

# Preparation of High Modulus Poly (vinyl Alcohol) by Drawing

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## Synopsis

The preparation of PVA films and fibers with high modulus and high strength was examined. The high drawing was attained when both the drawing just before melting and the relaxation at room temperature were repeated. The maximum draw ratio was 40 for the films prepared from the gels of high molecular weight (HMW)  $\alpha$ -PVA (DP = 12000)/water/dimethyl sulfoxide (DMSO) system (water/DMSO = 20/80). The degree of crystallinity of the dried gels prepared from the PVA/ethylene glycol (EG) system was high, 40–50%, and independent on the tacticity of PVA. The modulus of the fibers, prepared from the gels of HMW  $s$ -PVA (DP = 15300)/EG system, drawn 15 times to its original length was the highest (120 GPa).

## INTRODUCTION

Recently, numerous investigators have made efforts to prepare ultrahigh strength and ultrahigh modulus oriented polymers. The preparation methods are ample in variation. Namely, for ultrahigh molecular weight polyethylene (UHMW PE), gel-state spinning,<sup>1</sup> superdrawing of films obtained from gels,<sup>2</sup> superdrawing of single crystal mats,<sup>3</sup> two-step drawing of single crystal mats,<sup>4</sup> and the zone-drawing/annealing of films or fibers<sup>5</sup> have been investigated. Even from flexible polymers, the superdrawn materials of modulus close to theoretical values had been prepared. For poly (vinyl alcohol) (PVA), the preparation of high modulus materials has been tried by drawing fibers prepared by gel-state spinnings from glycerin (Gly), ethylene glycol (EG),<sup>6,7</sup> and water/dimethyl sulfoxide (DMSO) solutions,<sup>8</sup> and by flow-induced crystallization under the presence of seed crystals.<sup>9</sup>

Although the authors have tried to prepare high modulus films and fibers from the PVA ( $s$ -PVA) derived from vinyl trifluoroacetate,<sup>10–12</sup> which is more crystallizable than PVA ( $\alpha$ -PVA) derived from vinyl acetate, the former modulus was only slightly higher than the latter. In this article, we tried to prepare high strength and high modulus materials from precipitate mats, casting films, films prepared from gels of mixed water/DMSO or EG solutions, and fibers prepared by gel spinning from EG solutions for HMW  $\alpha$ -PVA and  $s$ -PVA.

## EXPERIMENTAL

### Samples and Solvents

$\alpha$ -PVAs which had the degrees of polymerization (DPs) of 2950, 7810, and 12,000 and the syndiotactic diad contents of 48.3, 50.9, and 50.0%, respectively

(supplied by Shin-Etsu Chemical Co. Ltd. and Unitika Chemical Co. Ltd.), were used. *s*-PVAs which had DPs of 1460, 1590, 1680, 2830, and 15,300 and the syndiotactic diad contents of 56.0, 57.2, 55.2, 56.0, and 57.4%, respectively, were used. Distilled water was used as a solvent. As organic solvents, DMSO, EG, diethylene glycol (DEG), triethylene glycol (TEG), 1,2-propanediol [1,2-Pr(OH)<sub>2</sub>], 1,3-propanediol [1,3-Pr(OH)<sub>2</sub>], 1,3-butanediol [1,3-Bu(OH)<sub>2</sub>], 1,4-butanediol [1,4-Bu(OH)<sub>2</sub>], 1,5-pentanediol [1,5-Pe(OH)<sub>2</sub>], 1,2,6-hexanetriol [1,2,6-Hx(OH)<sub>3</sub>], glycerin (Gly), and trimethylol propane (TMPr) of special grade of Wako Chemical Co. Ltd. were used without distillation.

### Determination of Dissolution and Precipitation Temperatures

Fiberlike flake *s*-PVA (0.03 g) dried under vacuum at 50°C was sealed with 3 mL of organic solvents in glass tubes (inner diameter, 12 mm). The dissolution temperature ( $T_d$ ) of *s*-PVA was determined at a heating rate of 1°C/min in a silicone oil bath. After the solutions were heated to  $T_d + 10^\circ\text{C}$ , the precipitation temperature ( $T_p$ ) was determined by gradual cooling.

