Effects of the Degree of Saponification and Concentration on the Thermal and Rheological Properties of Poly(vinyl alcohol)–Dimethyl Sulfoxide–Water Gels

Mineo WATASE and Katsuyoshi NISHINARI*

Chemical Research Laboratory, Faculty of Liberal Arts,
Shizuoka University, Ohya, Shizuoka 422, Japan
* Instrumentation Research Laboratory, National Food Research Institute,
Ministry of Agriculture, Forestry and Fisheries,
Tsukuba 305, Japan

ABSTRACT: Differential scanning calorimetry (DSC) and dynamic viscoelasticity measurements were carried out in order to clarify the relation between structure and gel properties of poly(vinyl alcohol) (PVA)–dimethyl sulfoxide (DMSO)–water systems. The gel-to-sol transition temperature T_m, endothermic enthalpy ΔH and elastic coefficient E of gels showed maximum at about 0.277 mf DMSO as a function of DMSO concentration. T_m, ΔH, and E of gels increased with increasing degree of saponification (DS) and concentration of the polymer. It was suggested that the number and structures of junction zones and the conformation of flexible chain molecules connecting junction zones are optimized to give maxima of E, T_m, and ΔH at a concentration of 0.277 mf DMSO. The gel containing 0.277 mf DMSO showed no endothermic DSC peak when heated from $-100°C$.
    KEY WORDS   Gel / Poly(vinyl alcohol) / Dimethyl Sulfoxide / Rheology / DSC / Absorbance /

It is well-known that the viscosity of poly(vinyl alcohol) (PVA) solution increases very slowly with time, and after a long time the transparent solution becomes opaque; then gelation occurs.[1] PVA solution forms a gel when subjected to repeated cycles of freezing and thawing.[2-8] Dynamic Young's modulus E' and the melting temperature T_m of PVA gels prepared by repeated cycles of freezing and thawing increased remarkably with increasing degree of polymerization (DP) from DP = 300 to DP = 1200, and beyond DP = 1200, they increased only gradually.[9] The degree of saponification (DS) is shown to have a strong influence on E' and T_m.[8] The increase of only 1 mol% in DS makes E' and T_m increase remarkably. PVA of DS = 96 mol% only showed the halo characteristic of amorphous materials, while PVA of 99.9 mol% showed a sharp crystalline peak in X-ray diffraction pattern.[10,11]

PVA gels are believed to consist of crystalline and amorphous regions. A crystalline region consists of junction zones, aggregation of ordered molecules, while an amorphous region consists of flexible chains which connect junction zones and is surrounded by solvent molecules.[12,13] The molecular forces which make the crystalline region are believed to consist mainly of hydrogen bonds rather than van der Waals forces since there are many hydroxyl groups in PVA molecules. The increase in DP increases the entanglement of flexible chains, while the increase in DS increases the number of crystalline regions and strengthens the structure of crystalline regions because bulky

acetyl groups, which inhibit the formation of hydrogen bonds for sterical reasons, are removed with increasing DS.

PVA is soluble both in dimethyl sulfoxide (DMSO) and in water, but does not form a strong gel without using repeated cycles of freezing and thawing. PVA forms a strong gel in DMSO–water mixture. Rheological and thermal properties of partially saponificated PVA–DMSO–water gels depend strongly on the concentration of DMSO.[14] The effect of DS and concentration of PVA on these properties of highly saponificated PVA–DMSO–water gels are examined in the present work.

EXPERIMENTAL

Materials

The PVA specimen used in this study was a gift from Kuraray Co. DP was fixed as 1700. DSs were 96.0 ± 0.5, 98.5 ± 0.5, and 99.9 mol%. The concentrations of gels ranged from 5 to 25% w/w. The method of preparation was the same as described previously.[14]

Dynamic Viscoelasticity Measurement

Dynamic Young's modulus E' and mechanical loss tangent $\tan \delta$ were observed at 2.5 Hz by use of a Rheolograph Gel from Toyo Seiki Seisakusho. The temperature was controlled using a silicone oil bath. Gels were kept at each measurement temperature for 30 min. The sample for rheological measurement was a cylindrically molded gel (20 mm diameter and 30 mm length).

Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) of gels was carried out by a Sensitive DSC SSC 560 U (Seiko Instruments & Electronics, Ltd.). Forty five mg each of the gels were sealed into silver pans of 70 μl. A DMSO solution was used as a reference, and the weight was made equal within ± 0.1 mg to that of the sample gel in order to obtain a flat baseline. The temperature was raised from 2°C at the heating rate of

$2°C \min^{-1}$ to observe an endothermic peak accompanying the transition from gel to sol.

In order to examine the interaction between DMSO water and PVA, DSC was carried out at low temperatures. 15 ± 0.1 mg each of gel were sealed into aluminium pans of 15 μl. Alpha alumina was used as a reference material. After lowering the temperature rapidly to $-120°C$ using liquid nitrogen, the temperature was kept for 10 min, and then raised at a rate of $2°C \min^{-1}$.

Measurement of Turbidity

After dissolution, PVA–DMSO solution was poured into a quartz cell, and the temperature was kept at 25°C. In order to examine the rate of the turbidity change, apparent absorbance at the wavelength of 600 nm was observed for 5% PVA–DMSO–water solution as a function of time.

RESULTS AND DISCUSSION

Figure 1(a) shows heating DSC curves of 15% (w/w) PVA–DMSO–water gels, with different DSs for various concentrations of DMSO in DMSO and water mixture. Figure 1(b) shows typical heating DSC curves of PVA–DMSO–water gels with two PVA concentrations, 5% (w/w) and 20% (w/w), for various DMSO concentrations.

Figure 2 shows the melting temperature T_m of PVA–DMSO–water gels as a function of DMSO concentration for various DSs (Figure 2(A)) and for various PVA concentrations (Figure 2(B)).

Figure 3 shows the endothermic enthalpy ΔH determined from the area enclosed by the endothermic peak and baseline as a function of DMSO concentration for various DSs (Figure 3(A)) and for various PVA concentrations (Figure 3(B)).

Both T_m and ΔH increased with increasing DMSO concentration up to about 0.277 mf DMSO and then decreased. This tendency was not dependent on DS and PVA concentration.
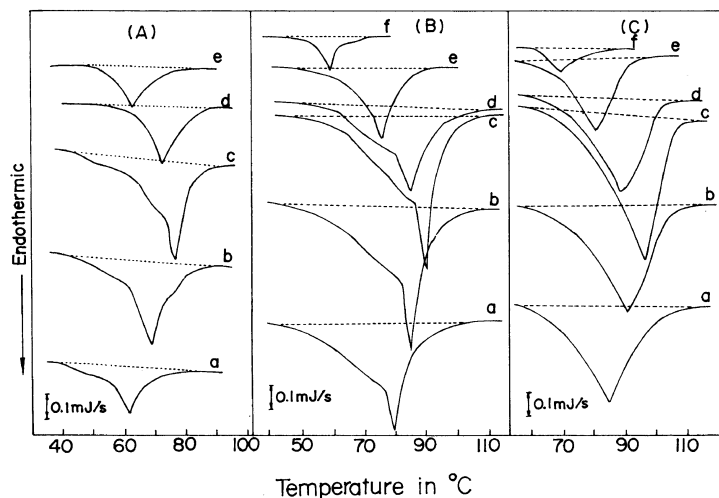
Figure 1(a). Heating DSC curves of 15% (w/w) PVA(DP = 1700)–DMSO–water gels with various DSs. (A), DS = 96 ± 0.5 mol%; (B), DS = 98.5 ± 0.5 mol%; (C), DS = 99.9 mol%. DMSO concentrations: (a), 0.104 mf; (b), 0.168 mf; (c), 0.277 mf; (d), 0.425 mf; (e), 0.582 mf; (f), 0.771 mf.
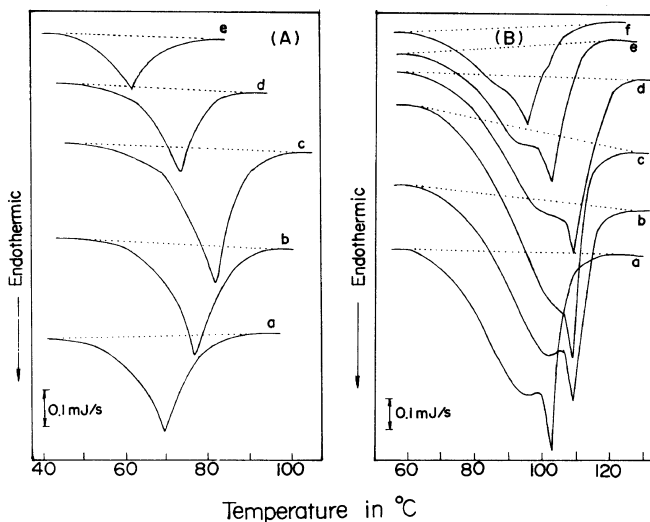

