Syndiotacticity-Rich Ultrahigh Molecular-Weight Poly(vinyl alcohol) Film. I. Determination of Optimum Polymer Concentration by Zone-Drawing Method in Film Preparation

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ABSTRACT: A new method using a simple zone-drawing technique has been suggested for determining the optimum initial concentration of a polymer solution that has suitable macromolecular entanglements. This method was developed to replace the incorrect inherent viscosity-measuring method for syndiotacticity-rich (syndiotactic diad content of 63.4%) ultrahigh molecular-weight (number-average degree of polymerization of 12,300) (UHMW) poly(vinyl alcohol) (PVA) solution. Syndiotacticity-rich UHMW PVA films were prepared from dimethyl sulfoxide (DMSO) solutions with different initial concentrations: of 0.1, 0.2, 0.3, 0.4, and 0.5 g/dL. In order to investigate the drawing behavior of the syndiotacticity-rich UHMW PVA films with different solution concentrations, the films were drawn under various zone-drawing conditions. Through a series of experiments, it was discovered that the initial concentration of PVA solution in DMSO caused significant changes in the draw ratio of the syndiotacticity-rich UHMW PVA film. That is, the one-step and maximum zone draw ratios of the film at an initial concentration of 0.3 g/dL exhibited its maximum values and gradually decreased at higher or lower concentrations. Thus, it was disclosed that the initial concentration of 0.3 g/dL is the optimum polymer concentration to produce a maximum draw ratio in this work. Based on the above results, it may be concluded that the optimum concentration of the initial PVA solution can be determined directly by measuring the zone draw ratio. The draw ratio, birefringence, crystallinity, degree of crystal orientation, tensile strength, and tensile modulus of the maximum drawn PVA film were 32.9, 0.0449, 0.61, 0.991, 1.91, and 46.2 GPa, respectively. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 77: 123–134, 2000

Key words: optimum concentration; syndiotacticity-rich UHMW PVA; zone draw ratio

INTRODUCTION

Poly(vinyl alcohol) (PVA) is a semicrystalline polymer whose molecular chains in the crystal region have much conformational similarity with those of the polyethylene (PE)-like all-trans chain structure.[1,2] On the other hand, microhardness exists in the PVA crystalline phase because inter- and intramolecular hydrogen bonds between the adjacent hydroxyl groups, which give rise to the difference in the crystal structure of PE. For this reason, it has been known that ultradrawing of PVA films and fibers is very difficult. In practice, PVA films and fibers have relatively low tensile moduli and strengths due to its poor drawability, compared with those of PE. In addition, in the case of syndiotacticity-rich high molecular-weight (HMW) PVA fibers and films whose mechanical and physical properties are much superior to those of atactic ones,[3–9] it is very difficult to obtain a higher draw ratio. The reason might be explained by the strong intermolecular hydrogen bonds in syndiotacticity-rich PVA, which may act as net points in both amorphous and crystalline regions and which reduce the occurrence of molecular slippage and of the unraveling of crystalline lamellae.[6,10,11] Therefore, to enhance the drawing and tensile properties of PVA film and fiber, gel drawings,[12] single crystal mats drawings,[13] and high-temperature zone drawings of film[14] and fiber[15,16] have been actively in progress.

As is well known, molecular weight,[17–20] molecular-weight distribution,[21] concentration of polymer solution,[22,23] and gelation–crystallization temperature[24–26] affect the drawing of polymers. Generally, the drawing increases as the molecular weight increases.[27] Above a certain molecular weight, however, this property depends principally on the initial concentration of the polymer solution.[20,22] This is the result of a reduced number of entanglements of the solution cast or spun polymers in comparison with those obtained from the melt.[28] That is, the macromolecules are thought to form a transient network, with entanglements acting as friction centers or nonlocalized junctions. Because the higher the entanglement density at higher solution concentration, the smaller the deformation of solidified HMW polymers, their drawing might be improved by a reduction of the number of entanglements. However, in the case of a dilute solution, which has fewer entanglements, the maximum draw ratio cannot be obtained because of a rare coil overlap and of chain slippage occurring at the drawing step. Therefore, a proper concentration of entanglements is needed to increase the maximum draw ratio, and this can be achieved by controlling solution concentration. So, a question has arisen as to how this concentration can be measured.

Sawatari et al.[19] determined optimum concentration of entanglements by means of the solution concentration through the measurement of solution viscosity for the purpose of preparing ultrahigh molecular-weight (UHMW) PE films with high drawability. This viscosity method, however, requires multiple steps and substantial time. Furthermore, in the case of syndiotacticity-rich UHMW PVA, it is difficult to determine optimum polymer concentration showing an abrupt change in the solution viscosity by the viscosity method. This is ascribable to syndiotacticity-rich UHMW PVA chain's ability to be easily shear oriented, such as shear thinning by gravitational force and phase-separation phenomena during viscometry.[29–33] Hence, a new method, not conventional viscometry, is necessary for determining the optimum polymer concentration of syndiotacticity-rich UHMW PVA.

Besides the viscosity method, there have been several methods for qualitatively determining the optimum concentration of chain entanglements in the case of PE. Based on the assumption that during film formation one entanglement per chain should decrease drawability by 20% compared to the absence of entanglement, Pennings and Smook[34] have determined the number of entanglements of film, using degree of shrinkage of the fully drawn films and the radius of gyration of the polymer. Also, Qin et al.[35] have calculated the density of entanglements of PE fibers, utilizing swelling differential scanning calorimetric analysis. But these two methods were constructed on a theoretical and analytical basis, not on an experimental basis directly related to the draw ratio of substance.

Zone-drawing technique[16,36] shows many advantages compared to hot-drawing experiments including reduced probability of microcrystallite formation, of back folding of molecular chains, and of thermal degradation of the sample. It has revealed that the maximum draw ratio is significantly related to the one-step zone draw ratio.[37–39]

Therefore, from studying the relationship between the maximum draw ratio of syndiotacticity-rich UHMW PVA film and its optimum solution

Table I   Two-Stage Zone-Drawing Conditions of PVA Films

Drawing Step	Solution Concentration (g/dL)	Initial Cross-Sectional Area of Film (mm^2)	Drawing Temperature (°C)	Drawing Stress (MPa)	Heat Band Speed (mm/min)	Draw Ratio
1	0.1	0.85	25	35[a]	1	1.5
1	0.2	0.85	25	35[a]	1	2.6
1	0.3	0.85	25	35[a]	1	3.7
1	0.4	0.85	25	35[a]	1	2.9
1	0.5	0.85	25	35[a]	1	2.8
2	0.1	0.12	220	18	1	7.2
2	0.2	0.11	220	18	1	7.6
2	0.3	0.13	220	18	1	8.9
2	0.4	0.13	220	18	1	7.1
2	0.5	0.12	220	18	1	6.9

[a] Maximum draw ratios at 25°C were obtained at this drawing stress. Under higher drawing stress of more than 35 MPa, a breakage of film occurred.

concentration, a convenient and simple method is introduced for determining the initial optimum polymer concentration of syndiotacticity-rich UHMW PVA solution at the maximum draw ratio, only knowing the one-step zone draw ratio and the concentration of solution.

