

# Preparation and Properties of Very Thin Films of Syndiotacticity-rich Poly(vinyl Alcohol)

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## Synopsis

Very thin films of poly(vinyl alcohol) could be prepared by utilizing the adsorption of polymer molecules at air/water interface from the aqueous solutions of the poly(vinyl alcohol) derived from vinyl trifluoroacetate. The films prepared by the bubble method were thinner than those obtained by the frame method. The minimum thickness of the former films was 260 Å and that of the latter was 1800 Å. These very thin films resisted water at temperatures below 55°C. The maximum Young's modulus of the drawn/annealed films prepared from these samples was 30 GPa. The permeability of water,  $J_w/\Delta P$ , was  $2-6 \times 10^{-3} \text{ cm} \cdot \text{s}^{-1} \cdot \text{atm}^{-1}$  (0–55°C) for the untreated film (thickness: 1800 Å) prepared by the frame method and  $0.8-2.2 \times 10^{-2} \text{ cm} \cdot \text{s}^{-1} \cdot \text{atm}^{-1}$  (5–55°C) for the untreated film (360 Å) prepared by the bubble method, and depended on the thickness of film.

## INTRODUCTION

Recently, we have developed a preparation method of very thin films by utilizing the adsorption of polymer molecules at the air/water interface for dilute aqueous solutions of syndiotacticity-rich poly(vinyl alcohol) (*s*-PVA),<sup>1</sup> regenerated silk fibroin,<sup>2</sup> and native silk fibroin.<sup>3</sup> The method is carried out by blowing a fixed volume of dilute aqueous solution that is sucked up into the tip of a glass tube. Therefore, we named this the "bubble method." The minimum thickness of very thin films obtained by the bubble method was 940 Å for *s*-PVA,<sup>1</sup> 450 Å for the regenerated silk fibroin,<sup>2</sup> and 390 Å for the native silk fibroin.<sup>3</sup> Since the films obtained from a ball form are not uniform flat films, a new method was also developed in which a liquid film was scooped out of the solution surface with circular or rectangular frames which we call the "frame method." The characteristic of the bubble and frame methods is that the films are formed without any substrate.

In this paper, the effects of degree of polymerization and polymer concentration on the production of ultrathin films by the bubble method and the relation between the film thickness and the polymer concentration for the thin films prepared by the frame method were examined. Moreover, the tensile strength and the permeability of water of the films were studied.

## EXPERIMENTAL

### Preparation of Samples and Solutions

Six unfractionated *s*-PVA samples were used. The degrees of polymerization ( $DP$ ) were 815, 1570, 1970, 3980, 4480, and 15300, and the syndiotactic diad contents were 52.3, 54.9, 58.0, 55.1, 58.6, and 57.4%, respectively. The first five samples were prepared from the polymers obtained by the bulk polymerization of vinyl trifluoroacetate (VTFA) at 60°C, using benzoyl peroxide as an initiator. The last sample was prepared from the polymer obtained by the bulk polymerization of VTFA at room temperature for two months without an initiator. The polymerization mechanism of this sample is unknown at present. An atactic PVA (*a*-PVA) derived from vinyl acetate was also used. The degree of polymerization was 1700 and the syndiotactic diad content was 45%. PVA was dissolved in water at about 130°C in a sealed glass tube.

### Preparation of Films by the Bubble and Frame Methods

The films were prepared at room temperature. Before preparation, opaque aqueous solutions were kept at a high temperature (ca. 95°C) until the opalescence vanished. The bubble method was carried out as follows: a fixed volume (0.025–0.033 mL) of aqueous *s*-PVA solution was sucked up into the tip of a glass tube (inner diameter: ca. 1 mm) and then blown by pushing out air in time intervals of 5–10 s by a pipetter. The frame method was carried out as follows: the aqueous *s*-PVA solution centrifuged was poured into a Petri disk (inner diameter: ca. 10 cm) and a liquid film was scooped out of the solution surface using circular or rectangular frames composed of steel wire (diameter: 0.5 mm).

