

# Preparation of High-Molecular-Weight Poly(vinyl alcohol) with High Yield by Solution Polymerization of Vinyl Acetate in Methanol Using 4,4'-Azobis(4-cyanovaleric acid)

Won S. Lyoo,<sup>1</sup> Du H. Song,<sup>1</sup> Won C. Lee,<sup>2</sup> Sung S. Han,<sup>1</sup> Seok K. Noh<sup>3</sup>

<sup>1</sup>*Division of Advanced Organic Materials, School of Textiles, Yeungnam University, Gyongsan 712-749, Korea*

<sup>2</sup>*School of Beauty Fashion Design, Kyungil University, Gyongsan, Korea*

<sup>3</sup>*School of Chemical Engineering and Technology, Yeungnam University, Gyongsan 712-749, Korea*

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**ABSTRACT:** Vinyl acetate (VAc) was solution-polymerized at 40°C and 50°C using 4,4'-azobis(4-cyanovaleric acid) (ACVA) as an initiator and methanol as a solvent, and effects of polymerization temperature and initiator concentration were investigated in terms of conversion of VAc into poly(vinyl acetate) (PVAc), degree of branching (DB) for acetyl group of PVAc, and molecular weights of PVAc and resulting poly(vinyl alcohol) (PVA) obtained by saponifying with sodium hydroxide. Slower polymerization rate by adopting ACVA and lower viscosity by methanol proved to be efficient in obtaining linear high-molecular-weight (HMW) PVAc with high conversion and HMW PVA. PVA having maximum

number-average degree of polymerization ( $P_n$ ) of 4300 could be prepared by the saponification of PVAc having maximum  $P_n$  of 7900 polymerized using ACVA concentration of  $2 \times 10^{-5}$  mol/mol of VAc at 40°C. Moreover, low DB of below 1 could be obtained in ACVA system, nevertheless of general polymerization temperatures of 40°C and 50°C. This suggests an easy way for producing HMW PVA with high yield by conventional solution polymerization without using special methods such as low-temperature cooling or irradiation. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 4831–4834, 2006

**Key words:** VAc; ACVA; high molecular weight; PVA

## INTRODUCTION

On account of high mechanical properties and excellent resistance to alkali and oxygen together with innocuous nature to human, poly(vinyl alcohol) (PVA) has attracted much attention as a basic material for high modulus and strength fiber, which can replace the carcinogenic asbestos fiber in construction materials, films for food and drug packages, polarization and barrier membranes, and materials for drug delivery systems. To maximize these properties of PVA, it is essential to prepare linear PVA of high molecular weight (HMW). Many studies such as adoption of new polymerization methods using special devices and utilization of new precursors such as poly(vinyl pivalate) have been progressed to obtain HMW PVA with few branches.<sup>1,2</sup>

As is well known, it is very difficult to obtain linear HMW poly(vinyl acetate) (PVAc), a representative precursor for HMW PVA, by free radical polymerization because it tends to chain transfer reactions, occurring

branching. Therefore, linear HMW PVA has been prepared only by special polymerization methods. Among them, initiation by irradiation has been mainly reported. These systems were developed in attempts to produce linear HMW PVAc, which could be used in the production of HMW PVA. Nikolaev et al. adopted a manganese chelate as initiator in a low temperature redox emulsion polymerization of vinyl acetate (VAc).<sup>3</sup> Rozenberg et al. made use of  $\gamma$ -radiation emulsion polymerization and obtained PVA of number-average degree of polymerization ( $P_n$ ) of 3200–5000.<sup>4</sup> Lanthier succeeded in obtaining PVA of  $P_n$  of 12,000 by  $\gamma$ -radiation polymerization of VAc at  $-15^\circ\text{C}$ .<sup>5</sup> Wu and West prepared PVA of  $P_n$  of over 10,000 by low-temperature-ultraviolet ray radiation bulk polymerization of VAc.<sup>6</sup>

However, these special polymerization methods require very complicated and expensive devices and hence difficult to be commercialized. In free radical polymerization of VAc, it may be possible to suppress the branching reaction by controlling polymerization temperature and rate using azoinitiator. Polymerization temperature is reported to have a paramount effect on branching reaction. As a rule, the degree of branching is diminished with decreasing polymerization temperature.<sup>7–9</sup>

Correspondence to: W. S. Lyoo (wslyoo@yu.ac.kr).

