

Gelation of Poly(vinyl Alcohol)/Ethylene Glycol Solutions and Properties of Gels

KAZUO YAMAURA, HIROSHI KITAHARA, TETSUYA TANIGAMI

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

Received 29 February 1996; accepted 14 September 1996

ABSTRACT: The melting temperature of the gels of the poly(vinyl alcohol) (PVA)/ethylene glycol (EG) system was measured. It was found that the temperature was independent of the thermal hysteresis. The apparent enthalpy of the fusion of the junction, ΔH , was 206 kJ/mol for a high molecular weight atactic PVA (HDP α -PVA), 172 kJ/mol for a low molecular weight syndiotacticity-rich PVA (LDP s -PVA), and 238 kJ/mol for an HDP s -PVA. The gels obtained by chilling at temperatures over 80°C or by gradual cooling are considered to have larger microcrystals. The Young's modulus of the HDP α -PVA drawn films were highest among the samples tested. The maximum and mean Young's moduli of the HDP α -PVA films drawn 15 times the original length were 37 and 26 GPa, respectively. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **64**: 1283–1289, 1997

INTRODUCTION

Recently, numerous investigators have made efforts to prepare ultrahigh strength and ultrahigh modulus oriented polymers. For poly(vinyl alcohol) (PVA), high modulus materials have been made using various methods, including drawing fibers prepared by gel-state spinings from glycerin (Gly),¹ ethylene glycol (EG),^{1–3} and water/dimethyl sulfoxide (DMSO) solutions,⁴ drawing ultrathin films prepared by the frame/bubble methods,⁵ flow-induced crystallization under the presence of seed crystals,⁶ repeating zone-drawn/heated treatment of as-spun fibers,⁷ and drawing fibers produced by melt-spinning.⁸

Despite the numerous articles dealing with the study of PVA/EG or PVA/EG/water systems, we feel that there are still many problems remaining unsolved in the range of lower polymer concentration for PVA with high molecular weight, considered to be more suitable for gel-spinning. In this article, the gelation of PVA/EG solutions and the thermal properties of the gels were examined.

EXPERIMENTAL

Samples

Two syndiotacticity-rich PVAs (s -PVA) derived from vinyl trifluoroacetate and atactic PVA (α -PVA) derived from vinyl acetate were used. The degrees of polymerization (DP) of the two s -PVAs were 15,300 (HDP s -PVA) and 1590 (LDP s -PVA) respectively, and the DP of α -PVA was 12,000 (HDP α -PVA, supplied by Unitika Chemical Co.). The contents of the syndiotactic diad [s -(diad) %] of the s -PVAs were 57.4 and 57.2, and the s -(diad) % of α -PVA was 50.0. EG of special grade made by Wako Chemical Co. was used without distillation.

Dissolution Temperature of PVA

Fibrous s -PVA samples placed in EG were heated at a rate of 0.5°C/min from the initial temperature of about 120°C, and during the process, the dissolution temperature (T_D) was determined.

Clouding and Gelation Temperatures of Solutions

After the dissolution of PVA in EG in a sealed test tube at 160–190°C, the clouding and gelation

Correspondence to: K. Yamaura.

© 1997 John Wiley & Sons, Inc. CCC 0021-8995/97/071283-07

temperatures (T_{CL} and T_G) of the solutions were determined by gradual cooling to room temperature. Moreover, the gelation time at quenching temperatures (T_Q) was measured after the solutions were quenched from 160°C to T_Q .

Melting Temperature of Gels

After the sealed test tube stood for 5 min to 24 h at T_Q , the melting temperature (T_M) of the gels was determined when the temperature of the gels was raised at a heating rate of 0.2°C/min from T_Q in poly(ethylene glycol) with the tube upside down. A certain temperature reached at which a gel fell to the bottom of the tube after air came inside it was regarded as the melting point.

Thermal Properties of Dry Gels

The 2.5 g/dL PVA solutions were quickly or gradually cooled to 30°C and then they stood at 30°C for 30 min. The gels were kept in a large excess of water to extract EG and then dried. The thermal analysis was carried out using a Rigaku Denki thermoflex differential scanning calorimeter at the heating rate of 10°C/min.

Preparation of Gel Films

After PVA was dissolved in EG at 160–180°C, the solutions were poured into a Petri dish in an oven controlled at 150°C and gelled by placing them in a freezer (0°C) or other ovens (50 and 100°C) for 24 h. The gels were kept in a large excess of water to extract EG and then dried.

