

Gels of Syndiotacticity-Rich Poly(vinyl Alcohol)–Water/Dimethyl Sulfoxide or –Water/Ethylene Glycol Solutions

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Synopsis

Gels of syndiotacticity-rich poly(vinyl alcohol) (*s*-PVA) in mixed solvents of water/dimethyl sulfoxide (DMSO) or water/ethylene glycol (EG) were made by chilling at the temperatures of 0–70°C from those solutions with the polymer concentrations below 10 g/dL. The melting points of the gels were measured warming the gel from the gelling temperature (T_{gel}) at a constant heating rate. The apparent enthalpy of fusion of a junction of gel, ΔH was estimated from the relation between the apparent melting temperature and the polymer concentration. The *s*-PVA gels made from the mixtures of the water/lower contents of DMSO or EG had a minimum at lower T_{gel} and a maximum ΔH at a higher T_{gel} . On the other hand, the *s*-PVA gels made from the mixtures of the water/higher contents of them had nearly a maximum ΔH at a higher T_{gel} . From those results, it was considered that the former gels received a high thermal history while the latter gels received only slight thermal history.

INTRODUCTION

In the previous papers,^{1–5} the authors have reported that aqueous solutions of syndiotacticity-rich poly(vinyl alcohol) (*s*-PVA) formed hard elastic gels easier than those of commercial poly(vinyl alcohol) (α -PVA) and that the melting point of the *s*-PVA gels was remarkably higher than that of α -PVA gels. It was considered that the gel junctions made of syndiotactic sequences for *s*-PVA were longer than those for α -PVA. Recently, the authors^{6–8} have reported that the dissolution state of *s*-PVA in water/dimethyl sulfoxide (DMSO) or water/ethylene glycol (EG) mixed solvents, like α -PVA,⁹ changed with the contents of DMSO or EG.

This paper reports the relationships between the melting point and the polymer concentration for *s*-PVA gels obtained by chilling the *s*-PVA solutions water/DMSO or water/EG mixtures at various temperatures.

EXPERIMENTAL

Sample and Solvents

s-PVA derived from vinyl trifluoroacetate (VTFA) was used. The bulk polymerization of VTFA was carried out at 60°C by using benzoyl peroxide as an initiator. Poly(vinyl trifluoroacetate) was converted to *s*-PVA by dissolving

in 2, 2'-diaminodiethylamine. The degree of polymerization was 1910 and the content of syndiotactic diad was 54.4%.

DMSO was the spectroscopy grade of Merck Co. Ltd. EG was a commercial product of the highest quality available.

Melting Point of Gel

The apparent melting points of gels were determined according to the Eldridge-Ferry method.¹⁰ Solutions were obtained by dissolving a known amount of *s*-PVA at about 130°C in test tubes with 2.5 cm³ water/DMSO (100/0, 90/10, 70/30, 50/50, 20/80, 0/100 V/V) or water/EG (100/0, 90/10, 70/30, 50/50) mixtures. The polymer concentration was represented as g/dL, which was estimated considering the additivity of the volumes of water and PVA (the density in amorphous state is 1.269 g/cm³). The solutions were held for 24 h at fixed temperatures (gelling temperature $T_{\text{gel}} = 0, 10, 20, 30, 40, 50, 60,$ and 70°C). The test tubes were placed upside down in a well-stirred poly(ethylene glycol) bath. The bath was warmed from the fixed temperatures at a rate of about 1°C/5 min. The temperature at which the gel fell to the bottom of the test tube was taken as melting point.

RESULTS AND DISCUSSION

Water DMSO Systems

The lowest concentrations above which the gels are formed are plotted against the chilling temperatures (gelling temperatures T_{gel}) in Figures 1 and 2. Although the relations for the aqueous solutions and the solutions of the mixture with 30 vol % DMSO are not shown in Figure 1, they coincide nearly with those with 10 vol % DMSO. In the case of the aqueous solutions, the lowest concentrations at $T_{\text{gel}} = 70$ and 40°C were 4 and 0.8 g/dL, respectively. In the case of solutions of the mixtures with 0–10 vol % DMSO and the solutions of the mixture with 30 vol % DMSO, the lowest concentrations had the minimum at $T_{\text{gel}} = 30$ –50°C and 20–40°C, respectively. In the previous paper,⁵ the similar results were obtained for the aqueous solutions of PVA derived from vinyl formate. This means that the mixtures of water and