### Preparation of Casting Films

After PVA was dissolved in water at 130°C in a sealed test tube, films were prepared by the casting method at room temperature and in an oven at 80°C. Solution concentrations were 1.3 and 2 g/dL. Thickness of films obtained from the former and latter solutions was 16 and 25–53 μm, respectively.

### Preparation of Precipitate Mats

PVA was put in a round flask with solvents and dissolved during stirring at 195°C [1,2-Pr(OH)<sub>2</sub>, 0.1%] or at 160°C (EG, 0.2%). After dissolution, the 1,2-Pr(OH)<sub>2</sub> solutions were cooled slowly to 150 or 145°C and most of the PVA was precipitated by standing for 6 h at those temperatures. PVA was perfectly precipitated by standing for 24 h after cooling to room temperature. The EG solutions were cooled slowly to 50°C or room temperature, or rapidly to 0°C, and PVA was precipitated by standing for 24 h at those temperatures. After removing the supernatant by decantation, the remaining solution was poured into a column (inner diameter, 4 cm) with glass filter and the precipitates were filtered off and dried under the stream of air. The precipitate mats with thickness of 0.3–1.0 mm were obtained.

### Preparation of Gel Films

After PVA was dissolved in water/DMSO (= 20/80; volume ratio) mixture at 120°C, the solutions were poured into a Petri dish and gelled by placing in a freezer (−40°C) for 24 h. The gels were kept in a large excess of water to extract DMSO and then dried. After PVA was further dissolved in EG at 160°C, the solutions were poured into a Petri dish, cooled rapidly to 0°C, and gelled by keeping at the temperature for 2–3 h. The gels were kept in a large excess of water to extract EG and then dried.

### Gel Spinning

After both *s*-PVA and *a*-PVA were dissolved in the sealed glass tube with EG at 160°C, the solutions were poured into the syringe heated at 150°C. The *s*-PVA solutions (about 130°C) and the *a*-PVA solutions (about 110°C) were extruded into a methanol bath of 0°C and kept there for 2–3 h to obtain gel filaments (diameter, about 3 mm). The gels were kept in a large excess of water to extract EG and dried.

### Drawing Methods

1. Cast films were drawn in steam (70–80°C).
2. Precipitate mats were softened in water at 50°C, pressed, and drawn in water at 90°C.
3. Precipitate mats, cast films, and gel fibers were drawn in an oven at 220–200°C and relaxed at room temperature. The drawing/relaxation cycles were repeated 10–20 times.
4. Precipitate mats and cast films were drawn in silicone oil at 220–200°C and relaxed at room temperature. The drawing/relaxation cycles were repeated 5–15 times.

### Measurements of Properties of Films and Fibers

Precipitates were observed using a Nikon Optihot-Pol polarizing microscope. Density was determined by the floating method in benzene–carbon tetrachloride mixture. Tensile properties were measured using the tensile tester of a TOM/5 type of Shinko Tsushin Kogyo at 20–22°C and relative humidity of about 50%. The lengths of the film and the fiber were 20 mm and the elongation rate was 10 mm/min. The heat treatment of the drawn film and fiber was carried out as follows. Both the ends of the section paper with film or fiber were fixed by adhesive on a glass plate. The glass plate was held in an oven. The annealing time and annealing temperature were 10 min and 200°C, respectively. The wide-angle X-ray diffraction patterns were recorded on a flat film camera for a Rigaku X-ray diffraction apparatus by using nickel-filter  $\text{CuK}\alpha$  radiation. The thermal analysis was carried out using a Rigaku Denki thermoflex differential scanning calorimeter. The heating rate was 10°C/min.

## RESULTS AND DISCUSSION

### Dissolution and Precipitation Temperatures

The dissolution and precipitation temperatures of *a*-PVA in various solvents have been reported by Monobe and Fujiwara.<sup>13</sup> In this article, the two temperatures for *s*-PVA with low (DP = 1460) and high (DP = 15,300) molecular weights (LMW and HMW) were decided. Table I shows the results obtained. The dissolution temperature ( $T_d$ ) of *s*-PVA in DMSO was below 100°C and was the lowest among those solvents used in this article. Therefore, DMSO is considered to be a good solvent of *s*-PVA. *s*-PVA is insoluble in water below 100°C and dissolves barely in a sealed tube at the temperatures above 110°C. In the case of solvents except water and DMSO,  $T_d$  of *s*-PVA in EG was the

