

Synthesis of Water-Soluble Syndiotacticity-Rich Low Molecular Weight Poly(vinyl alcohol) by Solution Copolymerization of Vinyl Pivalate/Vinyl Acetate in Tetrahydrofuran and Saponification

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ABSTRACT: Syndiotacticity-rich low molecular weight poly(vinyl alcohol) (PVA) was synthesized by solution copolymerization of vinyl pivalate (VPi) and vinyl acetate (VAc) in tetrahydrofuran (THF) at low temperature using 2,2'-azobis(2,4-dimethylvaleronitrile) (ADMVN) as an initiator and successive saponification of copoly(VPi/VAc). Effects of initiator and monomer concentrations and polymerization temperature on the polymerization behavior and molecular structure of PVA prepared were investigated. The polymerization rate of VPi and VAc in THF was proportional to the 0.96 power of ADMVN concentration, indicat-

ing the heterogeneous nature of THF polymerization. Low-temperature solution copolymerization of VPi and VAc in THF by adopting ADMVN proved to be successful in obtaining water-soluble PVA with number-average degree of polymerization of 180–360, syndiotactic diad content of 56–58%, and ultimate conversion of VPi and VAc into copoly(VPi/VAc) of over 80%, respectively. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 227–232, 2003

Key words: syndiotactic; water-soluble polymers; solution copolymerization; initiators; copoly(VPi/VAc)

INTRODUCTION

Poly(vinyl alcohol) (PVA) is a highly hydrophilic and water-soluble polymer, widely employed in various applications such as fibers for clothes and industries, films, membranes, medicines for drug delivery systems, and cancer cell-killing embolic materials. In addition, PVA fibers, gels, 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 are superior to those of any known polymers.^{1–3} These physical properties of PVA are controlled by the molecular weight and stereoregularity of PVA.

Actually, the control of the stereoregularity in vinyl polymerizations is important because physical and chemical properties of vinyl polymers are often significantly influenced by main-chain tacticity. Although

various effective methods for stereoregularity control have been devised for anionic and coordination polymerizations, only limited successful examples are known for free-radical polymerization because many classes of polymers are industrially produced by radical catalysis.⁴ Challenging attempts have been made to increase the syndiotacticity of PVA. The preparation of highly syndiotacticity-rich PVA was achieved by a choice of vinyl ester monomers with bulky pendent groups, such as vinyl trifluoroacetate^{5,6} and vinyl pivalate (VPi).^{7–17} Another way to obtain syndiotacticity-rich PVA includes the use of a proton-donating solvent¹⁸ like phenol, in solution polymerization of vinyl esters or a modification of the polymerization method such as low temperature photoinitiated polymerization.^{8,9}

However, in comparison with atactic PVA, high molecular weight syndiotacticity-rich PVA has been limited for biomaterial applications because of water-insoluble characteristics induced by the high compactness of the syndiotacticity-rich PVA, although syndiotacticity-rich PVA has superior properties. Therefore, to improve the water solubility of syndiotacticity-rich PVA, while maintaining the basic properties of syndiotacticity-rich PVA to some extent, fine control of

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TABLE I
Solution Copolymerization Conditions of VPi and VAc

VPi/VAc mole ratio	5/5
Polymerization temperature (°C)	30, 40, 50
Initiator concentration (mol/mol of VPi and VAc)	0.0003, 0.0005, 0.001
(VPi and VAc)/THF (v/v)	10/0, 9/1, 7/3, 5/5

the molecular weight of PVA is necessary. That is, for lower cost and various applications, therefore, it is essential to reduce the solubility temperature of PVA in water by controlling the stereoregularity as well as the molecular weight of PVA.

In this study, therefore, solution copolymerization of VPi/vinyl acetate (VAc) in THF with a high chain-transfer constant was conducted at polymerization temperatures of 30, 40, and 50°C to prepare low molecular weight PVA with high syndiotacticity and high yield. Also, the effects of initiator and solvent concentrations and polymerization temperature on the molecular parameters of PVA were investigated.