### Determination of Thickness of Films

The thickness of solid films prepared by the bubble method was determined from values of the polymer concentration, the weight of a drop, the diameter of bubble, and the weight of a solid film. We used 1.269 g/cc for the density of amorphous PVA, as the density for the solid films. The thickness of solid films prepared by the frame method was determined from the film area surrounded by a frame and the weight of a solid film. Moreover, the relation between the film thickness and the transmittance at 3300  $\text{cm}^{-1}$  due to hydroxyl groups in infrared (IR) spectrum was examined.

### Permeability

The experiments were carried out at 0–55°C under the atmospheric pressure, using two cells consisting of two detachable parts made of glass. The membrane was clamped between the cells with filter paper supports. The volume of permeated water was measured as a function of time. The volume flux of water  $J_w$  ( $\text{cm}^3/\text{cm}^2 \cdot \text{s}$ ) and the permeability of water  $J_w/\Delta P$  ( $\text{cm}/\text{s} \cdot \text{atm}$ ) were estimated. The effective membrane areas for the permeation were 7.07 (frame method) and 3.46  $\text{cm}^2$  (bubble method).

### Tensile Measurement

Fine tape-like samples were made of the sphere bubble and flat films by drawing in steam and annealing at 200°C for 10 min. The tensile measurements were carried out fastening a piece of the fine tape-like sample to the clamps of a Shinko Model TOM/5 tensile tester at a cross-head speed of 10 cm/min and an original sample length of 20 mm at 25°C and under the relative humidity of 65%.

## RESULTS AND DISCUSSION

### Preparation of Bubble Films

In the case of  $\alpha$ -PVA, no sphere bubble film could be prepared in a concentration range from 1 to 10 g/dL since the liquid drops fell from the glass tube before blowing.<sup>1</sup> In the case of *s*-PVA with  $DP = 815$ , a sphere bubble with solvent could be blown in a concentration range from 1 to 7 g/dL, but the sphere bubble burst during the vaporizing of solvent and no solid films were obtained. However, in the case of *s*-PVA with  $DP = 1570$ , a sphere bubble film was made successfully when aqueous solutions in a concentration range from 2.5 to 3.5 g/dL were pushed out slowly.<sup>1</sup> Hence, the degree of polymerization and stereoregularity of PVA molecules play an important role in the formation of a sphere bubble film. In this paper, *s*-PVA with  $DP = 3980$  was chiefly used. Sphere bubble films were made when its aqueous solutions in a concentration range from 1.0 to 3.0 g/dL were pushed out (Fig. 1). In the cases of *s*-PVA with  $DP = 1970$ , 4480, and 15,300, sphere bubbles were obtained only from the solutions in the concentration ranges from 2.0 to 3.5 g/dL, from 1.0 to 2.0 g/dL, and from 0.5 to 0.8 g/dL, respectively. The aqueous solutions of the polymer concentrations above the upper limit gelled easily at room temperature. In the case of aqueous *s*-PVA solutions with polymer concentrations below the low limit, the sphere bubble burst during the vaporizing of solvent or liquid drops fell from the glass tube before blowing. The attained diameters of sphere bubble were chiefly between 4 and 5 cm and the maximum diameter was about 6.2 cm in the case of *s*-PVA with  $DP = 3980$  and the polymer concentration  $C = 1.5$  g/dL. The film thickness was about 290 Å. Minimum thickness in the thin films obtained up to this time was 260 Å (see Table II).

### Preparation of Flat Films

In the case of  $\alpha$ -PVA, no liquid film could be scooped out of the solution surface by the frames, whereas the liquid films could be scooped out of the solution surface of *s*-PVA by the circular or rectangular frames (Figs. 2 and 3). The maximum diameter and side length were 7 and 5 cm, respectively. The dried films could be prepared from the solutions which did not gel at a short standing time at room temperature. The low limit of concentration was much lower in comparison with that in the bubble method. In this paper, *s*-PVA with  $DP = 1970$  was chiefly used. Figure 4 shows the effect of polymer concentration on the thickness of a flat solid film. At polymer concentrations above 0.6 g/dL the effect was high, on the other hand at polymer concentra-

