Structure of poly(vinyl alcohol) hydrogel prepared by repeated freezing and melting

Masanobu Nagura, Tomoki Hamano and Hiroshi Ishikawa
Faculty of Textile Science and Technology, Shinshu University, Ueda, Nagano 386, Japan
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Investigations have been made into the relationship between rubber elasticity, state of water, and fine structure in poly(vinyl alcohol) (PVA) hydrogels prepared by repeated freezing and melting of aqueous solution. The elasticity of the hydrogel increases with increasing hydrogen bond interaction between water and the molecular sheet of the PVA crystallite crosslink points, and between water and the amorphous chain between crosslinks. The effect is not due to an increase in the number and size of the crystallites.

(Keywords: poly(vinyl alcohol); hydrogen bond; crosslink; unfrozen water)

INTRODUCTION

The highly rubber elastic poly(vinyl alcohol) (PVA) hydrogel, which was prepared by repeated freezing and melting[1,2] of an aqueous solution of PVA, did not contain any compound except water, and was biocompatible *in vivo*. Thus this hydrogel could be useful as a biomedical material[3].

According to Nanbu[2], the elastic moduli of PVA hydrogels prepared from concentrated solutions are high and it is interesting to study the reason for such high rubber elasticity. However, this effect has not so far been studied in detail. We have reported in a previous paper[4] that water and PVA molecules interact strongly in such hydrogels particuarly when a large number of freezing cycles (N) is involved, while at the same time the crystallinity of the dried hydrogel decreases. On the other hand, Watase[5] concluded that the elasticity increases in conjunction with increasing crystallinity, since an elevation of the dissolving (i.e. 'melting') temperature was observed for hydrogels prepared from concentrated solutions.

In this paper, investigations have been made into the relationship between the rubber elastic properties, the state of water and the fine structure of PVA hydrogels using pulsed nuclear magnetic resonance (p.n.m.r.), differential scanning calorimetry (d.s.c.) and X-ray measurements.

EXPERIMENTAL

The PVA used, supplied by Kuraray Co. Ltd, was POVAL-120 (degree of polymerization 1700 and saponification 98.5 ± 0.5 mol%). Aqueous solutions of PVA with concentrations of 15, 20, 25 and 30 wt% were prepared in an autoclave, and hydrogels were generated from them by the procedure reported elsewhere[4]. Hydrogels corresponding to freezing cycle number $N = 10$ were used to study concentration effects because the samples had fully stable elasticity[2].

P.n.m.r. measurements were performed using Praxis II-10 instruments at 10.72 MHz. The spin-lattice relaxation time (T_1) was measured using the 90/90 pulse method. D.s.c. thermograms were measured using a Seiko denshi d.s.c. instrument DSC-10 at a heating rate of $5°\mathrm{C\,min^{-1}}$ from $-100°\mathrm{C}$ after cooling.

Wide angle X-ray scattering measurements were performed using a Rigaku Geigerflex 2028 diffractometer with CuKα radiation. Small angle X-ray scattering measurements were performed with point focusing optics[6] installed at the X-ray source from the 2.5 GeV storage ring in the Photon Factory of the National Laboratory for High Energy Physics at Tsukuba. In the present work, the scattering curves ($0.4 \leqslant 2\theta \leqslant 7.9°$) were obtained by superposing two curves which were measured by changing the specimen-to-detector distance.

RESULTS AND DISCUSSION

In general, an increase of elastic modulus of a rubber-like material is due to an increase in the density of crosslinks[7], for example, in this case, the number of crystallites. To study the density of crosslinks in the current hydrogels, it was considered valuable to elucidate a three-dimensional electron density correlation function, because the first peak of the correlation function should correspond to the distance between the centres of the crystalline domains, i.e. as crosslink points. The original scattering data normalized for PVA concentration are shown in *Figure 1*, where one channel was $2\theta = 0.012°$. Since these normalized intensity curves over the whole range of scattering angle decrease with increasing concentration, and since each curve has no special peak, the gels are homogeneous rather than demixed and heterogeneous. Thus the correlation function method can be applied to estimate the separation distance between the crystalline domains in these gels. The correlation function, $\gamma(r)$, was calculated by[8]

$$\gamma(r) = \frac{\displaystyle\int_0^\infty \theta^2 I(\theta)\sin(2\pi\theta r/\lambda)\,\mathrm{d}\theta/\{I_e(\theta)2\pi\theta r/\lambda\}}{\displaystyle\int_0^\infty \theta^2 I(\theta)\,\mathrm{d}\theta/I_e(\theta)} \tag{1}$$