EXPERIMENTAL

Materials

VPi and VAc (purchased from Shin-Etsu) were washed with an aqueous solution of NaHSO₃ and water and dried with anhydrous CaCl₂, followed by distillation in nitrogen atmosphere under reduced pressure. The initiator 2,2'-azobis(2,4-dimethylvaleronitrile) (ADMVN; Wako Pure Chemicals, Osaka, Japan) was recrystallized twice in methanol before use. Other extrapure grade reagents were used without further purification. Water used for all the procedures was deionized.

Solution copolymerization of VPi/VAc

VPi, VAc, and THF were poured into a three-neck round-bottom flask and flushed with nitrogen for 3 h to eliminate oxygen. At the predetermined polymerization temperature, ADMVN was added to the solution. When polymerization had been completed, the product polymer was reprecipitated several times from benzene/*n*-hexane to eliminate residual monomer and solvent. Conversion was calculated by measuring the weight of the polymer. Conversions were averages of five determinations. The detailed polymerization conditions are given in Table I.

Saponification of copoly(VPi/VAc)

The following is a typical example of saponification of copoly(VPi/VAc).⁷ In a flask equipped with a reflux condenser, a thermocouple, a dropping funnel, and a stirring device, 3 g of copoly(VPi/VAc) was dissolved

in 300 mL of THF. The copoly(VPi/VAc) solution in the flask and 20% potassium hydroxide/methanol/water (90/10 v/v) solution in the dropping funnel were flushed with nitrogen. The ratio of saponification agent/copoly(VPi/VAc) solution was 0.05/0.25 (v/v). The alkali solution was added to the copoly(VPi/VAc) solution while being stirred at 50–60°C. After the saponification reaction had been completed, the solid saponification product was filtered and washed several times with methanol. A quantitative yield of PVA was obtained. Residual ester groups could not be detected in the proton nuclear magnetic resonance (¹H-NMR) spectra of these specimens.

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 was stirred in a three-neck flask at 100°C for 72 h under an atmosphere of nitrogen. Then the mixture was poured into cold water to precipitate poly(vinyl acetate) (PVAc). PVAc thus produced was filtered and purified by repeating the reprecipitation from methanol and water.

Characterization

The molecular weight of PVA was calculated by using the following equation⁹:

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

where $[\eta]$ is the intrinsic viscosity and P_n is the number-average degree of polymerization of PVAc. The molecular weights of PVA were deduced from that of PVAc produced by acetylation of PVA.

The *S*-diad content of PVA was determined by using ¹H-NMR (Sun Unity 300; Varian Associates, Palo Alto, CA). The degree of saponification (*DS*) of PVA was determined by the ratio of *tert*-butyl and methylene proton peaks in the ¹H-NMR spectrum.

The degree of solubility of the PVA in hot water from 40 to 80°C after 3 h was calculated using the following equation⁷:

$$\text{degree of solubility} = 1 - (W_a/W_b) \quad (2)$$

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

RESULTS AND DISCUSSION

Solution copolymerization of VPi/VAc in THF

Generally, in a free-radical polymerization, the rate of polymerization (R_p) increases as the efficiency and

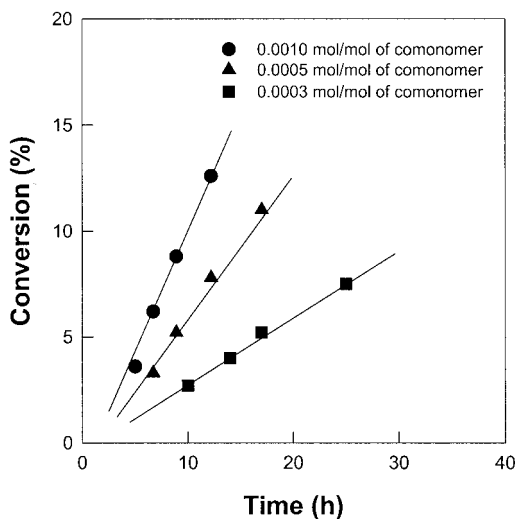


Figure 1 Plot of conversion of VPi/VAc into copoly(VPi/VAc) in early stage of polymerization at 30°C using comonomer/THF ratio of 9/1 (v/v).

