

Gelation of Poly(vinyl Alcohol) Solutions at Low Temperatures (20 to -78°C) and Properties of Gels

KAZUO YAMAURA,* KOH-ICHI KARASAWA, TETSUYA TANIGAMI, and SHUJI MATSUZAWA

Faculty of Textile Science and Technology, Shinshu University, 3-15-1 Tokida, Ueda-City, Nagano-Prefecture 386, Japan

SYNOPSIS

The flow points of atactic poly(vinyl alcohol) (*a*-PVA) gels with H_2O /dimethyl sulfoxide (DMSO) = 90/10 (v/v) chilled at 20 to -78°C for 24 h depended on the chilling temperature and were 0 – 30°C for gels with the initial polymer concentrations (C_i) of 2–5 g/dL, whereas those for H_2O /DMSO = 50/50 chilled at 0 to -78°C were independent of the chilling temperature and were 70 – 75°C . Syneresis occurred after eight cycles of freezing (-24°C) and thawing (20°C) for *a*-PVA hydrogels at concentrations above $C_i = 4$ g/dL and two such cycles for syndiotacticity-rich PVA (*s*-PVA) hydrogels at concentrations above $C_i = 1$ g/dL. The extent of syneresis per one cycle for *s*-PVA hydrogels was higher than that for *a*-PVA hydrogels at the initial cycles. In the *a*-PVA hydrogels with an initial polymer concentration of ca. 30 g/dL, syneresis was expected not to occur even after 20 cycles. If all the free water in the gels is assumed to have transuded by syneresis after 20 cycles, the residual water is bound water and is estimated to be six water molecules per one vinyl alcohol monomer unit. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Concentrated aqueous solutions of atactic poly(vinyl alcohol) (*a*-PVA) derived from vinyl acetate have been well known to gel after standing for a long time at 0 – 25°C .^{1–6} Dilute aqueous solutions of syndiotacticity-rich PVA (*s*-PVA) derived from vinyl trifluoroacetate have been also known to gel at 0 – 90°C ^{5,7–10} and the melting temperature of the *s*-PVA hydrogels is higher than that of *a*-PVA at the same polymer concentration.^{5,7,9,10} The *s*-PVA hydrogels behave as elastomers.¹¹ Recently, other kinds of gels were prepared by repeating the freezing/thawing of aqueous *a*-PVA solutions^{12–15} or by chilling at temperatures below 0°C PVA (*a*-PVA or *s*-PVA)/water/dimethyl sulfoxide (DMSO) solutions.^{15–20} The modulus and melting temperature of PVA gels prepared by repeated cycles of freezing and thawing increased remarkably with increasing number of cycles. PVA gels prepared by standing at -40°C for PVA solutions with DMSO contents of 40–80 vol %

are thermally more stable.¹⁴ Hydrogels of *s*-PVA prepared at 0°C exhibit syneresis by standing at elevated temperature.²¹ The gels have also been found to exhibit syneresis by repeated cycles of freezing and thawing.

As described above, no effect of solvent on the gelation in the wide low chilling temperature range between 0 and -78°C has been studied. In this report, water and a mixture of H_2O /DMSO = 90/10 and of H_2O /DMSO = 50/50 were used as solvents. When water is frozen in a glass tube, the tube is broken, whereas with a mixture of H_2O /DMSO = 90/10, breakage does not occur. Hydrogels in an unfrozen state at 0 and -5°C were prepared. A mixture of H_2O /DMSO = 90/10 was selected as a similar solvent to water.¹⁰ Since mixtures of volume ratios of H_2O /DMSO between 60/40 and 20/80 do not freeze,²² a mixture of H_2O /DMSO = 50/50 was selected as the solvent. The gel structure was studied from the flow temperature of gels and, in addition, the effect of stereoregularity was also studied. No investigation on syneresis of PVA hydrogels during repeated freezing/thawing cycles has been carried out so far. The syneresis accompanied by repeated freezing/thawing at -24°C /room temperature was

* To whom correspondence should be addressed.

compared for *a*- and *s*-PVA hydrogels. From the results, the structures of the gels are discussed. Moreover, the properties of dry gels were studied.

