

# Properties of Gels Obtained by Freezing/Thawing of Poly(vinyl Alcohol)/Water/Dimethyl Sulfoxide Solutions

KAZUO YAMAURA, MASAYASU ITOH, TETSUYA TANIGAMI,  
and SHUJI MATSUZAWA, *Faculty of Textile Science and  
Technology, Shinshu University, Tokida 3-15-1, Ueda-city,  
Nagano-prefecture 386, Japan*

## Synopsis

Melting points of poly(vinyl alcohol) (PVA) gels obtained by repeated freezing/thawing cycles of the solutions in mixed solvents of water and dimethyl sulfoxide (DMSO) were measured. PVA solutions in 1–30 and 90 vol % DMSO froze at  $-40^{\circ}\text{C}$ . The melting point of a gel increased with an increase in freezing/thawing cycles for all the solutions frozen and with an increase in freezing time in 10–30 vol % DMSO. The solutions in 1–5 vol % DMSO gelled even at very low polymer concentration of 1.0 g/dL by repeated freezing/thawing. The melting point of all the gels with a 5% polymer concentration reached ca.  $73^{\circ}\text{C}$  after 14 freezing/thawing cycles except for the gels in 90 vol % DMSO. However, the melting point of the gels with the same polymer concentration prepared at  $-40^{\circ}\text{C}$  using an unfrozen mixed solvent in 60 vol % DMSO was ca.  $77^{\circ}\text{C}$  and the largest. The maximum apparent enthalpy of fusion of the gels prepared by repeated freezing/thawing was ca. 40 kcal/mol. The gels in 90 vol % DMSO were transparent independent of cycles whereas those in 1–80 vol % DMSO were opaque. The degree of opaqueness increased with decreasing DMSO content.

## INTRODUCTION

The modulus of the gel prepared by freezing/thawing an aqueous atactic PVA solution was found to be higher than that of the gel prepared at temperatures above  $0^{\circ}\text{C}$  and increased with repeating the freezing/thawing cycle.<sup>1–3</sup> The structure of the gel has been investigated.<sup>1–12</sup> The conformation of PVA in mixed solvents of water and DMSO changes with the content of DMSO.<sup>13–16</sup> The melting point of the gel prepared at  $0^{\circ}\text{C}$  from the solution of a concentration of syndiotactic-rich PVA in the mixed solvent changes with the content of DMSO.<sup>17</sup> From preliminary experiments, we have found that PVA solutions in the ratio of water/DMSO of 90/10 form gels by freezing (at  $-18^{\circ}\text{C}$ )/thawing and that the melting points of the gels were greater than those of hydrogels for each fixed polymer concentration.<sup>18</sup> Hyon and Ikada have also found similar results with the latter.<sup>8</sup>

We were thus interested in the preparation of the gels from PVA solutions of mixed solvents of different ratios by repeated freezing/thawing and determining the melting points of the gels. The solutions were frozen at  $-40^{\circ}\text{C}$ ; at this temperature the mixed solvents in 0–30 and 90–100 vol % DMSO could be frozen. The effect of freezing time on gelation was also studied. The melting points of the gels prepared at  $-40^{\circ}\text{C}$  using unfrozen mixed solvents in 40–80 vol % DMSO were measured. Light transmittance of gels was observed in

order to help elucidate the mechanism of gelation for each solvent system. The polymer concentration of solutions was lowered to 0.6 g/dL to examine the critical polymer concentration of gelation. The gels of lower polymer concentrations seem to be useful for the preparation of the samples with high extensibility.

## EXPERIMENTAL

### Freezing of Mixed Solvents of Water and DMSO

Mixed solvents (2.5 mL volume) of various ratios were poured into glass tubes (12 mm in i.d.) to determine if they could be frozen at  $-40^{\circ}\text{C}$  and time required for freezing. DMSO was spectroscopic grade (Merck Co. Ltd.).

### Determination of Melting Point of Gels

PVA (Shin-etsu Kagaku Co. Ltd.) was used, which had a degree of polymerization of 2950, a 98.8% degree of hydrolysis, and syndiotactic diad content of 48.3%. The syndiotacticity was determined from the infrared spectrum.<sup>19</sup> Each 2.5 mL of mixed solvents of water and DMSO, and each fixed amount of polymer were added to glass tubes (12 mm in i.d.) and sealed 7 cm from the bottom.