EXPERIMENTAL

Materials

PVA was synthesized through the photoinitiated bulk polymerization of vinyl pivalate at 10°C and the saponification of poly(vinyl pivalate).[3,5,29,40] In order to determine its molecular weight, PVA was reacetylated into poly(vinyl acetate) (PVAc), and the number-average degree of polymerization (P_n) of PVAc was calculated by using eq. (1)[41]:

$$[\eta] = 8.91 \times 10^{-3}[P_n]^{0.62} \quad \text{(in benzene at 30°C)} \tag{1}$$

where $[\eta]$ is the intrinsic viscosity of PVAc/benzene solution.

Syndiotactic diad content and degree of saponification were determined from the spectrum of PVA obtained by proton–nuclear magnetic resonance spectroscopy (Varian, Sun Unity 300). The P_n, syndiotactic diad content, and degree of saponification of PVA used in this study were 12,300, 63.4%, and 99.9%, respectively.

Preparation of PVA Film

The relative viscosity of PVA solution was measured at 25°C by using a Ubbelohde capillary viscometer (viscometer number = 3, 3B, 3C, 4, 4B, 4C, 5, Sibata Co.). From these results, reduced viscosity for film casting was calculated. The concentrations of syndiotacticity-rich UHMW PVA solution in DMSO were 0.1, 0.2, 0.3, 0.4, and 0.5 g/dL, respectively. The homogenized solution was poured into a stainless-steel dish and dried under vacuum at 30°C for about 20 days. After the DMSO was removed from the films, dried films with a similar thickness of 85 μm were obtained.

Zone Drawing of Film

PVA films 5 mm wide and 10 cm long were zone-drawn at 220°C for preparation of a one-step zone-drawn film. In addition, to obtain the maximum draw ratio, films with the same initial cross-sectional areas were zone-drawn at 25°C, followed by 220°C. The two-stage zone-drawing conditions are listed in Table I. The draw ratio was regulated by varying the drawing stress, drawing temperature, and heat band speed. Zone drawing was carried out by moving a pair of narrow-band heaters 7 cm long, 2.5 cm wide, and 1 mm thick along the film (Fig. 1). The film was drawn under a tension controlled by different dead weights, on an Instron model 4201 (Fig. 2).

Crystallinity of Film

The density of the PVA film (d) was determined by a density-gradient tube method (benzene-carbon tetrachloride) at 30°C. The degree of crystallinity (X_c) was calculated by eq. (2):

$$1/d = X_c/1.345 + (1 - X_a)/1.269 \tag{2}$$
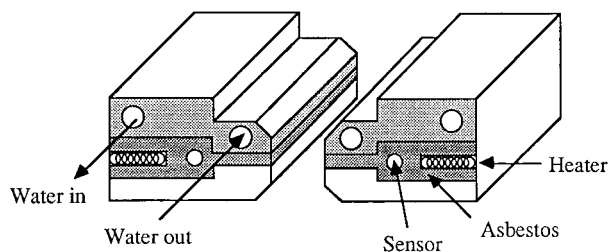
Figure 1 Schematic representation of band heater assembly.

where 1.345 (g/cm^3) and 1.269 (g/cm^3) are, respectively, the crystal[42] and amorphous[43] densities of PVA.

Polarizing Optical Microscopic Analysis

The birefringence of the film was measured on a polarizing optical microscope (POM) with a Senarmont compensator (Nikon, Optiphot-Pol 104). The birefringence was determined by dividing the optical path length by the thickness. Film surface was observed by a POM (Nikon, Optiphot-Pol 104).

Wide-Angle X-ray Diffraction Analysis

X-ray diffractograms were obtained using a X-ray diffractometer (Mac Science, MXP-18) with Ni-filtered CuKα radiation at 40 kV and 200 mA. The degree of crystal orientation was calculated by azimuthal scanning of the (020) diffraction (the crystal is monoclinic, and the chain axis is parallel to the b axis) at a scanning speed of 2°/min. A wide-angle X-ray diffraction (WAXD) photograph was obtained with a Statton camera with flat-plate geometry using Ni-filtered CuKα radiation at 40 kV and 45 mA. The X-ray pattern of the PVA was recorded on Kodak direct-exposure film using pinhole collimation under vacuum. The sample-to-film distances and exposure time for WAXD were 55 mm and 12 h, respectively.

Tensile Properties of Film

Load-elongation curves were recorded on an Instron model 4201 using a sample length of 4 cm and a crosshead speed of 20 mm/min. The cross-sectional areas of samples were different from one another with respect to the draw ratio. The tensile modulus was determined within 0.5% elongation. The tensile strength and modulus of the film were the average values of 20 samples.

RESULTS AND DISCUSSION

Effect of Initial Concentration on Drawability

The structure and physical properties of zone-drawn film may vary with the conditions of preparation and drawing of the film—that is, (1) the initial concentration of the polymer solution during preparation of the film and (2) the processing parameters, such as drawing stress, drawing temperature, and heat band speed during drawing of film, have marked influences on the drawing behavior of film. In this study the effects of those factors on the draw ratios of films were investigated.