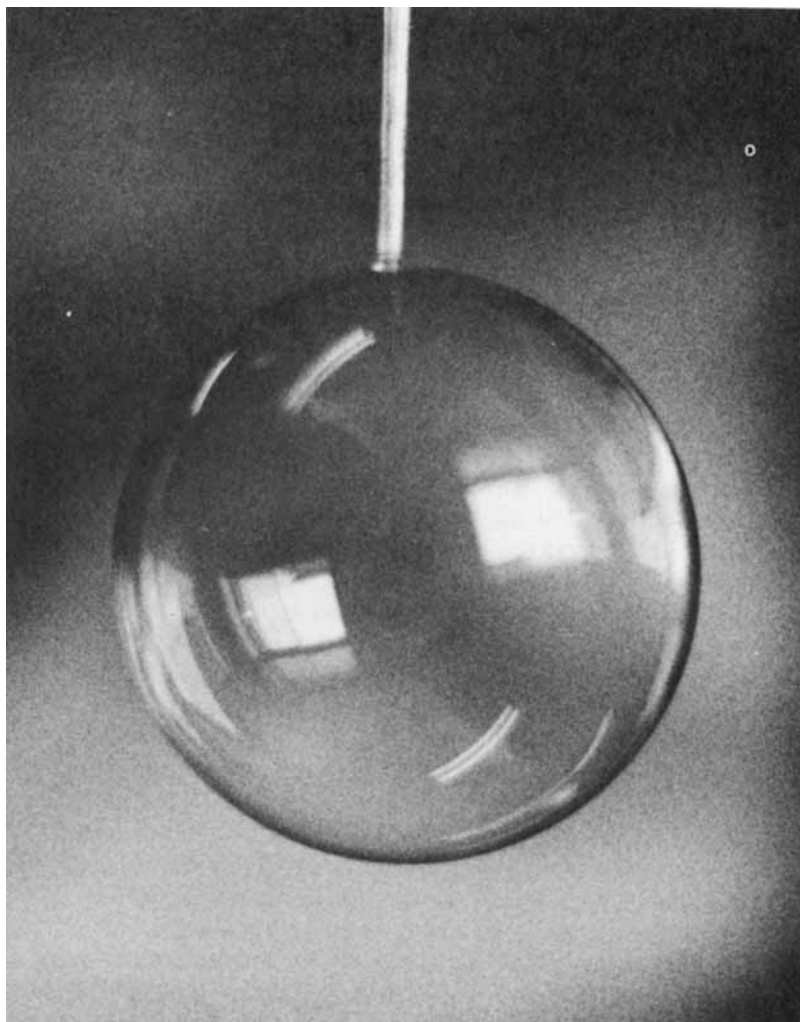


Fig. 1. Photograph of a sphere bubble prepared from the aqueous solution of  $C = 1.5$  g/dL for *s*-PVA with  $DP = 3980$ .

tions below 0.5 g/dL it was low. The polymer concentration of 0.5 g/dL for *s*-PVA with  $DP = 1970$  is considered to correspond to a CMC, that is, multilayers are considered to be formed at the interface of air/solution in the case of solutions of the polymer concentrations above 0.5 g/dL. Although the scooping of liquid films could be carried out shortly one after another in the case of solutions of polymer concentrations above 0.6 g/dL, it was difficult in the case of the polymer concentrations below 0.5 g/dL, that is, the time required for the adsorption of polymer molecules to the air/solution interface became much longer. The low limit of concentration for *s*-PVA with  $DP = 1970$  was 0.4 g/dL in the case of the frame method and 2.0 g/dL in the case of the bubble method, that is, the former was much lower. Polymer molecules in the aqueous *s*-PVA solutions with the air/solution interface are adsorbed to the interface immediately after the preparation of solution.<sup>4,5</sup> Therefore, the