concentration of the initiator increase. Figure 1 presents the initial conversion rate measured within 15% conversion in the solution copolymerization of VPi/VAc with molar ratio of 5/5 in THF at 30°C using ADMVN. The greater the initiator concentration, the higher the R_p .

The dependency of R_p on the initiator concentration can be determined with the initial-rate method.¹⁹ For small changes in the initiator concentration, R_p can be approximated to the corresponding ratio of increments. If a measurement is made at two different initiator concentrations of one component with the other held constant, the order with respect to that component can be simply determined by use of the following equations:

$$-(d[M]_1/dt) = (R_p)_1 = k[M]_1^{n_1}[I]_1^{n_2}[S]_1^{n_3} \quad (3)$$

$$-(d[M]_2/dt) = (R_p)_2 = k[M]_2^{n_1}[I]_2^{n_2}[S]_2^{n_3} \quad (4)$$

$$-(d[M]_3/dt) = (R_p)_3 = k[M]_3^{n_1}[I]_3^{n_2}[S]_3^{n_3} \quad (5)$$

$$(R_p)_1/(R_p)_2 = ([I]_1/[I]_2)^{n_{2a}} \quad (6)$$

$$(R_p)_2/(R_p)_3 = ([I]_2/[I]_3)^{n_{2b}} \quad (7)$$

$$(R_p)_3/(R_p)_1 = ([I]_3/[I]_1)^{n_{2c}} \quad (8)$$

$$n_2 = (n_{2a} + n_{2b} + n_{2c})/3 \quad (9)$$

where $[M]$, $[I]$, and $[S]$ are the concentrations of the monomer, initiator, and solvent, respectively, and k is the reaction rate constant.

This procedure can be used to determine all exponents like n_1 , n_2 , and n_3 . From the calculations, it was

found that the R_p value of VPi/VAc with molar ratio of 5/5 in THF was proportional to the 0.96 power of ADMVN concentration. This anomaly with respect to normal kinetic behavior is generally accounted for by the assumption that the precipitation of the growing chains severely restricts bimolecular chain termination and hence that the radicals do not reach a stationary concentration.^{20,21} In addition, some of the growing chains become buried in the dead polymer, which corresponds kinetically to monomolecular chain termination.²⁰ Therefore, the higher order with respect to ADMVN in the THF system (0.96) in this study might be attributed to monomolecular termination involving occlusion of growing chains attributed to the heterogeneous nature of the copolymerization of VPi/VAc.

Figure 2 illustrates conversion–time plots for polymerization temperatures of 30, 40, and 50°C at an initiator concentration of 0.0005 mol/mol of VPi/VAc with a molar ratio of 5/5 and comonomer/THF ratio of 9/1 (v/v). The rate of conversion was increased with increasing polymerization temperature. The conversions at 50°C increased up to 80% in spite of high polymerization temperature, which was absolutely impossible in bulk polymerization. This can be explained by an advantage of solution copolymerization of VPi/VAc in THF. At higher polymerization temperatures of 50 and 40°C, the conversion–time curves had the characteristic sigmoidal shape showing an increase in R_p with conversion. An increase in conversion with time was diminished during polymerization, probably because of the inefficient transfer and diffusion of heat resulting from the copoly(VPi/VAc) formed during the early stages of polymerization. It might be thought that the increase in rate is a conse-