EXPERIMENTAL

Samples

An *a*-PVA (Shin-etsu Kagaku Kogyo Co.) was used, which had a degree of polymerization (*DP*) of 2950 and syndiotactic dyad content [*s*-(dyad)] of 48.3%. A *s*-PVA derived from vinyl trifluoroacetate was also used, which had *DP* = 2830 and *s*-(dyad) = 56.0%. Deionized, distilled water was used as a solvent. DMSO was spectroscopic grade (Merck Co.).

Flow Point of Gels

The polymer was dissolved in the solvents in a well-stirred poly(ethylene glycol) bath heated at 120°C. The solutions were gelled in ice water at 0°C and in ice water with NaCl at -5°C. The solutions with DMSO were gelled in a freezer at -18 to -40°C and in methanol with dry ice at -78°C. The standing time was 24 h. The test tubes with gels were placed upside down in a well-stirred water bath. The bath was warmed from 0 to 25°C at a rate of about 1°C/5 min. At the temperatures above 25°C, the test tubes with gels were placed in a well-stirred poly(ethylene glycol) bath and warmed at the same rate. In this report, the temperature at which a gel fell to the bottom of the tube after air entered inside it was regarded as the flow point, T_M , which is shown as the melting point in the previous papers.^{5,7,9,10}

Water or Polymer Preserved in Gels

Aqueous solutions, 4 mL, were poured into plastic photofilm cases (diameter: 2.9 cm). The cases were used to protect the vessel from breakage by volume expansion during freezing. The cases with solutions or gels were held in a freezer at -24°C for 18 h and thawed at room temperature for 6 h. The freezing/thawing process is one cycle. After gelation, the mechanically stable gels were taken from the cases and weighed. Water squeezed on the surface of gels during thawing was wiped with filter paper. The percentage of preserved water, W_p , was estimated by the following equation:

$$W_p = \frac{\text{mass of gel (g)} - \text{mass of residual polymer (g)}}{\text{mass of solution (g)} - \text{mass of residual polymer (g)}} \quad (1)$$

The percentage of preserved polymer P_p was estimated by the following equation:

$$P_p = \frac{\text{mass of residual polymer (g)}}{\text{volume of solution (mL)} \times \text{initial polymer concentration (g/dL)}} \times 100 \quad (2)$$

Degree of Crystallinity of Dry Gels

After 25 cycles of freezing and thawing, gels were dried in air at room temperature and then in vacuum at 50°C for 24 h. The density of the dry gels, d , was determined by the floating method in benzene/carbon tetrachloride mixed solvents. The degree of crystallinity, x , was determined from the density of the dry gels using the following equation²³:

$$1/d = x/1.345 + (1 - x)/1.269 \quad (3)$$

RESULTS AND DISCUSSION

Effect of Solvents on Flow Point of Gels

Figure 1 shows the relationships between the flow points T_M and the initial polymer concentration C_i for *s*-PVA hydrogels chilled at 0 and -5°C for 24 h. Though both relations were similar, the plots for the hydrogels chilled at -5°C diverged widely. The aqueous solutions froze at the chilling temperature of -10°C for 24 h but did not freeze at -5°C. Therefore, the freezing points of these aqueous PVA solutions lay between -5 and -10°C. The solutions chilled in the neighborhood of the freezing point are considered to freeze inhomogeneously. The enthalpy of the thermal dissociation of the junctions of spatial network, ΔH , estimated by the Eldridge-Ferry equation²⁴ was 20.6 kcal/mol for *s*-PVA hydrogels chilled at 0°C. In this report, the gels prepared from aqueous solutions were named hydrogels (Figs. 1 and 4-9).