Figure 3 shows the one-step zone draw ratios of PVA films drawn under various drawing stresses with a drawing temperature of 220°C and a heat band speed of 1 mm/min as a function of initial solution concentrations. The draw ratio increased with an increase in the drawing stress. In addition, a maximum value up to 15.1 could be obtained at a drawing stress of 18 MPa. This result can be explained by an increased deformation of the molecular chains with increasing drawing stress above the glass-transition temperature. Under a higher drawing stress, of more than 18 MPa, a breakage of film occurs. The maximum value of the draw ratio appeared at a solution concentration of 0.3 g/dL. At a lower or higher concentration, the draw ratio decreased gradually. This is attributed to a suitable number of entanglements for the film prepared at a solution
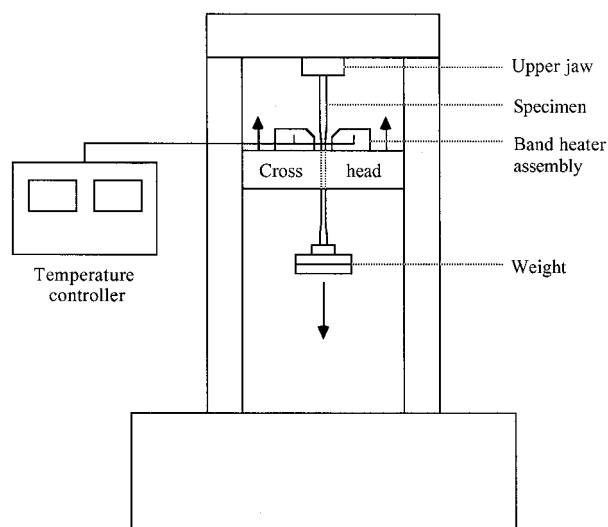
Figure 2 Schematic representation of zone-drawing apparatus.
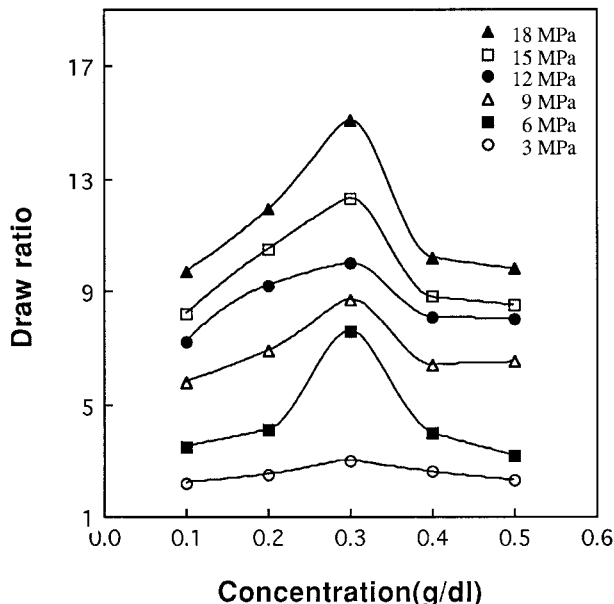
Figure 3 One-step zone draw ratio of PVA film drawn under various drawing stresses, drawing temperature of 220°C, and heat band speed of 1 mm/min with concentration of PVA solution.

concentration of 0.3 g/dL. Generally, for effective drawing, film must have a suitable number of entanglements, which can be evaluated by a determination of the optimum solution concentration. Optimum initial concentrations of polymer solutions vary with molecular weight, linearity, and stereoregularity of polymers and type of solvent, and so forth. However, in this study those effects were negligible because the same types of polymer with the same molecular weight and the same solvent were used in all experiments. Therefore, the initial concentration of 0.3 g/dL is the optimum concentration, which contains suitable entanglements. The general viscometric method for a determination of optimum solution concentration is complicated and requires a long time; thus, the zone-drawing method could be a better one.

Figure 4 shows the one-step zone draw ratios of PVA films drawn under various drawing temperatures, with a drawing stress of 18 MPa and a heat band speed of 1 mm/min as a function of the initial solution concentrations. The draw ratio increased for each film with increasing drawing temperature, from which it can be inferred that as the drawing temperature reaches the crystal melting temperature (240–250°C) of undrawn syndiotacticity-rich (syndiotactic diad content of more than 60%) UHMW PVA film, the degree of

freedom of syndiotactic PVA chains increases. The largest value was obtained at a concentration of 0.3 g/dL, so this can be presumed the optimum concentration manifesting the highest draw ratio.

Figure 5 shows the one-step zone draw ratios of PVA films drawn under various heat band speeds, with a drawing stress of 18 MPa and a drawing temperature of 220°C as a function of the initial solution concentrations. It was shown that the slower the heat band speed, the larger the draw ratio. This may point to the softening of film becoming easier because of the longer residence time for film between two heat bands. That is, the more uniform heat transfer to the sample of slower heat band speed had a great effect on the draw ratio of PVA film. As identified in Figures 3, 4, and 5, the one-step zone draw ratio of film prepared at a concentration of 0.3 g/dL was the largest among all the films of different concentrations. Thus, it was supposed that film prepared at this concentration has suitable entanglements to attain an effective draw ratio.

The effect of the concentration of the PVA solution in DMSO on the maximum draw ratio of PVA film drawn under drawing conditions described in Table I is shown in Figure 6. The maximum draw ratio of the film was 32.9, with the largest for a concentration of 0.3 g/dL, and it steeply decreased at higher and lower concentra-
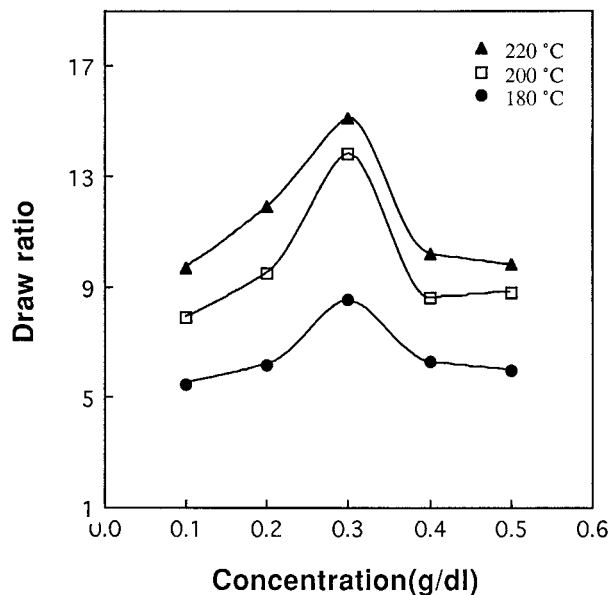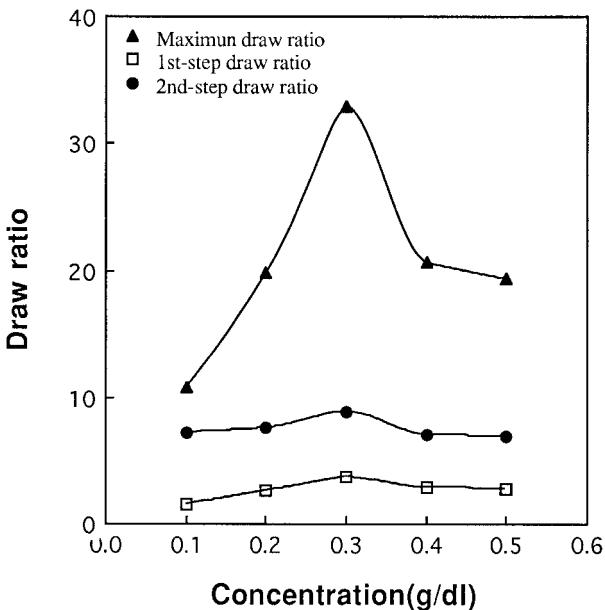

