

4,4'-아조비스(4-시아노발레릭산)을 이용한 아세트산비닐의 메탄올계 저온 용액중합

곽진우, 류원석
영남대학교 섬유패션학부

Low-Temperature Solution Polymerization of Vinyl Acetate in Methanol Using 4,4'-Azobis(4-cyanovaleric acid) in Methanol

Jin Woo Kwak and Won Seok Lyoo

School of textiles, Yeungnam University, Kyongsan, Korea

1. Introduction

Poly(vinyl alcohol) (PVA) obtained by the saponification of poly(vinyl ester) is a linear semicrystalline polymer; these polymers have been widely used as fibers for clothes and industries, binders, films, membranes, medicines for drug delivery system, and cancer cell-killing embolic materials. PVA fibers have high tensile and compressive strength, tensile modulus, and abrasion resistance because of the highest crystalline lattice modulus. To maximize these physical properties, molecular weight, degree of saponification, and syndiotacticity should be increased. In general, PVA is prepared by four polymerization methods of vinyl acetate (VAc) - bulk, solution, suspension, and emulsion - and then the saponification of prepared poly(vinyl acetate) (PVAc). Among these polymerization methods, solution polymerization has advantage of easy control of polymerization exotherm and of higher conversion than those of bulk polymerization and of higher purity than those of emulsion and suspension polymerization[1-2]. In this study, VAc was solution-polymerized at 40 and 50 °C in methanol using 4,4'-azobis(4-cyanovaleric acid) (ACVA) as an initiator for obtaining high molecular weight PVAc with higher conversions. The effect of polymerization conditions on the polymerization behavior of VAc and molecular parameters of PVAc and PVA were examined.

2. Experimental

2.1. Materials

VAc was washed with an aqueous solution of NaHSO₃ and water and dried over anhydrous CaCl₂, followed by distillation under reduced pressure of nitrogen. The initiator, ACVA, the solvent, methanol, and other reagents were used without further purification. VAc was placed in a three-necked round bottom flask and flushed with dry nitrogen. Methanol was added into a flask and flushed with nitrogen for 3 h to eliminate oxygen. At the predetermined polymerization temperature, ACVA was added to the solution. At the completion of polymerization, the unreacted monomer was distilled out. PVAc was reprecipitated several times from acetone/*n*-hexane and then dried under vacuum at 50 °C for 24 h.

2.2. Saponification of PVAc

To a solution of 2 g of PVAc in 100 mL of methanol, 2.5 mL of 40% NaOH aqueous solution was added, and the mixture was stirred for 5 h at room temperature to yield PVA. The PVA produced was filtered and washed well with methanol.

2.3. Characterization

The conversion of VAc into PVAc was obtained from the percent ratio of the weight of polymer formed to the weight of monomer used and the molecular weight of PVAc and the degree of branching (DB) were calculated by using eq. (1) and eq. (2) respectively[3].

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

where $[\eta]$ is the intrinsic viscosity and P_n is a number-average degree of polymerization of PVAc. On the other hand, molecular weight of PVAc was determined from that of PVAc produced by acetylation of PVA using eq. (2)[4].

$$DB = \frac{DP_1}{DP_2} - 1 \quad (2)$$

where DP_1 is P_n of PVAc and DP_2 is P_n of PVA prepared by saponifying PVAc.

3. Result and discussion

Generally, the conversion of VAc into PVAc is increased as the polymerization temperature is increased. Figure 1 presents typical tendency of conversion increasement in the solution polymerization of VAc in methanol. That is, the rate of conversion was very high during the early stage of polymerization at 50 and 40 °C, but the ultimate conversion was lower in both cases. Increase of conversion with time was diminished during polymerization, probably as a result of the inefficient transfer and diffusion of heat because of the PVAc formed during the early stage of polymerization[5].

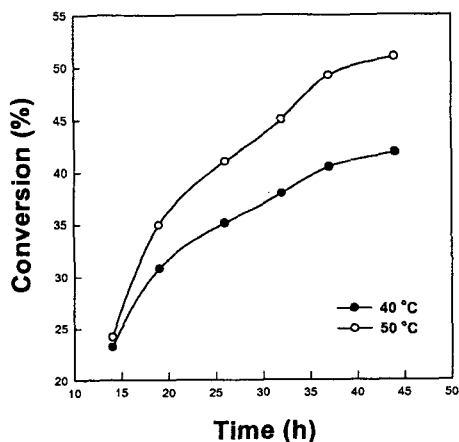


Figure 1. Plots of conversion of VAc into PVAc obtained by solution polymerization of VAc at 50 and 40 °C vs. polymerization time.

