

피발산비닐과 아세트산비닐의 테트라히드로푸란계 용액공중합에 의한 수용성 저분자량 교대배열 폴리비닐알코올의 제조

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Preparation 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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1. Introduction

Poly(vinyl alcohol) (PVA) is a representative hydrophilic and water-soluble polymer and widely employed in various applications such as fibers for clothes and industries, films, membranes, medicines for drug delivery system, and cancer cell-killing embolic materials. Moreover, 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 which are superior to those of any known polymers[1,2].

These physical properties of PVA are controlled by the molecular weight and stereoregularity of PVA. So, challenging attempts have been made to increase syndiotacticity of PVA. Preparation of syndiotacticity-rich PVA (s-PVA) has been achieved by a choice of vinyl ester monomers with bulky pendent groups, such as vinyl trifluoroacetate[3] and vinyl pivalate (VPi)[4-6]. However, comparing with atactic PVA, high molecular weight s-PVA has been limited for applications of biomaterial due to water-nonsoluble characteristic 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 extent, fine control of the molecular weight of PVA may be required.

So, in this study, solution copolymerization of VPi/vinyl acetate (VAc) in tetrahydrofuran (THF) with high chain transfer constant was conducted at polymerization temperature of 30, 40, and 50 °C to obtain 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.

2. Experimental

2.2 Solution Copolymerization of VPi/VAc

VPi, VAc, and THF were poured into a three-necked round bottom flask and flushed with nitrogen for 3 h to eliminate oxygen. At the predetermined polymerization temperature, 2,2'-azobis(2,4-dimethylvaleronitrile) (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 three determinations.

2.3 Saponification of Copoly(VPi/VAc)

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 °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.

2.4 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 necked 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.

2.5 Characterizations

The molecular weight of PVA was calculated by using eq. 1:

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

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

Syndiotactic diad content of PVA was determined by using $^1\text{H-NMR}$ (Varian, Sun Unity 300). The degree of saponification of PVA was determined by the ratio of *tert*-butyl and methylene proton peaks in the $^1\text{H-NMR}$ spectrum. The degree of solubility of the PVA in hot water from $40 \text{ }^\circ\text{C}$ to $80 \text{ }^\circ\text{C}$ after 3 h was calculated using eq. 2:

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

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

3. Results and Discussion

Effects of polymerization temperature and conversion on the (P_n)s of PVA obtained by the saponification of copoly(VPi/VAc) are shown in Figure 1. It is presented that P_n of PVA remained almost constant up to approximately 40-50% conversion and then P_n of PVA slightly decreased at higher conversions of over 40-50%. This was ascribed by frequent chain transfer reactions between polymers resulting in termination and branch formation reactions at higher conversions, whereas chain transfer reactions between monomers were prevail at lower ones. P_n of PVA was increased with a decrease in the polymerization temperature. This was due to a lower polymerization rate at lower polymerization temperature. (PVA)s having various (P_n)s 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 of 180-360 could be prepared from copoly(VPi/VAc) solution polymerized in THF at conversion of ca. 50-80%. Thus, it concludes that the solution copolymerization of VPi/VAc in THF using ADMVN and saponification are effective methods to increase both yield and water solubility of PVA by molecular weight and stereoregularity decrease. Figure 2 exhibits (P_n)s of PVA against ADMVN concentration at different comonomer/THF ratios. Copoly(VPi/VAc) was sampled

at similar conversions of about 20% to precisely clarify the effects of comonomer and initiator concentrations. Higher THF concentrations lowered P_n of PVA, which arises from the fact that disproportionation reactions were favored by chain transfer as THF content increased.

4. References

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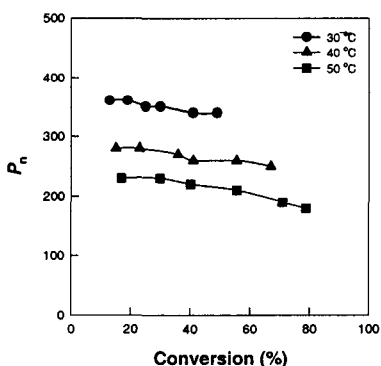


Figure 1. (P_n)s of PVA from copoly(VPi/VAc) polymerized using ADMVN concentration of 0.0005 mol/mol of comonomer and comonomer/THF ratio of 9/1 (v/v) at three different polymerization temperatures with conversions.

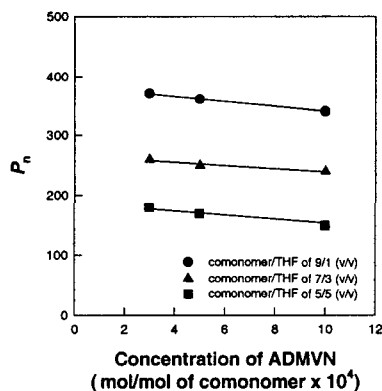


Figure 2. (P_n)s of PVA from copoly(VPi/VAc) polymerized at 30 °C with ADMVN concentrations.