Figure 2 shows the relationships between the flow points T_M and the initial polymer concentration C_i for the gels of *a*-PVA with H₂O/DMSO = 90/10 (v/v) chilled at 0 to -78°C for 24 h. The solutions froze at chilling temperatures below -18°C. C_{gel} (4.2-1.0 g/dL) decreased with lowering of the chilling temperature (0 to -78°C). The results are expected from the phase diagram of H₂O/DMSO obtained by Rasmussen and MacKenzie.²² However, the dependence of flow point on the chilling tem-

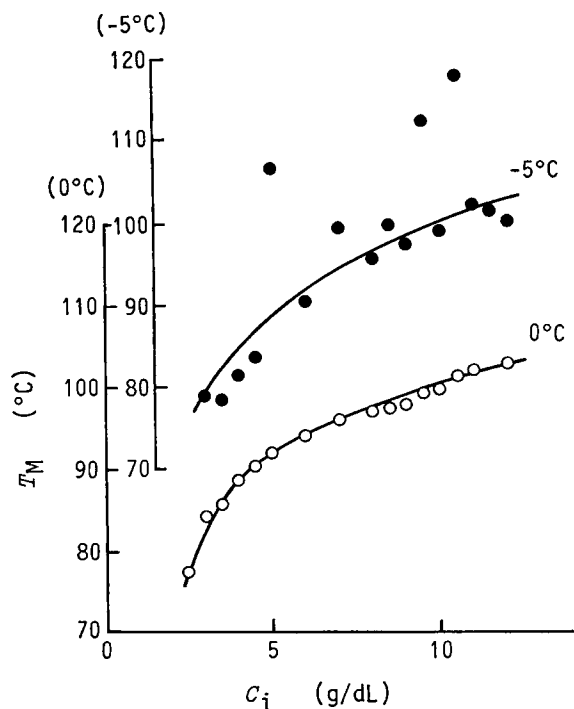


Figure 1 Relationships between the flow temperature, T_M , and the initial polymer concentration, C_i , for the hydrogels of *s*-PVA chilled at 0 and -5°C for 24 h.

perature was not apparent and the flow points were 0 – 30°C . ΔH was 16.6 – 28.0 kcal/mol (20 to -78°C) for *a*-PVA gels with $\text{H}_2\text{O}/\text{DMSO} = 50/50$, 6 – 8 kcal/mol (-18 to -40°C), 11 kcal/mol (0°C), and 18 kcal/mol (-78°C) for *a*-PVA gels with $\text{H}_2\text{O}/\text{DMSO} = 90/10$.

Figure 3 shows the relationships between the flow points, T_M , and the initial polymer concentration, C_i , for the gels of *a*-PVA with $\text{H}_2\text{O}/\text{DMSO} = 50/50$ (v/v) chilled at 20 to -78°C for 24 h. The *a*-PVA solutions did not freeze at temperatures above -40°C but froze partially at -78°C . The solutions chilled in the neighborhood of -78°C are expected to freeze inhomogeneously from the phase diagram obtained by Rasmussen and MacKenzie.²² Therefore, the plots obtained for the hydrogels chilled at -78°C diverged widely. The flow points were 65 – 78°C and higher than for *a*-PVA gels with $\text{H}_2\text{O}/\text{DMSO} = 40/60$ (60 – 75°C) and $60/40$ (52 – 70°C) and were independent of the chilling temperature. However, the critical gelling polymer concentration, C_{gel} , was 2.8 g/dL at the chilling temperature of 20°C and higher than that at 0 to -78°C (about 1.2 g/dL). In the case of aqueous *a*-PVA solutions, the flow point of the gel increased by increasing the number of freezing/thawing cycles. However, in the case of the *a*-PVA solution with 40 – 60 vol % DMSO,

the gels with a high flow point were obtained without freezing/thawing by chilling merely at lower temperatures of 0 to -40°C .