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We prepared HMW PVA by bulk and solution polymerizations of VAc at polymerization temperature of below 30°C using several chemical initiators. However, in these cases, it is also difficult to commercialize low polymerization temperature system using chemical initiation because of expensive cooling devices.<sup>10–13</sup>

In this study, to solve this problem, we used 4,4'-azobis(4-cyanovaleic acid) (ACVA), which can initiate VAc at 40°C and 50°C, in the solution polymerization of VAc in methanol. ACVA is insoluble in VAc and soluble in methanol. So, it is expected to obtain lower polymerization rate and higher molecular weight in spite of common polymerization temperature of 40°C and 50°C.

## EXPERIMENTAL

### Solution polymerization of VAc

VAc was washed with an aqueous solution of NaHSO<sub>3</sub> and water and dried over anhydrous CaCl<sub>2</sub>, followed by distillation under reduced pressure of nitrogen. The initiator, ACVA, the solvent, methanol, and other extra-pure grade reagents were used without further purification. VAc and solvent (methanol) were poured into a three-necked round-bottom flask and flushed with nitrogen for 3 h to eliminate oxygen. At the predetermined polymerization temperature, ACVA was added to the solution. When polymerization had been completed, the unreacted monomer was distilled out. PVAc was purified by reprecipitation several times from acetone/*n*-hexane and the dried under vacuum

at 40°C for 24 h. Conversion was calculated by measuring the weight of the polymer.

### Saponification of PVAc<sup>7,8</sup>

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.

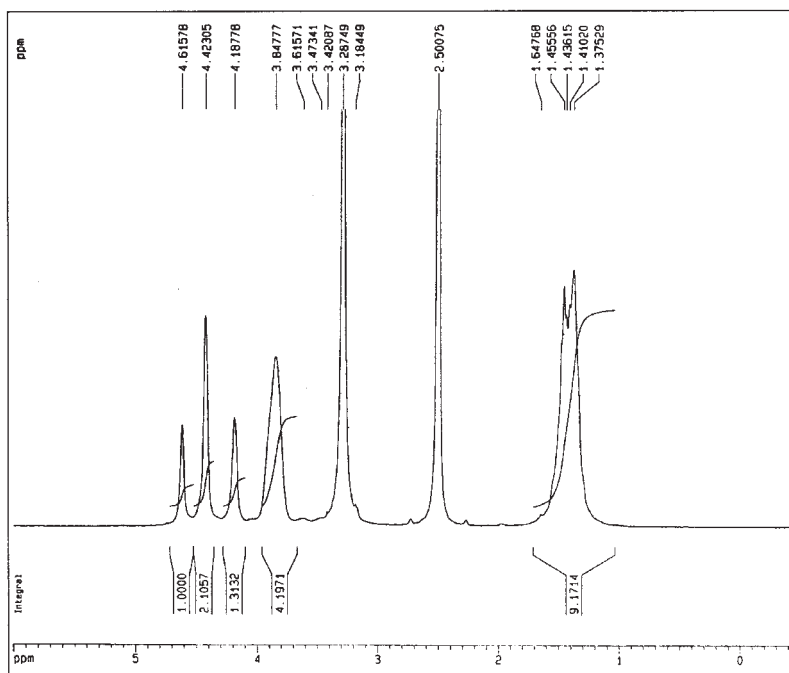
### Characterization

For measurement of molecular weight, PVA was reacylated as follows. PVA (1 g), 2 mL of pyridine, 20 mL of acetic anhydride and 20 mL of acetic acid were placed in a three-necked flask. The mixture was stirred at 100°C for 24 h under a nitrogen atmosphere, and then the mixture was poured into cold water to precipitate PVAc. PVAc thus obtained was filtered and purified by repeated dissolution and precipitation from methanol and water, respectively.

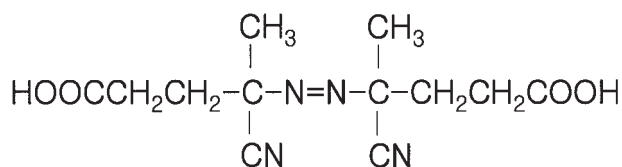
The molecular weight of PVAc and the degree of branching (DB) were calculated by using eq. (1) and eq. (2), respectively.<sup>3</sup>

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

where  $[\eta]$  is the intrinsic viscosity and  $P_n$  is a number-average degree of polymerization of PVAc. Molecular weight of PVA was determined from  $P_n$  of reacylated



**Figure 1** <sup>1</sup>H-NMR spectrum of PVA with degree of saponification of 99.9% and S-diad content of 53.9% prepared by completely saponification of PVAc obtained by solution polymerization of VAc at 40°C.



Scheme 1 Chemical structure of ACVA.