TABLE I  
Dissolution and Precipitation Temperatures ( $T_d$  and  $T_p$ ) for Low and High  
Molecular Weight *s*-PVAs (LMW and HMW *s*-PVA)<sup>a</sup>

Solvent	LMW <i>s</i> -PVA		HMW <i>s</i> -PVA	
	$T_d$	$T_p$	$T_d$	$T_p$
Water	110 <sup>b</sup>	c	127 <sup>b</sup>	c
DMSO	64.5	c	86	c
EG	147	86	153	93
DEG	202.5	144	205	159
1,2-Pr(OH) <sub>2</sub>	181	135	184.5	146
1,3-Pr(OH) <sub>2</sub>	164.5	c	170	c
1,3-Bu(OH) <sub>2</sub>	212	158.5	217	167
1,4-Bu(OH) <sub>2</sub>	194	143	198	150
1,5-Pe(OH) <sub>2</sub>	203.5	161	210	169
1,2,6-Hx(OH) <sub>3</sub>	188	139	197	145
Gly	159.5	93	164	97
TMPr	189.5	139	195	150

<sup>a</sup> Polymer concentration: 0.1 g/dL.

<sup>b</sup> Y. Go, S. Matsuzawa, Y. Kondoh, K. Nakamura, and T. Sakamoto, *Kobunshi Kagaku*, **25**, 55 (1968).

<sup>c</sup> Precipitates were not recognized.

lowest, 147°C (HMW, 153°C), and  $T_d$  of *s*-PVA in 1,3-Bu(OH)<sub>2</sub> was the highest, 212°C (HMW, 217°C). *s*-PVA has been reported to dissolve in TEG at 260°C.<sup>14</sup>  $T_d$  of *s*-PVA in water was higher than that of *a*-PVA, the difference was about 55°C and was the largest among all the solvents used in this study. Among the organic solvents used in this study, the difference of  $T_d$  of *s*-PVA and *a*-PVA was lowest in 1,4-Bu(OH)<sub>2</sub> (8°C), and highest in DEG (30°C). In the case of TEG, the difference was large (54°C).<sup>12,13</sup> Although the differences of  $T_d$ 's of HMW and LMW *s*-PVAs in water and DMSO were 17 and 22°C, respectively, the difference in organic solvents except DMSO, used in this study, was only 2.5–9°C.

The precipitation temperatures ( $T_p$ ) of *s*-PVA in various solvents by slow cooling are also shown in Table I. The dilute *s*-PVA solution with DMSO as solvent was transparent even after the solution was kept for a long time at room temperature. The dilute LMW *s*-PVA aqueous solution was transparent after keeping for a short time at room temperature, and it was semitransparent after keeping for a long time at room temperature. The dilute HMW *s*-PVA aqueous solution was semitransparent just after reaching room temperature by slow cooling. No precipitates developed after keeping for longer time at room temperature. No precipitates developed from dilute *s*-PVA solution with 1,2-Pr(OH)<sub>2</sub> as solvent. Except these three solvents, precipitates were observed and the temperatures were designated as  $T_p$  in Table I. The smallest and largest differences between the dissolution and precipitation temperatures were 38.5 and 67°C, respectively. The difference was independent of molecular weight. Monobe and Fujiwara<sup>3</sup> have reported that single crystals were formed from the dilute *a*-PVA solutions using TEG, 1,2-Pr(OH)<sub>2</sub>, or 1,3-Bu(OH)<sub>2</sub> as solvents. Tsuboi et al.<sup>14</sup> have also reported that single crystals were formed from the

dilute *s*-PVA solution using TEG as solvent. The authors investigated the precipitates of *s*-PVA obtained from its 1,2-Pr(OH)<sub>2</sub> or 1,3-Bu(OH)<sub>2</sub> solutions using an optical polarizing microscope, and only the precipitates from 1,2-Pr(OH)<sub>2</sub> solution showed slight polarizability. Since the authors used the commercial organic solvents without distillation, it is speculated that water in air dissolved into those solvents and obstructed the production of single crystals.<sup>14</sup>