The films obtained were cut into a width of 2 mm. The tapelike films were drawn in an oven at 200°C and relaxed at room temperature. The drawing/relaxation cycle was repeated 5–20 times.

Measurements of Properties of Films

The density of films was determined by the floating method in a benzene–carbon tetrachloride mixture. Tensile properties were measured using a tensile tester of a TOM/5 type of Shiko Tsushin Kogyo at the temperature of 20–22°C and the relative humidity of about 50%. The length of the films were 20 mm and the rate of elongation was 10 mm/min. The heat treatment was carried out as follows: Both ends of the graph paper with the film were fixed by adhering them to a glass plate. Then, the glass plate was held in an oven in which

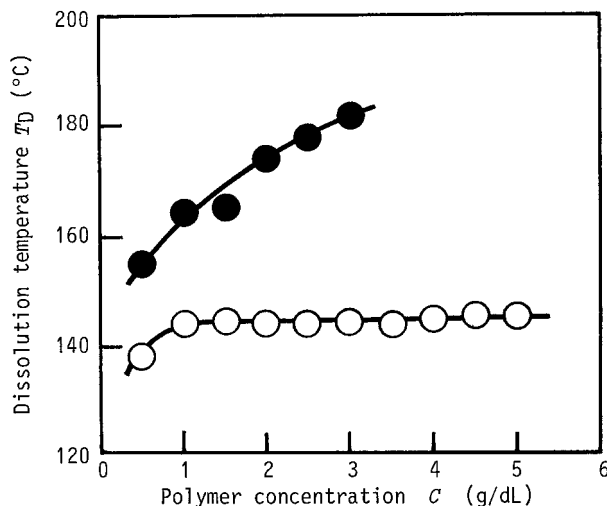


Figure 1 Relations between the dissolution temperature and the polymer concentration for the fibrous (○) LDP and (●) HDP *s*-PVA samples.

the annealing time and annealing temperature were 10 min and 200°C, respectively.

RESULTS AND DISCUSSION

Dissolution Temperature of PVA

Figure 1 shows the relations between the dissolution temperature (T_D) of fibrous *s*-PVA samples and the polymer concentration (C). For the LDP *s*-PVA sample, the concentration dependence of T_D was little and T_D was 144–148°C in the range of $C = 1.0$ – 5.0 g/dL. The dissolution temperature of LDP α -PVA was reported to be 123°C.⁹ Recently, for LDP PVA, the concentration dependence of T_D was reported and T_D was 120–190°C (weight fraction: 0.02–0.8).¹⁰ In the range of the same concentration, the T_D of LDP *s*-PVA was ca. 20°C higher than that of LDP α -PVA. For the HDP *s*-PVA sample, T_D increased from 155°C ($C = 0.5$ g/dL) to 182°C ($C = 3$ g/dL).

Although the dissolution temperature of the HDP α -PVA sample was examined, it was not determined for the granule sample used in this study which stuck on the bottom of the test tube. To dissolve the granule sample, the test tube with the sample must be shaken without intermission. The dissolution of the granule HDP α -PVA was initiated at 135–140°C and finished at about 155°C. Therefore, the solutions of HDP α -PVA had to be prepared at 160°C.

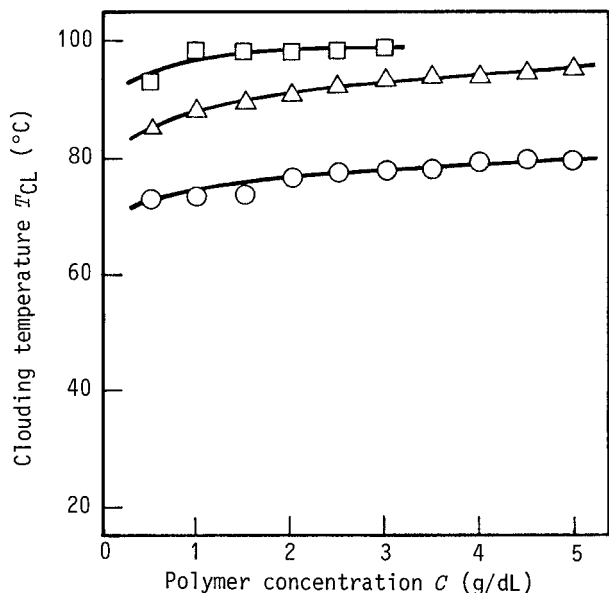


Figure 2 Relations between the clouding temperature and the polymer concentration for PVA/EG solutions during gradual cooling: (○) HDP a -PVA; (△) LDP s -PVA; (□) HDP s -PVA.