The polymer was dissolved in the solvents in a well-stirred poly(ethylene glycol) bath heated at  $120^{\circ}\text{C}$ . The solutions were frozen in a freezer at  $-40^{\circ}\text{C}$  and thawed in a thermoregulator bath at  $10^{\circ}\text{C}$ . Freezing for 1 h at  $-40^{\circ}\text{C}$  and thawing for 1 h at  $10^{\circ}\text{C}$  were regarded as one cycle. The melting points of gels were determined at a heating rate of  $0.2^{\circ}\text{C}/\text{min}$  from  $10^{\circ}\text{C}$  in a water bath after the glass tubes were put upside down. The temperature at which a gel fell to the bottom of the tube after air entered inside it was regarded as the melting point.

## RESULTS AND DISCUSSION

### Freezing of Water / DMSO Mixed Solvents

Figure 1 shows the times that water/DMSO mixed solvents began and completed freezing at  $-40^{\circ}\text{C}$ . It took less than 10 min for solvents with DMSO less than 20 vol % to begin freezing,  $15 \pm 3$  min for 30 vol %, ca. 2 h for 40 vol %, and  $5 \pm 2$  min for  $> 90$  vol %. It took  $30 \pm 5$  min for the mixed solvent in 30 vol % DMSO to be frozen completely and  $20 \pm 3$  min for the others, but the mixed solvent in 40 vol % DMSO did not freeze completely. Mixed solvents in volume ratios of water and DMSO of 99 : 1, 95 : 5, 80 : 20, 75 : 25, 70 : 30, 10 : 90, and 0 : 100 were found to freeze at  $-40^{\circ}\text{C}$ .

### Melting Points of Freezing/Thawing Gels of PVA/DMSO Solutions

#### *Effects of Cycles*

Figure 2 shows the dependence of the melting points of gels in 1 vol % DMSO on polymer concentration for each fixed cycle. The melting point of the gel increased with an increase in the number of cycles. This corresponds to

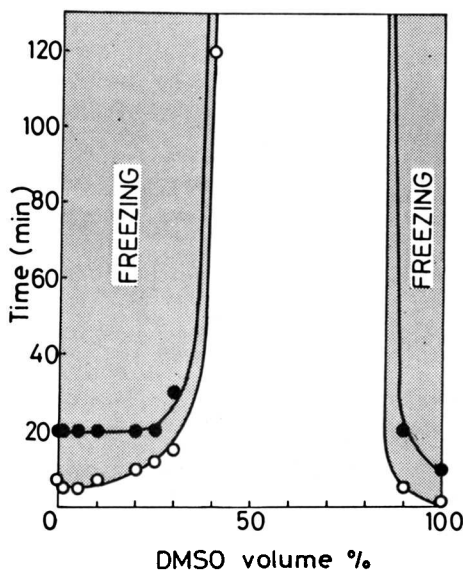


Fig. 1. Initial and final times of freezing of water/DMSO mixed solvents (2.5 mL volume) at  $-40^{\circ}\text{C}$ : (○) initiation time; (●) finishing time.

an increase in modulus for gels obtained by freezing/thawing aqueous PVA solutions.<sup>4</sup> After eight cycles, however, the melting points did not increase remarkably with increasing cycles kept around  $70^{\circ}\text{C}$ . Although gelation occurred even for solutions of low polymer concentration of around 1.0%, the melting points of the gels were impossible to determine because the gels were peeled off from glass tube wall by hard syneresis. The melting points of the gels in 1–5 vol % DMSO depended on the freezing/thawing cycles, but scarcely depended on freezing time because it took a short time to freeze completely.

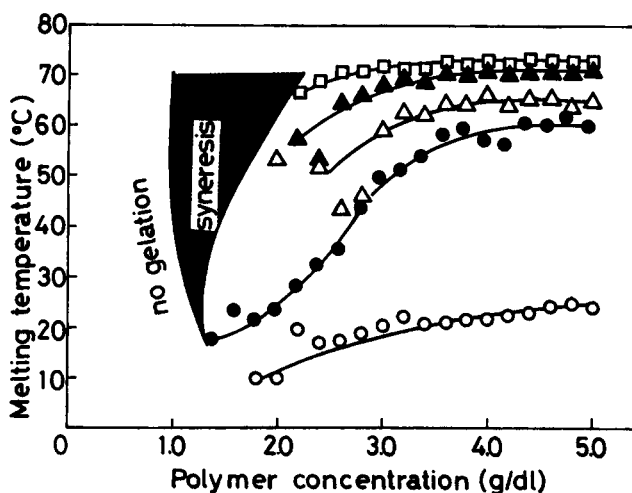


Fig. 2. Dependence of melting points on polymer concentration and freezing/thawing cycles for the gels in 1 vol % DMSO at  $-40^{\circ}\text{C}$ . Cycles: (○) 1; (●) 3; (△) 4; (▲) 8; (□) 14.