Figure 4 One-step zone draw ratio of PVA film drawn under various drawing temperatures, drawing stress of 18 MPa, and heat band speed of 1 mm/min with concentration of PVA solution.
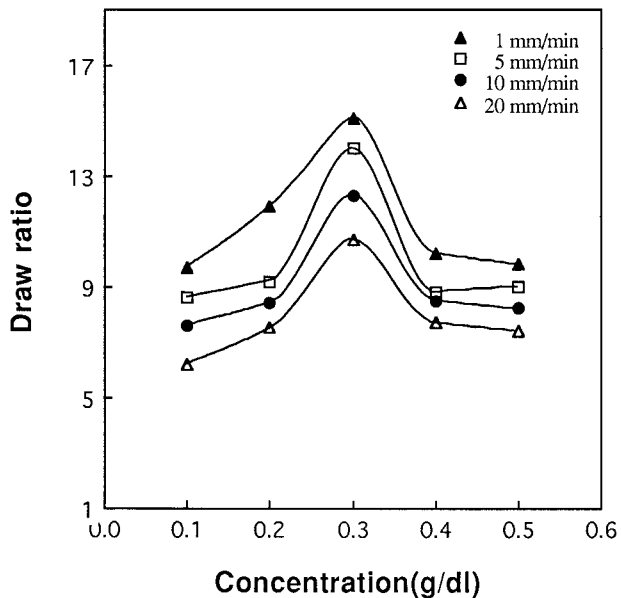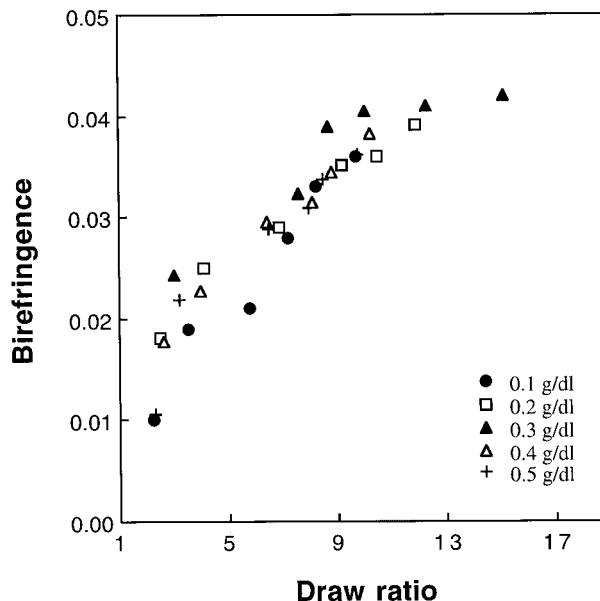
Figure 5 One-step zone draw ratio of PVA film drawn under various heat band speeds, drawing stress of 18 MPa, and drawing temperature of 220°C with concentration of PVA solution.
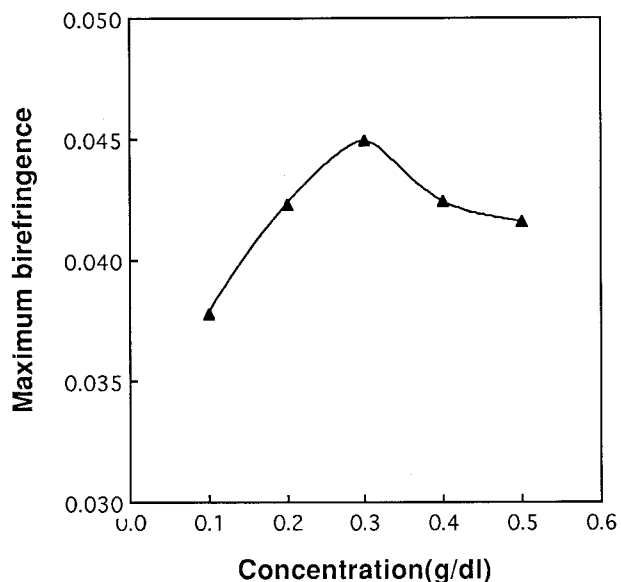

Figure 7 Birefringence of PVA film one-step zone-drawn under various drawing stresses, drawing temperature of 220°C, and heat band speed of 1 mm/min with draw ratio.

tions. This tendency was similar to the results observed for the one-step zone-drawn film at various zone-drawing conditions, as described above.

Figure 6 Maximum draw ratio of PVA film drawn at 25°C, followed by 220°C, first-step draw ratio of PVA film drawn at 25°C, and second-step draw ratio of PVA film drawn at 220°C.

That is, it can be inferred from this result that the maximum zone draw ratio is dependent upon a one-step zone draw ratio. Therefore, it can be predicted that the present method for determining the optimum initial concentration of syndiotacticity-rich UHMW PVA solution by a one-step zone draw ratio is correct and suitable.

Effect of Initial Concentration on Orientation

Figure 7 shows the birefringences of PVA films that have been one-step zone-drawn under various drawing stresses with a drawing temperature of 220°C and a heat band speed of 1 mm/min with draw ratios. Two things are worth noting in the figure. First, the maximum birefringence appeared at a solution concentration of 0.3 g/dL irrespective of drawing stress. At lower or higher concentrations, birefringence decreased because the difference in draw ratio using the one-step zone drawing might cause variation in the birefringence. Second, birefringence of the film increased with an increase in the draw ratio. The effect of the initial polymer concentration on the birefringence of the maximum drawn PVA film is shown in Figure 8. This figure demonstrates that the degree of overall orientation of the PVA film cast at 0.3 g/dL, the concentration of maximum drawability, is higher than those cast at other

Figure 8 Effect of solution concentration of PVA on the birefringence of maximum-drawn PVA film.