Change in Water Preservation of Hydrogels with Freezing/Thawing Cycles

Figures 4 and 5 show the relationships between the percentage of water, W_p , preserved in gels and the freezing/thawing cycles for the hydrogels of *a*-PVA and *s*-PVA with the initial polymer concentration of $C_i = 0.8$ (a) and 10 g/dL (b), respectively.

The aqueous PVA solutions with $C_i = 0.6$ and 0.8 g/dL represent the same syneresis behavior. The aqueous *s*-PVA solutions gelled at one cycle and the aqueous *a*-PVA solutions gelled after three or four cycles, but the gels deformed during syneresis. Significant syneresis occurred after five cycles for the *s*-PVA hydrogel and 12 cycles for the *a*-PVA hydrogel.

For the hydrogels with initial polymer concentrations above 1 g/dL, the syneresis occurred at two cycles for the *s*-PVA hydrogel and eight cycles for the *a*-PVA hydrogel. The initial extent of syneresis

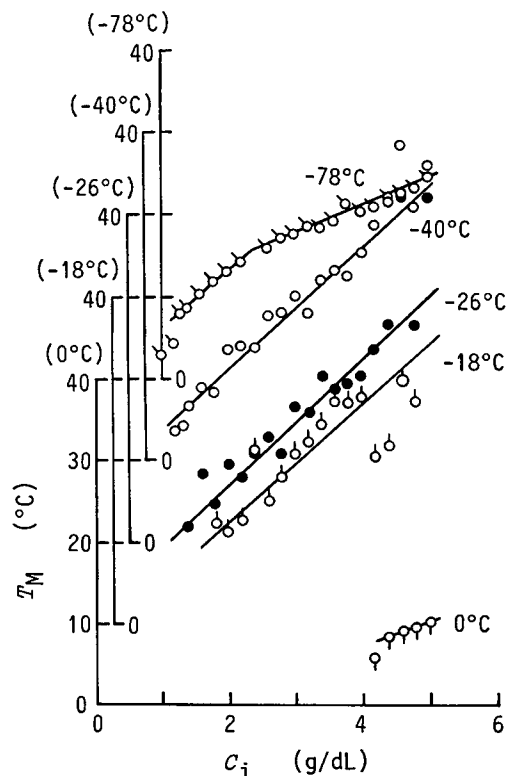


Figure 2 Relationships between the flow temperature, T_M , and the initial polymer concentration, C_i , for the gels of *a*-PVA with water/DMSO = $90/10$ chilled at 20 to -78°C for 24 h.

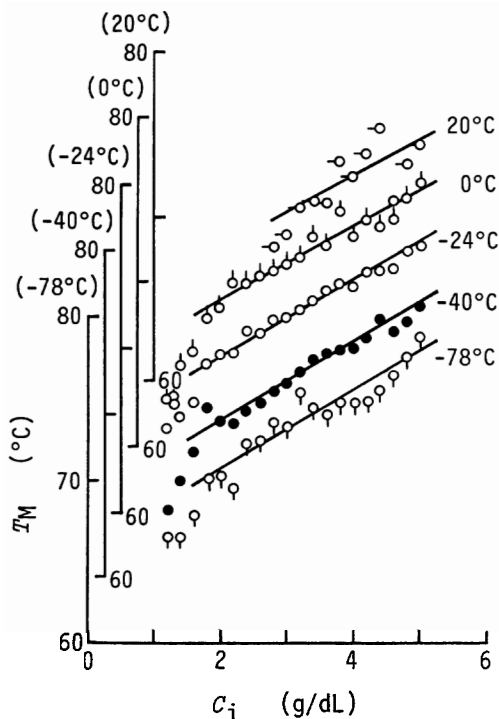


Figure 3 Relationships between the flow temperature, T_M , and the initial polymer concentration, C_i , for the gels of α -PVA with water/DMSO = 50/50 (v/v) chilled at 20 to -78°C for 24 h.

per one cycle of s -PVA hydrogels was higher than that of α -PVA hydrogels. This is due to the high crystallizability of s -PVA.²⁵ When the number of cycles is over five cycles, the s -PVA hydrogels were stable and the extent of syneresis became very low.