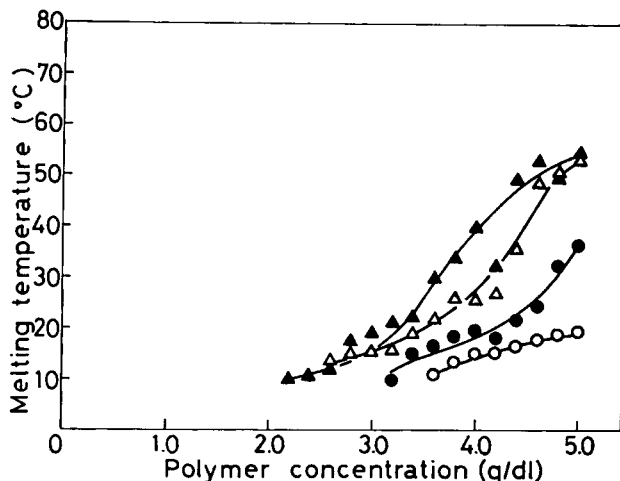


Fig. 3. Dependence of melting points on polymer concentration and freezing/thawing cycles for the gels in 20 vol % DMSO at  $-40^{\circ}\text{C}$ . Cycles: (○) 1; (●) 2; (Δ) 3; (▲) 4.

Figures 3 and 4 show the dependence of the melting points of gels in 20 and 30 vol % DMSO on polymer concentration for each fixed cycle, respectively. For each fixed polymer concentration, the melting points of gels in 20 vol % DMSO were lowest in the range of 1–30 vol % DMSO. This seems to be related to the interaction between the polymer and solvent molecules. The intrinsic viscosity  $[\eta]$  of a PVA in 20 vol % DMSO solution is the largest in the range of 0–30 vol % DMSO.<sup>13,16</sup> PVA and solvent molecules interact most strongly in 20 vol % DMSO, and this leads to increased dissolution of PVA molecules; therefore, the ability to form microcrystals seems to be lower. The melting points of gels in 30 vol % DMSO also depended on polymer concentration and cycles. For each fixed polymer concentration and cycle, the melting

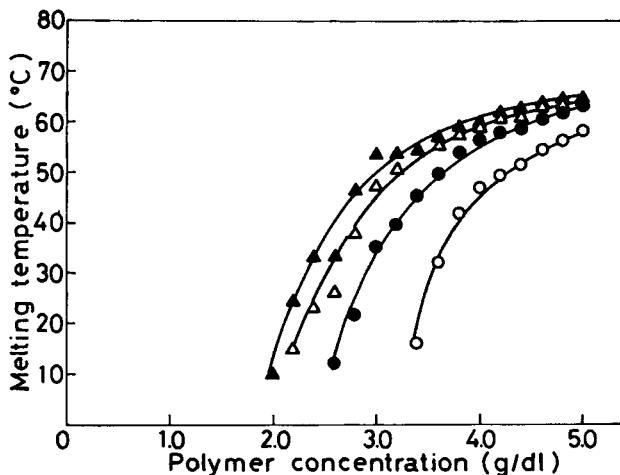


Fig. 4. Dependence of melting points on polymer concentration and freezing/thawing cycles for the gels in 30 vol % DMSO at  $-40^{\circ}\text{C}$ . Cycles: (○) 1; (●) 2; (Δ) 3; (▲) 4.