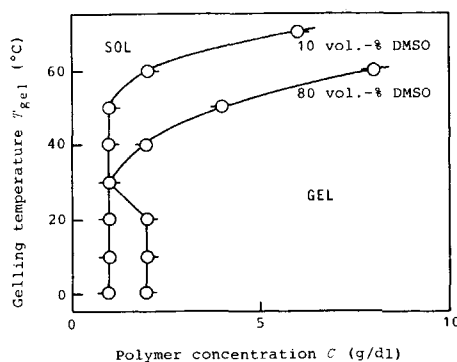


Fig. 1. Lowest concentration of gelation for the *s*-PVA solutions with 10 and 80 vol % DMSO at various gelling temperatures.

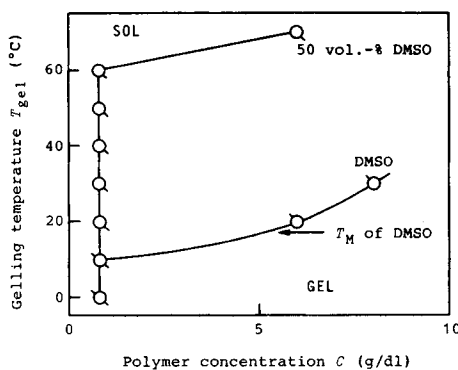


Fig. 2. Lowest concentration of gelation for the s-PVA solutions with 50 and 100 vol % DMSO at various gelling temperatures.

DMSO below 30 vol % are good solvents below 30–40°C and poor solvents above 30–40°C, which seems to be the lower consolute temperature pointed out by Peppas.¹¹

DMSO is a good solvent for α -PVA,¹² but not for s-PVA because the DMSO solutions of s-PVA gel, though the gelling temperature is low and the polymer concentration is high. Since the melting temperature of DMSO is 18.42°C (see Fig. 2), the DMSO solutions of s-PVA chilled at 0–10°C are considered to gel by freezing followed by thawing. The gels of higher polymer concentrations showed syneresis. The degree of syneresis increased with the increase in the polymer concentration, and the polymer was relegated to a center line of a glass tube. Syneresis was also recognized for the gels made from the 8.0 and 10.0 g/dL solutions of the mixture with 50 vol % DMSO at 0–70°C and for those made from the 8.0 and 10.0 g/dL solutions of the mixture with 80 vol % DMSO at 30–40°C.

Eldridge and Ferry have presented the relation (1) for the concentration C against the melting point of gel, T_M ,¹⁰

$$\log C = A - \frac{\Delta H}{2.303RT_M} \quad (1)$$

where A is a constant, ΔH the apparent enthalpy of fusion of a junction of gel, and R the gas constant. The relations between the melting point of gel and the polymer concentration are shown in Figure 3 for gels made from the solutions of the mixture with 10 vol % DMSO chilled at 10 and 40°C, and in Figure 4 for gels made from the solutions of the mixture with 10 vol % DMSO chilled at 50°C. The reproducibility of melting points for the gels chilled at the temperatures below 40°C was high and that for gels made from the solutions of the mixture with 50 vol % DMSO also was high up to $T_{gel} = 60^\circ\text{C}$. This is due to the fact that the solutions with 50 vol % DMSO gels easier than the solutions of the mixtures other than 50 vol % DMSO.⁸ The poor reproducibility of higher gelling temperatures is considered to be due to the fact that the construction of stable crosslinks is interfered by thermal motion.

From the slopes shown in Figures 3 and 4 the apparent enthalpies of fusion of a junction ΔH were estimated using eq. (1). ΔH is plotted against T_{gel} in

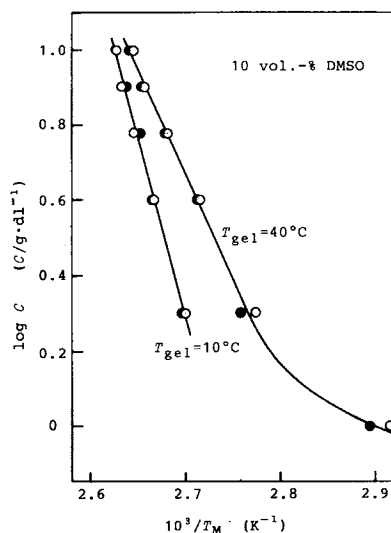


Fig. 3. Plots of $\log C$ against $1/T_M$ for the s-PVA gels with 10 vol % DMSO chilled at 10 and 40°C.

