Preparation of Water-Soluble Syndiotacticity-Rich High Molecular Weight Poly(vinyl alcohol) Microfibrillar Fibers Using Copolymerization of Vinyl Pivalate and Vinyl Acetate and Saponification

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ABSTRACT: Water-soluble high molecular weight (HMW) syndiotactic poly(vinyl alcohol) (s-PVA) microfibrillar fibers were prepared by the saponification with various conditions such as amount of alkali solution, saponification temperature, and saponification concentration from copoly-(vinyl pivalate (VPi)/vinyl acetate (VAc)) copolymerized using various VPi/VAc feed ratios. To produce s-PVA microbrillar fibers having various water-soluble temperatures for many industrial applications, the intrinsic viscosities, syndiotactic diad (S-diad) contents, and degrees of saponification (*DS*)s of PVAs were finely controlled to 1.2–3.6 dL/g, 56.3–58.3%, and 91.4–98.3%, respectively. Through a series of experiments, it was found that the amount of alkali may alter the structure of the saponified polymers, primarily the *DS*, and the structural variation changes viscosity. That is, intrinsic viscosity was sharply decreased as the amount of alkali solution was increased. *DS* was increased with an increase in the amount of alkali solution. S-diad content was increased with an increase in the VPi content. HMW s-PVA microfibrillar fibers having S-diad content of 56.3–58.3% prepared by the saponification of copoly(VPi/VAc) were completely soluble in water at 100°C. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 88: 1482–1487, 2003

Key words: water soluble; syndiotactic; fibers

INTRODUCTION

Poly(vinyl alcohol) (PVA) fibers and films are potentially high-performance materials because they have high tensile and impact strengths, high tensile modulus, high abrasion resistance, excellent alkali resistance, and oxygen barrier property that is superior to those of any known polymers[1–3].

PVA is commercially produced by the radical polymerization of vinyl acetate (VAc), followed by saponification of the obtained polymers. In general, the radical polymerization of VAc gives an atactic polymer. Much attention has been paid to the synthesis of stereoregular PVA, because the properties of PVA significantly depend on the stereochemical structure of the main chain. It is known that the solvent and temperature effects on the stereochemistry of the radical polymerization of VAc are generally small,[4–14] whereas the polymerizations of bulky vinyl ester monomers, such as vinyl pivalate (VPi)[15–30] and vinyl diphenylacetate,[31] give polymers rich in syndiotacticity.

Recently, Lyoo et al.[15,17,19,30] reported that PVA fiber of well-oriented microfibrillar structure is formed during saponifying high molecular weight (HMW) poly(vinyl pivalate) (PVPi) to PVA. During the saponification process of atactic poly(vinyl acetate) (PVAc) to PVA with similar molecular weight, fibrillation was not observed at all. Moreover, HMW syndiotacticity-rich PVAs [(s-PVA)s] with lower syndiotactic diad (S-diad) contents have shapeless morphologies but those with S-diad content over 56% are fibrous with high degree of crystallinity and orientation of the crystallites[18].

Actually, water-soluble PVA has been extensively used for materials of drug delivery system or immobilization of enzyme[32–34]. But, in comparison with atactic PVA (a-PVA), HMW s-PVA has been limited for applications of biomaterial due to water-nonsoluble characteristics induced by the high compactness of the s-PVA, although s-PVA has a superior property. Therefore, to improve the water solubility of s-PVA maintaining basic properties of s-PVA to some

TABLE I
Polymerization Conditions of VPi and VAc

Polymerization temperature (°C)	40
Initiator concentration (mol/mol of comonomer)	0.0001, 0.0005
VPi/VAc (mol/mol)	2/8, 3/7, 4/6

extent, fine control of stereoregularity of PVA should be required. In addition, water-soluble s-PVA of microfibrillar structure is expected to be a powerful candidate in various biomedical and environmental applications such as porous support for enzyme, cancer-cell killing embolic material, gene delivery material, protein release material, etc., which maintain stability in blood.

In this study, to prepare HMW s-PVA microfibrils with S-diad content of 56.3–58.3%, which is the maximum S-diad value in representing water solubility above 100°C, copolymerization of VPi/VAc and subsequent saponification were conducted. Also, three important parameters [molecular weight, degree of saponification (DS), and tacticity] of s-PVA were controlled to obtain microfibrils with various water-soluble temperatures. That is, the effects of copolymerization and saponification conditions on the intrinsic viscosity (molecular weight), stereoregularity, and DS were investigated.