Figure 6 shows the effects of the number of cycles on the percentage of water, W_p , preserved in hydrogels as a function of polymer concentration. The polymer concentration, C_1 , was estimated by the following equation:

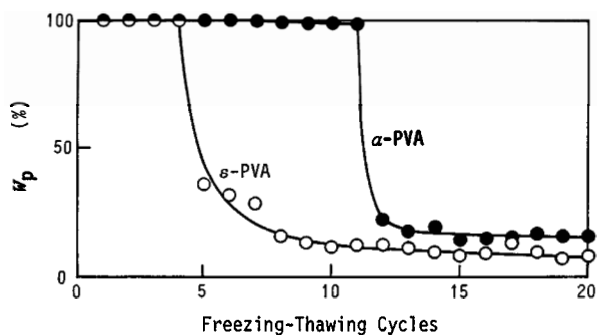


Figure 4 Relationships between the percentage of water preserved in gels, W_p , and the freezing-thawing cycles for the hydrogels of s -PVA and α -PVA with the initial polymer concentration of 0.8 g/dL.

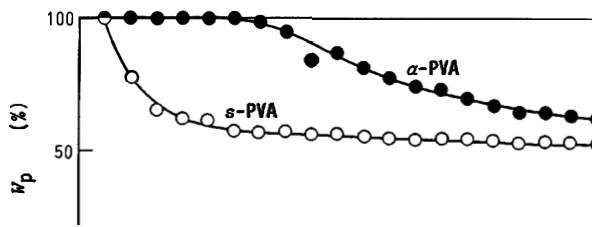


Figure 5 Relationships between the percentage of water preserved in gels, W_p , and the freezing-thawing cycles for the hydrogels of s -PVA and α -PVA with the initial polymer concentration of 10 g/dL.

C_1 (wt %)

$$= \frac{\text{mass of residual polymer (g)}}{\text{mass of gels after one cycle (g)}} \times 100 \quad (4)$$

For the α -PVA hydrogels with initial polymer concentrations over 4 g/dL, syneresis was not apparent until six or seven cycles. The modulus of 10% α -PVA hydrogels increased with an increase in the number of cycles until eight cycles.²⁶ The flow point of α -PVA hydrogels increased with an increase in the number of cycles,¹⁴ namely, the junctions in α -PVA hydrogels grew without syneresis until six or

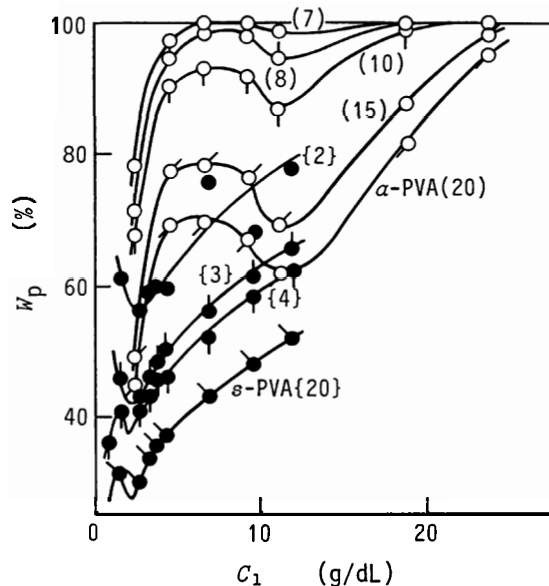


Figure 6 Relationships between the percentage of water, W_p , preserved in gels and the polymer concentration, C_1 , after one cycle for the hydrogels of (●) s -PVA and (○) α -PVA. The nos. in parentheses indicate the freezing-thawing cycles.

seven cycles. If the PVA gels are assumed to behave as elastomers and the Poisson's ratio is assumed to be nearly equal to 0.5, generally, the modulus E is shown by the following equation:

$$E = \frac{3\nu_e RT}{V} = \frac{3\rho RT}{M_c} \quad (5)$$

where ν_e is the number of moles of chains in network; V , the volume of the gel; ρ , the density of the gel; M_c the molecular mass between junctions; R , the gas constant; and T , the absolute temperature. Until six or seven cycles, as the volume of gels did not change, it is expected that ν_e increases and M_c decreases.

