $r_{DH}$ . With a decrease in  $r_{DH}$ , the gel became weak because of the destruction of the microcrystallites during the swelling process, and the polymers dissolved without cracks.

To summarize the experimental results, the changes in the nanoscopic network structures before and after elution are schematically summarized in Figure 6. In order to confirm these conclusions, microscopic studies of polymer gel networks of swollen states in water are important subjects for future investigations. To understand the nano-, micro-, and mesoscopic network structure of PVA gels, it is desirable to use several scattering techniques. For example, a small-angle neutron scattering provides valuable information from the contrast in scattering length density that is a complementary technique of SAXS.

Finally, two problems related to the principles of the elution phenomena, as pointed out in Introduction section, should be stressed. The first is that the elution of polymers is an important phenomenon in physically crosslinked gels, which strongly depend on  $n_{DP}$  and  $r_{DH}$  values. The other problem is related to the definition of gels. Although PVA cast gels with both high  $n_{DP}$  and  $r_{DH}$  values are well-established gels because they do not flow in a limited amount of water, PVA gels with either low  $n_{DP}$  or low  $r_{DH}$  values were found to break into pieces or dissolved. Nevertheless, all of the samples used here were referred to as gels. This is because it was difficult to distinguish a structured liquid from an elastic gel in the present experiment. These issues are important and should be re-considered in a future study.

## CONCLUSION

The elution of polymers from physically crosslinked PVA cast gels and their  $n_{DP}$ - and  $r_{DH}$ -dependences

were examined quantitatively using a TOC analyzer. Elution was detected for each of the gels, and depended on both  $n_{DP}$  and  $r_{DH}$  values.

To decrease the polymer elution or increase the strength of a gel it was necessary to use PVA powders with both high  $n_{DP}$  and  $r_{DH}$  values in the preparation of the gel by a cast-drying method. On the other hand, the gels became weak and dissolved when either  $n_{DP}$  or  $r_{DH}$  was low. In the case of a low  $n_{DP}$ , the microcrystallites were firm and the amorphous region was weak, which caused cracks on the surface. In the case of a low  $r_{DH}$ , the microcrystallites were weak and the amorphous region was strong, which caused the dissolution of polymers from backbone networks without cracks. The macroscopic change in  $W_t/W_d$  and the conformation with and without cracks were well explained by the microscopic network structures, characterized by  $D$  and  $L$ .

The authors would like to thank Prof. Eiko Nakamura for her kind assistance with the use of the TOC analyzer and Prof. Masaaki Sugiyama for his kind help with the SAXS experiments, performed under the approval of the Photon Factory Advisory Committee.

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