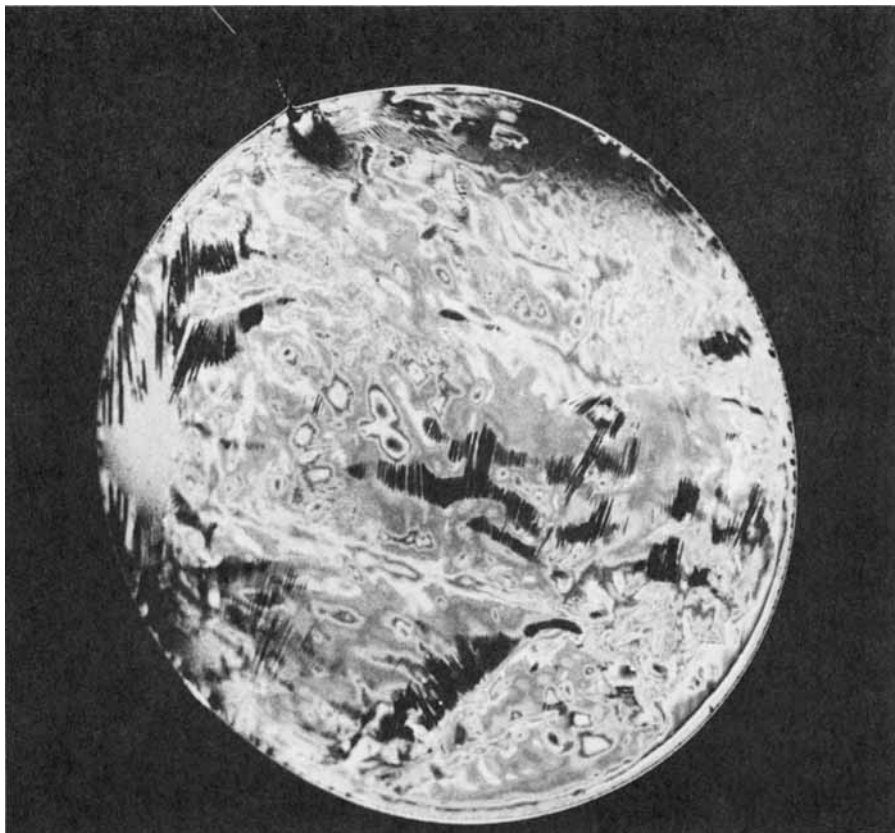


Fig. 2. Photograph of a solid film prepared by the circular frame for *s*-PVA with  $DP = 1590$  ( $C = 2.0$  g/dL).

polymer concentration at the interface is considered to become higher than that in the solution, and the liquid film can be scooped out of the solution surface by the frames. In the bubble method, the solution has scarcely reached the air/solution interface before blowing. As soon as the liquid drop appears from the tip of glass tube, the polymer molecules must be adsorbed immediately at the air/solution interface formed by blowing. As adsorption increases with the increase in the polymer concentration,<sup>4,5</sup> solutions with high polymer concentrations produce stable bubbles.

Figure 5 shows the relation between the transmittance  $I$  (%) at  $3300\text{ cm}^{-1}$  in infrared (IR) spectra and the thickness of solid film estimated from the weight. If the transmittance in the absence of film is  $I_0$  (100%), the absorption coefficient  $a$  is obtained from the following equation:

$$\log(I/I_0) = -ax$$

where  $x$  is the thickness of solid film. From the plots shown in Figure 5, the average value of absorption coefficient  $a$  was estimated to be  $1.415 \times 10^{-5}$ . The straight line in Figure 5 is that for  $a = 1.415 \times 10^{-5}$ . The plots in Figure 5 deviated from the straight line in the range of higher thickness. Though the