EXPERIMENTAL

Materials

VPi and VAc purchased from Aldrich was washed with an aqueous solution of $NaHSO_3$ and water and dried with anhydrous $CaCl_2$, followed by distillation in nitrogen atmosphere under reduced pressure. The initiator, 2,2′-azobis(2,4-dimethylvaleronitrile) (ADMVN) (Wako Co.) was recrystallized twice in methanol before use. Other extra-pure grade reagents were used without further purification. Water used for all the procedures was deionized.

Copolymerization of VPi and VAc

VPi and VAc, precursor monomers for PVA, were copolymerized at 40°C using a low-temperature initiator, ADMVN[18]. Mixtures of VPi and VAc in different mole ratios were flushed with nitrogen for 3 h thoroughly in a 250-mL three-necked round-bottom flask. At the predetermined polymerization temperature,

ADMVN was added. When polymerization had been completed, the product polymer was reprecipitated several times from benzene/n-hexane to eliminate residual monomer. The polymerization conditions are listed in Table I.

Saponification of copoly(VPi/VAc)

In a flask equipped with a reflux condenser, a thermocouple, a dropping funnel, and a stirring device, 2.5 or 5 g of copoly(VPi/VAc) was dissolved in 250 mL of methanol. The 40% sodium hydroxide/water solution was added to the copoly(VPi/VAc) solution while being stirred at 30 and 40°C. After the saponification reaction had been completed, the solid saponification product was beaten mechanically, filtered, and washed several times with methanol. A quantitative yield of PVA was obtained. The saponification conditions are listed in Table II.

Acetylation of PVA

A mixture of 1 g of PVA, 2 mL of pyridine, 20 mL of acetic anhydride, and 20 mL of acetic acid were stirred in a three-necked flask at 100°C for 72 h under an atmosphere of nitrogen. Then the mixture was poured into cold water to precipitate PVAc, which was filtered and purified by repeating the reprecipitation from methanol and water.

Characterizations

The intrinsic viscosities of the PVAs were determined from the viscosities of the benzene solutions of the fully acetylated specimens[17]. S-diad content of PVA was determined from the ratio of the components of hydroxyl proton triplet at 4.1–4.7 ppm obtained by using ^{1}H-NMR (Varian, Sun Unity 300). The DS of PVA was determined by the ratio of tert-butyl and methylene proton peaks in the ^{1}H-NMR spectrum. The degree of solubility of the s-PVA specimen in hot water from 50 to 100°C after 2 h was calculated using eq. (1)

Degree of solubility (wt. %)

$$= (W_b - W_a)/W_b \times 100 \quad (1)$$

TABLE II
Saponification Conditions of Copoly(VPi/VAc)

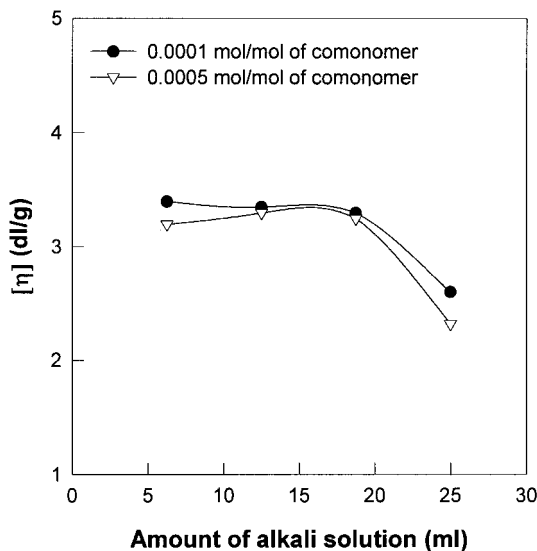|	
Saponification temperature (°C)	30, 40
Saponification polymer concentration (g/dL)	1, 2
Type of catalyst	40% sodium hydroxide/water solution

Figure 1 Intrinsic viscosity of s-PVA saponified from copoly(VPi/VAc) polymerized using VPi/VAc mol ratio of 3/7, at saponification temperature of 30°C and saponification polymer concentration of 2% (g/dL) with amount of alkali solution.

where W_a is the weight of dried specimen after treatment and W_b is the weight of dried specimen before treatment.