Figure 1(b). Heating DSC curves of PVA(DP = 1700, DS = 99.9 mol%)–DMSO–water gels with various PVA concentrations. PVA concentrations: (A), 5% (w/w); (B), 20% (w/w). DMSO concentrations: (a), 0.104 mf; (b), 0.168 mf; (c), 0.277 mf; (d), 0.425 mf; (e), 0.582 mf; (f), 0.771 mf.

Figure 4(a) shows dynamic Young's modulus E' and mechanical loss tangent $\tan \delta$ of 15% PVA–DMSO–water gels as a function of temperature with different DSs for various DMSO concentrations. E' and $\tan \delta$ of PVA–DMSO–water gels were observed as functions of temperature for various PVA concentrations and DMSO concentrations, and typical examples for 5% (w/w) and 25% (w/w) PVA concentrations are shown in Figure 4(b). E' also showed a similar tendency to T_m and H; E' as a function of DMSO concentration showed a maximum at 0.277 mf DMSO irrespective of DS's (Figure 5(a)) and of PVA
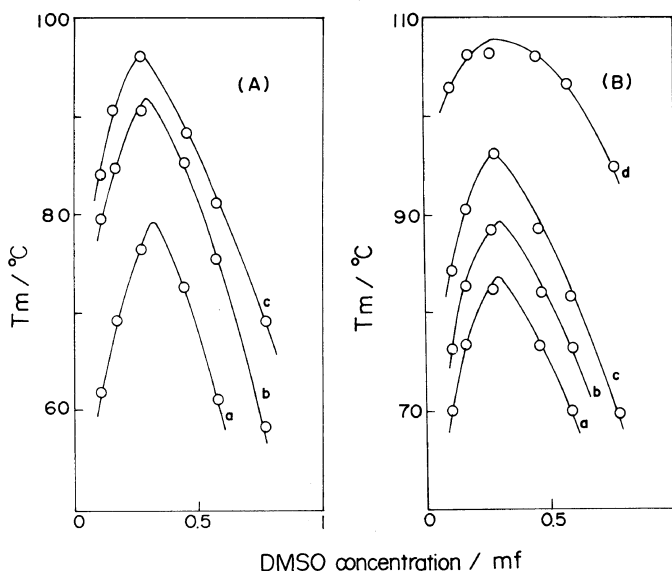
Figure 2. Relation between the melting point T_m of PVA(DP = 1700)–DMSO–water gels and DMSO concentration. (A), PVA concentrations: 15% (w/w), a, DS = 96.0 mol%; b, DS = 98.5 mol%, c, DS = 99.9 mol%. (B), DS = 99.9 mol%, PVA concentrations: a, 5% (w/w); b, 10% (w/w); c, 15% (w/w); d, 25% (w/w).
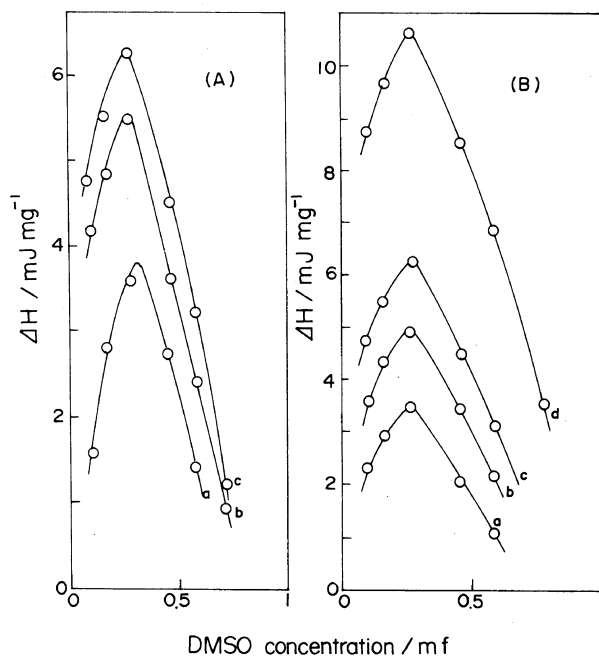