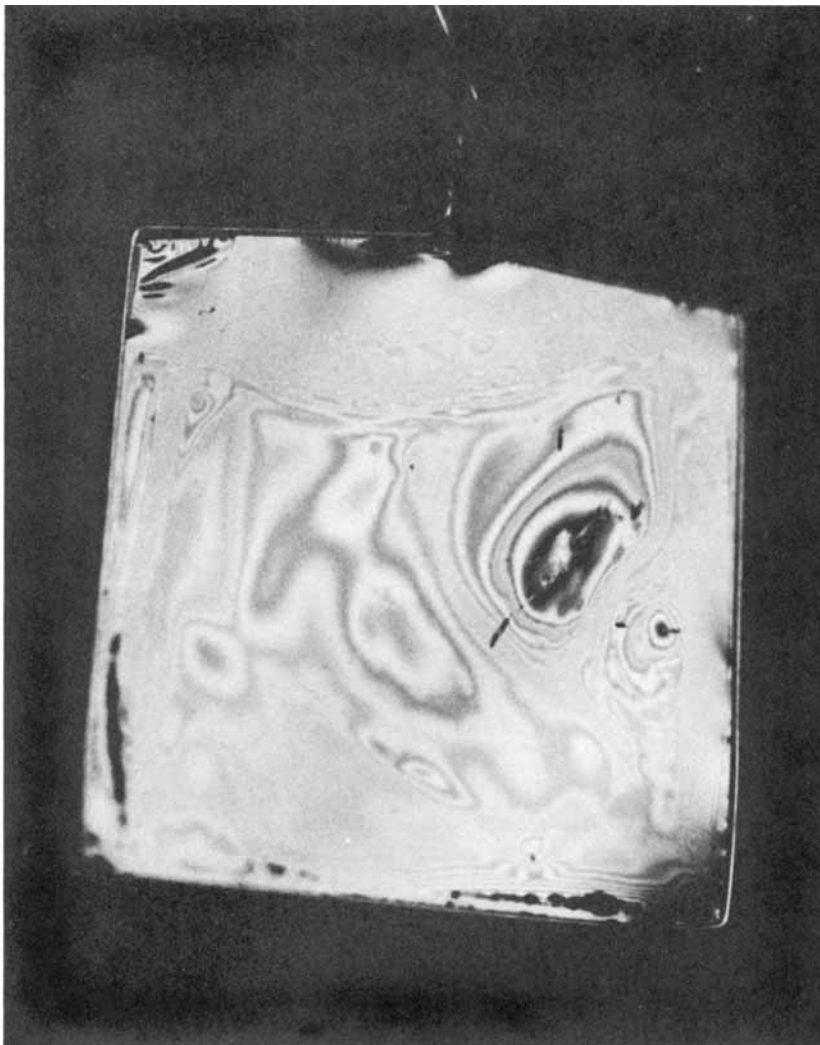


Fig. 3. Photograph of solid film prepared by the rectangular frame for *s*-PVA with  $DP = 1590$  ( $C = 1.0$  g/dL).

reason is not clear at present, the preservation of water in the films is considered as a reason.

#### **Young's Modulus and Strength at Break**

Tables I and II show the tensile properties for the drawn/annealed tape-like samples prepared by the bubble and frame methods, respectively. The draw ratios of bubble films in steam were independent of the film thickness and Young's moduli of thin films were higher than those of thick films. The bubble film for *s*-PVA with  $DP = 15300$  could be drawn highly in comparison to that with low degree of polymerization, but the maximum value of Young's modulus was inverse. Young's modulus of the bubble films was generally higher than that of frame films and the maximum value was about 30 GPa.

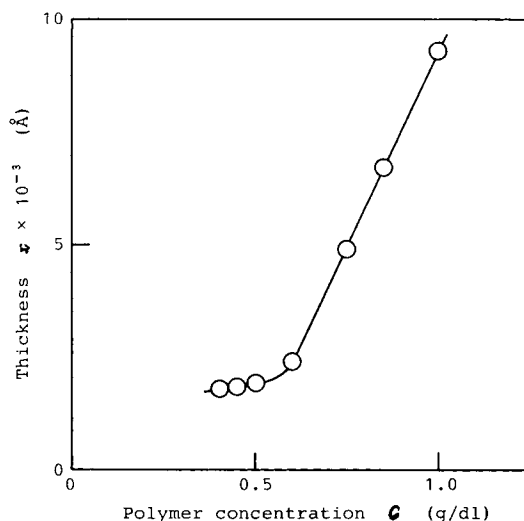


Fig. 4. The relation between the film thickness and the polymer concentration for the solid films prepared by the frame method from aqueous solutions of *s*-PVA with  $DP = 1970$ .

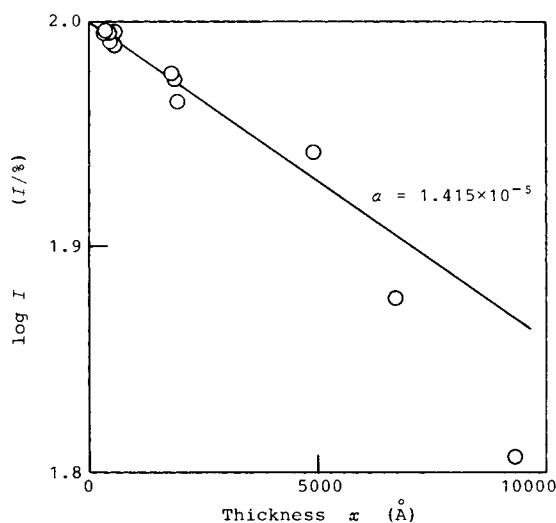


Fig. 5. The relation between the transmittance  $I$  (%) at  $3300\text{ cm}^{-1}$  in IR spectra and the thickness for the thin *s*-PVA films prepared by the frame and the bubble methods.