Clouding and Gelation Temperatures of Solutions

To study the gelation behavior of s - and a -PVAs in EG, the systems with low polymer concentration of 0.5–5 wt % were used. Figure 2 shows the relations between the clouding temperature and the polymer concentration for the three samples. The clouding temperature of s -PVA solutions (85–98°C) is higher than that of a -PVA solutions (72–80°C).^{2,10,11–13} PVA precipitates from the dilute EG solution by standing for a long time at 70–100°C.^{2,14–16} The precipitation temperature is higher than the clouding temperature in the case of gradual cooling. Figure 3 shows the relations between the gelation temperature and the polymer concentration. The gelation temperature (60–90°C) was 10–15°C lower than the clouding temperature. T_{CL} and T_G depended strongly on the tacticity and the molecular weight of PVA.

Figure 4 shows the relations between the quenching temperature and the gelation time for 2 g/dL solutions. For s -PVA, the molecular weight dependence of the gelation time was low at the quenching temperatures below 60°C. However, the tacticity dependence of the gelation time was high. The gelation time for the s -PVA solution was very short and 120 s more or less at the quenching temperatures below 60°C, but for the a -PVA solutions, it was below 30°C. Figure 5 shows the relations between the quenching temperature and the gelation time for HDP s -PVA solutions. The poly-

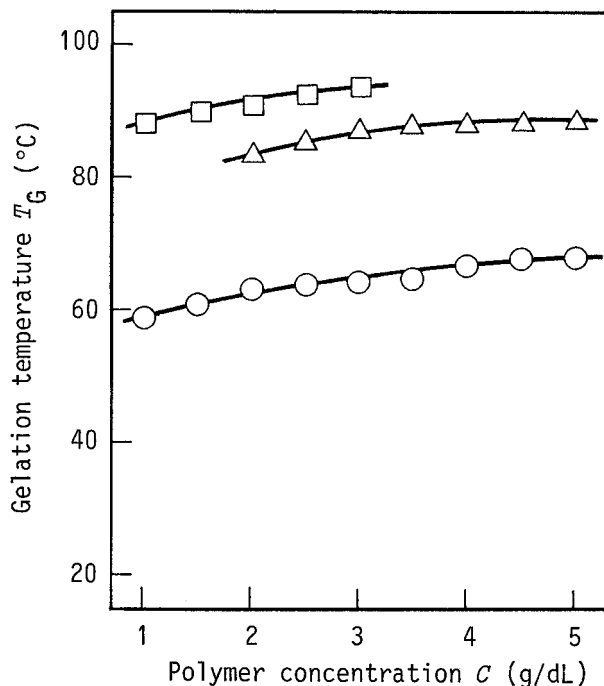


Figure 3 Relations between the gelation temperature and the polymer concentration for PVA/EG solutions during gradual cooling: (○) HDP a -PVA; (△) LDP s -PVA; (□) HDP s -PVA.

mer concentration dependence of the gelation time was recognized, but even the 1 g/dL HDP s -PVA solutions can gel in a very short time.

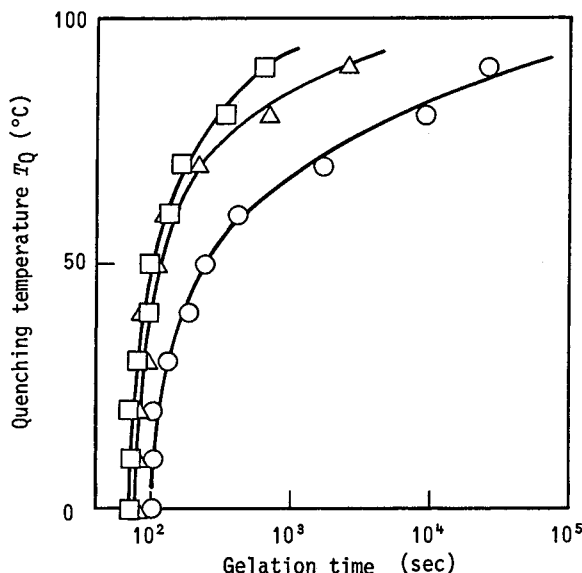


Figure 4 Relations between the quenching temperature and the gelation time for 2.0 g/dL PVA/EG solutions: (○) HDP a -PVA; (△) LDP s -PVA; (□) HDP s -PVA.