orientation with draw ratio (Fig. 12), the steady increase of birefringence with draw ratio (Fig. 7) might be explained by the effect of amorphous orientation. Figure 13 presents the WAXD photographs of three PVAs with similar draw ratios but prepared from different initial concentrations. It showed a high degree of orientation of the crystallites. Moreover, the highest orientation ap-
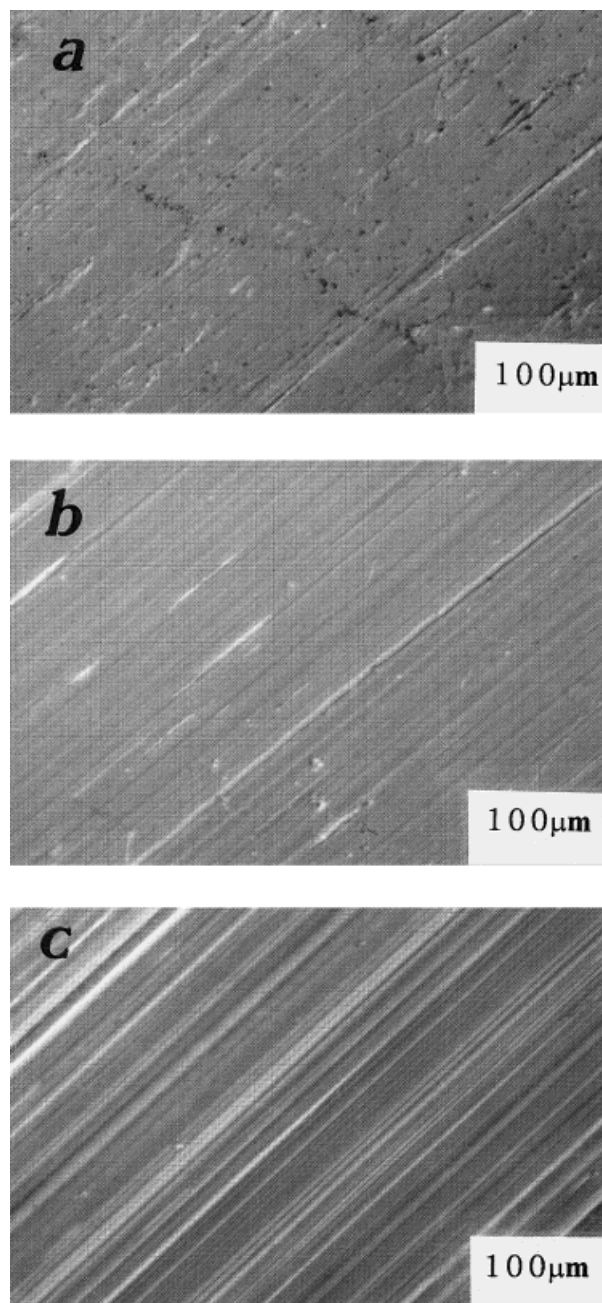
Figure 9 Polarizing micrographs of the surfaces of one-step zone-drawn PVA film: (a) draw ratio of 4.1; (b) draw ratio of 8.2; (c) draw ratio of 15.1.

concentrations. The maximum birefringence of the PVA film with a draw ratio of 32.9 cast at 0.3 g/dL was 0.0449. Figure 9 shows polarizing micrographs of the surfaces of drawn PVA films. A fibrillar structure clearly developed with an increase in the draw ratio.
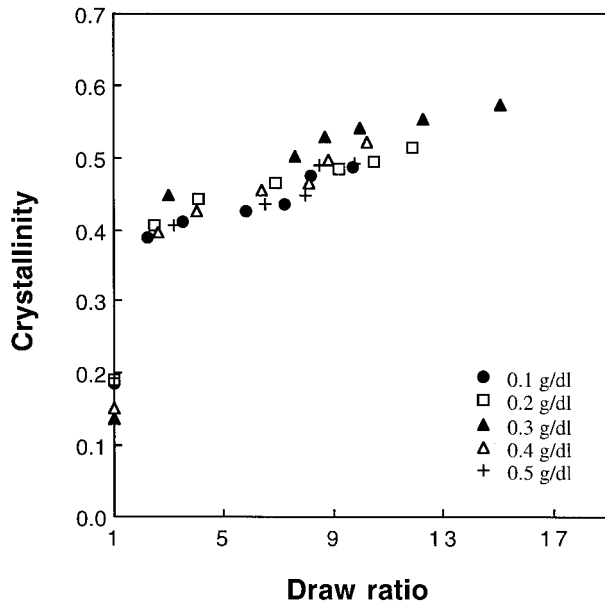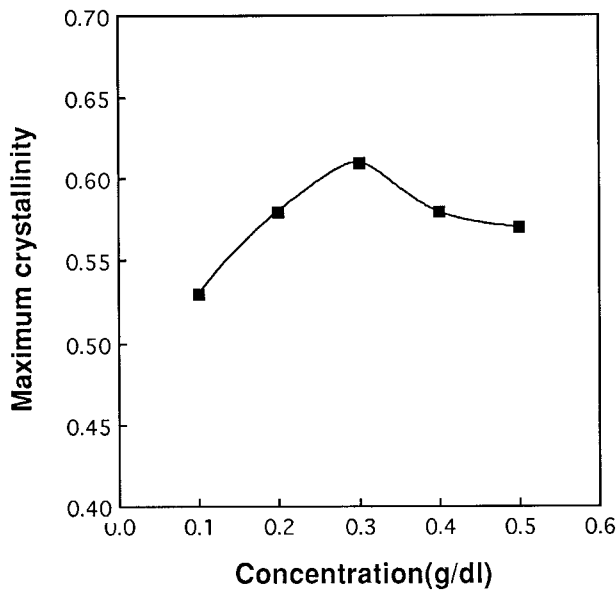
Figure 10 shows the crystallinities of PVA films one-step zone-drawn under various drawing stresses, with a drawing temperature of 220°C and a heat band speed of 1 mm/min with draw ratios. It can be seen that the crystallinity was high at the low draw ratio, around 3, and that it increased slightly with a further increase in the draw ratio. The effect of the initial polymer concentration on the crystallinity of the maximally drawn PVA film is shown in Figure 11. The maximum crystallinity of the PVA film with a draw ratio of 32.9 cast at 0.3 g/dL was 0.61. At lower or higher concentrations crystallinity decreased.

The degrees of crystal orientation of PVA films one-step zone-drawn under various drawing stresses, with a drawing temperature of 220°C and a heat band speed of 1 mm/min with draw ratios are shown in Figure 12. It was noted that the degree of crystal orientation was already high at the low draw ratio, around 3, and increased mildly with the draw ratio. This might be explained by the film's being heated sufficiently due to a higher drawing temperature of 220°C and a slower heat band speed of 1 mm/min. Since there was virtually no increase in the degree of crystal
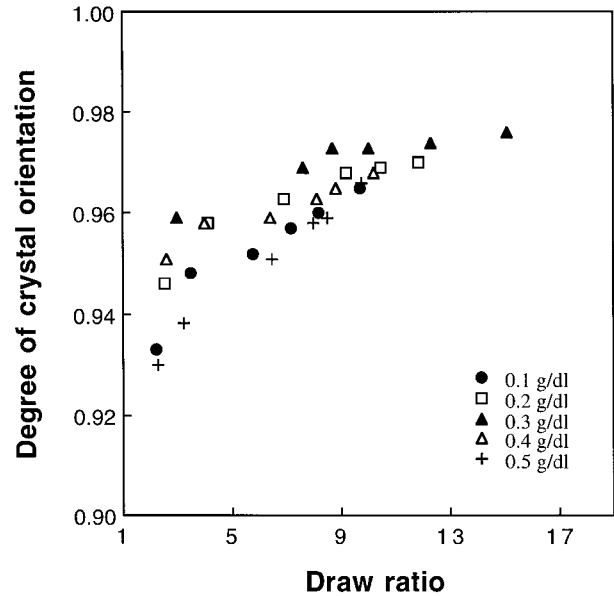
Figure 10 Crystallinity of PVA film one-step zone-drawn under various drawing stresses, drawing temperature of 220°C, and heat band speed of 1 mm/min with draw ratio.