Figure 3. Relation between the endothermic enthalpy ΔH and DMSO concentration. (A), PVA concentrations: 15% (w/w), a, DS = 96.0 mol%; b, DS = 98.5 mol%; c, DS = 99.9 mol%. (B), DS = 99.9 mol%, PVA concentrations: a, 5% (w/w); b, 10% (w/w); c, 15% (w/w); d, 25% (w/w).
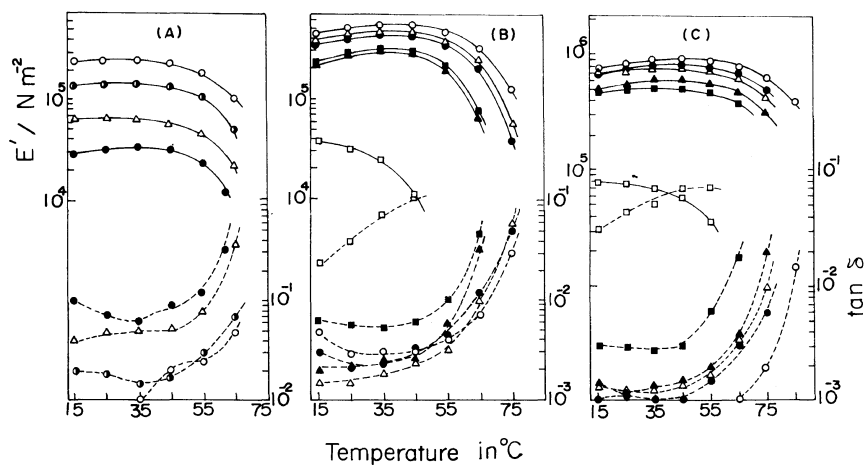
Figure 4(a). Temperature dependence of dynamic Young's modulus E' and mechanical loss tangent tan δ of PVA(DP = 1700)–DMSO–water gels. PVA concentration, 15% (w/w). (A), DS = 96.0 mol%; (B), DS = 98.5 mol%; (C), DS = 99.9 mol%. E', solid line; tan δ, broken line. DMSO concentrations: △, 0.104 mf; ●, 0.168 mf; ◑, 0.217 mf; ○, 0.277 mf; ▲, 0.452 mf; ■, 0.582 mf; □, 0.771 mf.
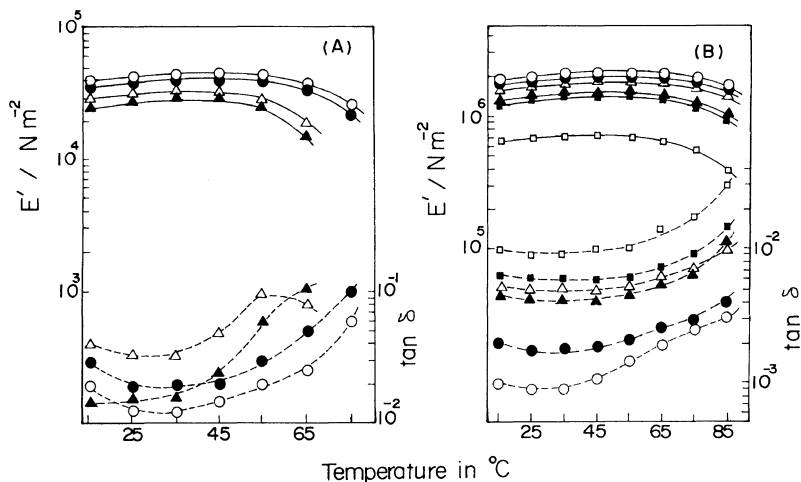

