Structure and mechanical properties of poly(vinyl alcohol) gels swollen by various solvents

Toshikazu Takigawa, Hisahiko Kashihara, Kenji Urayama and Toshiro Masuda*
Research Center for Biomedical Engineering, Kyoto University, Shogoin, Sakyo-ku, Kyoto 606, Japan
(Received 15 March 1991; revised 20 June 1991; accepted 8 August 1991)

The swelling and mechanical properties of poly(vinyl alcohol) (PVA) hydrogel, and PVA gels obtained by swelling precursors in various solvents were investigated. On the basis of the experimental results, the structure of the gels in various solvents was estimated. PVA gels have a uniform structure with flexible PVA chains in a mixed solvent of dimethyl sulphoxide (DMSO) and water. On the other hand, those swollen in methanol, ethanol and formamide have a two-phase structure, which is composed of PVA-rich and solvent-rich phases. The PVA chains in the PVA-rich phase are crosslinked by hydrogen bonding.

(Keywords: poly(vinyl alcohol); gel; structure; swelling; mechanical properties)

INTRODUCTION

Poly(vinyl alcohol) (PVA) hydrogels are good biomaterials, and studies on their preparation and mechanical properties have been carried out by many researchers$^{1-4}$. According to the preparation method developed by Hyon *et al.*[3], currently the best way to obtain highly transparent and strong PVA hydrogels, hydrogels are prepared in several steps where precursor gels are formed, as shown in the next section. In a previous paper[5], we reported the mechanical properties of PVA hydrogels, which are the final products obtained through the preparation method. That work suggested that swelling and mechanical properties of PVA hydrogels are affected only by annealing temperature in the course of the hydrogel preparation process. It was somewhat surprising that the initial PVA concentration did not affect the swelling and mechanical properties of the hydrogels. In order to understand the experimental results, it is necessary to clarify the relationship of structure, swelling and mechanical properties in the precursor gels as well as the hydrogels. This kind of understanding should also be important for designing PVA hydrogels with suitable mechanical properties for medical use. In this study, we examined swelling and mechanical properties of PVA hydrogel and PVA gels obtained by swelling precursors in various solvents. A proposal for the structure of these materials is made, based on the swelling and mechanical behaviour of the gels.

EXPERIMENTAL

Samples

PVA used in this study was supplied by Unitika Co., Japan. The preparation process of PVA hydrogel is schematically shown in *Figure 1*, which also contains the sample codes used for the PVA hydrogel and PVA gels obtained by swelling precursors in various solvents. The sample, PVA GEL (DMSO/W), was prepared by dissolving PVA in a mixture of water and dimethyl sulphoxide (DMSO) (1:4 by weight) at 105°C, and then maintaining the sample at −20°C for 24 h. The polymer concentration at which PVA was initially dissolved into the solvent was designated by c_0. PVA GEL (W), PVA GEL (MeOH) and PVA GEL (EtOH) were obtained from PVA GEL (DMSO/W) by exchanging the mixed solvent with water, methanol and ethanol, respectively. PVA GEL, W and PVA GEL, Solv. were also prepared, respectively, from PVA GEL (EtOH) by drying in a vacuum oven at 30°C and then swelling in water and the organic solvents. The solvent used and the solubility parameter (δ) obtained from the literature[6], are listed in *Table 1*. In order to prepare PVA HYDROGEL, PVA GEL (EtOH) was dried in a vacuum oven at 30°C, and then annealed in an oil bath. The annealing temperature (T_a) was 125°C. The PVA HYDROGEL was finally obtained by swelling the annealed gel in water.

Swelling

Swelling experiments were carried out at room temperature. The degree of swelling of the gels was measured by weight, and expressed in weight per cent using either PVA content (W_p) or solvent content (W_s), which is equal to $100 - W_p$.