Figure 12 Degree of crystal orientation of PVA film one-step zone-drawn under various drawing stresses, drawing temperature of 220°C, and heat band speed of 1 mm/min with draw ratio.

peared at a solution concentration of 0.3 g/dL; nevertheless, there were similar draw ratios of about 9. At lower or higher concentrations, the orientation of the film decreased gradually. This indicates that film prepared at a solution concentration of 0.3 g/dL, which has a suitable number

Figure 11 Effect of solution concentration of PVA on the crystallinity of maximum-drawn PVA film.

of entanglements, is more oriented than those at other concentrations. This result strongly coincides with that in Figure 12. The effect of the initial polymer concentration on the degree of crystal orientation of the maximally drawn PVA film is shown in Figure 14. All values were about 0.977–0.985. The highest value of 0.985 was obtained with a concentration of 0.3 g/dL.

### Effect of Initial Concentration on Tensile Property

Figure 15 shows the tensile strength [Fig. 15(a)] and the tensile modulus [Fig. 15(b)] of PVA films one-step zone-drawn under various drawing stresses, with a drawing temperature of 220°C and a heat band speed of 1 mm/min with draw ratios. The effect of the initial polymer concentration on the tensile strength [Fig. 16(a)] and the tensile modulus [Fig. 16(b)] of the maximum drawn PVA film is shown in Figure 16. It is clear that the tensile strength and tensile modulus of the PVA film increased significantly with draw ratio. It is also noted from Figures 15 and 16 that tensile strength and tensile modulus of the PVA film showed a maximum value at 0.3 g/dL concentration. The maximum tensile strength and tensile modulus obtained in the maximum drawn PVA film cast at 0.3 g/dL were 1.91 GPa and 46.2 GPa, respectively.
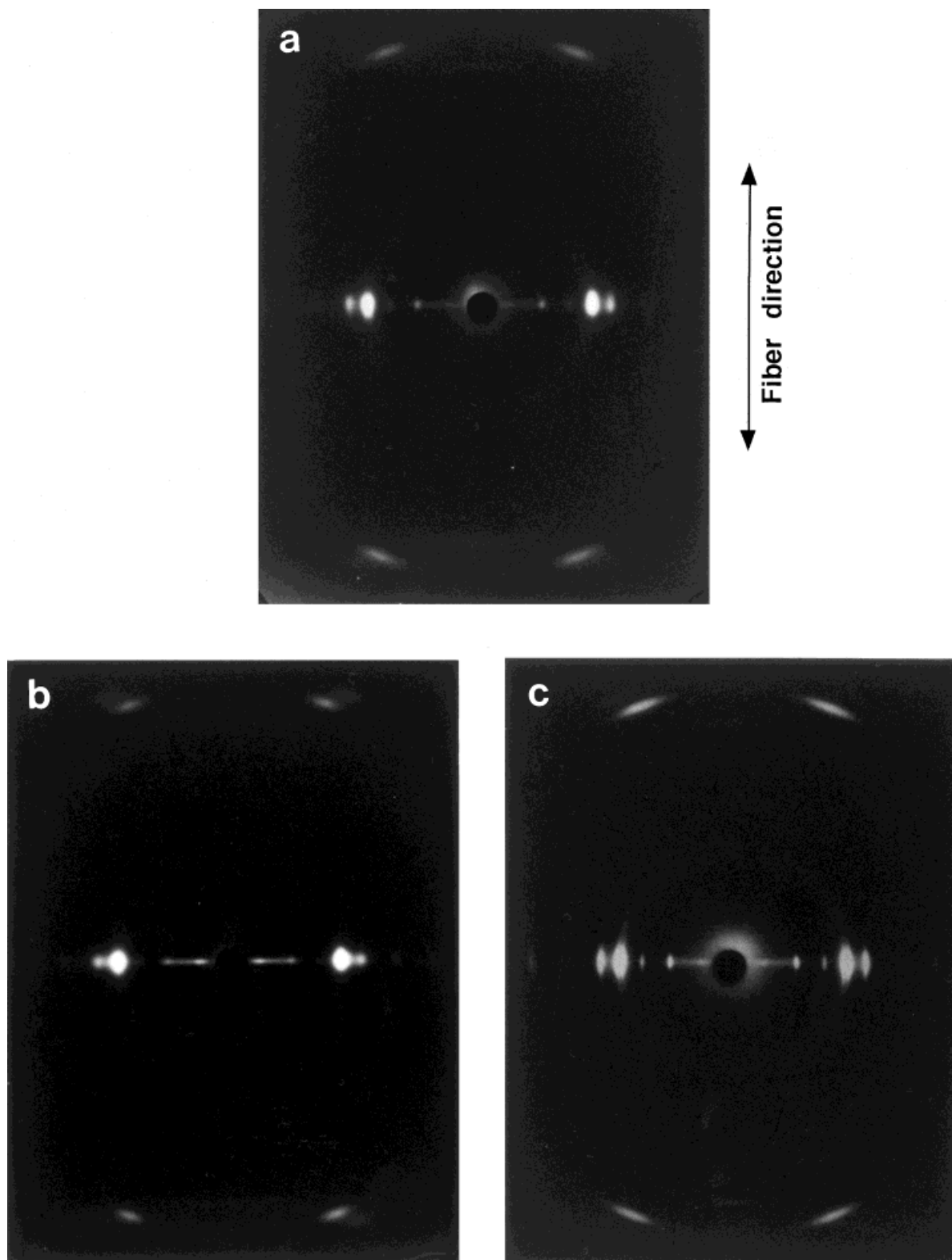
Figure 13   WAXD photographs of the one-step zone-drawn PVA film having similar draw ratios prepared at three initial concentrations: (a) 0.2 g/dL, draw ratio of 9.2; (b) 0.3 g/dL, draw ratio of 8.7; (c) 0.4 g/dL, draw ratio of 8.8.