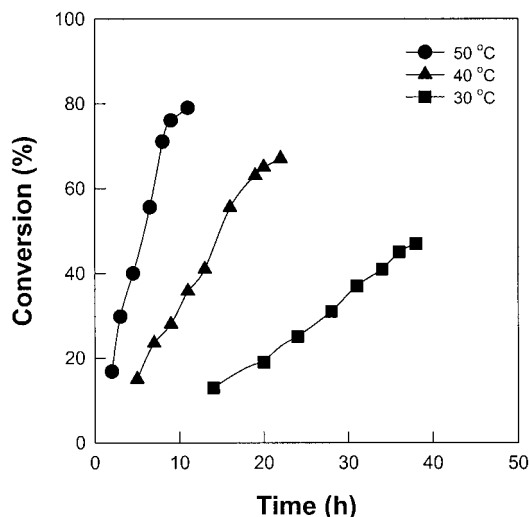


Figure 2 Plot of conversion of VPi/VAc into copoly(VPi/VAc) solution polymerized using ADMVN concentration of 0.0005 mol/mol of comonomer and comonomer/THF ratio of 9/1 (v/v) at three different polymerization temperatures with polymerization time.

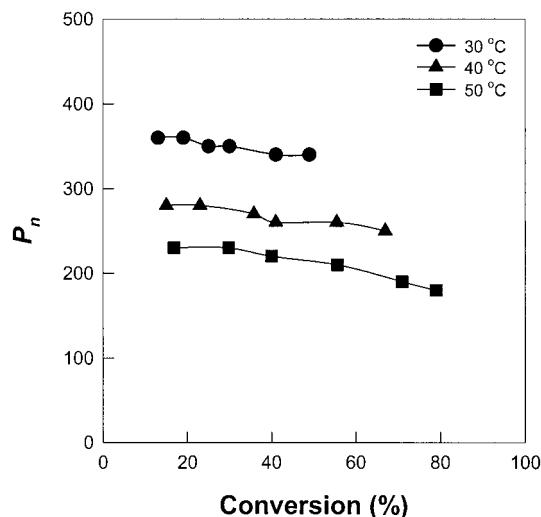


Figure 3 Plot of P_n values of PVA from copoly(VPi/VAc) copolymerized using ADMVN concentration of 0.0005 mol/mol of comonomer and comonomer/THF ratio of 9/1 (v/v) at three different polymerization temperatures with conversions.

quence of diffusion-controlled termination reactions in solution copolymerization of VPi/VAc. In contrast, at 30°C, the conversion linearly increased without any abrupt changes in the slope. This might be explained by smaller heating effects during polymerization at lower polymerization temperature using ADMVN, and that heat generated during solution copolymerization can be easily removed at a lower polymerization temperature, which minimizes the autoacceleration of polymerization. High ultimate conversions (50–80%) were obtained at all conditions, compared with the case of bulk copolymerization of VPi/VAc using ADMVN (25–40%). This explains the fact that solution copolymerization by ADMVN and THF is useful for producing copoly(VPi/VAc) in high yields.

Molecular weight of PVA

The effects of polymerization temperature and conversion on the P_n values of PVA obtained by saponifying copoly(VPi/VAc) are shown in Figure 3. It is shown that the P_n of PVA remained almost constant up to approximately 40–50% conversion and then the P_n of PVA decreased slightly at higher conversions of over 40–50%. This was attributed to frequent chain-transfer reactions between polymers, resulting in termination and branch formation reactions at higher conversions, whereas chain-transfer reactions between monomers prevailed at lower conversions. P_n values of PVA increased with a decrease in the polymerization temperature, attributed to a lower polymerization rate at lower polymerization temperature. PVA polymers having various P_n values of 180–360 could be prepared by the saponification of copoly(VPi/VAc)s. It

should be noted that water-soluble PVA with P_n values of 180–360 could be prepared from copoly(VPi/VAc) solution polymerized in THF at conversion of about 50–80%. Therefore, it can be concluded that the solution copolymerization of VPi/VAc in THF using ADMVN and saponification is an effective method to increase both the yield and the water solubility of PVA by molecular weight and stereoregularity decrease.