Measurements

The stress–strain curves of PVA gel samples were measured at room temperature (23–25°C) in solvent using an Orientec RTM250 Tensile Tester with a specially designed bath. Mechanical behaviour of PVA gels was described by using stress (σ) and strain (ε), defined as

---

* To whom correspondence should be addressed

0032-3861/92/112334-06

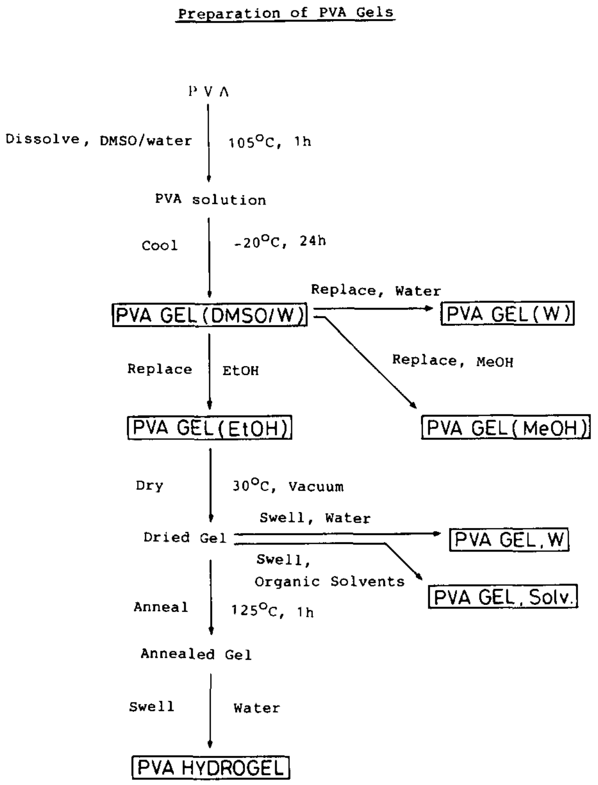

Figure 1 Schematic representation of the preparation of PVA hydrogels. Precursor gels at each stage are also shown

Table 1 Solubility parameters of solvents used for swelling dried PVA GEL (EtOH)

Solvent	δ ((cal cm^{-3})$^{1/2}$)
Water	23.4
Formamide	19.2
Methanol	14.5
Ethanol	12.7
Butylolactone	12.6
Diethylene glycol	12.1
2-Propanol	11.5
2-Methyl-1-propanol	10.5
2-Methyl-2,4-pentanediol	9.7

follows[7]:

$$\sigma = \sigma_E \lambda \quad (1)$$

$$\varepsilon = \ln \lambda \quad (2)$$

where λ is the extension ratio, and σ_E the engineering stress. In obtaining equation (1), we assumed that the volume of a gel was unchanged before and after deformation for all gels examined in this study.

RESULTS

Figure 2 shows the double logarithmic plots of σ *versus* ε of PVA GEL (DMSO/W). In the low ε region, each curve can be approximated by a line with the slope of unity. The curves start to deviate upwards from the straight line at an intermediate ε. The initial Young's modulus E_0 for each gel can be obtained from the low ε region in *Figure 2*. The value of E_0 increases with increasing W_p of the gels.

In *Figure 3*, similar plots for PVA GEL (W), PVA GEL (MeOH), and PVA GEL (EtOH) are shown. The

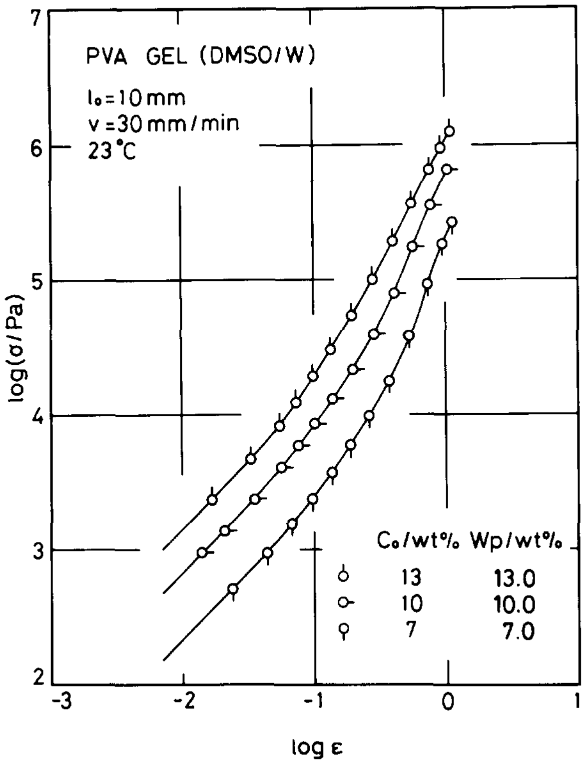

Figure 2 Double logarithmic plots of stress (σ) against strain (ε) for PVA GEL (DMSO/W)