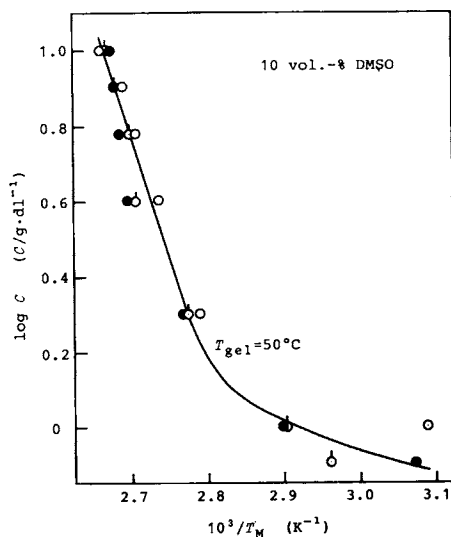


Fig. 4. Plots of $\log C$ against $1/T_M$ for the s-PVA gels with 10 vol % DMSO chilled at 50°C.

Figure 5. The gels made from the solutions of the mixtures of the contents of DMSO below 30 vol % had a minimum and a maximum ΔH . The gels made from the solutions of the mixture with 50 vol % DMSO had a maximum, but not a minimum ΔH . The gels made from the solutions of the mixtures with the contents of DMSO above 80 vol % had neither minimum nor maximum. The minimum gelling concentration for the aqueous solutions at $T_{gel} = 0-20^\circ\text{C}$ is higher than that at $T_{gel} = 30-50^\circ\text{C}$. From this fact ΔH 's of the gels chilled at 30–50°C are expected to be higher than that at $T_{gel} = 0-20^\circ\text{C}$. As shown in Figure 5, however, the reverse relation was found. The resemble fact is also

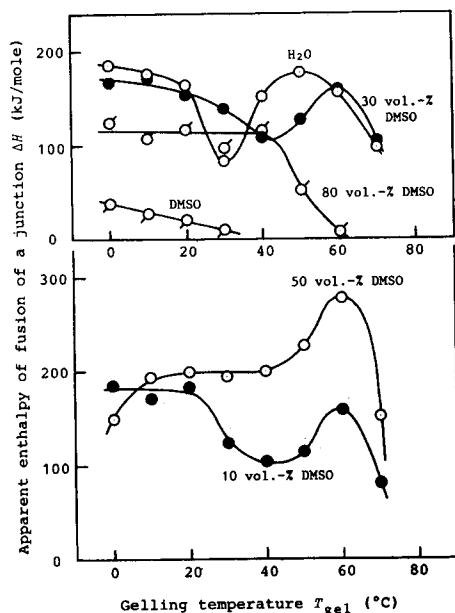


Fig. 5. Relationships between the apparent enthalpy of fusion ΔH and the gelling temperature T_{gel} for the *s*-PVA gels with 0–100 vol % DMSO.

found for the melting temperature of gels. T_M of the gels with the polymer concentration of 10 g/dL and the contents of 0–30 vol % DMSO in the solvent mixtures was about 108°C for gels chilled at 0°C, about 101°C for chilled at 50°C, and about 108°C for gels chilled at 70°C. These are considered to be concerned with the partial dissolution, the production or propagation and the perfect redissolution of microcrystals in the gels with the rise in temperatures from 0–30°C as described in the previous papers for the aqueous gel and the thin film in water of *s*-PVA.^{5,13,14} The initial partial dissolution of microcrystals plays an important role for the reproduction and propagation of microcrystals with the rise in temperature. The gels obtained at $T_{gel} = 30$ –50°C have not the small, unstable microcrystals, and the growth of microcrystals is considered to be very few. For gels chilled at 0–30°C, the reproduction of microcrystals at 55–60°C with the rise in temperature was ascertained by weak regelling of the solutions produced by melting at about 40–50°C.