RESULTS AND DISCUSSION

Roles of copolymerization and saponification conditions in the molecular parameters of PVA

Generally, it is known that structure and properties of PVA were greatly affected by the molecular weight, *DS*, and stereoregularity of PVA. Figure 1 shows the effects of the polymerization initiator (ADMVN) concentration and saponification alkali concentration on the intrinsic viscosity of s-PVA saponified from copoly(VPi/VAc) prepared using VPi/VAc mol ratio of 3/7 at saponification temperature of 30°C and saponification concentration of 2% (g/dL). At the highest alkali concentration, the intrinsic viscosity was outstandingly decreased. This implies that more amount of alkali solution may affects the main chain as well as the branch of copoly(VPi/VAc) during saponification reaction. Furthermore, the intrinsic viscosity of s-PVA prepared from copoly(VPi/VAc) using lower ADMVN concentration shows relatively higher value. This result agrees with theoretical prediction, that molecular weight of copoly(VPi/VAc) is increased with a decrease in the initiator concentration. Effects of the VPi/VAc feed ratio, the amount of alkali solution, and saponification temperature on the intrinsic viscosity of s-PVA saponified from copoly(VPi/VAc) polymerized at 40°C are shown in Figure 2. Regardless of saponification reaction conditions, intrinsic viscosity of s-PVA increased with an increase of VPi content. This
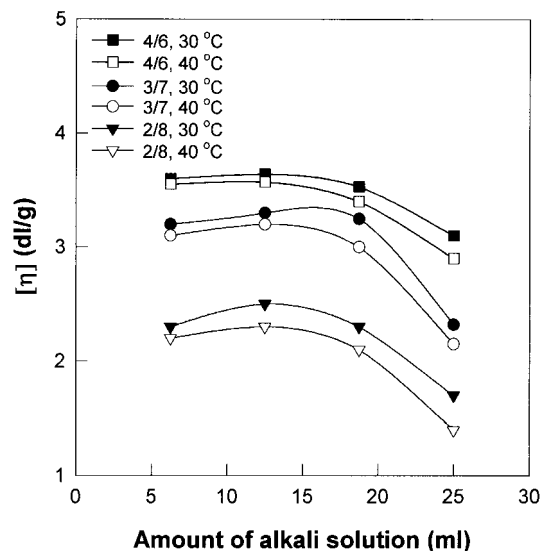
might be explained by a higher syndiotacticity of PVA chains with more VPi content. Also, intrinsic viscosity of s-PVA was slightly decreased with an increase of the saponification temperature. This implies that chain breakage and side reactions might occurred at higher saponification temperature. Figure 3 shows the effects of the amount of saponification agent, the saponification polymer concentration, and saponification temperature on the intrinsic viscosity of s-PVA saponified from copoly(VPi/VAc) prepared using VPi/VAc mol ratio of 2/8. The intrinsic viscosity of s-PVA saponi-
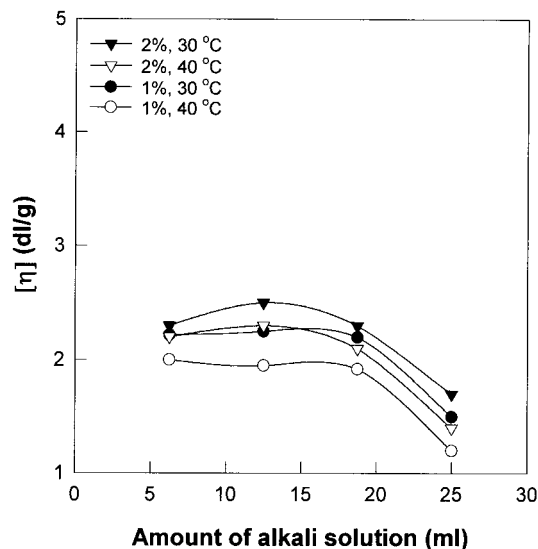

Figure 2 Intrinsic viscosity of s-PVA saponified from copoly(VPi/VAc) polymerized using initiator concentration of 0.0005 mol/mol of comonomer at saponification polymer concentration of 2% (g/dL) with amount of alkali solution.