PVAc. The degree of saponification of PVA was determined by weight loss after saponification and by the ratio of methyl proton and methylene proton peaks in the  $^1\text{H}$ -NMR spectrum. Figure 1 shows a  $^1\text{H}$ -NMR spectrum in dimethyl sulfoxide of completely saponified PVA obtained from PVAc polymerized at  $40^\circ\text{C}$ . The DB for the acetyl group of PVAc was calculated by eq. (2)

$$\text{DB} = (\text{DP}_1/\text{DP}_2) - 1 \quad (2)$$

where  $\text{DP}_1$  is  $P_n$  of PVAc and  $\text{DP}_2$  is  $P_n$  of PVA prepared by saponifying PVAc.

## RESULTS AND DISCUSSION

The initiator, ACVA (Scheme 1) is monomer-nonsoluble initiator, hence the radical formation process was occurred in solvent phase. Free radicals formed in methanol moved to monomer phase gradually. Therefore, in case of solution polymerization of VAc using ACVA as initiator, it is expected that the polymerization rate was slower and molecular structure of prepared precursor was more linear in comparison with the general solution polymerization of VAc.

In general, the rate of polymerization is increased as the efficiency of initiator is enhanced in a free radical polymerization process. Hence, the rate of conversion is increased by raising the polymerization temperature or increasing initiator content as presented in Figure 2. That is, the rate of conversion was very high during the early stage of polymerization at  $40^\circ\text{C}$  and  $50^\circ\text{C}$ , 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. Maximum ultimate conversion of over 65% was obtained in ACVA system. Kim et al.<sup>12</sup> reported that maximum conversion of bulk polymerized PVAc was 24% at  $50^\circ\text{C}$ . Thus, conversion of ACVA system is much higher than that of bulk system, despite of polymerization system for HMW PVA.

The kinetic chain length,  $\nu$ , is expressed by eq. (3),

$$\nu = k_p[M]/2(fk_d k_t[I])^{1/2} \quad (3)$$

where  $[M]$  is the concentration of monomer,  $f$  is the efficiency of initiator,  $[I]$  is the concentration of initiator,

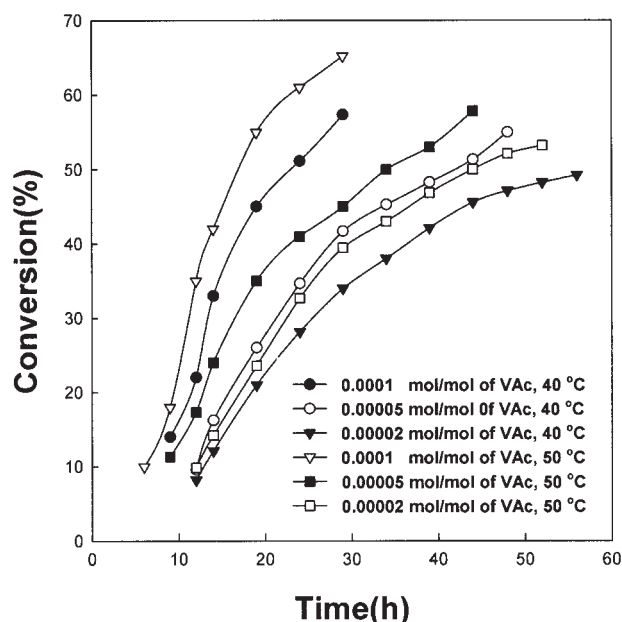


Figure 2 Conversions of VAc into PVAc obtained by solution polymerization of VAc at  $40^\circ\text{C}$  and  $50^\circ\text{C}$  using methanol/VAc of 1/9 (mol/mol) at three different ACVA concentrations with polymerization times.

and  $k_d$ ,  $k_p$ , and  $k_t$  are reaction rate constants of initiator decomposition, propagation, and termination, respectively. Referring to eq. (3), the degree of polymerization may be decreased as the efficiency and content of initiator are increased. The  $P_n$  of PVAc and PVA obtained by saponifying the corresponding PVAc is plotted against conversion in Figure 3. In accordance