where θ is Bragg's scattering angle, λ is the X-ray

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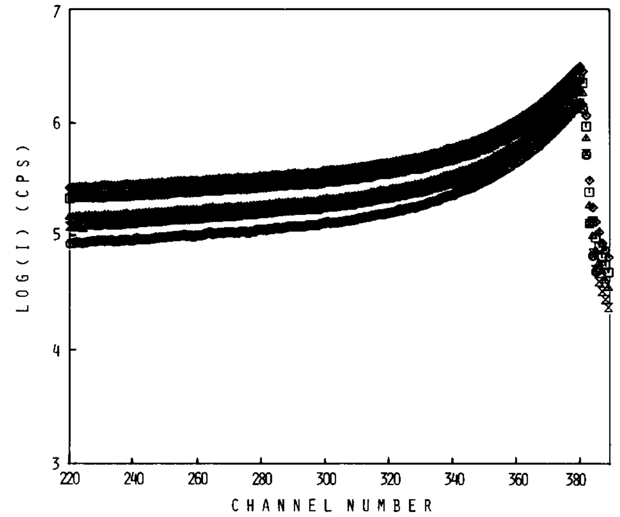

Figure 1 Original data normalized for PVA concentration: ◇, 10; □, 15; △, 20; ⧖, 25; ○, 30 wt%

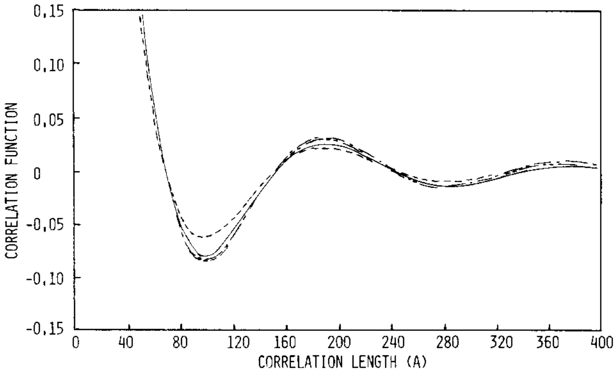

Figure 2 Dependence of three-dimensional electron density correlation function on PVA concentration: - - -, 10; ——, 15; — — —, 25; — — — —, 30 wt%

wavelength (1.42 Å*), and $I(\theta)$ and $I_e(\theta)$ are the scattering intensities from the sample and an electron, respectively. As shown in *Figure 2* there is an obvious first peak at about 190 Å in every curve. This suggests that the number of crystalline domains is constant in spite of the change in concentration. Thus the increase of the elastic modulus is not caused by an increase in the number of the crystallites, i.e. crosslink points.

Wide angle X-ray scattering curves were measured to investigate structural changes in the crystallites present in the hydrogels. Only the (101) reflection peak could be observed overlapping the halo-ring reflected by the water in the hydrogel. *Figure 3* shows the concentration dependence of the reciprocal value of the half width (a width of about 2° in 2θ) of the reflection peak, which is proportional to the crystal size[9]. Since the crystal size is independent of the concentration, the crystallite does not grow in size when the concentration increases, and hence it can also be said that the increase in elastic modulus[2] is not due to an increase in crosslink size.

Figure 4 shows the dependence on concentration of the (101) spacing, which corresponds to the distance between the molecular sheets formed by intermolecular hydrogen bonds[10]. The intersheet distance expands slightly with increasing concentration, but this increase is not large enough to affect the crystal size, as described above. It means, however, that, through crystallization, more water molecules remain in the intersheets of the more concentrated hydrogels than in the gels made at lower concentrations, and/or the molecular sheet is disordered. The latter explanation suggests the formation of weak crystal, however, and hence cannot explain the increase of the elastic modulus. Thus the former explanation can be accepted as more realistic.