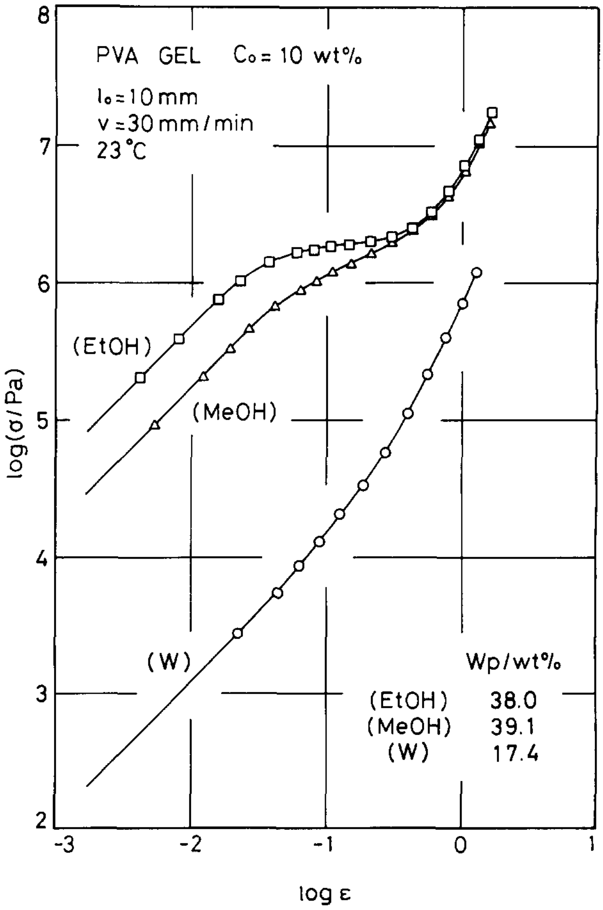

Figure 3 Double logarithmic plots of stress (σ) against strain (ε) for PVA GEL (EtOH), PVA GEL (MeOH) and PVA GEL (W)

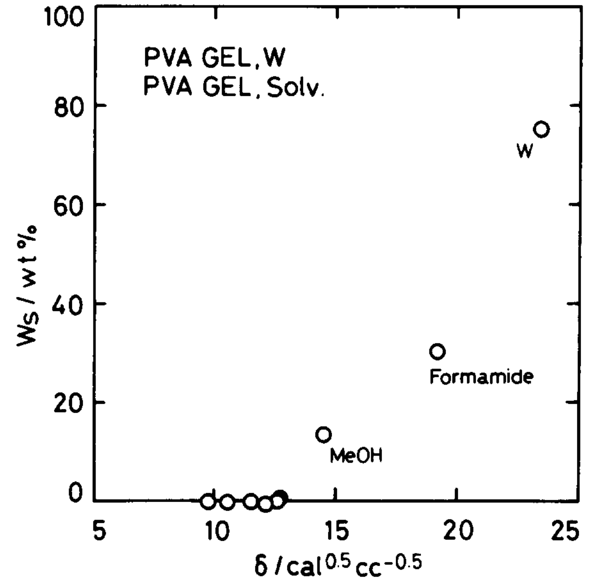

Figure 4 Solvent content (W_s) plotted against solubility parameter (δ) for PVA GEL. W and PVA GEL, Solv