Figure 4(b). Temperature dependence of dynamic Young's modulus E' and mechanical loss tangent tan δ of PVA(DP = 1700)–DMSO–water gels. DS = 99.9 mol%, PVA concentrations: (A), 5% (w/w); (B), 25% (w/w). E', solid line; tan δ, broken line. DMSO concentrations: △, 0.104 mf; ●, 0.168 mf; ○, 0.277 mf; ▲, 0.452 mf; ■, 0.582 mf; □, 0.771 mf.

concentration (Figure 5(b)).

Of course, the values themselves of T_m, ΔH, and E' increased with increasing DS or PVA concentration at a fixed DMSO concentration.

In order to examine DMSO concentration dependence of T_m, ΔH, and E', DSC was carried out at low temperatures. Figure 6 shows

the heating DSC curves of 15% (w/w) PVA (DS = 99.9 mol%)–DMSO–water gels with different DMSO concentrations. The endothermic peak accompanying the melting of frozen solvent shifted to lower temperatures with increasing DMSO concentrations up to around 0.277 mf DMSO and then it shifted
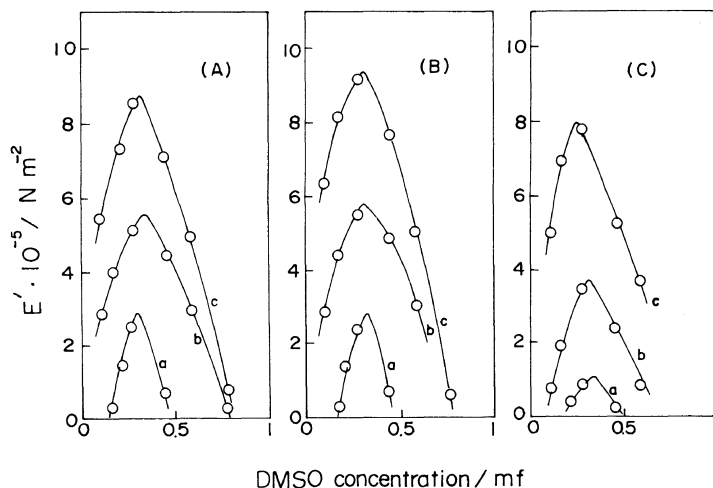
M. WATASE and K. NISHINARI