It was observed that film having optimum macromolecular entanglements cast from 0.3 g/dL solution represented higher drawability, degree of orientation, tensile strength, and tensile modulus than other films. When the cast film is stressed for drawing, it is assumed that the applied force is first concentrated on the interfibrillar ties that connect microfibrils and that it is then transferred into the intrafibrillar ties that crystal blocks in a microfibril. Among the tie molecules, the shortest tie molecules are dominantly forced, and the next longer tie molecules are forced subsequently. Therefore, the film's representing high tensile strength and tensile modulus means the polymer has the suitable length of tie molecules and uniform length distribution. The PVA film cast at 0.3 g/dL represented higher tensile strength and tensile modulus than the PVA films cast at other concentrations because the film had suitable interfibrillar tie molecules and uniform length distribution. The PVA films cast at higher concentrations had too many tie molecules, which prevented the orientation of chains, so tensile strength and tensile modulus were lowered. The PVA films cast at lower concentrations had fewer tie molecules, so tensile strength and tensile modulus were lowered because of the slippage of molecular chains.
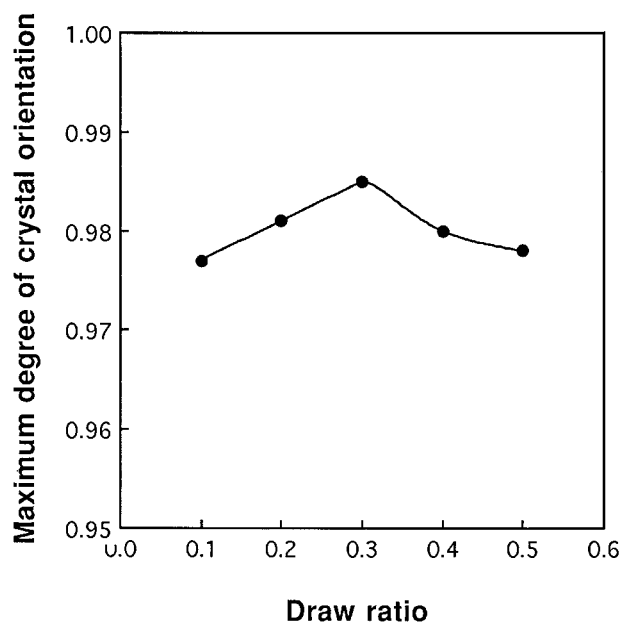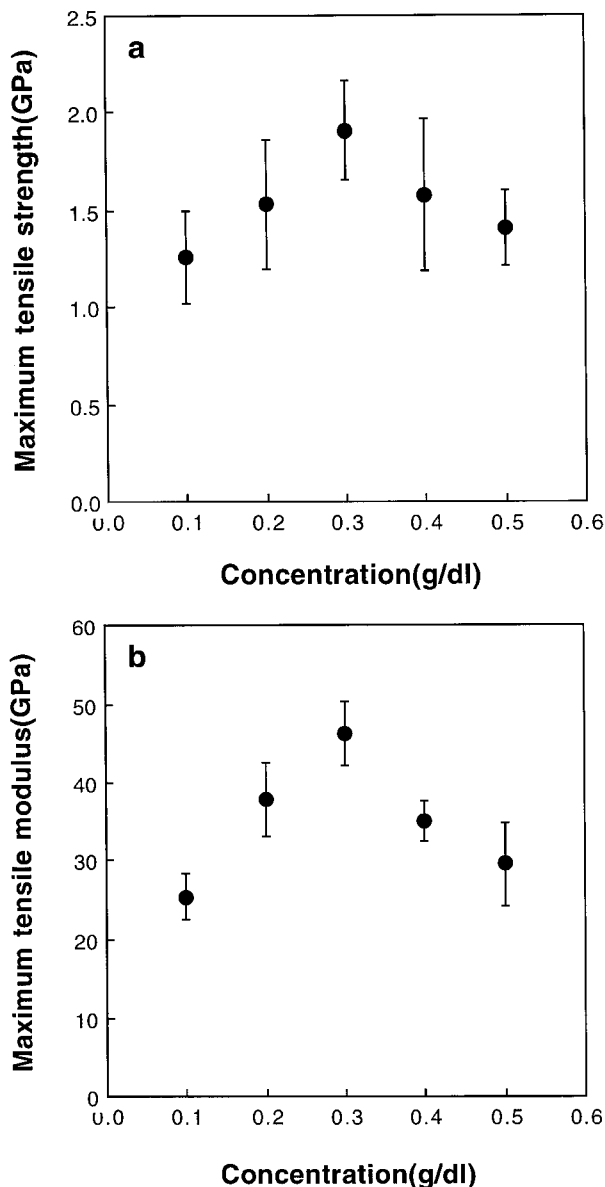

Figure 14   Effect of solution concentration of PVA on the degree of crystal orientation of maximum-drawn PVA film.
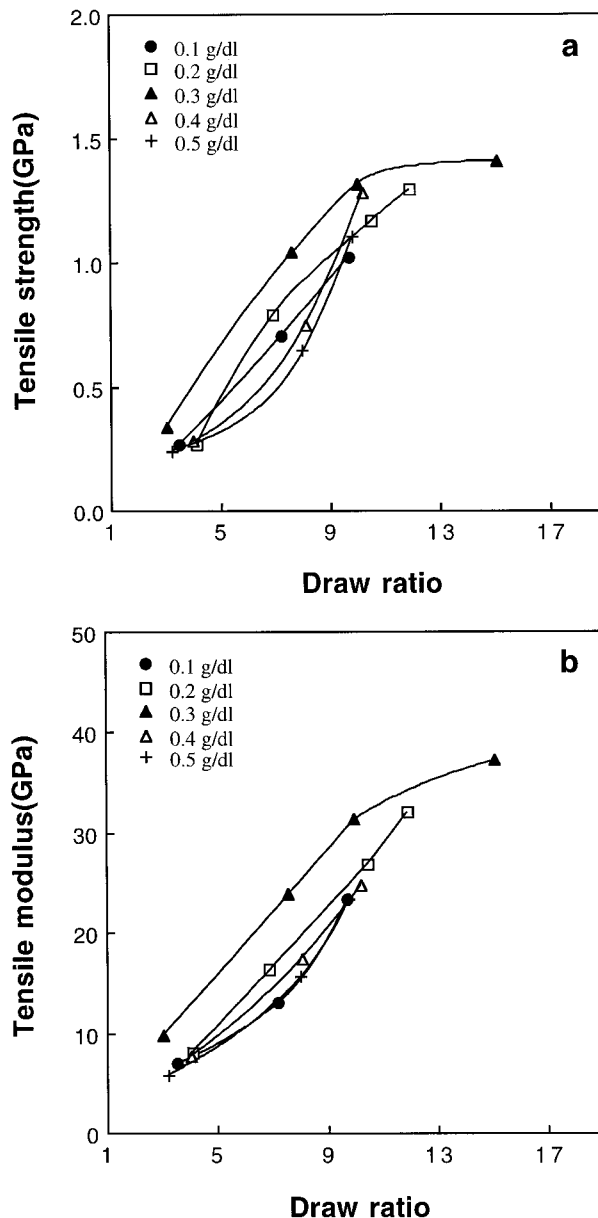
Figure 15   Tensile strength (a) and tensile modulus (b) of PVA film one-step zone-drawn under various drawing stresses, drawing temperature of 220°C, and heat band speed of 1 mm/min with draw ratio.

CONCLUSIONS

The optimum processing condition for high-strength and high-modulus syndiotacticity-rich UHMW PVA film was investigated by measuring the birefringence, crystallinity, degree of crystal orientation, and tensile properties in terms of the initial polymer concentration and draw ratio. Syndiotacticity-rich (syndiotactic diad content of

Figure 16 Effect of solution concentration of PVA on the tensile strength (a) and tensile modulus (b) of maximum drawn PVA film.