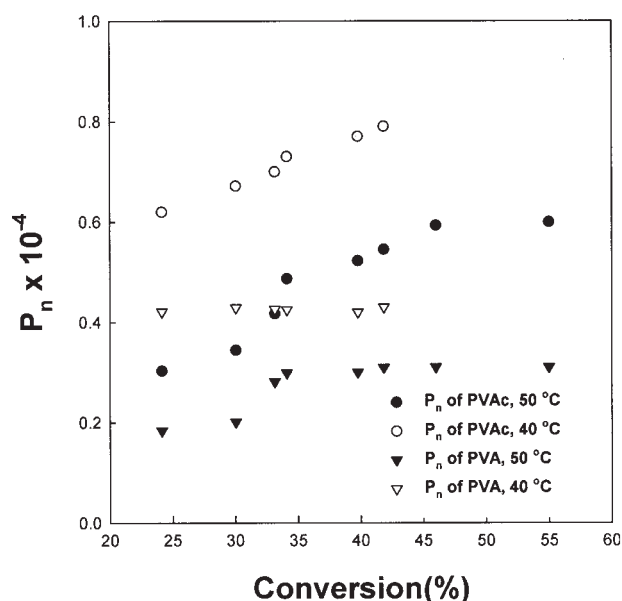
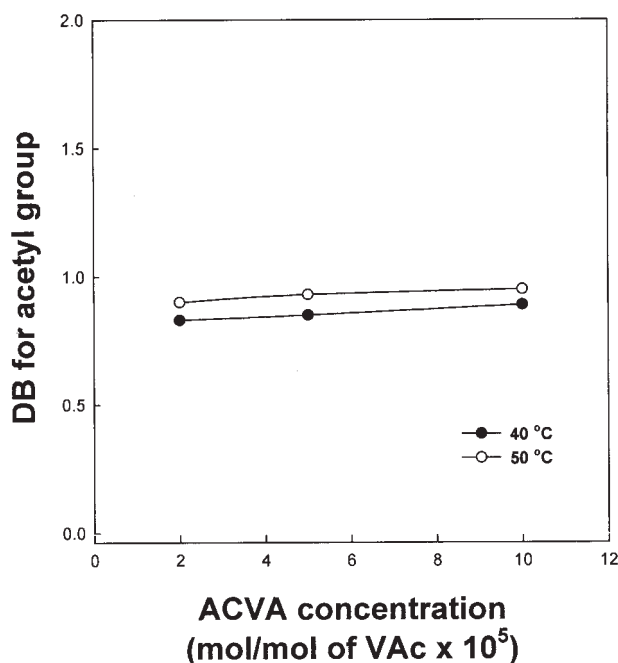


Figure 3  $P_n$ 's of PVAc obtained by solution polymerization of VAc at  $40^\circ\text{C}$  and  $50^\circ\text{C}$  using ACVA concentration of  $2 \times 10^{-5}$  mol/mol of VAc and methanol/VAc of 1/9 (mol/mol) and resulting PVA with conversions.



**Figure 4** DBs for acetyl group of PVAc obtained by solution polymerization of VAc at 40°C and 50°C using methanol/VAc of 1/9 (mol/mol) with ACVA concentrations (The PVAc was obtained at similar conversion of about 30%).

with theoretical prediction, the  $P_n$  of PVAc and PVA was generally increased with decreasing initiator content or decreasing polymerization temperature. In the case of PVAc,  $P_n$  was notably increased with increasing conversion. On the other hand, the  $P_n$  of PVA remained constant irrespective of conversion although it was decreased with increasing polymerization temperature. PVA with maximum  $P_n$  of 4300 could be obtained by saponifying PVAc with  $P_n$  of 7700 polymerized using ACVA concentration of  $2 \times 10^{-5}$  mol/mol of VAc at 40°C. Maximum  $P_n$  of bulk polymerized PVAc was 10,000 at 30°C and PVA with maximum  $P_n$  of 6000 was obtained by Kim et al.<sup>12</sup>

As a rule, the difference between  $P_n$ 's of PVAc and PVA is mostly due to branched structures, which may be broken down when saponified. Effects of polymerization temperature and initiator content on the DB for the acetyl group of PVAc at a similar conversion of about 30% is shown in Figure 4. DB was increased with increasing ACVA content and polymerization temperature. In general, optimum solvent in solution polymerization should have low chain transfer constant to minimize frequent branching reactions generated dur-

ing solution polymerization. But, the chain transfer constant of methanol used as solvent in these experimental have reported as a solvent with high chain transfer constant. Therefore, it is difficult to obtain linear PVAc using methanol as solvent. In spite of the fact, HMW linear PVAc could be prepared using methanol with low polymerization temperature and monomer-nonsoluble initiator. By the fact described above, lower DB of below 1 was obtained in this ACVA system.

## CONCLUSIONS

It is not easy to obtain HMW linear PVAc and resulting HMW PVA by solution polymerization of VAc in methanol using azoinitiator due to the high chain transfer to solvent and chain branching reaction caused by fast propagation rate of VAc. However, by adoption of unique azoinitiator, which is not solved in VAc such as ACVA, it was possible to obtain PVA of a  $P_n$  of up to 4300. This suggests an easy way of producing HMW PVA with high yield by conventional solution polymerization at polymerization temperature of 40°C and 50°C without using any special devices like low-temperature cooling system or irradiation device. In the near future, we will report on the effects of monomer-nonsoluble initiator on the preparation of stereoregular PVA.

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