The precipitate mats of *s*-PVA were prepared using 1,2-Pr(OH)<sub>2</sub> as a solvent. The dried mats were hard in the case of HMW *s*-PVA, and brittle and chalklike in the case of LMW *s*-PVA. The degree of crystallinity of the former mats was about 30%. The wide angle X-ray diffraction pattern of the mat is shown in Figure 1 (through direction). The wide angle X-ray diffraction pattern to the direction of edge was also analogous to the pattern shown in Figure 1. It may suggest that the crystals are randomly oriented in different directions. For HMW *s*-PVA and *a*-PVA (DP = 7830), though the precipitates were formed from the dilute solution with EG as a solvent, the polarization was not observed. Those precipitate mats were hard and the degrees of crystallinity of the former and latter were 46 and 15%, respectively.

#### Drawing at Low Temperatures

After the film and fiber of PVA were heated at higher temperature (above 200°C) for a long time (above 5 min), their color changed to dark brown. The authors previously carried out drawing in steam,<sup>12</sup> in an oven at 100°C,<sup>10</sup> and in a silicone oil bath at 100°C to prevent coloring.<sup>8</sup> In this article, the hard mats in air were softened in water at 50°C and the drawing of the soft mats in

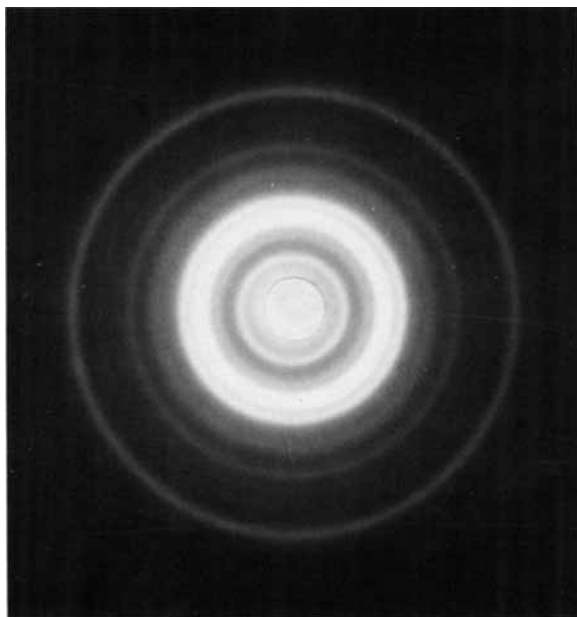


Fig. 1. Wide angle X-ray pattern (through direction) of precipitate-mat obtained from 1,2-Pr(OH)<sub>2</sub> solution of HMW (DP = 15300) *s*-PVA.

water at 90°C was stopped immediately before breaking. The soft precipitate mats were pressed to twice their original size before drawing in water at high temperature, but contracted to 1.5 times the original size when the press was free. After the pressed mats were cut to tapelike, they were drawn to 4.5 times the original size in hot water (90°C). The wide angle X-ray diffraction pattern of the drawn mats was analogous to that shown in Figure 1, that is, the orientation of crystals was not recognized. Therefore, both the Young's modulus (maximum 4.5 GPa) and the strength at break (maximum 0.09 GPa) were still low.

Recently, for the ultrathin films obtained by the bubble and frame methods, the authors have reported that drawing in steam was possible up to about 5.5 times the original length and the Young's modulus of the drawn films annealed at 200°C was about 30 GPa.<sup>12</sup> When the casting film of PVA was drawn in steam, the drawing was possible up to 5, 5.6, 5.2, 4.6, and 4.7 times the original lengths for the HMW *a*-PVA (DP = 7810, thickness = 25 μm), HMW *s*-PVA films (16 and 30 μm) cast at room temperature, and HMW *s*-PVA films (30 and 53 μm) cast in an oven at 80°C, respectively. The maximum Young's modulus for *a*-PVA film was 24 GPa, that for *s*-PVA thin film casted at 80°C was 26 GPa, and the mean Young's modulus of both of them was 16 GPa. The values were higher than those of cast films and fibers of LMW *s*-PVA prepared previously.<sup>10,11</sup> This is considered to be due to the molecular weight effect.