The growth of microcrystals in gels obtained for gels made from the solutions of the mixture with 50 vol % DMSO chilled at 0–50°C is considered to take place similarly as the gels made from the solutions of the mixtures of the contents of DMSO below 30 vol %. However, as the melting points of gels made from 0.8 g/dL solutions at $T_{gel} = 0$ –50°C were above 70°C and ΔH was the largest at $T_{gel} = 60$ °C, the inference described above cannot be ascertained. T_M of the gels made from the solutions of the mixtures with 50 vol % DMSO and the polymer concentration of 10 g/dL was 111–113°C at $T_{gel} = 0$ –50°C and roughly independent on T_{gel} . ΔH of gels obtained from the solutions of mixture with 80 vol % DMSO was nearly constant at $T_{gel} = 0$ –40°C, and decreased with the increase in T_{gel} at the gelling temperatures

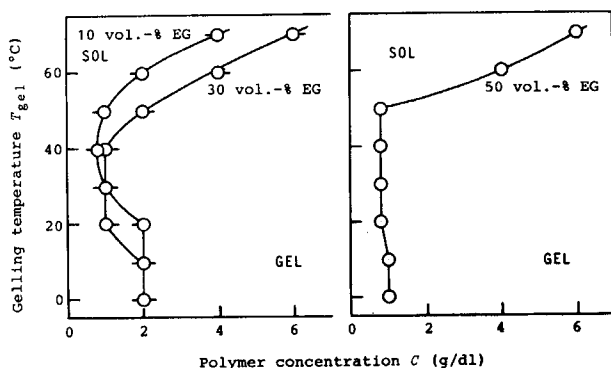


Fig. 6. Lowest concentration of gelation for the *s*-PVA solutions with 10, 30, and 50 vol % EG at various temperatures.

above 40°C. T_M of gels with $C = 10$ g/dL made at 0–50°C was about 105°C. ΔH of the gels of the DMSO solutions decreased with the increase in T_{gel} . Therefore, both the DMSO and the mixtures with 80 vol % DMSO are considered to behave as good solvents for *s*-PVA. ΔH of the gels made at 60°C from the solutions of the mixture with 50 vol % DMSO was the highest and was 278 kJ/mol.

Water / EG Systems

Naitoh⁹ has reported that α -PVA dissolved in water/EG mixed solvents in the range of 0–70 vol % EG. The gelling experiment was carried out using the solutions of the mixtures with 10, 30, and 50 vol % EG. The lowest concentrations above which the gels are formed are plotted against T_{gel} in Figure 6. The relation between the lowest concentration and T_{gel} for gels made for the solutions of the mixture with 10 vol % EG coincided with that for gels made

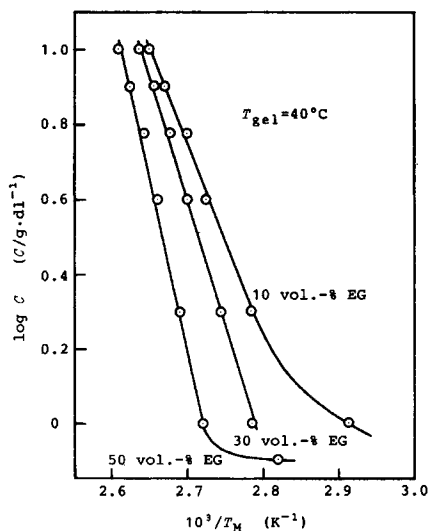


Fig. 7. Plots of $\log C$ against $1/T_M$ for the *s*-PVA gels with 10, 30, and 50 vol % EG chilled at 40°C.

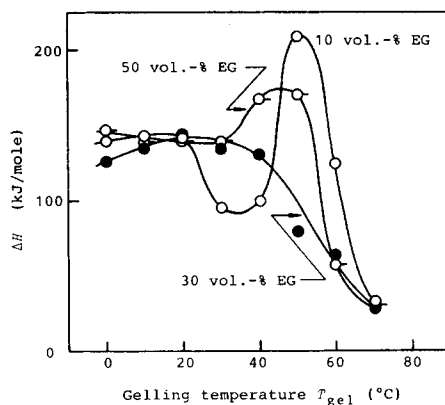


Fig. 8. Relationships between ΔH and T_{gel} for the s-PVA gels with 10, 30, and 50 vol % EG.

from aqueous solutions. The solutions of the mixture with 50 vol % EG, 0.6 g/dL solution did not gel in the range of $T_{gel} = 20\text{--}50^\circ\text{C}$.