Figure 4 exhibits plots of P_n values of PVA against ADMVN concentration at different comonomer/THF ratios. Copoly(VPi/VAc) was sampled at similar conversions of about 20% to clarify the effects of comonomer and initiator concentrations. A larger amount of THF lowered the P_n value of PVA, which arises from the fact that disproportionation and branch-forming reactions were favored by chain transfer as the THF content increased.

Characteristics of saponified PVA

The syndiotacticity of PVA depends on polymerization conditions as well as side-group bulkiness of the monomer. In this study, we considered the effects of polymerization solvent, polymerization temperature, and conversion on the stereoregularity of PVA (Figs. 5 and 6). We had earlier investigated the effect of monomer ratios in bulk copolymerization of VPi and VAc on the syndiotacticity of PVA.⁷ The *S*-diad contents, varying continuously from 52.8 to 61.5%, were obtained by variation of the monomer feeds. Also, in the case of solution polymerization of VPi, we studied the effect of solvents such as dimethyl sulfoxide (DMSO) and tertiary butyl alcohol (TBA) in solution polymerization of VPi on the syndiotacticity of PVA.¹³ Polar aprotic solvents like DMSO promoted isotactic config-

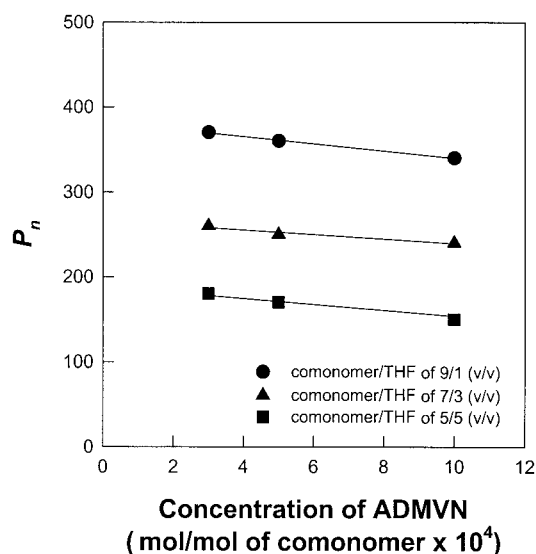


Figure 4 Plot of P_n values of PVA from copoly(VPi/VAc) copolymerized at 30°C with ADMVN concentrations.

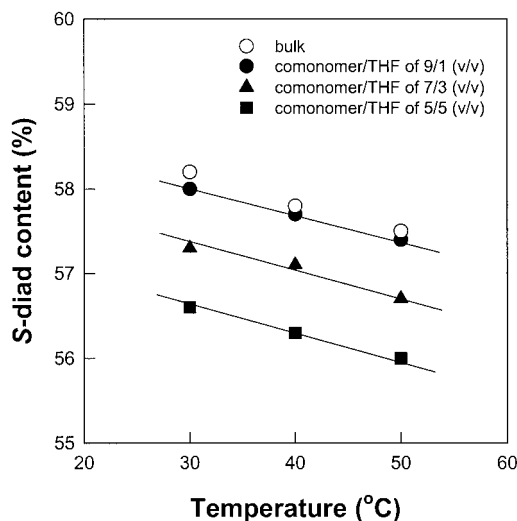


Figure 5 Plot of *S*-diad content of PVA from copoly(VPi/VAc) copolymerized using ADMVN concentrations of 0.0005 mol/mol of comonomer with polymerization temperature.