### Drawing at High Temperatures

As described above, the drawing at low temperatures was still not enough to get ultrahigh Young's modulus and the maximum Young's modulus was about 30 GPa. In this section, the drawing at high temperatures (above 200°C) was tried disregarding coloring. The HMW *a*-PVA (DP = 7810) films cast at room temperatures and the HMW *s*-PVA films cast at 80°C were drawn at 220–200°C in an oven and relaxed in air at room temperature. The cycles were repeated 10–15 times and the draw ratio was 9.2 for the former and 9.3 for the latter. The drawing of *s*-PVA casting films reached to six times its original length if it was carried out carefully in an oven at 200°C.<sup>10</sup> Here, the film was first drawn to five times of its original length and the drawn films were relaxed in air. The following drawing was carried out up to 1.05–1.1 times predrawing length and the films were relaxed in air again. This was repeated 10–15 times. The cast films of LMW *s*-PVA (DP = 1680) were drawn to 12.3 times original length. The maximum Young's moduli were 50.1, 41.8, and 53.4 GPa and the mean Young's moduli were 45, 37, and 33 GPa, respectively, for the HMW *a*-PVA, HMW *s*-PVA, and LMW *s*-PVA cast films. Although the maximum Young's modulus of LMW *s*-PVA films was highest in three samples, the mean value was lowest. This suggests that the orientation of polymer chains does not extend fully, that is, the slippage between crystals in the films might occur since the crystallinity of *s*-PVA was higher than that of *a*-PVA and the entanglement between polymers was incomplete for LMW PVA. The high Young's modulus of HMW *a*-PVA is considered to be due to the uniform orientation of polymer chains. Namely, the entanglement between polymers are presumed still to remain when the melting of crystals progressed considerably, thus leading to uniform orientation even at low draw ratio.

Although the films drawn in steam just before breaking were drawn repeatedly at high temperature, the draw ratios for both of films of *a*-PVA and *s*-PVA were at most 8.7 times the original length, the maximum Young's moduli were 45 and 33 GPa, and the mean values were 33 and 21 GPa, respectively. These values are lower than that of films drawn only at high temperatures. Since the drawing in steam was performed at a sitting just before breaking, the polymer chains were fixed without sufficient uncoiling of entanglement. Therefore, sufficient orientation of polymer chains was not attained by repeated drawing at high temperatures.

A material of higher Young's modulus was found to be produced from the HMW *a*-PVA by drawing in air. The drawing in a silicone oil was also tried. At temperatures above 217°C, the films were drawn in the melting state endlessly. Therefore, the Young's modulus of the drawn films was very low. The DSC thermographs of HMW *a*-PVA and HMW *s*-PVA undrawn cast films are shown in Figure 2. The melting of HMW *a*-PVA films started at 216.5°C and reached melting peak at 228.5°C. Since the drawn films were still in a solid state near 216.5°C, the repeated drawing was tried at 216.5°C by the same method in an oven and the draw ratio was 9.6 times the original length. Although further drawing was tried, it was impossible to draw due to slippage at the fixed parts. If the fixed parts are modified, a higher draw ratio will be attained. The maximum Young's modulus and the mean value were 44 and 30 GPa.

Figure 3 shows the relationship between Young's modulus and the draw ratio for the precipitate mats prepared by the three methods from dilute PVA/EG solution and drawn in a silicone oil at 200°C. The effects of the precipitation methods and the syndiotacticity on Young's modulus were not clearly recog-

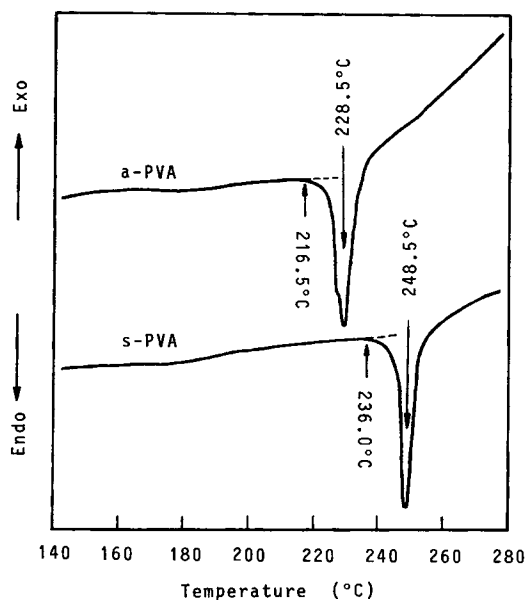


Fig. 2. DSC thermographs of *a*-PVA (DP = 7810) and *s*-PVA (DP = 15300) undrawn cast films dried at 50°C.