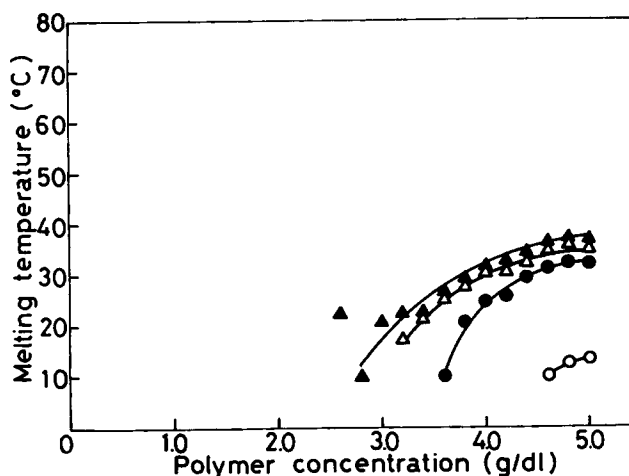


Fig. 5. Dependence of melting points on polymer concentration and freezing/thawing cycles for the gels in 90 vol % DMSO at  $-40^{\circ}\text{C}$ . Cycles: (○) 1; (●) 2; (△) 3; (▲) 4.

points of gels in 25 vol % DMSO were higher than those of gels in 20 vol % DMSO and lower than those of gels in 30 vol % DMSO. During freezing and thawing, volume expansion was not observed and bubbles were not produced for the gels in 30 vol % DMSO. The syneresis was not as prevalent for gels in 1 vol % DMSO.

In Figure 5, the melting points of gels in 90 vol % DMSO are shown as a function of polymer concentration for each fixed cycle. For each polymer concentration and cycle, the melting points were lower than those of the gels in other DMSO vol %. The gels were transparent, and the melting points were almost independent on cycles after the first cycle. Syneresis hardly occurred. DMSO is well known to be a good solvent for PVA.<sup>20</sup> This lowers the ability of gelation of 90 vol % DMSO solutions and leads to low melting-point gels. The melting point of a gel prepared by letting a syndiotactic-rich PVA (*s*-PVA) DMSO solution stand at temperatures over  $0^{\circ}\text{C}$  is lower than that of a gel prepared from its aqueous solution of the same polymer concentration.<sup>17</sup>

#### *Effects of Freezing Time*

The melting point was independent on freezing time from 0.5 h up to 40 h for the gels in 1 and 5 vol % DMSO as shown in Figure 6 for the gels in 1 vol % DMSO, whereas it depended on freezing time strongly for the gels in 30 vol % DMSO as shown in Figure 7. In the latter, the melting point increased with increasing freezing time, although the increment decreased with increasing polymer concentration. In the former, the melting point is independent on freezing time because the solutions are frozen completely before junctions are formed perfectly. In the latter, the solutions are considered not to have frozen perfectly. Before freezing or gelling, the spinodal decomposition is considered to occur in the solutions at lower temperatures as is recognized for PVA hydrogels,<sup>21</sup> so that they separate to polymer-poor phases and polymer-rich phases. The latter phases are considered to freeze slower than the former. It seems that the melting point increases as the junctions grow with freezing

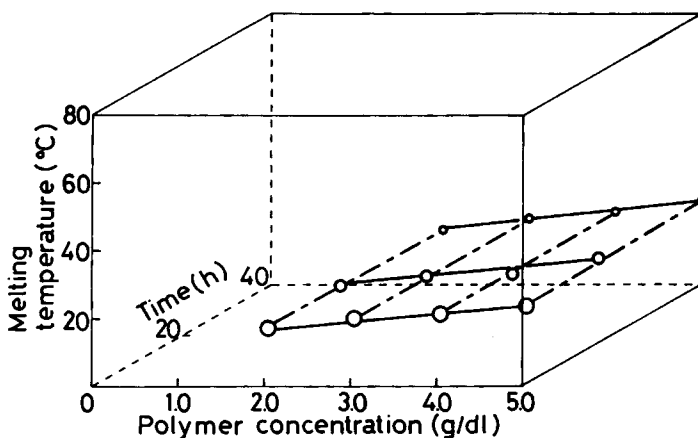


Fig. 6. Dependence of melting points on polymer concentration and freezing time for the gels in 1 vol % DMSO at  $-40^{\circ}\text{C}$ . Freezing time: 1, 17, and 40 h.