Figure 3 Intrinsic viscosity of s-PVA saponified from copoly(VPi/VAc) polymerized using initiator concentration of 0.0005 mol/mol of comonomer and VPi/VAc mol ratio of 2/8 with amount of alkali solution.
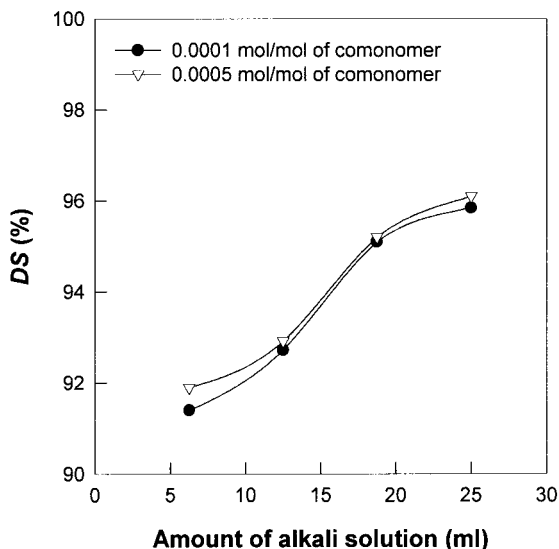
Figure 4 *DS* of s-PVA saponified from copoly(VPi/VAc) polymerized using VPi/VAc mol ratio of 3/7 at saponification temperature of 30°C and saponification polymer concentration of 2% (g/dL) with amount of alkali solution.
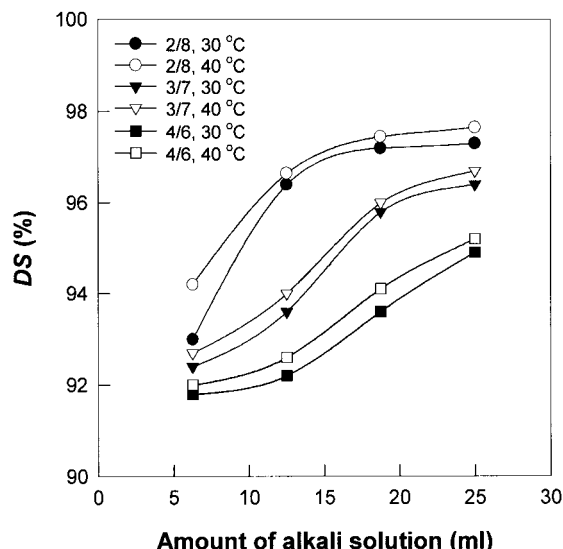

Figure 5 *DS* of s-PVA saponified from copoly(VPi/VAc) polymerized using initiator concentration of 0.0005 mol/mol of comonomer at saponification polymer concentration of 2% (g/dL) with amount of alkali solution.

fied at saponification polymer concentration of 1% (g/dL) indicated a lower level than that of s-PVA saponified at concentration of 2% (g/dL). This can be explained by the fact that the more frequent contact between polymer chain and alkali at lower polymer concentration resulted in chain breakage and side reactions more easily.

Figure 4 shows the effects of the initiator concentration and the amount of saponification alkali on *DS* of s-PVA saponified from copoly(VPi/VAc) prepared using VPi/VAc mol ratio of 3/7 at saponification temperature of 30°C. Two things are worth noting in Figure 4. First, as the amount of alkali increased, the *DS* abruptly increased. Second, *DS* of s-PVA from copoly(VPi/VAc) prepared using a lower ADMVN concentration showed a relatively lower one. This might be ascribed to the fact that in the higher molecular weight polymer, the saponification reaction may bring about complete saponifications and side reactions more difficult owing to a higher viscosity of system. Effects of the VPi/VAc feed ratio, the amount of alkali solution, and saponification temperature on the *DS* of s-PVA saponified from copoly(VPi/VAc) polymerized at 40°C are presented in Figure 5. *DS* of s-PVA increased with an increase in the amount of alkali solution and with an increase in the saponification temperature. Especially, the higher the VPi content, the lower the *DS*. Thus, this explains the fact that copoly(VPi/VAc) with a high VPi content was not saponified effectively using sodium hydroxide as catalyst. According to Lyoo et al.[15,17–19,30] and Yamamoto et al.,[35] HMW PVPi was saponified using potassium hydroxide as a catalyst. This means that although the preparation of fully saponified s-PVA from copoly-