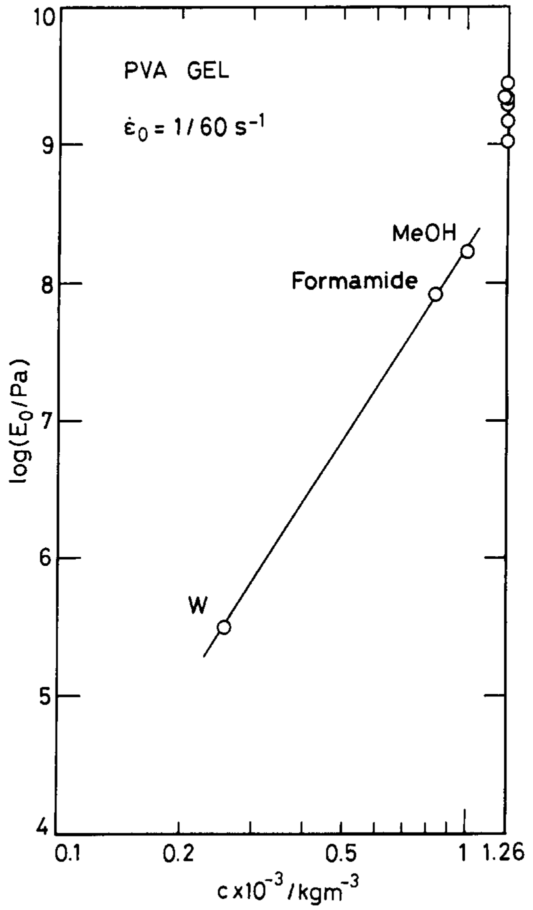

Figure 5 Double logarithmic plots of Young's modulus (E_0) against polymer concentration (c) for PVA GEL, W and PVA GEL, Solv

value of W_p is also shown in the figure. For these gels, c_0 was fixed at 10 wt%. The value W_p of PVA GEL (W) was 17.4 wt%; W_p increased by the exchange of DMSO/W with water. W_p was also increased by organic solvent exchange as shown for PVA GEL (MeOH) and PVA GEL (EtOH), which were a little opaque. The W_p values for the gels are high compared with that for PVA GEL (W), but there is no difference between W_p values of PVA GEL (MeOH) and PVA GEL (EtOH). The stress–strain curve of PVA GEL (W) is very similar to that of PVA GEL (DMSO/W) (*Figure 2*). The curves for PVA GEL (MeOH) and PVA GEL (EtOH) can be approximated by a line with the slope of unity in the low ε region, but shoulders are observed in the middle ε region.

The solvent contents (W_s) of the gels prepared by drying PVA GEL (EtOH) and then immersing them in various solvents listed in *Table 1*, are plotted in *Figure 4* as a function of δ of the solvent. The initial polymer concentration c_0 of the specimens was 10 wt% in all cases. These gels are designated by PVA GEL, W and PVA GEL, Solv. Here, W stands for water, and Solv. refers to each of the organic solvents used for swelling; for example, MeOH (methanol), EtOH (ethanol), etc. As can be seen from this figure, the solvents, except water, formamide and methanol, do not swell the dried gel. The value of W_s increases with increasing δ for methanol, formamide and water.

Figure 5 shows plots of E_0 against polymer concentration (c) for PVA GEL, W and PVA GEL, Solv. The values of E_0 for gels swollen in water, formamide and methanol fall on a line with a slope of 4.7. The value E_0 for the non-swollen PVA gels in the solvents with $\delta \leqslant 12.7$ $(\mathrm{cal\,cm^{-3}})^{1/2}$ shows upward deviation from the line.

Figure 6 shows double logarithmic plots of σ *versus* ε of PVA HYDROGEL of $c_0 = 10\%$ and $T_a = 125°\mathrm{C}$. The curve in the low ε region can be approximated by a line with the slope of unity. A shoulder is observed around $\log \varepsilon = -1$.

DISCUSSION

PVA GEL (DMSO/W)

As reported by Naito[8], water and DMSO act as solvents for PVA, and DMSO is a better solvent than water. The solubility of PVA in a mixture of DMSO and water depends on the composition. PVA precipitates in mixtures with DMSO content of 40–70 vol% at 30°C[8]. However, it has also been reported[8] that mixtures of

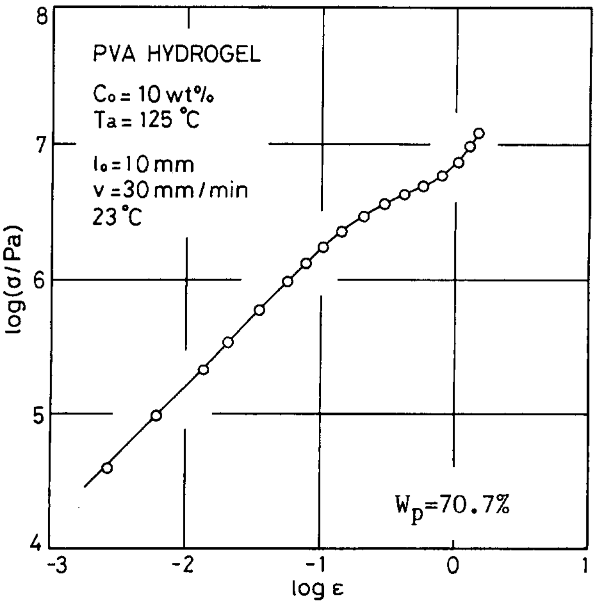

Figure 6 Double logarithmic plots of stress (σ) *versus* strain (ε) for PVA HYDROGEL with $c_0 = 10$ wt% and $T_a = 125°\mathrm{C}$