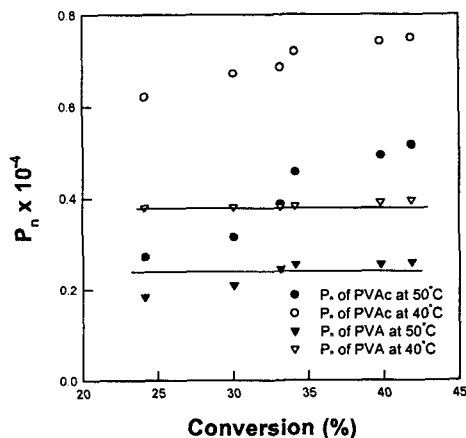


Figure 2. Plots of P_n of PVAc obtained by solution polymerization of VAc at 50 and 40 °C and resulting PVA vs. conversions.

Effect of polymerization temperature on the conversion of VAc into PVAc and P_n of PVAc obtained by solution polymerization of VAc and resulting PVA is shown in Figure 2. The P_n of PVAc was increased with increasing conversion, but the P_n of PVA was almost uniform because of the occurrence by means of frequent chain transfer reactions above a certain extent of initial conversion in solution polymerization. As a rule, the branches occurred by chain transfer and

termination by disproportionation are hydrolyzed via saponification process. Thus, (P_n)s of PVA are almost uniform regardless of each (P_n)s of precursor, PVAc.

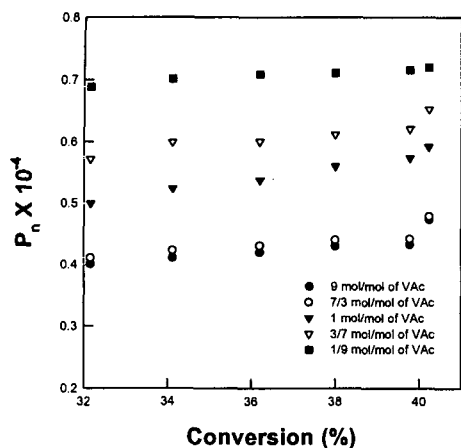


Figure 3. Plots of P_n of PVAc obtained by solution polymerization of VAc at 40 °C and vs. the content of solvent.

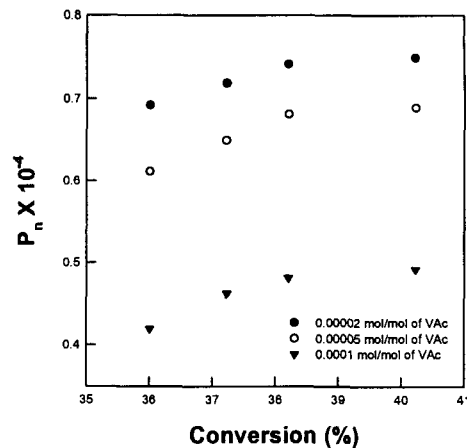


Figure 4. Plots of P_n of PVAc obtained by solution polymerization of VAc at 40 °C vs. initiator concentrations.

Figure 3 shows the effect of solvent content affects the P_n of PVAc in solution polymerization of VAc at 40 °C. As shown in Figure 3, the P_n of PVAc decreased as the content of solvent was increased. This may due to the attack toward the solvent of radicals generated from the initiator, which can cause the decrease of P_n of PVAc. Figure 4 illustrates conversion- P_n plots for temperatures 40 °C versus each initiator concentration. The P_n of PVAc increased as the initiator concentration was decreased.

4. Conclusion

Molecular weight of PVAc at lower temperature is higher than that of PVAc at higher temperature. PVA having maximum P_n of 3,900 could be prepared by saponification of PVAc having maximum P_n of 7,500 obtained 2×10^{-5} mol/mol of VAc of ACVA at 40 °C. And, the P_n of PVAc decreased as the content of solvent was increased.

5. References

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