Figure 5 shows d.s.c. thermograms for the dissolution of the crystallites in the hydrogel. The endothermic peak temperatures, i.e. the dissolving or 'melting' temperatures

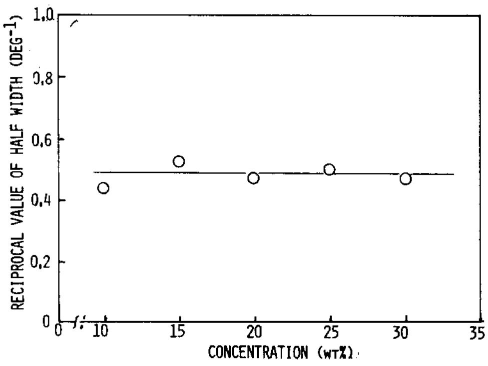

Figure 3 Dependence of reciprocal of half width of (101) reflection on PVA concentration

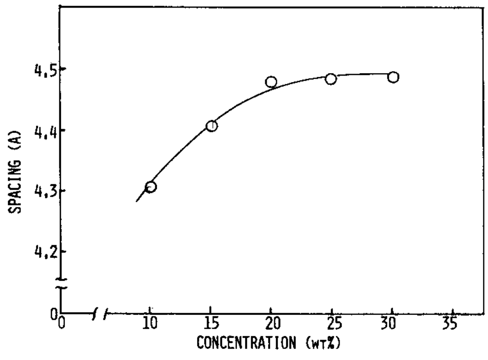

Figure 4 Dependence of (101) spacing on PVA concentration

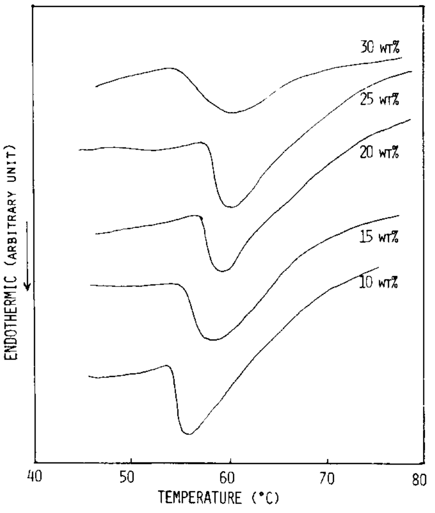

Figure 5 D.s.c. thermograms of dissolution of crystallites in hydrogels

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* 1 Å = 10^{-1} nm

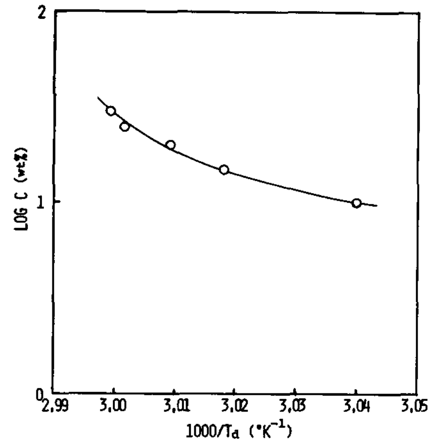

Figure 6 Dependence of logarithm of PVA concentration on reciprocal of absolute gel 'melting' temperature

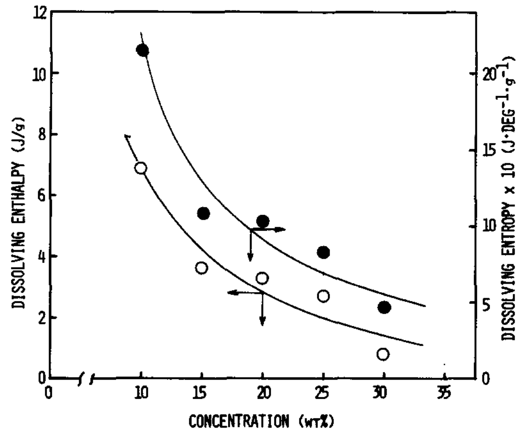

Figure 7 Dependence of concentration of dissolving enthalpy (○) and dissolving entropy (●) on PVA solution concentration

(T_d), increase with increasing concentration. According to Eldridge *et al.*[11], the logarithm of the concentration (log *C*) has a linear relation with the reciprocal absolute 'melting' temperature of gels wholly stabilized by slow gelation. This relation was deduced theoretically by assuming an increase in the degree of crosslinking with increasing polymer concentration, and from the slope of this plot an enthalpy for the formation of crosslinks can be estimated. As shown in *Figure 6*, a log *C* against reciprocal of absolute temperature plot (Eldridge–Ferry plot) conforms roughly to Eldridge's result, though there is a clear deviation from linearity. This indicates an increase in the crosslinking with concentration. As mentioned above, however, the size and number of the crystallite crosslinks are independent of concentration. Thus it may be assumed that the increase in the gel 'melting' temperature is not related to the crystallite crosslink points, but is rather due to the formation of another intermolecular association, i.e. other crosslinking mechanisms.