DMSO and water with DMSO content higher than 70 vol% can dissolve PVA and do not precipitate. The solvent we used in this study contains DMSO 78 vol%, suggesting that the mixture is a solvent for PVA. This means that the network structure is homogeneous and the polymer chain strands between crosslink points are flexible. We have also observed[9,10] that PVA clusters shrink due to the formation of intramolecular hydrogen bonding in DMSO/water dilute solutions of PVA, prepared by the same process as the PVA GEL (DMSO/W).

We have already reported[5] that PVA hydrogels show a shoulder on the log σ–log ε curve, and that the shoulder is closely related to a breakdown process of the microcrystalline domains which behave as crosslink points. However, the plots in *Figure 2* do not show the shoulder. This result implies that domains, which are smaller in size, act as crosslink points in PVA GEL (DMSO/W). The domains are composed of a few polymer chains, while the microcrystalline domains in PVA HYDROGEL comprise more chains. When strain is applied to the systems, stress concentrates on the microcrystalline domains in PVA HYDROGEL and the microcrystalline domains break down at a critical strain, showing a shoulder on the log σ–log ε curve. In the case of PVA GEL (DMSO/W), the crosslink domains, on the contrary, are small and uniformly dispersed in the gel, and the chains between the domains are flexible. Stress concentrations do not occur easily and the gel behaves like a crosslinked rubber, implying that no shoulder on log σ–log ε curve is observed.

In concentrated solutions of PVA, where entanglements of PVA chains are already formed uniformly, intermolecular hydrogen bonding rather than intramolecular hydrogen bonding will occur when they are cooled. Crosslinks, due to hydrogen bonding between PVA chains, start to form upon cooling to $-20°C$. The crosslink points can be considered to occur from entanglement points occurring in solution before cooling[1]. A sequence of hydrogen bonds, which are formed at the entanglement points when the solution is kept at $-20°C$ and the temperature is then raised, can be referred to as a zipper-like domain[11]. The domains caused by this molecular association act as crosslinks in PVA GEL (DMSO/W). In a thermodynamical sense, the zipper-like domains might be regarded as microcrystalline domains because they have a melting point dependent on the length.

PVA GEL (W), PVA GEL (MeOH) and PVA GEL (EtOH)

As mentioned previously, W_p of PVA GEL (W) is higher than that of PVA GEL (DMSO/W), suggesting that PVA GEL (W) shrunk during the solvent exchange process. The shrinkage may be because water is a slightly poorer solvent than DMSO/W. However, since the plots of log σ *versus* log ε for PVA GEL (W) (*Figure 3*) are very similar in shape to that of PVA GEL (DMSO/W) (*Figure 2*), the structure of the gel is considered to be almost identical to that of PVA GEL (DMSO/W).

The W_p values for PVA GEL (MeOH) and PVA GEL (EtOH) are high compared with that for PVA GEL (W). This is because methanol and ethanol are poor solvents for PVA. As mentioned previously, PVA GEL (EtOH) and PVA GEL (MeOH) were slightly opaque, suggesting that phase separation occurs in the gels. The experimental results on the mechanical properties also suggest a phase-separated structure for the gels. The log σ–log ε curves of the gels showed a shoulder. The shoulder might be attributed to the formation of large microcrystalline domains or aggregation of microcrystallites, both of which make the gels turbid, during solvent exchange. Such crystalline domains cannot be dissolved even though the gels are again immersed in water. We can therefore expect the gels to show a shoulder on the log σ–log ε curve as for PVA HYDROGEL. On the other hand, PVA GEL (W), which is prepared through PVA GEL (EtOH), does not show a shoulder. Therefore, we can conclude that PVA GEL (EtOH) and PVA GEL (MeOH) have a two-phase structure. In the course of solvent exchange, the gel size decreases due to the decrease of solvent power in the gels. The decrease of solvent power also causes phase separation, which brings a heterogeneity into the gels; it occurs first in the surface area, and then the two-phase area diffuses to the central part of the gel. The gels became turbid during the first few days of immersion, but the turbidity was unchanged during a further 2 weeks. The degree of shrinkage of the gels shows a constant value after about 1 week, and a phase-separated structure composed of the PVA-rich phase and solvent-rich phase is formed in the gels. The crosslink domains formed initially by the molecular association in PVA GEL (DMSO/W) might grow. Most PVA chains exist in the PVA-rich phase where hydrogen bonding between PVA chains also exists. The degree of shrinkage of the gels might be controlled by the type of solvent used for solvent exchange from the mixed solvent. However, W_p of PVA GEL (MeOH) and PVA GEL (EtOH) is almost identical (39.1 and 38.0 wt%, respectively, as shown in *Figure 3*). The reason might be that both solvents are very poor, and precipitation and shrinkage of PVA occur too rapidly to reach the equilibrium state.