Figure 5(a). Dependence of E' of 15% (w/w) PVA(DP = 1700)–DMSO–water gels on DMSO concentration for various DS's at different temperatures. (A), 25°C; (B), 45°C; (C), 65°C. a, DS = 96.0 mol%; b, DS = 98.5 mol%; c, DS = 99.9 mol%.
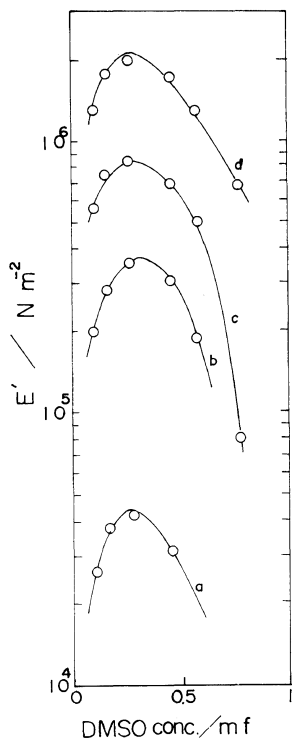

Figure 5(b). Dependence of E' of PVA(DP = 1700)–DMSO–water gels on DMSO concentration at 25°C for various PVA concentrations. DS = 99.9 mol%. PVA concentration: a, 5% (w/w); b, 10% (w/w); c, 15% (w/w); d, 25% (w/w).

to higher temperatures. The gel containing 0.277 mf DMSO did not show an endothermic peak.

Heat of fusion $\Delta H_{m.f.}$ (open circle) and endothermic peak temperature $T_{m.f.}$ (closed circle) of frozen 15% (w/w) PVA–DMSO–water gels are shown in Figure 7. The heat of fusion was calculated from the area enclosed by the endothermic peak and base line shown in Figure 6, assuming the heat of fusion for water as 6.008 kJ mol^{-1} and that for DMSO as 13.94 kJ mol^{-1}. Here, it is assumed that below 0.277 mf DMSO, only free water freezes, and that above 0.277 mf, only free DMSO freezes. Since PVA–DMSO–water gels whose DMSO concentrations ranged from 0.2 mf to 0.4 mf did not show any endothermic peak when heated from −100°C, neither $\Delta H_{m.f.}$ nor $T_{m.f.}$ is shown at this DMSO concentration range in Figure 7.

DMSO, $(CH_3)_2SO$ is known to have a large dielectric constant and to be a polar solvent, and its affinity with water is very strong. Research on interactions of DMSO with water by viscometry,[15–17] ultrasound velocity,[18] NMR,[19] neutron scattering[20] show the structure of a hydrated compound of DMSO to be
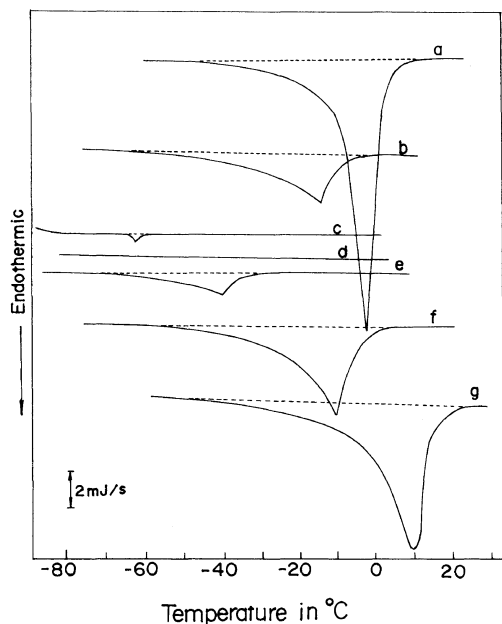
Figure 6. Low temperature DSC heating curves of 15% (w/w) PVA–DMSO–water gels. DS = 99.9 mol%. DMSO concentrations: a, without DMSO; b, 0.104 mf; c, 0.168 mf; d, 0.277 mf; e, 0.452 mf; f, 0.771 mf; g, 1 mf. Heating rate, 2°C min^{-1}; reference, alpha alumina; sample weight, 15 mg.

Figure 7. Heat of fusion $\Delta H_{m.f.}$ (○) and $T_{m.f.}$ (●) of 15% (w/w)PVA–DMSO–water gels as a function of DMSO concentration.