uration, resulting from electrostatic interaction between the solvent molecules and pivaloyl groups. In contrast, in the solution polymerization of VPi in TBA, the hydrogen-bonding interaction between the solvent molecules and pivaloyl groups increases the steric hindrance between the monomers. Thus, syndiotactic configuration is favored when alcohol is used as a solvent.¹³ In Figures 5 and 6, the effect of the solvent THF on the syndiotacticity of PVA is depicted. THF caused a decrease in the *S*-diad content; that is, the *S*-diad content of PVA from copoly(VPi/VAc) obtained by solution copolymerization at 30°C using comonomer/THF of 5/5 (v/v) dropped to lower levels (56%) than that of PVA obtained by bulk polymer-

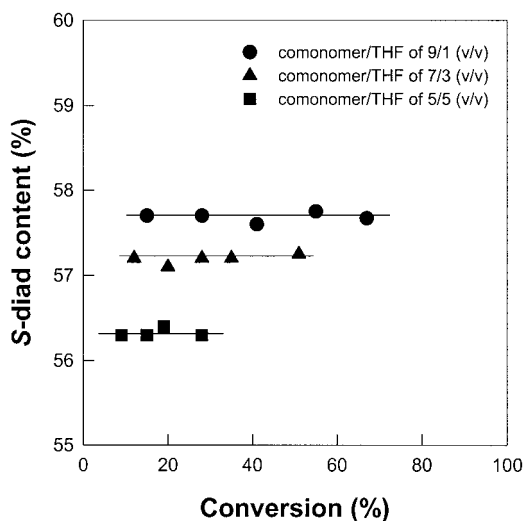


Figure 6 Plot of *S*-diad content of PVA from copoly(VPi/VAc) copolymerized using ADMVN concentrations of 0.0005 mol/mol of comonomer at 40°C with conversion.

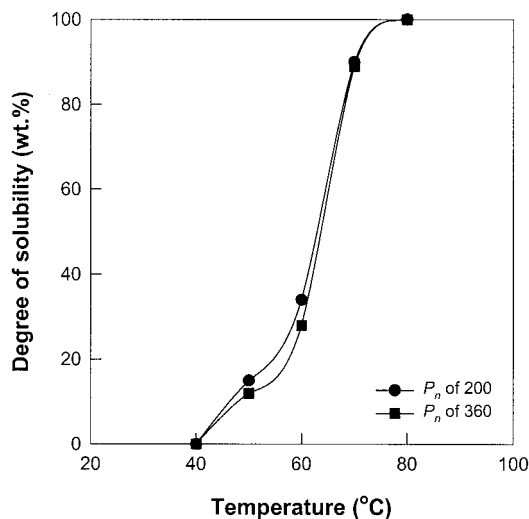


Figure 7 Plot of degree of water solubility of PVA specimens having similar *S*-diad contents of 57% and *DS* of 99.9% and different *P_n* values of 360 and 200 with solubility test temperature.

ization. However, the difference between the two values was small. The *S*-diad content of PVA increased with lowering the polymerization temperature, as shown in Figure 5. Meanwhile, the *S*-diad content seems not to have a close relationship with conversion of VPi and VAc into copoly(VPi/VAc), as shown in Figure 6.

Figure 7 presents the water solubility of two PVA polymers prepared in this study. PVA was completely soluble above 80°C because of its low molecular weight and syndiotacticity.

CONCLUSIONS

To obtain low molecular weight copoly(VPi/VAc) with high syndiotacticity and high conversion for a precursor of water-soluble low molecular weight syndiotacticity-rich PVA, VPi/VAc with a molar ratio of 5/5 was solution copolymerized using ADMVN and THF at 30, 40, and 50°C. It is difficult to prepare copoly(VPi/VAc) with high conversion, high syndiotacticity, and low molecular weight by free-radical polymerization in bulk because of the polymerization exotherm and high viscosity during copolymerization of VPi and VAc. However, ADMVN and THF seem to be advantageous in lowering the polymerization temperature down to about 30°C and in activating chain-transfer reaction, respectively. Furthermore, this solution copolymerization is a powerful method for enhancing conversion.