After eight cycles, syneresis occurs and the volume of the gel decreases. The extent of syneresis depends on the initial polymer concentration. It increased through a maximum at the initial polymer concentration of ca. 11 g/dL. Though the freezing and thawing of water in gels promotes the propagation of junctions, the unfrozen water in gels prevents the junctions from propagating. The amount of unfrozen water in gels is known to be influenced by the density of cross-links of polymers and to be largest at an intermediate density.²⁷ For the α -PVA hydrogels in this article, it is assumed from Figure 6 that the amount of unfrozen water is largest at the polymer concentration of ca. 7 g/dL. For the s -PVA hydrogels, as the ability of gelation is higher

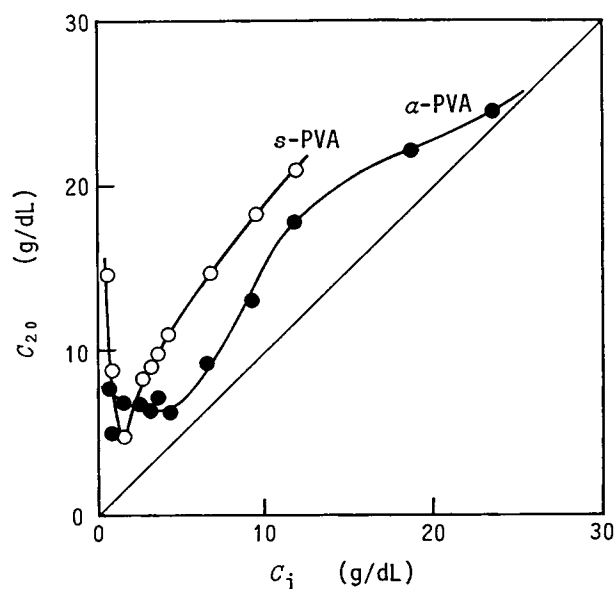


Figure 7 Relationships between the polymer concentration, C_{20} , after 20 cycles of freezing-thawing and the initial polymer concentration, C_i , for the hydrogels of s -PVA and α -PVA.

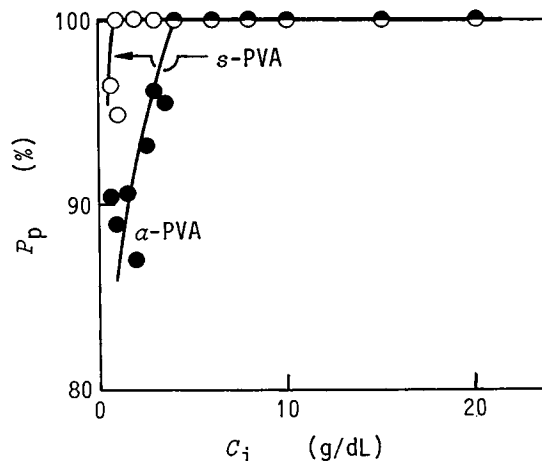


Figure 8 Relationships between the percentage of polymer, P_p , preserved in gels after 25 cycles of freezing-thawing and the initial polymer concentration, C_i .

than that for the α -PVA hydrogels, significant syneresis occurred already at two cycles and continued until five cycles.

Figure 7 shows the relations between the polymer concentration, C_{20} , of hydrogels after 20 cycles and the initial polymer concentration, C_i . For the α -PVA hydrogels, the percentage of water preserved in gels is gradually approaching 100% in the high initial polymer concentration and the syneresis is expected not to occur for α -PVA hydrogels with $C_i = 27$ –30 g/dL. If water and PVA molecules are assumed to interact perfectly at this polymer concentration, six water molecules are estimated to bind with a base unit of PVA.