Though the draw ratios of cast films were higher than that of the bubble and frame films, the maximum values of Young's modulus for the latter films were larger than that of the former (ca. 20 GPa).<sup>6</sup> These results indicate that the polymer molecules in thinner films are uncoiled easier than those in thicker films, that is, the former are entangled loosely in comparison with the latter. Similarly, the strength at break of bubble films was generally higher than that of frame films and the maximum value was 1.5 GPa. In the case of frame films, both Young's modulus and the strength at break of films were lowered with the decrease in the polymer concentration, that is, the thickness of film. The

TABLE I  
Young's Modulus and Strength at Break for the Thin Film Prepared by the Frame Method

<i>DP</i>	Polym. conc. (g/dL)	Draw ratio	Young's modulus (GPa)	Strength at break (GPa)	Strain (%)
1570	2	5	14.1-23.2	0.34-0.61	6.6-8.1
	1	4.5	6.6-14.8	0.19-0.58	6.1-11.0
1970	1.0	4.5-5.3	7.6-30.0	0.15-1.02	—
	0.75	4.1-5.1	3.0-10.8	0.11-0.41	—
	0.6	4.8-5.1	5.5-15.0	0.074-0.40	—
	0.5	2.6-4.1	2.4-8.1	0.076-0.31	—

TABLE II  
Young's Modulus and Strength at Break for the Very Thin Films Prepared by the Bubble Method

<i>DP</i>	Conc. (g/dL)	Balloon diam. (cm)	Thickness (Å)	Draw ratio	Young's modulus (GPa)	Strength at break (GPa)	Strain (%)
1570	3	4.8	940	3	4.7-10.7	0.12-0.34	7.2-12.4
3980	1.5	$\left\{ \begin{array}{l} 3 \\ 4 \\ 5 \end{array} \right.$	1160	4.3-5.5	3.5-27.7	0.14-1.15	1.3-10.8
			650		3.5-25.0	0.26-1.50	2.0-16.5
			420		5.2-31.4	0.20-1.10	3.1-10.5
15300	$\left. \begin{array}{l} 0.8 \\ 0.5 \end{array} \right\}$	4	410	5-6	3.4-21.2	0.10-0.67	7.1-20.0
			260	5-6	8.8-24.4	0.30-0.71	5.7-11.3

section of the thinner films was rougher than that of the thicker films, that is, it was very difficult to straight cut the thinner films owing to the softness and the electrostatic effect. Therefore, the thinner films could not be drawn highly before the tensile measurement.

### Permeability of Water

Figure 6 shows the temperature dependence of the permeability of water for three untreated thin films with the different thickness prepared by the frame method. Figure 7 shows the temperature dependence of the permeability of water for an untreated very thin film and two very thin films annealed at different temperatures prepared by the bubble method. Though these films were very thin, they were resistant to water even at 55°C. In the case of the unannealed thin films, the permeability of water increased with the decrease in the thickness of film as shown in Figures 6 and 7. In particular, the permeability of water for the unannealed very thin film prepared by the bubble method,  $J_w/\Delta P$ , was  $0.8-2.2 \times 10^{-2} \text{ cm} \cdot \text{s}^{-1} \cdot \text{atm}^{-1}$  (5-55°C) and much higher than that ( $1 \times 10^{-6}$  at 25°C) for  $\alpha$ -PVA film of the thickness in the dry-state of 0.2 mm.<sup>7</sup> Here it should be noted that the very thin  $\alpha$ -PVA film cannot be prepared. If the thickness of the film which contains water,  $\Delta x$ , is estimated from the degree of swelling,  $J_w \Delta x/\Delta P$  at 25°C was  $2.9-5.5 \times 10^{-8}$  for the samples shown in Figure 6,  $5.2 \times 10^{-8}$  for the untreated samples shown in Figure 7, and  $1.8 \times 10^{-7} \text{ cm}^2 \cdot \text{s}^{-1} \cdot \text{atm}^{-1}$  for  $\alpha$ -PVA film shown above, respectively.  $J_w \Delta x/\Delta P$  values of  $s$ -PVA were slightly low in comparison with that of  $\alpha$ -PVA. This is considered to be due to the difference in the