Figure 7 shows the relations between the polymer concentration and T_M for gels made from the solutions of the mixtures with 10, 30, and 50 vol % EG chilled at 40°C . Equation (1) is applicable to the region of higher polymer concentrations in Figure 7. Figure 8 shows the relations between ΔH and T_{gel} . The gels made from the solutions of the mixture with 10 vol % EG have a minimum at about $T_{gel} = 35^\circ\text{C}$ and a maximum ΔH at $T_{gel} = 50^\circ\text{C}$. However, ΔH for the gels made from the solutions of the mixture with 30 vol % EG was nearly constant in the range of $T_{gel} = 0\text{--}40^\circ\text{C}$ and decreased with the increase in gelling temperatures above 40°C , that is, microcrystals are considered to dissolve and then to be reproduced in the range of $T_{gel} = 0\text{--}40^\circ\text{C}$. Intrinsic viscosity $[\eta]$ for α -PVA in water/EG mixed solvents had minimum at 30 vol % EG.⁹ The authors had found that s-PVA in water/EG mixed solvents with over 30 vol % EG was adsorbed only slightly to the interface of air/solutions. Therefore, the mixed solvents with EG contents over 30 vol % are considered to be poor solvents for s-PVA. T_M of the gels made from the solutions of the polymer concentration of 10 g/dL and the mixtures with 10 and 30 vol % EG was 108°C for the gels chilled at $0\text{--}20^\circ\text{C}$ and about 106°C for the gels chilled at $30\text{--}50^\circ\text{C}$. In the case of the gels made from the solutions of the mixture with 50 vol % EG, both the gelling temperature at maximum ΔH and the lower consolute temperature (see Fig. 6) coincided roughly each other; therefore, microcrystals are considered to grow only slightly. T_M of gels made from the solutions of the polymer concentration of 10 g/dL and the mixture with 50 vol % EG was about 111°C for gels chilled at $0\text{--}60^\circ\text{C}$.

CONCLUSION

A similar tendency was found for the dependency of T_{gel} on the apparent enthalpy of fusion of a junction of gel, ΔH , for both of an aqueous solution and the solutions of the water/lower contents of DMSO or EG mixtures. The microcrystals in those gels were found first to dissolve, to be reproduced or to grow, and then to redissolve with the rise in temperature. The values of ΔH obtained in this experiment are considered not to represent the raw values for

gels obtained at each gelling temperatures. Therefore, in order to determine real ΔH for gels obtained at lower gelling temperatures, we must select higher temperature than T_{gel} as an initial temperature of heating.

A similar tendency was also found for the dependency of T_{gel} on ΔH for gels made from both of the solutions of the water/50 vol % DMSO or /50 vol % EG mixtures and only ΔH has maximum. The gels made at lower T_{gel} are considered to receive only slightly a thermal history.

References

1. Y. Go, S. Matsuzawa, and K. Nakamura, *Kobunshi Kagaku*, **25**, 62 (1968).
2. K. Ogasawara, T. Nakajima, K. Yamaura, and S. Matsuzawa, *Progr. Colloid Polym. Sci.*, **58**, 145 (1975).
3. K. Ogasawara, T. Nakajima, K. Yamaura, and S. Matsuzawa, *Colloid Polym. Sci.*, **254**, 456 (1976).
4. K. Ogasawara, T. Nakajima, K. Yamaura, and S. Matsuzawa, *Colloid Polym. Sci.*, **254**, 553 (1976).
5. S. Matsuzawa, K. Yamaura, R. Maeda, and K. Ogasawara, *Makromol. Chem.*, **180**, 229 (1979).
6. K. Yamaura, K. Hirata, S. Tamura, and S. Matsuzawa, *J. Polym. Sci., Polym. Phys. Ed.*, **23**, 1703 (1985).
7. S. Matsuzawa, K. Yamaura, Y. Inoue, S.-Y. Pak, and N. Yoshimoto, *Sen-i Gakkaishi*, **35**, T-462 (1979) (in English).
8. K. Yamaura, M. Hamaguchi, N. Rokudai, S. Tamura, and S. Matsuzawa, *Sen-i Gakkaishi*, **38**, T-381 (1982) (in English).
9. R. Naitoh, *Kobunshi Kagaku*, **15**, 597 (1958).
10. J. E. Eldridge and J. D. Ferry, *J. Phys. Chem.*, **58**, 992 (1954).
11. N. A. Peppas, *Makromol. Chem.*, **176**, 3433 (1975).
12. M. Negishi, S. Yanagibori, K. Yoshida, and M. Shiraishi, *Kobunshi Kagaku*, **14**, 239 (1957).
13. K. Yamaura and S. Matsuzawa, *J. Appl. Polym. Sci.*, **29**, 4009 (1984).
14. K. Yamaura and S. Matsuzawa, *J. Appl. Polym. Sci.*, **30**, 3225 (1985).

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