$(CH_3)_2 \cdot SO \cdot 2H_2O$ or $(CH_3)_2 \cdot SO \cdot 3H_2O$. It is not yet concluded whether the di-hydrated compound model or tri-hydrated model is correct. The DMSO concentration of 0.277 mf is intermediate between these two models. It is suggested from low temperature DSC that the behaviour of PVA–DMSO–water systems differs depending on the content of DMSO: (i) at the DMSO concentration range <0.2 mf, the solvent consists of DMSO–water complex and free water, (ii) at the DMSO concentration range between 0.2 mf and 0.4 mf, almost no free DMSO nor free water, (iii) at the DMSO concentration range >0.4 mf, the solvent consists of DMSO–water complex and free DMSO.

PVA with higher DS dissolves in DMSO and in water, but it does not form a strong gel in a single solvent. It forms a strong gel only in a mixture of DMSO and water. Below 0.2 mf DMSO, free water content decreases with in-
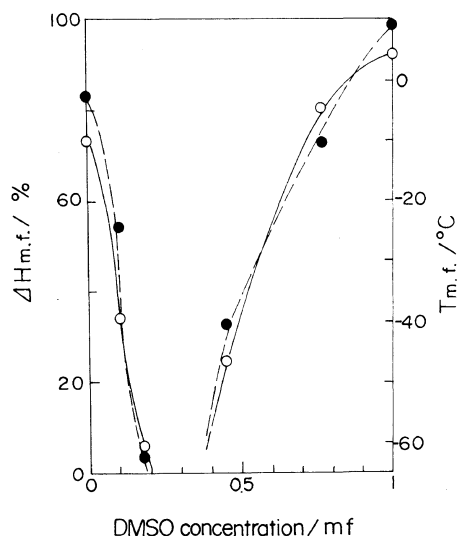
creasing DMSO content. Beyond 0.4 mf DMSO, free DMSO content increases with increasing DMSO content but the ratio of solvated DMSO decreases. As is described in Introduction, the balance between the crystallinity and solubility of PVA gels shifts to solubility side with increasing free water or free DMSO. Therefore, the maximum crystallinity appears at the DMSO content range from 0.2 mf to 0.4 mf. At this DMSO concentration range, the solvated DMSO and water reach a maximum, and thus the free DMSO or free water content takes a minimum.

As is well known, aqueous solutions of PVA with higher DS become turbid with the lapse of time, and gelation occurs concurrently. Since PVA–DMSO–water systems show similar behaviour, measurement of turbidity change will be useful for understanding the gelation process of this system. The apparent absorbance of 5% (w/w) PVA–DMSO–water solution at 25°C observed at the wavelength of 600 nm is shown in Figure 8 as a function of time. The solution without DMSO became turbid very slowly. The solution containing
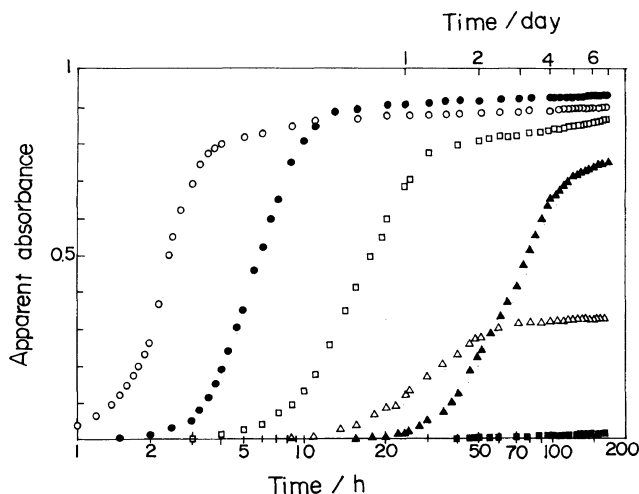
Figure 8. Time course of apparent absorbance for 5% w/w PVA(DP = 1700, DS = 99.9 mol%)–DMSO–water solutions at various DMSO concentrations. DMSO concentrations: ■, without DMSO; ▲, 0.094 mf; □, 0.129 mf; ●, 0.168 mf; ○, 0.277 mf; △, 0.452 mf.