Percentage of Preserved Polymer

Figure 8 shows the relations between the percentage of polymer, P_p , preserved in gels after 25 cycles and the initial polymer concentration, C_i . The hydrogels

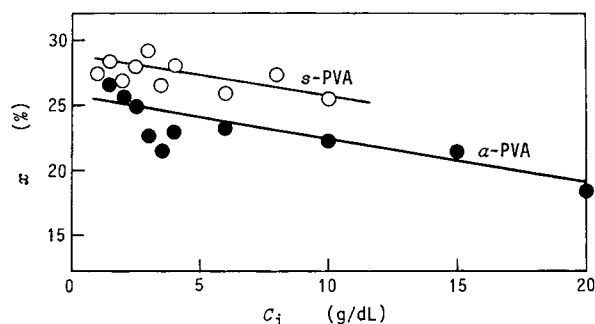


Figure 9 Relationships between the degree of crystallization, x , of hydrogels dried after 25 cycles of freezing-thawing and the initial polymer concentration, C_i .

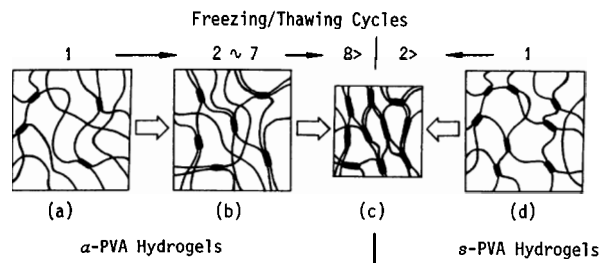


Figure 10 Scheme of the gel structure.

with initial polymer concentrations above 1 g/dL for *s*-PVA and 4 g/dL for *α*-PVA completely preserved the polymer in the gels through syneresis.

Degree of Crystallinity of Dry Gels

Figure 9 shows the relations between the degree of crystallinity x of *α*-PVA and *s*-PVA hydrogels dried after 25 cycles and the initial polymer concentration, C_i . The degree of crystallinity of *s*-PVA dry gels was higher than that of *α*-PVA dry gels at the same initial polymer concentrations and, for both the degree of crystallinity decreased with an increase in the initial polymer concentration, namely, syneresis through the freezing/thawing cycle increases the size and number of junctions in gels and the degree of crystallinity of dry gels.

CONCLUSION

The flow point of *α*-PVA gels with $H_2O/DMSO = 90/10$ ($0-30^\circ C$) was lower than that of *s*-PVA hydrogels ($70-75^\circ C$). The difference in flow points of *α*- and *s*-PVA gels is due to the difference in stereoregularity.

Based on the experimental results, a model for the structure of PVA gels with polymer concentrations below 20 g/dL prepared by chilling at 20 to $-78^\circ C$ was proposed. Figure 10 shows a scheme of the structure of PVA gels. At a same polymer concentration, the *s*-PVA hydrogels [Fig. 10(d)] after one freezing/thawing cycle have more small junctions and flexible chain segments than do *α*-PVA hydrogels [Fig. 10(a)]. This is due to higher crystallinity of *s*-PVA in comparison with *α*-PVA. The *α*-PVA gels with $H_2O/DMSO = 50/50$, unfrozen at -10 to $-78^\circ C$, show a similar structure to the *s*-PVA hydrogels [Fig. 10(d)]. The mixed solvent of $H_2O/DMSO 50/50$ is a poorer solvent than is water.²⁸ Therefore, the *s*-PVA hydrogels [Fig. 10(d)] and the *α*-PVA gels with $H_2O/DMSO = 50/50$ have a similar structure. The junctions and flexible chain segments in gels of *α*-PVA hydrogels [Fig. 10(b)] increase slowly by phase separation with an increase

in the number of cycles in comparison with that of *s*-PVA hydrogels.

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