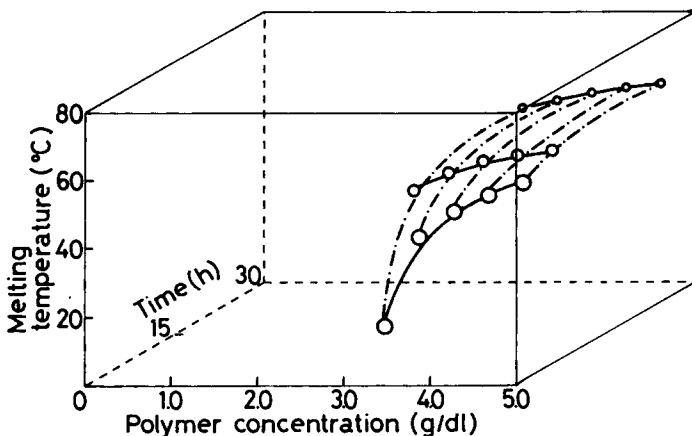


Fig. 7. Dependence of melting points on polymer concentration and freezing time for the gels in 30 vol % DMSO at  $-40^{\circ}\text{C}$ . Freezing time: 1, 6, and 24 h.

time in polymer-rich phases. The independence of the melting points of gels with higher polymer concentrations on freezing time suggests the formation of the stable junctions even after a short freezing time. Watase et al.<sup>2,7</sup> have reported that the modulus increased with an increase in freezing time for gels prepared from PVA aqueous solutions of 10%.

#### *Effects of DMSO Content on Melting Points of Freezing / Thawing Gels*

Figure 8 shows the dependence of the melting points of the gels prepared by one freezing/thawing cycle on the polymer concentration for several water/DMSO ratios. The solvent power of the mixtures for PVA decreases in the order water/DMSO = 10/90, 80/20, 70/30, and 99/1. For each fixed concentration between 3.6 and 5.0 g/dL, the melting point decreases with

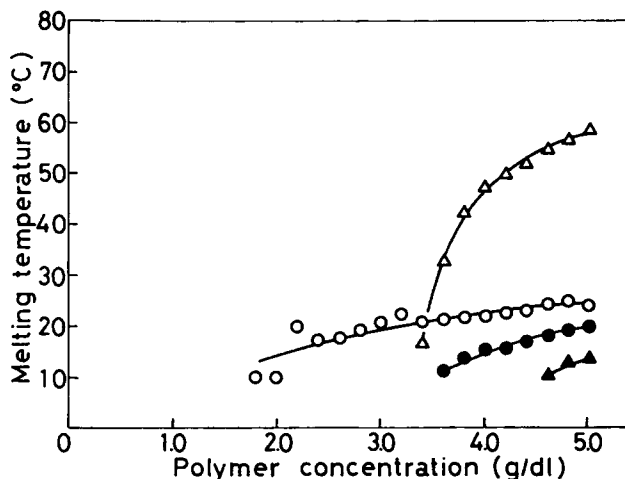


Fig. 8. Dependence of melting points on polymer concentration and mixing ratio of water/DMSO for the gels obtained by thawing for 1 h at 10°C after freezing for 1 h at -40°C. Mixing ratios of water/DMSO: (○) 99/1; (●) 80/20; (△) 70/30; (▲) 10/90.

increasing solvent power except for the gels in 30 vol % DMSO. The critical concentration below which no gelation occurs, decreases with decreasing DMSO content except for the case in 30 vol % DMSO. In the case of solutions in 30 vol % DMSO, spinodal decomposition is considered to occur easily, and it takes more time for the polymer-rich phases to freeze. Therefore, the association between polymer chains in the polymer-rich phase before freezing is easier, and larger junctions are formed. This is considered to be a reason for the production of high-melting-point gels. Since the spinodal decomposition occurs only partly under a few cycles for low polymer concentration solutions and a spongelike continuous connection of polymer-rich phases are hindered, they do not gel.

The solutions in 1 vol % DMSO gelled in a wide range of polymer concentration as shown in Figure 8. This is considered to be due to the freezing of the solutions in such a short time as complete spinodal decomposition cannot occur. The gelation of the solutions in 1 vol % DMSO, therefore, is independent on the freezing time and dependent on freezing/thawing cycles.

#### Melting Points of Gels Prepared Using Unfrozen Water/DMSO Mixed Solvents

Mixed solvents in 40–80 vol % DMSO did not freeze. However, the PVA solutions prepared using those solvents were found to form gels at -40°C. The dependence of melting points of the gels in 40 and 60 vol % DMSO on polymer concentration is shown in Figure 9. The melting points of the gels of higher polymer concentrations are near 77°C. The values are highest among PVA/water/DMSO gels prepared in this study. The similar result has been found by Hyon and Ikada.<sup>8</sup> The detailed results for unfrozen gels in 40–80 vol % DMSO will be reported in the future.