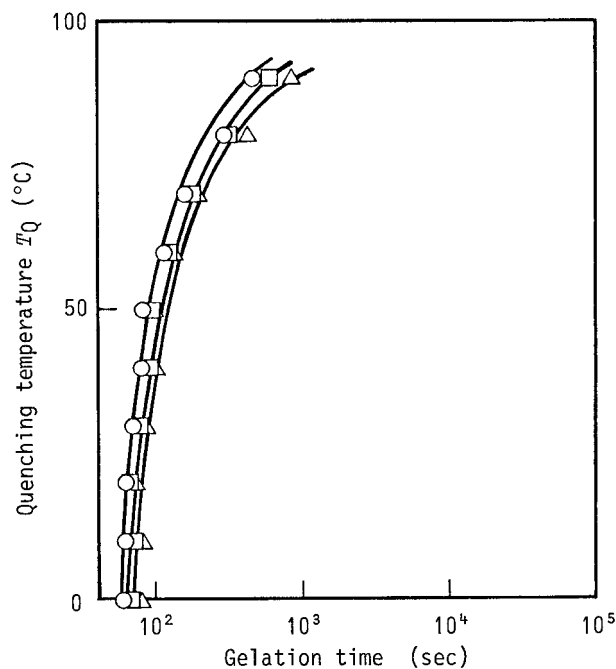


Figure 5 Relations between the quenching temperature and the gelation time for HDP *s*-PVA solutions. Polymer concentration: (○) $C = 3$ g/dL; (□) 2 g/dL; (△) 1 g/dL.

Melting Temperature of Gels

The critical polymer concentration C^* of the gelation after solutions were chilled for 24 h was 1.5 g/dL at 0–100°C for the HDP *s*-PVA solution or at 0–40°C for HDP *α*-PVA and 2.0 g/dL at 50–100°C for HDP *α*-PVA. C^* for the LDP *s*-PVA solution was 2.0 g/dL at 0–60°C and 3.0 g/dL at 90–120°C.

Figure 6 shows the relations between the polymer concentration and the melting temperature for HDP *α*-PVA gels quenched at 0–100°C for 24 h, i.e., Eldridge–Ferry's plot.¹⁷ The melting temperature of gels with the same concentration was independent of the quenching temperature and the spots of the temperature on the figure were scattered. However, the melting temperature of the PVA/EG systems depended strongly on the polymer concentration, the molecular weight, and the tacticity. Figure 7 shows the relations between the polymer concentration and the melting temperature for the three PVA gels. The straight lines in Figures 6 and 7 were drawn by the method of least squares. The apparent enthalpy change of gel melting ΔH_M [$\ln C = -(\Delta H_M/RT_M) + \text{const}$]¹⁷ for HDP *α*-PVA was 206 kJ/mol. ΔH_M 's for both *s*-PVAs were 172 ($DP = 1590$) and 238 kJ/mol ($DP = 15,300$), respectively. The melting temperature for gels of the LDP *α*-PVA/EG/water

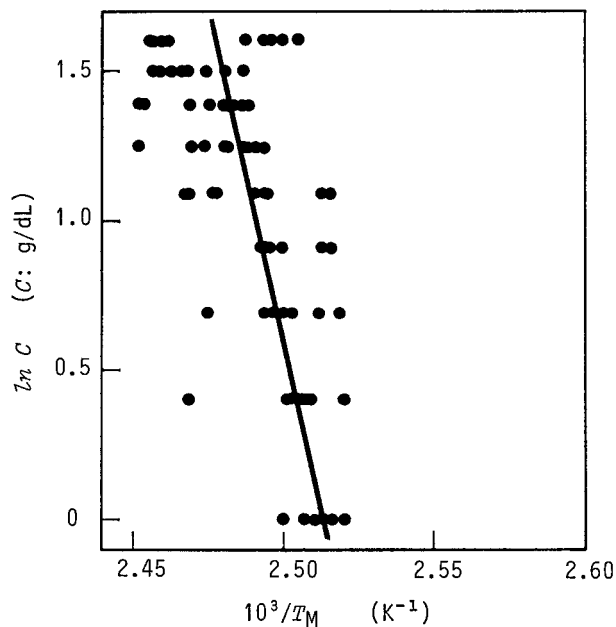


Figure 6 Eldridge–Ferry's plot for HDP *α*-PVA/EG gels obtained by quenching at 0–100°C for 24 h.

systems was measured using differential scanning calorimetry¹⁸ and it was shown that ΔH_M obtained by Eldridge–Ferry's plot increased with increase in EG content.