As can be seen from *Figure 3*, PVA GEL (EtOH) and PVA GEL (MeOH) show high E_0 values compared with PVA GEL (W) having a homogeneous structure. The value of E_0 of PVA GEL (EtOH) is higher than that of PVA GEL (MeOH). The values of E_0 of PVA GEL (MeOH) and PVA GEL (EtOH) with two-phase structures are affected by various factors such as morphology, composition of PVA- and solvent-rich phases, as well as PVA content in PVA-rich phase. The morphology of PVA GEL (MeOH) and PVA GEL (EtOH) seems to be almost identical, because both gels form a bicontinuous structure composed of the PVA- and solvent-rich phases. The difference of E_0 of the gels with two-phase structure is determined by the combination of PVA content in the PVA-rich phase and the composition of the two phases. The higher the concentration in the PVA-rich phase becomes, the lower the composition of PVA-rich phase when W_p is kept constant, as in the case of PVA GEL (MeOH) and PVA GEL (EtOH). The higher value of E_0 of PVA GEL (EtOH) shows that the effect of concentration of PVA in the PVA-rich phase is more dominant than the effect of composition. The E_0 value of the PVA-rich phase is affected by the glass transition temperature (T_g) of the PVA-rich phase or the crosslink density due to hydrogen bonds in the phase. T_g of PVA has been reported[6] to be 85°C, but T_g of the PVA-rich phase is dependent on c: T_g decreases with decreasing PVA concentration. T_g will be a determining factor of E_0 when T_g of the PVA-rich phase of both or one of the gels is higher than room temperature. On the other hand, the crosslink density is a determining factor of E_0 when T_g of the PVA-rich phase of both gels is below room temperature. Although we cannot clarify at present which determines E_0 of the PVA-rich phase for the gels, the crosslink density as well as T_g increases with increasing PVA concentration. Independently of which is the determining factor, it may be considered that the flexibility of chains decreases with increasing PVA concentration, and the flexibility determines E_0. The higher PVA concentration in the PVA-rich phase for PVA GEL (EtOH) compared with PVA GEL (MeOH) is because ethanol is a poorer solvent than methanol, as can be seen from the data shown in *Figure 4*. The shoulders on the stress–strain curves for PVA GEL (EtOH) and PVA GEL (MeOH), shown in *Figure 3*, appear to be related to the breakdown process of the PVA-rich phase.

PVA GEL, W and PVA GEL, Solv.