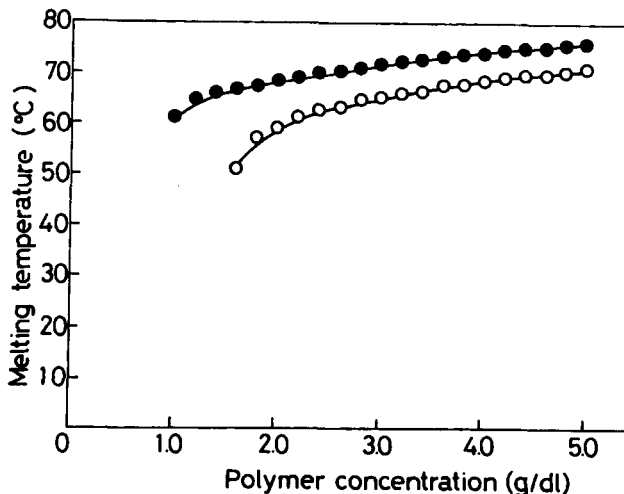


Fig. 9. Dependence of melting points on polymer concentration and mixing ratio of water/DMSO for the unfrozen gels obtained by chilling for 1 h at  $-40^{\circ}\text{C}$ . Mixing ratios of water/DMSO: (○) 60/40; (●) 40/60.

### Apparent Enthalpy of Fusion of Gels

The apparent enthalpy changes of gel melting  $\Delta H_M$  were estimated using the relation  $\ln C = (\Delta H_M/RT_M) + \text{const}$  ( $C$  = polymer concentration,  $R$  = gas constant,  $T_M$  = absolute temperature of gel melting), presented by Eldridge and Ferry.<sup>22</sup> In the gels in 1 vol % DMSO, the linear relationships were established in the polymer concentration range in Figure 2 after one cycle and 4 to 14 cycles. The apparent enthalpy changes were ca. 18 for the former and ca. 40 kcal/mol for the latter. The latter value is higher than that<sup>23</sup> obtained so far for atactic PVA hydrogels chilled at  $0^{\circ}\text{C}$  and similar to that<sup>17</sup> of syndiotactic-rich PVA gels chilled at  $20$ – $78^{\circ}\text{C}$ . The linear relationships were not obtained for the gels after two or three cycles. This means that the extent of growth of junctions in gels in higher polymer concentrations with repeated cycles is large in comparison with that in lower polymer concentrations. The similar relationships were obtained for the results shown in Figure 3 (20 vol % DMSO), Figure 4 (30 vol % DMSO), and Figure 5 (90 vol % DMSO). The linear relationships were obtained for the gels prepared using the unfrozen mixed solvents in the polymer concentration range shown in Figure 9. The apparent enthalpy changes were 20 and 30 kcal/mol for the gels in 40 and 60 vol % DMSO, respectively.

### Light Transmittance

The light transmittance of gels increased with increasing DMSO content. The opaqueness of gels in 1–5 vol % DMSO is primarily due to the presence of small air bubbles. At the beginning of freezing/thawing cycle, the gels were semitransparent and small bubbles were observed between the gels and glass tubewall. The gels became more opaque, and the amount of bubbles increased with increasing cycles. The volume of the frozen gels did not contract to the initial one after thawing. This suggests that extremely minute air bubbles



remain in the gels. The presence of the bubbles is considered to be a reason of cloudiness of the gels, which is supported by a porous structure obtained by drying cryogels of aqueous PVA solutions.<sup>8</sup> The gels in 5 vol % DMSO had the same tendency. Secondary, the opaqueness due to spinodal decomposition to polymer-rich and polymer-poor phases is considered. At the beginning, the gels prepared from solutions in 20–30 vol % DMSO were semitransparent and became opaque with an increase in the number of cycles. However, they did not become opaque like the gels in 1 vol % DMSO. The refractive indices of PVA<sup>24</sup> and DMSO are  $d^{25} = 1.51$  and  $d^{20} = 1.4783$ , respectively, that is, very close. The reflection of light due to two phases decreases with increasing DMSO content for the gels in 0–90 vol % DMSO. An increase in opaqueness of gels with increasing cycles is due to the growth of junctions.