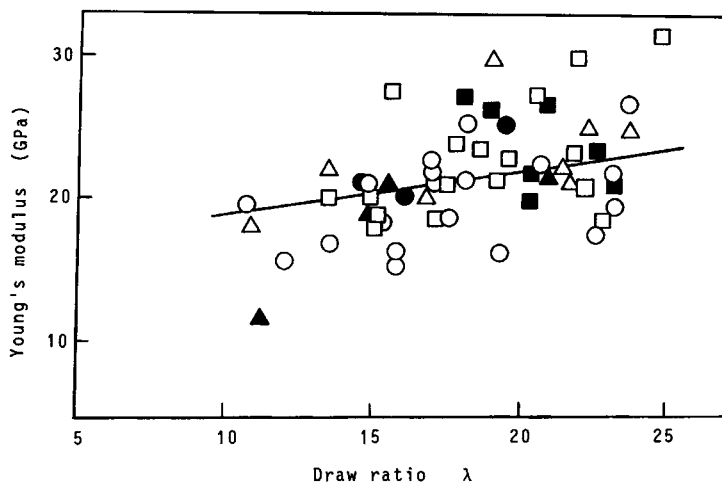


Fig. 3. Young's modulus of *a*-PVA (U, DP = 7810) and *s*-PVA (S, DP = 15300) precipitate-mats obtained from those EG solutions. Precipitation method: (A) gradual cooling up to room temperature; (B) held for 24 h quenching up to 50°C; (C) held for 24 h quenching up to 0°C; (O) SA; (Δ) SB; (□) SC; (●) UA; (▲) UB; (■) UC.

nized. The maximum draw ratio was 30 times the original length and the maximum Young's modulus was 32 GPa. Although the draw ratio was high, Young's modulus was not so much high.

Hyon et al. have found that the gel obtained from an *a*-PVA/water/DMSO mixture (water/DMSO = 20/80, volume ratio) had high Young's modulus. In this study, therefore, the gels of *a*-PVA and *s*-PVA were made using the same mixed solvent at  $-40^{\circ}\text{C}$ . After drawing and relaxation for the dried gels were repeated 10–15 times, the Young's modulus was determined. During drying, the LMW *a*-PVA (DP = 2950) gels obtained from the 2 and 10 g/dL solutions contracted to  $\frac{2}{3}$  and  $\frac{1}{2}$  the original length, respectively, whereas those from the 5 g/dL solution contracted slightly. For the gels prepared from the 10 g/dL solution, although the draw ratio was high (30), the maximum Young's modulus was low (18 GPa). For the gels from the 2 g/dL solution, the maximum draw ratio and Young's modulus were 28 and 35 GPa, respectively. For the gels from the 5 g/dL solution, although the maximum draw ratio was low (20), the Young's modulus was high (45 GPa, Fig. 4). For the HMW *a*-PVA (DP = 12000) gels obtained from the 1 g/dL solution contracted to  $\frac{2}{3}$  the original length during drying, the maximum draw ratio was 40 and the maximum Young's modulus was 62 GPa (Fig. 5). Namely, for the gels of *a*-PVA obtained from water/DMSO mixture, the Young's modulus was dependent on the molecular weight. The gels of HMW *s*-PVA from the 2 g/dL solution contracted to  $\frac{1}{2}$  the original length during drying and the maximum Young's modulus was 35 GPa at a draw ratio of 25. When the draw ratio raised over 25, the Young's modulus lowered reversely. This is due to high crystallinity of *s*-PVA. Namely, the breaking of crystals occurs during drawing at  $220^{\circ}\text{C}$  to lower the Young's modulus with the increase in the draw ratio.