0.277 mf DMSO became turbid faster than the other solutions. This observation corresponds very well to the findings shown in Figures 1 to 5.

Although DS has a decisive effect on rheological and thermal properties of PVA gels without DMSO prepared by repeated cycles of freezing and thawing,[8] the fact that the ratio of DMSO and water, 0.277 mf DMSO, at which E', T_m, ΔH and the rate of gelation become maximum is independent of DS or the concentration of PVA is noteworthy. Since the crosslinking junction in PVA gels is made by mainly hydrogen bonds between hydroxyl groups, the number of crosslinking junctions increases with increasing DS. The number of crosslinking junctions per unit volume also increases with increasing concentration of PVA. Therefore, the strong interaction between water and DMSO is more influential than DS or PVA concentration for this behaviour. The formation of hydrated compound of DMSO means the absence of free water and free DMSO, which is not influenced by DS or PVA concentration.

REFERENCES

1. N. A. Peppas, *Makromol. Chem.*, **176**, 3433 (1975).
2. S. V. Rogozhin, V. I. Lozinsky, E. S. Vainerman, L. V. Domotenko, S. M. Mamtsis, S. A. Ivanova, M. I. Shtil'man, and V. U. Korshak, *Dokl. Akad. Nauk., SSSR*, **278**, 129 (1984).
3. V. I. Lozinshi, L. V. Domotenko, E. S. Vainerman, A. M. Mamtsis, and S. V. Rogozhin, *Polym. Bull.*, **15**, 333 (1986).
4. F. Yokoyama, I. Masada, S. Shimamura, T. Ikawa, and K. Monobe, *Colloid Polym. Sci.*, **264**, 19 (1986).
5. M. Nagura and H. Ishikawa, *Polym. Commun.*, **25**, 313 (1984).
6. T. Hatakeyama, A. Yamauchi, and H. Hatakeyama, *Eur. Polym. J.*, **20**, 61 (1984).
7. M. Watase and K. Nishinari, *Polym. Commun.*, **24**, 269 (1983).
8. M. Watase and K. Nishinari, *Makromol. Chem.*, **189**, 871 (1988).
9. M. Watase and K. Nishinari, Proc. 31st IUPAC Macromolecular Symp., Microsymp. IV, Merseburg, GRD, 1987, p 136.
10. M. Watase and K. Nishinari, *Makromol. Chem.*, **190**, 155 (1989).
11. M. Watase and K. Nishinari, *J. Polym. Sci., Polym. Phys. Ed.*, **23**, 1803 (1985).
12. T. Matsuo and H. Inagaki, *Makromol. Chem.*, **53**, 130 (1962).
13. D. Braun and E. Walter, *Colloid Polym. Sci.*, **258**, 376 (1980).
14. M. Watase and K. Nishinari, submitted to this journal.

15. S. A. Schichman and R. L. Amey, *J. Phys. Chem.*, **75**, 98 (1971).
16. J. M. G. Cowie and P. M. Toporowske, *Can. J. Chem.*, **39**, 2240 (1961).
17. R. K. Wolford, *J. Phys. Chem.,* **68**, 3392 (1964).
18. D. E. Bowen, M. A. Priesand, and M. P. Eastman, *J. Phys. Chem.*, **78**, 2611 (1974).
19. K. J. Packer and D. J. Tomlinson, *Trans. Faraday Soc.*, **67**, 1302 (1971).
20. G. T. Safford, P. C. Schaffer, P. S. Leung, G. F. Doebbler, G. W. Brady, and E. F. X. Lyden, *J. Chem. Phys.*, **50**, 3140 (1969).