The melting temperature of PVA hydrogels depends on the quenching temperature, the standing time, the initial temperature of heating, and the heating rate.^{19–22} Table I shows the effect of the standing time on the melting temperature of

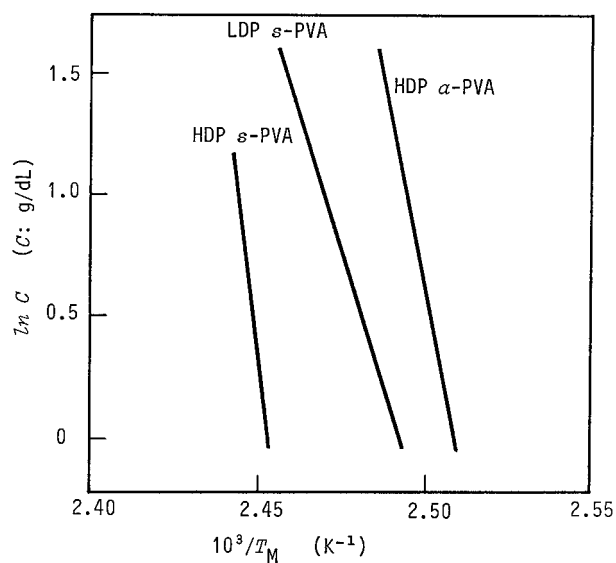


Figure 7 Eldridge–Ferry's plot for PVA/EG gels obtained by quenching at 0–100°C for 24 h.

Table I Melting Temperatures of Gels Chilled at 40°C for HDP α -PVA/EG Solutions (Heating Was Initiated from 105°C)

Standing Time	Polymer Concentration (g/dL)									
	0.5	1.0	1.5	2.0	2.5	3.0	3.5	4.0	4.5	5.0
	Melting Temperature of Gels (°C)									
5 min	—	123.0	129.0	127.1	127.1	127.0	127.5	127.5	129.2	129.6
10 min	—	126.0	127.0	126.5	127.2	128.0	132.0	132.2	132.0	130.8
30 min	—	124.8	126.0	127.0	127.1	127.0	132.0	129.2	132.0	130.9

gels obtained by chilling HDP α -PVA/EG solutions at 40°C. The melting temperature of gels with the same polymer concentrations was independent of the standing time. Identical results were obtained for *s*-PVA/EG gels. Moreover, in comparison with PVA hydrogels, the melting temperature of the gels for the *s*-PVA/EG systems was recognized to be independent of the heating rate (Table II) and the initial temperature of heating, namely, thermal hysteresis.

From the results described above, the gelation process and the gel structure of the PVA/EG system is considered to be independent of the gelation conditions. Although the LDP *s*-PVA solutions with the polymer concentration below 1.5 and 2.5 g/dL were still sol after chilling for 24 h at 0–60°C and 70–120°C, respectively, they were opaque. The opaque sol changed into transparent solutions after being heated to 136–146°C. The transition temperature of the solution from opaque to transparent solutions was ca. 5°C higher than the melting temperature of the gels. In the case of *s*-PVA hydrogels, its solution was transparent in the vicinity of the melting temperature. Since EG as a solvent is poorer than is water for PVA, the clear phase separation of PVA crystallites and EG is considered to be performed

through the gelation. The transition temperature (142–146°C) to the transparent solution for the gels obtained by being chilled at 90–120°C was higher than that (136–140°C) for the gels obtained by being chilled at 0–80°C, namely, the thermally more stable microcrystals were formed by chilling at higher temperatures.