Through a series of calculations using the initial-rate method, it was found that the solution copolymerization rate of VPi and VAc at 30°C was proportional to the exponent 0.96 of ADMVN concentration. This high value (0.96) might be explained by monomolecular

termination involving occlusion of growing chains attributed to the heterogeneous nature of the polymerization of VPi and VAc in THF.

Solution copolymerization of VPi and VAc by ADMVN and saponification produced water-soluble low molecular weight syndiotacticity-rich PVA with P_n values of 180–360, an S-diad content of 56–58%, and with maximum conversion of VPi and VAc into copoly(VPi/VAc) of 50–80%. The P_n values and syndiotacticity were higher with PVA from copoly(VPi/VAc) at lower temperatures. Isotactic configuration was favored when THF was used because of the electrostatic interaction between the solvent molecules and piv-aloyl and acetyl groups.

Finally, this solution copolymerization is expected to be an easy way of producing water-soluble syndiotacticity-rich PVA with high yield by simple chemical initiation without using special devices such as irradiation. It is expected that these PVA polymers can be used as environmentally friendly fibers such as water-soluble fiber for nonwoven fabric, embolic fiber for cancer-cell killing, ultralow denier fiber, and pulp for paper-based products because of its high fineness, excellent alkali resistance, good biocompatibility, and good binding property.⁸ In the near future, we will report on the preparation of PVA having various stereoregularities with high yield using solution copolymerization and saponification.

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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.; Wiley: New York, 1985.
3. Masuda, M. In: *Polyvinyl Alcohol Development*; Finch, C. A., Ed.; Wiley: New York, 1991.
4. Yuki, H.; Hatada, K. *Adv Polym Sci* 1979, 31, 1.
5. Yamaura, K.; Hirata, K.; Tamura, S.; Matsuzawa, S. *J Polym Sci Part B: Polym Phys* 1985, 23, 1703.
6. Nakamae, K.; Nishino, T.; Ohkubo, H.; Matsuzawa, S.; Yamaura, K. *Polymer* 1992, 33, 2581.
7. Lyoo, W. S.; Blackwell, J.; Ghim, H. D. *Macromolecules* 1998, 31, 13.
8. Lyoo, W. S.; Ha, W. S. *Polymer* 1996, 37, 3121.
9. Lyoo, W. S.; Ha, W. S. *J Polym Sci Part A: Polym Chem* 1997, 35, 55.
10. Lyoo, W. S.; Kim, B. J.; Ha, W. S. *J Korean Fiber Soc* 1996, 33, 231.
11. Kwarck, Y. J.; Lyoo, W. S.; Ha, W. S. *Polym J* 1996, 28, 851.
12. 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. *Angew Makromol Chem* 1999, 271, 46.
13. Lyoo, W. S.; Kim, J. H.; Ghim, H. D. *Polymer* 2001, 42, 6317.
14. Yamamoto, T.; Yoda, S.; Sangen, O.; Fukae, R.; Kamachi, M. *Polym J* 1989, 21, 1053.
15. 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.
16. Lyoo, W. S.; Kim, J. H.; Choi, J. H.; Kim, B. C.; Blackwell, J. *Macromolecules* 2001, 34, 3982.
17. Lyoo, W. S.; Chvalun, S. N.; Ghim, H. D.; Kim, J. P.; Blackwell, J. *Macromolecules* 2001, 34, 2615.
18. Matsuzawa, S.; Yamaura, K.; Noguchi, H.; Hayashi, H. *Macromol Chem* 1973, 165, 217.
19. Cox, B. G. *Modern Liquid Phase Kinetics*; Oxford, UK: Oxford University Press, 1994.
20. Bamford, C. H.; Jenkins, A. D. *J Polym Sci* 1956, 20, 405.
21. Bernas, A.; Bodard, M. *J Polym Sci* 1960, 48, 167.