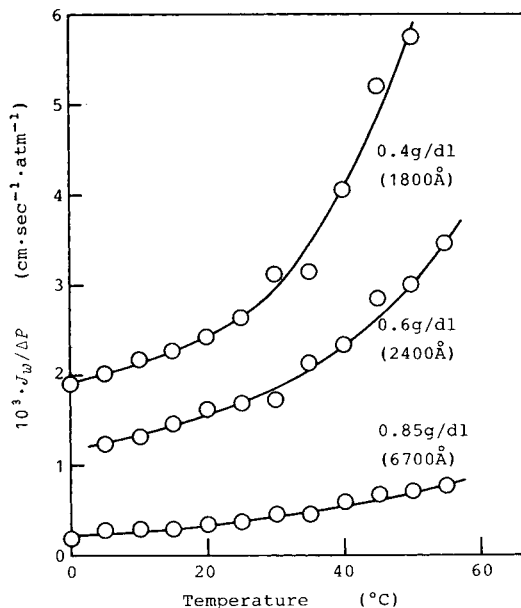


Fig. 6. Temperature dependence of permeability of water for the thin film prepared by the frame method for s-PVA with  $DP = 1970$ .

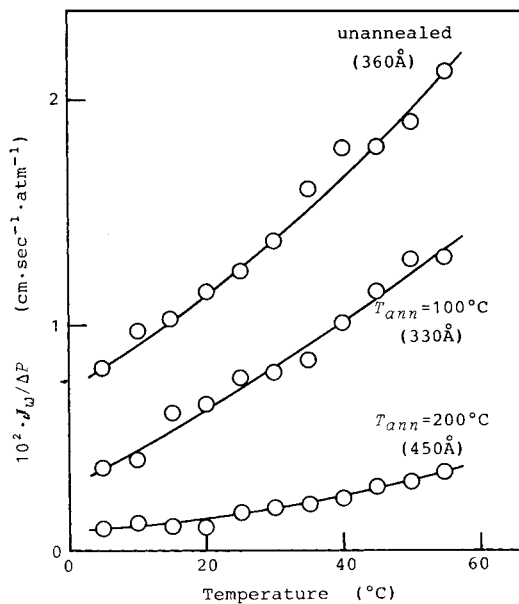


Fig. 7. Temperature dependence of permeability of water for the very thin films prepared by the bubble method for s-PVA with  $DP = 3980$  ( $C = 1.5$  g/dL).

stereoregularity for both samples, that is, the difference in the resistance to water for films of both samples. Though the films obtained in this paper are very thin, they resist water and  $J_w/\Delta P$  values are very high. Therefore, the separation of the solute from the aqueous solution is expected to be achieved at high speed by use of the very thin films.

### CONCLUSIONS

The results obtained in this paper are as follows:

1. The very thin *s*-PVA film could be prepared by utilizing the adsorption of polymer molecules at air/water interface.
2. Though the extensibility of the very thin films prepared in this paper was lower than that of the film prepared by the casting method, Young's modulus for the former was higher than that of the latter.
3. Young's modulus of the ultrathin films prepared by the bubble method increased with the decrease in the film thickness.
4.  $J_w \Delta x/\Delta P$  of the thinner film prepared by the frame method was higher than that of the thicker film.

From these results, the *s*-PVA films prepared by the bubble, the frame, and the cast methods are supposed to have roughly a three-layer structure. The layers at both sides are supposed to consist of the molecules of the loops (hydrophilic parts: isotactic, atactic parts, and short syndiotactic sequences) and the trains (hydrophobic: long syndiotactic sequence) connected in a line alternately and the intermediate layer is supposed to consist of random coiled molecules. Though the amounts of the layers of both sides would be independent of the film thickness, that of the intermediate layer would decrease with the decrease in the film thickness. Therefore, the intermediate layer would influence the extensibility, the modulus, the permeability, etc. The layer structure must be ascertained experimentally in the future.

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