Properties of Dry Gels

Table III shows the crystallinity of various undrawn films. The crystallinity of the films obtained by being chilled at 100°C was higher than that at 0–50°C. As is obvious in Figures 4 and 5, the solutions gelled in a very short time at lower temperatures. Therefore, sufficient propagation of microcrystals was interfered with at lower temperatures. Table IV shows the melting temperature of dry gels found in the DSC curves. The melting temperature of the dry gels obtained by gradual cooling were higher than that of the dry gels obtained by quick cooling. The melting temperature of the former dry gels coincided with that²³ of solution-grown crystal mats. The former gels are expected to have larger microcrystals than those of the latter dry gels. The melting peaks of the former gels were broad and those of

Table II Melting Temperatures of Gels Obtained by Chilling at 100°C for 30 Min for LDP *s*-PVA/EG Solutions (Heating Was Initiated from 115°C)

Heating Rate (°C/min)	Polymer Concentration (g/dL)				
	3.0	3.5	4.0	4.5	5.0
	Melting Temperature (°C)				
0.2	133.0	139.2	143.9	138.9	141.2
1.0	134.8	141.9	142.0	139.1	143.6

Table III Crystallinity of Undrawn Films (C = 2.5 g/dL, Chilling Time: 24 h)

Sample	Gelation Temperature (°C)	Crystallinity (%)
HDP <i>s</i> -PVA	0	37.6
HDP <i>s</i> -PVA	50	36.8
HDP <i>s</i> -PVA	100	49.1
HDP α -PVA	0	32.7
HDP α -PVA	100	37.1
LDP <i>s</i> -PVA	0	39.1

the latter gels were sharp. In the case of the latter gels, the propagation of large microcrystals is restrained by gelling at a shorter time. The crystallinity of drawn films obtained from EG solutions was higher than that obtained from aqueous solutions.²⁴ As described in the previous section, it is indicated that EG as a solvent is poorer than is water for PVA.

Figure 8 shows the relations between the Young's modulus and the draw ratio. The drawability of *s*-PVA films was lower than that of *a*-PVA films. As the former films were brittle, it is considered that a large number of defects were generated in the drawn films. The Young's modulus of the HDP *a*-PVA drawn films were highest. The maximum and mean Young's moduli of the HDP *a*-PVA drawn 15 times the original length were 37 and 26 GPa, respectively. The values were lower than those for HDP *s*-PVA gel fibers obtained in the previous article² and for the solution-grown crystal mats.²³

CONCLUSIONS

The melting temperature (T_M) of the gels of atactic or syndiotactic poly(vinyl alcohol) (*a*- or *s*-PVA)/ethylene glycol (EG) systems was chiefly examined and we obtained the following results:

1. T_M was independent of quenching temperature, quenching time, initial temperature of heating, and heating rate, i.e., independent of the gelation conditions and thermal hysteresis.

Table IV Melting Temperatures (Peak Temperature in DSC Curves) of Dry Gels (Cooling Temperature 30°C, Chilling Time 30 min)

Sample	Cooling Method	Melting Temperature (°C)
LDP <i>a</i> -PVA	Quick	220
	Gradual	227
HDP <i>a</i> -PVA	Quick	231
	Gradual	238.5
LDP <i>s</i> -PVA	Quick	243
	Gradual	243.5
HDP <i>s</i> -PVA	Quick	247.5
	Gradual	248.5

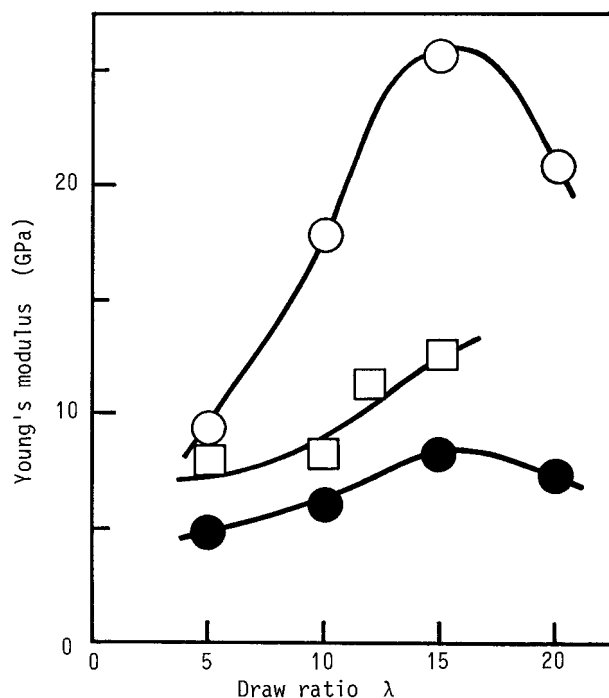


Figure 8 Relations between the Young's modulus and the draw ratio for the gel films: (○) HDP *a*-PVA, 0°C; (●) LDP *s*-PVA, 50°C; (□) HDP *s*-PVA, 50°C.