When the 1% EG, DEG, 1,2-Pr(OH)<sub>2</sub>, 1,3-Bu(OH)<sub>2</sub>, 1,4-Bu(OH)<sub>2</sub>, and 1,5-Pe(OH)<sub>2</sub> solutions of HMW *a*-PVA (DP = 12000) were quickly cooled to



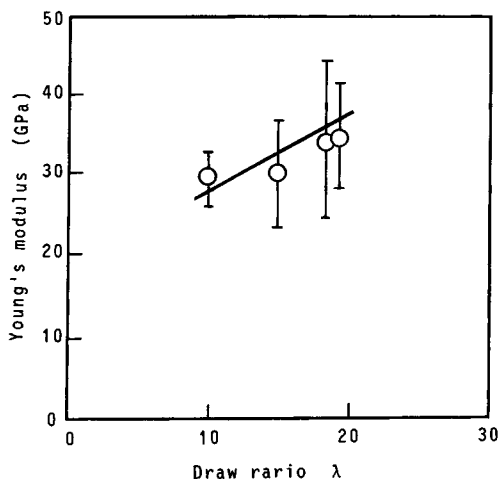


Fig. 4. Young's modulus of gel-films obtained by chilling 5 g/dL water/DMSO (= 20/80) solution of  $\alpha$ -PVA (DP = 2950) at  $-40^{\circ}\text{C}$ .

$18^{\circ}\text{C}$  (in tap water), only the EG solution gelled. The gels from the 1.35% EG solution contracted to  $\frac{2}{3}$  the original length during drying. Figure 6 shows the relation between the Young's modulus and the draw ratio. The maximum draw ratio was 16 and the maximum Young's modulus was 70 GPa. The thickness of the gel fibers of HMW  $s$ -PVA and  $\alpha$ -PVA was not uniform. Figure 7 shows the relations between the Young's modulus and the draw ratio. The maximum Young's modulus was 120 GPa though the draw ratio was low (15). This value of Young's modulus was the highest in which the authors obtained so far. The draw ratio was lower than that of HMW  $\alpha$ -PVA/water/DMSO system. This is considered to be related to the fact that the degree of crystallinity of gels from EG solution was higher than that of gels from water/DMSO solution.

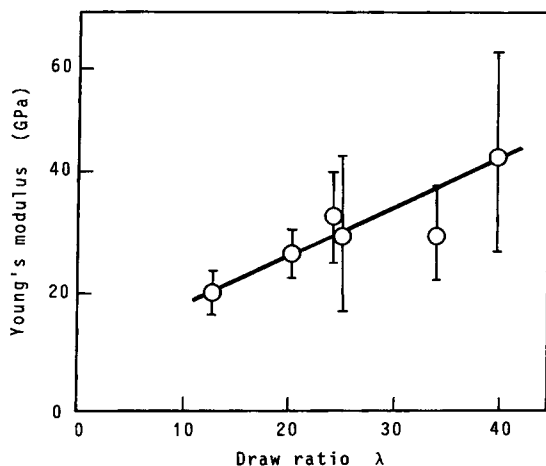


Fig. 5. Young's modulus of gel-films obtained by chilling 1 g/dL water/DMSO (= 20/80) solution of  $\alpha$ -PVA (DP = 12000) at  $-40^{\circ}\text{C}$ .

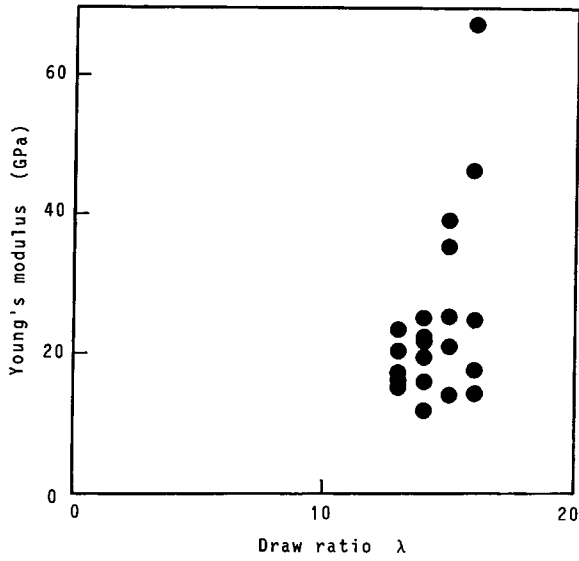


Fig. 6. Young's modulus of gel-films obtained by chilling 1.35 g/dL EG solution of  $\alpha$ -PVA (DP = 12000) at 0°C.