(VPi/VAc) using sodium hydroxide as a catalyst is not easy, the control of *DS* is easy relatively. Figure 6 presents the effects of the amount of saponification agent, the saponification polymer concentration, and saponification temperature on the *DS* of s-PVA saponified from copoly(VPi/VAc) prepared using VPi/VAc mol ratio of 2/8. The *DS* of s-PVA saponified at saponification polymer concentration of 1% (g/dL) showed a higher level than that at concentration of 2% (g/dL). In the case of 1% (g/dL), copoly(VPi/VAc) is easily converted to PVA by much alkali solution be-
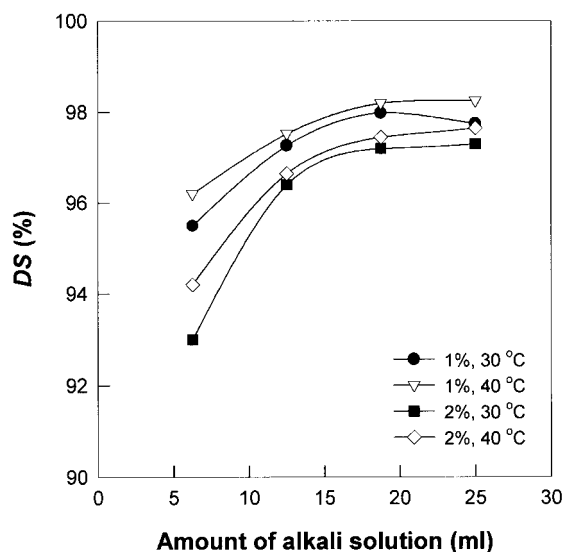

Figure 6 *DS* of s-PVA saponified from copoly(VPi/VAc) polymerized using initiator concentration of 0.0005 mol/mol of comonomer and VPi/VAc mol ratio of 2/8 with amount of alkali solution.

cause of a relatively smaller quantity of polymer in alkali solution. This might be explained by a higher possibility of conversion to PVA with more amount of alkali solution. This result is well coincident with the data in the previous Figure 3.

To improve the water solubility of HMW s-PVA maintaining basic properties of s-PVA to some extent, fine control of the stereoregularity of PVA is necessary. Effects of the VPi/VAc feed ratio, the amount of alkali solution, and saponification temperature on the S-diad content of s-PVA saponified from copoly(VPi/VAc) polymerized at 40°C are shown in Figure 7. S-diad contents of s-PVA were increased with an increase in the VPi content. Thus, water-soluble (s-PVA)s having various syndiotacticities were obtained by fine control of VPi/VAc feed ratio. Generally, vinyl trifluoroacetate and VPi have been applied frequently to the preparation of syndiotacticity-rich PVA. In particular, VPi is the best among the vinyl ester monomers in the production of syndiotacticity-rich PVA owing to the strong steric hindrance of the *tert*-butyl group in VPi. By using VPi shown the best syndiotacticity, recently, Lyoo et al. have prepared ultrahigh molecular weight PVA microfibrillar fiber with a maximum number-average degree of polymerization of 18,300 and an S-diad content of 64.1% via UV-initiated bulk polymerization of VPi at low temperature[17].

Degree of solubility in water of s-PVA

Effect of VPi/VAc mol ratio on the water solubility of s-PVA is presented in Figure 8. The degree of solubility of s-PVA prepared using VPi/VAc mol ratios of 2/8 and 3/7, respectively, showed a similar tendency.
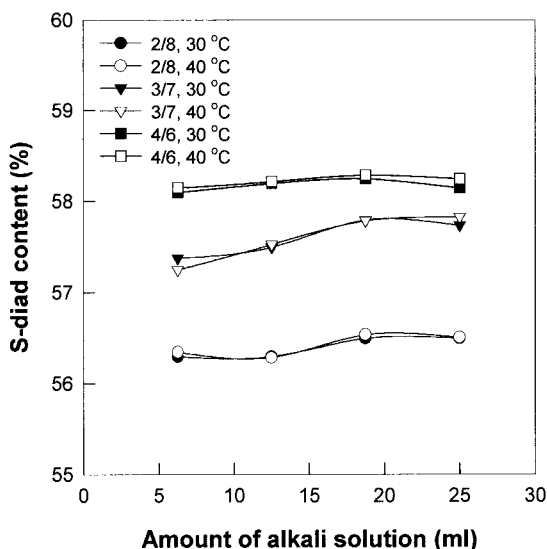