To clarify the nature of this other intermolecular association, the concentration dependence of the 'melting' enthalpy, ΔH, calculated directly from the endothermic peak area, and the 'melting' entropy (ΔS), calculated by

$$\Delta S = \Delta H / T_d \qquad (2)$$

were investigated as shown in *Figure 7*. Both ΔH and ΔS decrease with increasing concentration. In general, during the dissolution of a crystal in a solvent, the solvent first permeates into the crystal, and then the solute molecules forming the crystal disperse into the solvent. Thus ΔH and ΔS are the total of the enthalpy and entropy for permeation and dispersion, respectively. If water molecules remain in the crystallites of the more concentrated hydrogels, the enthalpy and entropy for permeation will be small, while those for dispersion will not change. Thus the total dissolving enthalpy and entropy of the hydrogel decrease with increasing concentration, as shown in *Figure 6*. In other words, these results support the view that water molecules exist in the intersheets of the crystallites of the hydrogel.

Next, we will study the state of water in the hydrogels. There are three states of water absorbed in a hydrophilic material: usual or free water, and bound and bonded states[12]. One can observe the separate melting of free and bound water, which appear, respectively, as a sharp peak at 0°C and as a broad peak or a shoulder on the sharp peak below 0°C, but one cannot observe that of water bonded to the polymer molecule, i.e. the unfrozen water. Since the water remaining in the intersheet is probably tightly bonded to the PVA molecules in the crystallite, it is worth studying the unfrozen water. When the water content is measured as a function of the heat of fusion (ΔH) for the melting of water, the content of unfrozen water is defined as the water content at $\Delta H = 0$. In *Figure 8* the content of unfrozen water is presented as a function of concentration, and shows the largest value for the hydrogel prepared from the most concentrated solution. The intersheet distance expands with increasing PVA concentration, as described above, and the content of the unfrozen water increases in proportion to the intersheet distance. Thus part of the unfrozen water arises from the water molecules existing in the intersheet. When the hydrogels are repeatedly treated to freezing and melting, the unfrozen water becomes stable, and hydrogen bonds strongly to the OH groups of PVA molecules in the molecular sheets. This results in an increase in the elastic moduli of the hydrogels.

Figure 9 shows the dependence on *N* of the spin-lattice relaxation time for five concentrations. For each concentration, T_1 decreases with increasing *N* and becomes constant above $N = 6$. For whole values of *N*, T_1 decreases with increasing concentration. It is already known that T_1 is ≈ 2000 ms for pure water[13], and decreases with increasing interactions by hydrogen bonds between water and polymer molecules[14]. Thus the above result means that water molecules in the hydrogels are bound more strongly to the PVA molecules, as *N* and the concentration increase. From *Figure 8*, it is clear

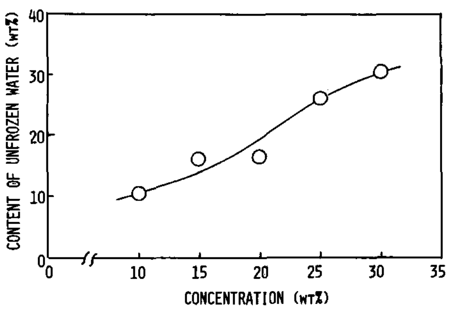

Figure 8 Dependence of the content of unfrozen water on PVA concentration

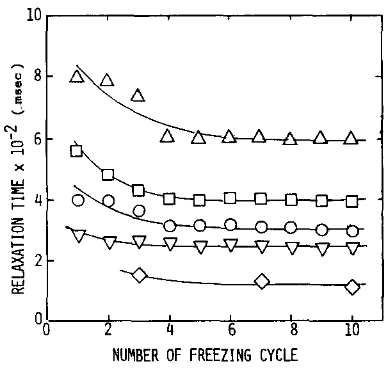

Figure 9 Dependence of spin-lattice relaxation time on freezing cycle: △, 10; □, 15; ○, 20; ▽, 25; ◇, 30 wt%

that both bound water and unfrozen water increase with increasing PVA concentration. Since part of the unfrozen water exists in the crystalline region described above, this bound and unfrozen water probably interacts with the amorphous chains between the crosslink points, through hydrogen bonds, and probably also contributes to the increase in elastic modulus.

CONCLUSIONS

Hydrogen bonds between bound and unfrozen water and PVA molecules are the main cause of the increase in elastic modulus and the roughly linear Eldridge–Ferry plot of the gels studied here. Increases in the size and number of the crystallites which constitute the crosslink points are not the origins of this effect.

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