PVA film. That is, the one-step and maximum zone draw ratios and tensile properties of the film at an initial concentration of 0.3 g/dL exhibited its maximum values and gradually decreased at higher or lower concentrations. In case of maximum drawn PVA film, the draw ratio of 32.9, tensile strength of 1.91 GPa, and tensile modulus of 46.2 GPa were obtained. Such high tensile properties were well correlated with the maximized birefringence and crystal orientation at the optimum initial polymer concentration of 0.3 g/dL.

REFERENCES

1. Sakurada, I.; Ito, T.; Nakamae, K. J Polym Sci 1966, C15, 75.
2. Lyoo, W. S.; Kim, B. J.; Ha, W. S. J Korean Fiber Soc 1996, 33, 231–239.
3. Lyoo, W. S.; Ha, W. S. Polymer 1996, 37, 3121.
4. Lyoo, W. S.; Blackwell, J.; Ghim, H. D. Macromolecules 1998, 31, 4253.
5. Lyoo, W. S.; Ha, W. S. Polymer 1999, 40, 497.
6. Nakamae, K.; Nishino, Y.; Ohkubo, H.; Matsuzawa, S.; Yamaura, K. Polymer 1992, 33, 2581.
7. Sakurada, I. In Polyvinyl Alcohol Fibers; Lewin, M., Ed.; Marcel Dekker: New York, 1985; pp 3–9 and pp 361–386.
8. Marten, F. L. In Encyclopedia of Polymer Science and Technology; Mark, H. F.; Bikales, N. M.; Overberger, C. G.; Menges, G.; Kroschwitz, J. I., Eds.; John Wiley and Sons: New York, 1985; Vol. 17, pp 167–180 and p 188.
9. Masuda, M. In Polyvinyl Alcohol Developments; Finch, C. A., Ed.; John Wiley and Sons: New York, 1991; pp 403–422 and p 711.
10. Nagura, M.; Matsuzawa, S.; Yamaura, K.; Ishikawa, H. Polym J 1982, 14, 69.
11. Nagura, M.; Matsuzawa, S.; Yamaura, K.; Ishikawa, H. Polym Commun 1983, 24, 250.
12. Grubb, D. T.; Kearney, F. R. J Appl Polym Sci 1990, 37, 695.
13. Kanamoto, T.; Kiyooka, S.; Tovmasyan, Y.; Sano, H.; Narukawa, H. Polymer 1990, 31, 2039.
14. Lyoo, W. S.; Han, S. S.; Choi, J. H.; Cho, Y. W.; Ha, W. S. J Korean Fiber Soc 1995, 32, 1023.
15. Garrett, P. D.; Grubb, D. T. Polym Commun 1988, 29, 60.
16. Kunugi, T.; Kawasumi, T.; Ito, T. J Appl Polym Sci 1990, 40, 2101.
17. Smith, P.; Lemstra, P. J.; Pijpers, J. P. L. J Polym Sci Polym Phys 1982, 20, 2229.
18. Hallam, M. A.; Cansfield, D. L. M.; Ward, I. M.; Pollard, G. J Mater Sci 1986, 21, 4199.

63.4%) UHMW (P_n of 12,300) PVA films were prepared from DMSO solutions with initial concentrations of 0.1, 0.2, 0.3, 0.4, and 0.5 g/dL. In order to investigate the drawing behavior of the syndiotacticity-rich UHMW PVA films with different solution concentrations, the films were drawn under various zone-drawing conditions. From evaluating several results, it was recognized that the initial concentration of PVA solution in DMSO caused significant changes in the draw ratio of the syndiotacticity-rich UHMW

19. Sawatari, C.; Okumura, T.; Matsuo, M. Polym J 1986, 18, 741.
20. Bastiaansen, C. W. M. J Polym Sci Polym Phys 1990, 28, 1475.
21. Liu, B. L.; Murakami, N.; Sumita, M.; Miyasaka, K. J Polym Sci Polym Phys 1989, 27, 2441.
22. Smith, P.; Lemstra, P. J.; Booji, H. C. J Polym Sci Polym Phys 1981, 19, 877.
23. Kanamoto, T.; Tsurata, A.; Tanaka, K.; Porter, R. S. Polym J 1983, 15, 327.
24. Ogita, T.; Suzuki, N.; Kawahara, Y. Polymer 1992, 33, 698.
25. Jang, B. N.; Kim, S. Y. J Korean Fiber Soc 1993, 30, 162–170.
26. Ji, B. C.; Jeong, G. S.; Yoon, W. S.; Han, S. S.; Lyoo, W. S. Polym Testing 1999, 18, 299–311.
27. Nunes, R. W.; Martin, J. R.; Johnson, J. F. Polym Eng Sci 1982, 22, 205.
28. Douglas, M. J. F.; Freed, F. Macromolecules 1983, 16, 741.
29. Lyoo, W. S. Ph.D. Thesis, Seoul National University, 1994.
30. Lyoo, W. S.; Ha, W. S.; Lee, C. J.; Kim, B. C. Pacific Polym Con (Branch of ACS) Proc, 1995.
31. Lyoo, W. S.; Ha, W. S.; Lee, C. J.; Kim, B. C. Polym Eng Sci 1997, 37, 1259.
32. Lyoo, W. S.; Ha, W. S.; Lee, C. J.; Kim, B. C. IUPAC MACRO Seoul '96 Proc, Korea, 1996.
33. Lyoo, W. S.; Kim, B. C.; Ha, W. S. Polym J 1998, 30, 424.
34. Pennings, A. J.; Smook, J. Colloid Polym Sci 1984, 26, 712.
35. Qin, J.; Hu, P.; Zhao, J.; Wu, Z.; Qian, B. J Appl Polym Sci 1994, 51, 1433.
36. Kunugi, T.; Akiyama, I. Polymer 1982, 23, 1199.
37. Ji, B. C.; Yoon, W. S.; Kim, S. Y. J Korean Fiber Soc 1993, 30, 328.
38. Han, S. S.; Kim, S. Y. J Korean Fiber Soc 1994, 31, 1012–1020.
39. Kunugi, T.; Ohmori, S. Polymer 1988, 29, 814.
40. Lyoo, W. S.; Ha, W. S. J Polym Sci Polym Chem 1997, 35, 55.
41. Nakajima, I. Kobunshi Kagaku 1954, 11, 142.
42. Sakurada, I.; Fuchino, K.; Okada, A. Kaken Hokoku 1950, 23, 78.
43. Sakurada, I.; Nukushina, Y.; Sone, Y. Kobunshi Kagaku 1955, 12, 506.
44. Gurp, M. V. Int J Polym Mat 1993, 22, 219.