Figure 7 S-diad content of s-PVA saponified from copoly-(VPi/VAc) polymerized using initiator concentration of 0.0005 mol/mol of comonomer at saponification polymer concentration of 2% (g/dL) with amount of alkali solution.
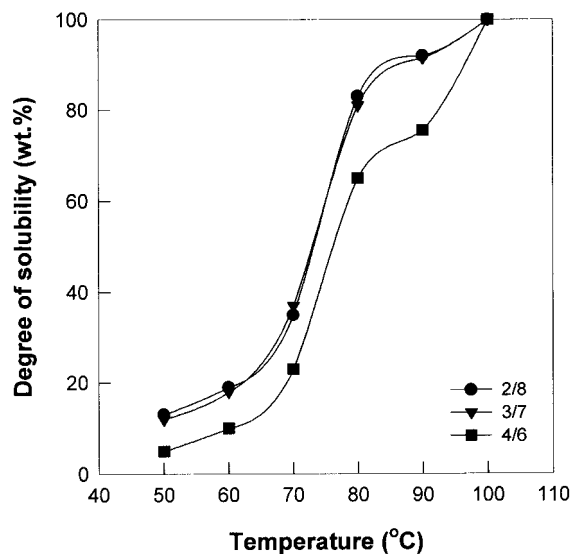

Figure 8 Degree of water solubility of s-PVA with similar *DS* of about 95% saponified from copoly(VPi/VAc) polymerized using initiator concentration of 0.0005 mol/mol of comonomer at saponification temperature of 30°C and saponification polymer concentration of 2% (g/dL) with amount of alkali solution.

In the case of s-PVA using a VPi/VAc ratio of 4/6, it was soluble perfectly at 100°C, although it has a relative resistance on the water below 100°C, owing to higher syndiotacticity. In particular, the degree of solubility of PVA increased markedly over 70°C regardless of the VPi/VAc feed ratio. In this study, s-PVA prepared using the VPi/VAc mol ratio of over 5/5 was not soluble completely at 100°C. Therefore, it is evident that these copolymerizations, including the VPi/VAc feed ratio control and subsequent saponification, are useful and easy methods for the preparation of water-soluble HMW s-PVA having various water-soluble behaviors.

CONCLUSIONS

As reported in our previous study,[15,17,19] HMW s-PVA microfibrils with high syndiotacticity of over 60% hardly dissolve in hot water owing to strong inter- and intramolecular hydrogen bondings between the adjacent hydroxyl groups. In this study, to obtain water-soluble HMW s-PVA microfibril maintaining basic property of s-PVA, syndiotacticity of PVA was controlled by copolymerization of VPi/VAc. Also, by diversifying saponification conditions such as amount of alkali solution, saponification temperature, and saponification polymer concentration, intrinsic viscosity and *DS* were also controlled. The intrinsic viscosities, S-diad contents, and (*DS*)s of PVAs were 1.2–3.6 dL/g, 56.3–58.3%, and 91.4–98.3%, respectively. Higher intrinsic viscosity was obtained at higher VPi content and higher saponification polymer concentration, and

lower initiator concentration and lower saponification temperature. *DS* increased with an increase in the amount of alkali solution and with a decrease in the VPi content. Syndiotacticity of PVA increased with an increase in the VPi content. The S-PVA microfibrillar fiber having a S-diad content of 56.3–58.3% prepared by copolymerization of VPi/VAc dissolved completely in water at 100°C. In the near future, we will report on the properties and applications of this water soluble s-PVA microfibrillar fiber.