### CONCLUSIONS

1. The melting points of gels in 1–20 vol % DMSO increased with increasing freezing (at  $-40^{\circ}\text{C}$ )/thawing cycles. The attained melting point of gels with 5% polymer concentration was ca.  $72.5^{\circ}\text{C}$ .
2. The melting points of gels in 30 vol % DMSO increased with increasing freezing time. The attained melting point was ca.  $73^{\circ}\text{C}$ .
3. For each fixed polymer concentration and cycle, the melting point of a gel in 30 vol % DMSO was highest among the gels prepared using frozen solvents.
4. The melting point of the gel with 5% polymer concentration prepared using unfrozen mixed solvent in 60 vol % DMSO was ca.  $77^{\circ}\text{C}$ .
5. The maximum apparent enthalpies of fusion of the gels prepared by repeated freezing/thawing and that for the gels prepared using an unfrozen mixture were 40 and 30 kcal/mol, respectively.
6. Light transmittance of the gels increased with increasing DMSO content.

The authors gratefully acknowledge the courtesy of Mr. N. Nakamura, Shin-etsu Kagaku Co. Ltd., who supplied the PVA sample.

### References

1. M. Nambu, *Japan Pat.*, 82-130543 (1982).
2. M. Watase, K. Nishinari, and M. Nambu, *Polym. Commun.*, **24**, 52 (1983).
3. M. Watase, *Nippon Kagaku Kaishi*, No. 7, 973 (1983).
4. M. Watase, *Nippon Kagaku Kaishi*, No. 9, 1254 (1983).
5. M. Watase and K. Nishinari, *Polym. Commun.*, **24**, 270 (1983).
6. K. Nishinari, M. Watase, K. Ogino, and M. Nambu, *Polym. Commun.*, **24**, 345 (1983).
7. M. Watase, K. Nishinari, and M. Nambu, *Cryo-Letters*, **4**, 197 (1983).
8. S.-H. Hyon and Y. Ikada, *Rept. Poval Committee*, **83**, 91 (1983).
9. M. Nagura, M. Nagura, and H. Ishikawa, *Polym. Commun.*, **25**, 313 (1984).
10. M. Watase and K. Nishinari, *J. Polym. Sci., Polym. Phys. Ed.*, **23**, 1803 (1985).
11. V. I. Lozinsky, E. S. Vainerman, L. V. Domotenko, A. M. Matisis, E. F. Titova, E. M. Belavtseva, and S. V. Rogozhin, *Colloid & Polym. Sci.* **264**, 19 (1986).
12. V. I. Lozinsky, L. V. Domotenko, E. S. Vainerman, A. M. Mamtsis, and S. V. Rogozhin, *Polym. Bull.*, **15**, 333 (1986).
13. R. Naitoh, *Koubunshi Kagaku*, **15**, 597 (1958).
14. K. Imai and U. Maeda, *Koubunshi Kagaku*, **16**, 499 (1959).
15. K. Yamaura, M. Hamaguchi, N. Rokudai, S. Tamura, and S. Matsuzawa, *Sen-i Gakkaishi*, **38**, T-381 (1982) (in English).

16. K. Yamaura, K. Hirata, S. Tamura, and S. Matsuzawa, *J. Polym. Sci., Polym. Phys. Ed.*, **23**, 1703 (1985).
17. K. Yamaura, H. Katoh, T. Tanigami, and S. Matsuzawa, *J. Appl. Polym. Sci.*, **34**, 2347 (1987).
18. K. Yamaura, K. Karasawa, T. Tanigami, and S. Matsuzawa, *Rept. Poval Committee*, **88**, 36 (1986).
19. S. Murahashi, S. Nozakura, M. Sumi, H. Yuki, and K. Hatada, *Koubunshi Kagaku*, **23**, 605 (1966).
20. M. Negishi, S. Yanagibori, K. Yoshida, and M. Shiraishi, *Koubunshi Kagaku*, **14**, 239 (1957).
21. M. Komatsu, T. Inoue, and K. Miyasaka, *J. Polym. Sci., Polym. Phys. Ed.*, **24**, 303 (1986).
22. J. E. Eldridge and J. D. Ferry, *J. Phys. Chem.*, **58**, 992 (1954).
23. H. Maeda, T. Kawai, and R. Kashiwagi, *Koubunshi Kagaku*, **13**, 193 (1956).
24. R. H. Wiley, *Ind. Eng. Chem.*, **38**, 959 (1946).

Received November 3, 1988

Accepted May 31, 1988