The degrees of crystallinity of the undrawn gel films of *s*-PVA and  $\alpha$ -PVA, 45.6 and 50.1%, were high in comparison with that of casting film of *s*-PVA, 25.4%. Moreover, the degree of crystallinity was 70.4% for the former fibers drawn 14 times the original length and 74.3% for the latter fibers drawn eight times. Figure 8 shows the relationship between the strength at break and the draw ratio for the same samples shown in Figure 7. The maximum strength was 5

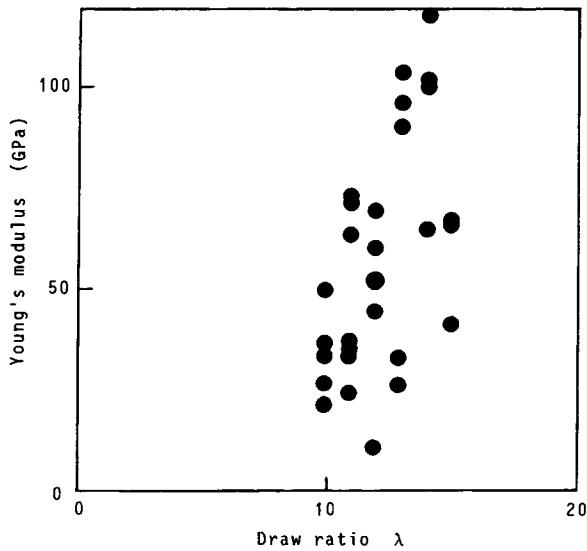


Fig. 7. Young's modulus of fibers obtained by gel-spinning 2% EG solution of *s*-PVA (DP = 15300) into methanol (0°C).

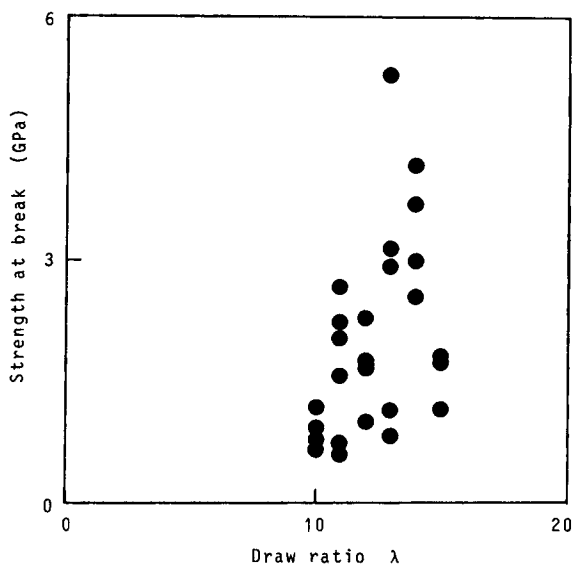


Fig. 8. Strength at break of fibers shown in Figure 7.

GPa. This value also was the highest the authors obtained so far. From these results, if uniform gel fibers are spun from HMW PVA/EG system continuously, fibers with higher Young's modulus and strength are expected to be prepared.

### CONCLUSION

1. The high drawing of PVA films and fibers is attained when both the drawing just before melting and the relaxation at room temperature are repeated.
2. The maximum draw ratio and the Young's modulus of the gel films prepared from the HMW  $\alpha$ -PVA (DP = 12,000)/water/DMSO system (water/DMSO = 20/80) were 40 times and 62 GPa, respectively.
3. Among the casting films, the Young's modulus of films of HMW  $\alpha$ -PVA (DP = 7910) was the highest (50.3 GPa).
4. When 1,2-Pr(OH)<sub>2</sub> was used as a solvent of PVA, the precipitates obtained had polarizability. However, it has not been recognized in the use of other organic solvents.
5. Among the 1% PVA solutions made with various organic solvents, only the solution with EG gelled by rapid cooling to 18°C from ca. 200°C.
6. The degree of crystallinity of dried gels prepared from the PVA/EG system was high (40–50%), independent of the tacticity of PVA.
7. The maximum and mean Young's moduli of the gel fibers of HMW  $s$ -PVA (DP = 15,300)/EG system drawn 15 times the original length were 120 and 90 GPa, respectively.

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Received January 17, 1989

Accepted August 9, 1989