We examined the swelling behaviour of dried gels in various solvents. The solubility of a polymer with solubility parameter δ_p in a solvent (δ) should be determined by $|\delta - \delta_p|$. In the particular case in which a single polymer is considered, δ_p is constant and the solubility might be a function of δ of solvents. W_s of the swollen gel was analysed as a function of δ. Although the difference of W_s of PVA–solvent systems cannot be completely described by δ because of hydrogen bonding interactions in the systems, δ of solvents will be a crude measure of the extent to which the dried gel absorbs the solvent. A similar case was treated by Dror *et al.*[12] for polyurethane–solvent systems. Since PVA GEL, Solv. (Solv. refers to the organic solvent with $\delta \leqslant 12.7$ $(\text{cal cm}^{-3})^{1/2}$ in *Table 1*) was not swollen in the solvent, it is in a glassy state showing high E_0. PVA GEL, W, PVA GEL, Formamide, and PVA GEL, MeOH were swollen in each solvent. The value of W_p of PVA GEL, W was slightly higher than that of PVA GEL (W), while PVA GEL, MeOH shows much higher W_p than PVA GEL (MeOH). For the ethanol system, PVA GEL, EtOH does not swell, while PVA GEL (EtOH) contains 62 wt% of the solvent. These results suggest that the drying process from PVA GEL (EtOH), through which PVA GEL, W and PVA GEL, Solv. are prepared, is an important factor for determining W_p of the systems. As stated previously, PVA GEL (EtOH) has a two-phase structure. When PVA GEL (EtOH) is dried, the gel size decreases with increasing time of drying. In this process, however, the phase-separated structure composed of PVA-rich phase and solvent-rich phase, is maintained to a critical polymer concentration where gels become homogeneous. At concentrations higher than the critical concentration, the two phases tend to mix with each other thermodynamically, but the existence of hydrogen bonding between PVA chains prevents them from mixing. As mentioned previously, hydrogen bonding is formed in the PVA-rich phase in PVA GEL (EtOH), and the formation of hydrogen bonding is also enhanced during drying. Hence, it is expected that the degree of phase mixing is very low in the dried gel. This implies that the structure of the dried gel is microporous. PVA GEL, W and PVA GEL, MeOH are prepared by immersing the dried gel into each of the solvents. The W_p of the gel is chiefly determined by the extent to which crosslinks formed by molecular association as well as hydrogen bonds are broken by swelling; in other words, the degree of breakage depends on the solvent type used. As can be seen from *Figures 3*, *4* and *5*, the small difference in W_p and E_0 between PVA GEL, (W) and PVA GEL, W shows that the structure of these gels is almost identical, suggesting that hydrogen bonds which occur in the solvent exchange process and the drying process, can easily be eliminated by swelling in water, while the crosslinks are maintained. This is because hydrogen bonding between two PVA chains occurring in the solvent exchange and drying stages is weak compared with the crosslinks formed by the molecular association in PVA GEL (DMSO/W).

When methanol is used as a swelling solvent, the solvent can break only a small amount of the hydrogen bonds, the formation of which is enhanced further by the drying process, resulting in the large difference in W_p between PVA GEL (MeOH) and PVA GEL, MeOH. PVA GEL, MeOH contains most of the solvent in a porous structure. The structure of PVA GEL, MeOH can be considered to be almost identical to that of PVA GEL (MeOH); both have a phase-separated structure. Formamide is a better solvent than methanol for PVA, but similar structure can also be considered for PVA GEL, Formamide, because E_0 of the gel is comparable with that of PVA GEL (EtOH) with almost the same W_p. On the other hand, as ethanol is a poorer solvent than methanol for PVA, ethanol cannot be absorbed by the dry gel.

Dynamic Young's modulus (E') for the PVA GEL (DMSO/W) system[13] is proportional to $c^{2.4}$ in the region of c higher than about 75 kg m^{-3}. In this system the structure of the gel is unchanged even when c varies. The c dependence of E' of PVA GEL (DMSO/W) was influenced only by the network density. On the other hand, the c dependence of E_0 for the system composed of PVA GEL, W, PVA GEL, Formamide and PVA GEL, MeOH, shown in *Figure 5*, is stronger than that for the PVA GEL (DMSO/W) system. The reason for the strong concentration dependence is that the concentration dependence of E_0 in the first is affected by various factors: the difference of the phase structure, PVA concentration in PVA-rich phase, and so on.

PVA HYDROGEL

We have shown[5] that when PVA HYDROGEL experiences an annealing process, crystallinity increases with increasing T_a. The shoulder on $\log \sigma$–$\log \varepsilon$ plots in *Figure 6* is related to a breakdown process of the microcrystalline domains[5]. As can be seen from *Figures 2* and *6*, E_0 of the gel is lower than those of PVA GEL (EtOH) and PVA GEL (MeOH) in spite of high W_p. This suggests that the flexibility of chains in PVA HYDROGEL is higher compared with those of PVA GEL (MeOH) and PVA GEL (EtOH). The structure of the gel is considered to consist of microcrystalline domains and flexible PVA chains, though most of the chains are restricted by the microcrystalline domains.