References

1. Sakurada, I. In Polyvinyl Alcohol Fibers; Lewin, M., Ed.; Marcel Dekker: New York, 1985.
2. Martin, F. L. In Encyclopedia of Polymer Science and Technology; Mark, H. F.; Bikales, N. M.; Menges, C. G.; Kroschwitz, J. I., Eds.; John Wiley & Sons: New York, 1985.
3. Masuda, M. In Polyvinyl Alcohol-Development; Finch, C. A., Ed.; John Wiley & Sons: New York, 1991.
4. Lyoo, W. S.; Lee, S. G.; Kim, J. P.; Han, S. S.; Lee, C. J. Colloid Polym Sci 1998, 276, 951.
5. Lyoo, W. S.; Han, S. S.; Choi, J. H.; Cho, W. W.; Ha, W. S. J Korean Fiber Soc 1995, 32, 1023.
6. Lyoo, W. S.; Kim, B. C.; Lee, C. J.; Ha, W. S. Eur Polym J 1997, 33, 785.
7. Lyoo, W. S.; Lee, S. M.; Koo, K.; Lee, J. S.; Ghim, H. D.; Kim, J. P.; Lee, J. J Appl Polym Sci 2001, 82, 1897.
8. Lyoo, W. S.; Lee, C. J.; Park, K. H.; Kim, N.; Kim, B. C. Int J Polym Mater 2000, 46, 181.
9. Lyoo, W. S.; Ha, W. S. Fibers Polym 2001, 2, 108.
10. Lyoo, W. S.; Ha, W. S. J Korean Fiber Soc 1996, 33, 156.
11. Lyoo, W. S.; Kwark, Y. J.; Ha, W. S. J Korean Fiber Soc 1996, 33, 321.
12. Lyoo, W. S.; Ghim, H. D. Polymer(Korea) 1996, 20, 860.
13. Kim, S. G.; Lee, W. S.; Jo, S. M.; Kim, B. C.; Lyoo, W. S.; Han, J. R. J Korean Fiber Soc 1999, 36, 354.
14. Lyoo, W. S.; Han, S. S.; Choi, J. H.; Ghim, H. D.; Yoo, S. W.; Lee, J.; Hong, S. I.; Ha, W. S. J Appl Polym Sci 2001, 80, 1003.
15. Lyoo, W. S.; Ha, W. S. Polymer 1996, 37, 3121.
16. Kwark, Y. J.; Lyoo, W. S.; Ha, W. S. Polym J 1996, 28, 851.
17. Lyoo, W. S.; Ha, W. S. J Polym Sci Part A Polym Chem 1997, 35, 55.
18. Lyoo, W. S.; Blackwell, J.; Ghim, H. D. Macromolecules 1998, 31, 4253.
19. Lyoo, W. S.; Ha, W. S. Polymer 1999, 40, 497.
20. Choi, J. H.; Lyoo, W. S.; Ko, S. W. Macromol Chem Phys 1999, 200, 1421.
21. Cho, J. D.; Lyoo, W. S.; Chvalun, S. N.; Blackwell, J. Macromolecules 1999, 32, 19.
22. Lyoo, W. S.; Han, S. S.; Kim, J. H.; Yoon, W. S.; Lee, C. J.; Kwon, I. C.; Lee, J.; Ji, B. C.; Han, M. H. Die Angew Makromol Chem 1999, 271, 46.
23. Lyoo, W. S.; Chvalun, S. N.; Ghim, H. D.; Kim, J. P.; Blackwell, J. Macromolecules 2001, 34, 2615.
24. Lyoo, W. S.; Kim, J. H.; Ghim, H. D. Polymer 2001, 42, 6317.
25. Choi, J. H.; Ko, S. W.; Kim, B. C.; Blackwell, J.; Lyoo, W. S. Macromolecules 2001, 34, 2964.
26. Lyoo, W. S.; Kim, J. H.; Choi, J. H.; Kim, B. C.; Blackwell, J. Macromolecules 2001, 34, 3982.
27. Lyoo, W. S.; Kim, J. H.; Koo, K.; Lee, J.; Kim, S. S.; Yoon, W. S.; Ji, B. C.; Kwon, I. C.; Lee, C. J. J Polym Sci Part B Polym Phys 2001, 39, 1263.
28. Lyoo, W. S.; Kim, B. J.; Ha, W. S. J Korean Fiber Soc 1996, 33, 231.
29. Lyoo, W. S.; Yeum, J. H.; Ghim, H. D.; Ji, B. C.; Yoon, W. S.; Kim, J. P. J Korean Fiber Soc 2000, 37, 487.
30. Ha, W. S.; Lyoo, W. S.; Choi, Y. G. US Pat. 2000, 6,124,033.
31. Nakano, T.; Makita, K.; Okamoto, Y. Polym J 1998, 30, 681.
32. Li, J. K.; Wang, N.; Wu, X. H. J Controlled Release 1998, 56, 117.
33. Huang, J.; Kao, H.; Wu, X. Y. J Controlled Release 2000, 67, 45.
34. Morita, R.; Honda, R.; Takahashi, Y. J Controlled Release 2000, 68, 115.
35. Yamamoto, T.; Yoda, S.; Sangen, O.; Fukae, R.; Kamachi, M. Polym J 1989, 21, 1053.