2. T_M depended strongly on polymer concentration, molecular weight, and tacticity.
3. The thermally more stable microcrystals in gels were formed by chilling at higher temperature or slow cooling.
4. The drawability of dry-gel films of *a*-PVA was higher than that of *s*-PVA.
5. The maximum and mean Young's moduli of drawn ($\times 15$) film of *a*-PVA with high molecular weight were 37 and 26 GPa, respectively.

We are grateful to Prof. Dr. S. Matsuzawa of Shinshu University for his valuable advice.

REFERENCES

1. Y. D. Kwon, S. Kavesh, and D. C. Prevorsek, U.S. Pat. 440,711 (1985).
2. K. Yamaura, T. Tanigami, N. Hayashi, K. Kosuda, S. Okuda, Y. Takemura, M. Itoh, and S. Matsuzawa, *J. Appl. Polym. Sci.*, **40**, 905 (1990).
3. R. Schellekens and C. Bastiaansen, *J. Appl. Polym. Sci.*, **43**, 2311 (1991).
4. S.-H. Hyon and Y. Ikada, U.S. Pat. 4,765,935 (1988); W.-I. Cha, S.-H. Hyon, and Y. Ikada, *J. Polym. Sci. Polym. Phys. Ed.*, **32**, 297 (1994).
5. K. Yamaura, K. Ikeda, M. Fujii, R. Yamada, T. Tan-

- igami, and S. Matsuzawa, *J. Appl. Polym. Sci.*, **34**, 989 (1987).
6. K. Yamaura, M. Daimoh, T. Tanigami, and S. Matsuzawa, *J. Appl. Polym. Sci.*, **36**, 1707 (1988).
7. T. Kunugi, T. Kawasumi, and T. Ito, *J. Appl. Polym. Sci.*, **40**, 2101 (1990).
8. T. Tanigami, L.-H. Zhu, K. Yamaura, and S. Matsuzawa, *Sen-i Gakkaishi*, **50**, 53 (1994).
9. K. Monobe and H. Fujiwara, *Kobunshi Kagaku*, **21**, 179 (1964).
10. W. Stokes and H. Berghmans, *J. Polym. Sci. Polym. Phys. Ed.*, **29**, 609 (1991).
11. G. Rehage, *Kunststoffe*, **53**, 605 (1963).
12. K. Monobe and H. Fujiwara, *Kobunshi Kagaku*, **21**, 179 (1964).
13. W. Stokes, H. Berghmans, P. Moldenaers, and J. Mewis, *Br. Polym. J.*, **20**, 361 (1988).
14. H. E. Harris, J. F. Kenney, G. W. Willcockson, R. Chiang, and H. N. Friedlander, *J. Polym. Sci. A-1*, 665 (1966).
15. K. Tuboi and T. Mochizuki, *Kobunshi Kagaku*, **24**, 366 (1967).
16. T. Kanamoto, S. Kiyooka, Y. Tajima, and H. Sano, in *The Fifth Annual Meeting, PPS (Kyoto)*, 1989, p. 132.
17. J. E. Eldridge and J. D. Ferry, *J. Phys. Chem.*, **58**, 992 (1954).
18. K. Nishinari and M. Watase, *Polym. J.*, **25**, 463 (1993).
19. S. Matsuzawa, K. Yamaura, R. Maeda, and K. Ogasawara, *Makromol. Chem.*, **180**, 229 (1987).
20. K. Yamaura, T. Takahashi, T. Tanigami, and S. Matsuzawa, *J. Appl. Polym. Sci.*, **33**, 1983 (1987).
21. K. Yamaura, H. Katoh, T. Tanigami, and S. Matsuzawa, *J. Appl. Polym. Sci.*, **34**, 2347 (1987).
22. K. Yamaura, I. Kurose, and T. Tanigami, *J. Appl. Polym. Sci.*, **60**, 897 (1996).
23. T. Kanamoto, S. Kiyooka, Y. Tovmasyan, H. Sano, and H. Narukawa, *Polym. J.*, **31**, 2039 (1990).
24. K. Yamaura, M. Tada, T. Tanigami, and S. Matsuzawa, *J. Appl. Polym. Sci.*, **31**, 493 (1986).