Structure of PVA gels

Based on the experimental results, we can estimate the structure of PVA gels. A scheme of the proposed structure for each gel is shown in *Figure 7*. From PVA solutions with c_0 greater than the gelation threshold (c_G), PVA GEL (DMSO/W) with small crosslink domains and flexible chains is formed. PVA GEL (W) has almost the

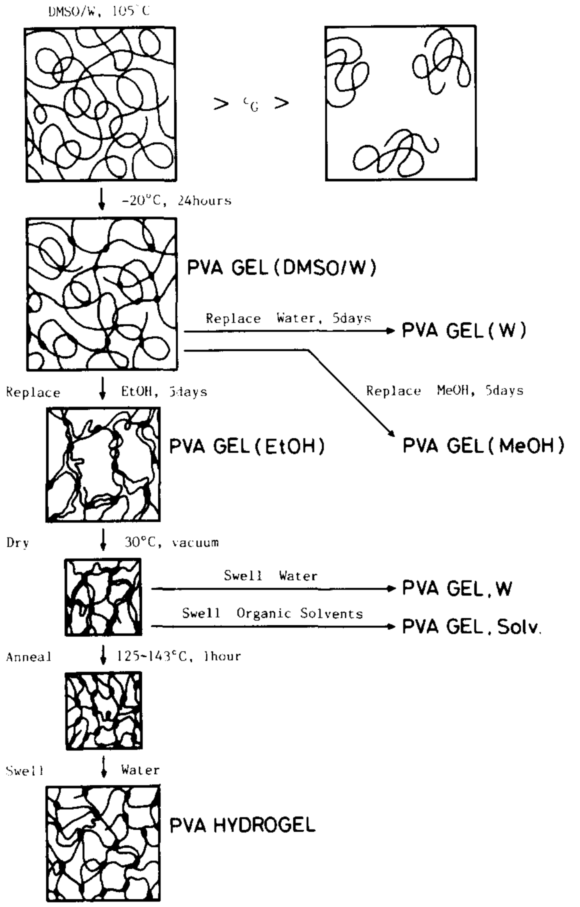

Figure 7 Schematic representation of structure of various PVA gels

same structure as PVA GEL (DMSO/W). On the other hand, PVA GEL (EtOH) and PVA GEL (MeOH) have a two-phase structure composed of PVA-rich and solvent-rich phases. The size of the gels is smaller than for PVA GEL (DMSO/W). The dried gel obtained from PVA GEL (EtOH) shows a similar structure to PVA GEL (EtOH) and PVA GEL (MeOH), but the size is much reduced. PVA GEL, W, which is prepared from the dried PVA GEL (EtOH), has a similar structure to PVA GEL (W). PVA GEL, MeOH and PVA GEL, FORMAMIDE have almost the same structure as PVA GEL (EtOH). After annealing the dried gel at high temperatures (T_a), the gels have a structure consisting of a flexible chain region and microcrystalline domains, because microporous structure is diminished and crystallinity increases by annealing. The crystallinity increases with increasing annealing temperature. PVA HYDROGEL, formed by immersing the annealed gel into water, has microcrystalline domains and flexible chains.

REFERENCES

1 Nambu, M. *Kobunshi Ronbunshu* 1990, **47**, 659
2 Hyon, S.-H., Cha, W.-I. and Ikada, Y. *Kobunshi Ronbunshu* 1989, **46**, 673
3 Hyon, S.-H., Cha, W.-I. and Ikada, Y. *Polym. Bull.* 1989, **22**, 119
4 Watase, M. and Nishinari, K. *Polym. J.* 1989, **21**, 567
5 Takigawa, T., Kashihara, H. and Masuda, T. *Polym. Bull.* 1990, **24**, 613
6 'Polymer Handbook' (Eds J. Brandrup and E. H. Immergut), Interscience, New York, 1966
7 Kamei, E. and Onogi, S. *Appl. Polym. Symp.* 1975, **27**, 19
8 Naito, R. *Kobunshikagaku* 1958, **15**, 597
9 Takigawa, T., Urayama, K. and Masuda, T. *Chem. Phys. Lett.* 1990, **174**, 259
10 Takigawa, T., Urayama, K. and Masuda, T. *J. Chem. Phys.* 1990, **93**, 7310
11 Nishinari, K., Koide, S., Williams, P. A. and Phillips, G. O. *J. Phys. (Paris)* 1990, **51**, 1759
12 Dror, M., Elsabee, M. Z. and Berry, G. C. *J. Appl. Polym. Sci.* 1981, **26**, 1741
13 Takigawa, T., Kashihara, H., Urayama, K. and Masuda, T. *J. Phys. Soc. Japan* 1990, **59**, 2598