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ORIGINAL CONTRIBUTION

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Low temperature suspension polymerization of vinyl acetate using 2,2′-azobis(2,4-dimethylvaleronitrile) for the preparation of high molecular weight poly(vinyl alcohol) with high yield

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Abstract To obtain high molecular weight (HMW) poly(vinyl acetate) (PVAc) with high conversion and high linearity for a precursor of HMW poly(vinyl alcohol) (PVA), vinyl acetate (VAc) was suspension-polymerized using a low-temperature initiator, 2,2′-azobis (2,4-dimethylvaleronitrile) (ADMVN), and the effects of polymerization conditions on the polymerization behavior and molecular structures of PVAc and PVA prepared by saponifying PVAc were investigated. On the whole, the experimental results well corresponded to the theoretically predicted tendencies. Suspension polymerization was slightly inferior to bulk polymerization in increasing molecular weight of PVA. In contrast, the former was absolutely superior to the latter in increasing conversion of the polymer, which indicated that the suspension polymerization rate of VAc was faster than the bulk one. These effects could be explained by a kinetic order of ADMVN concentration calculated by initial-rate method and an activation energy difference of polymerization obtained from the Arrhenius plot. Suspension polymerization at 30 °C by adopting ADMVN proved to be successful in obtaining PVA of HMW (number-average degree of polymerization (P_n)): (4200–5800) and of high yield (ultimate conversion of VAc into PVAc: 85–95%) with diminishing heat generated during polymerization. In the case of bulk polymerization of VAc at the same conditions, maximum P_n and conversion of 5200–6200 and 20–30% was obtained, respectively. The P_n, lightness, and syndiotacticity were higher with PVA prepared from PVAc polymerized at lower temperatures.

Key words High molecular weight – PVAc – high conversion – PVA – VAc – low temperature – ADMVN – suspension polymerization

Introduction

Poly(vinyl alcohol) (PVA) obtained by the saponification of poly(vinyl ester) like poly(vinyl acetate) (PVAc) is a linear semicrystalline polymer, which has been widely used as fibers for clothes and industries, films, membranes, medicines for drug delivery system, and cancer cell-killing embolic materials [1–4]. PVA fibers have high tensile and compressive strengths, tensile modulus, and abrasion resistance due to its highest crystalline lattice modulus. To maximize these physical properties, molecular weight, degree of saponification, and syndiotacticity should be increased [1, 2]. In particular, to increase the molecular weight which is a fundamental factor affecting physical properties, improvement of polymerization methods of vinyl acetate (VAc) [5–12] or the use of other vinyl ester monomers such as vinyl pivalate [13–20] is necessary.

In general, four polymerization methods of VAc (bulk, solution, emulsion, and suspension) have been known. In bulk polymerization, high molecular weight (HMW) PVAc can be obtained but the increased polymerization rate arising from the higher polymerization heat [21] results in a side reaction and it is difficult to control the viscosity of the reaction mixture. Thus, HMW PVAc with high conversion is hardly obtained at the same time [11]. To reduce the polymerization heat and the viscosity of the medium, solution polymerization of VAc was tried [12, 22, 23]. However, branch formation caused by frequent chain transfer reactions to monomer makes it unfavorable to obtain linear HMW PVAc for the precursor of HMW PVA. It was known that molecular weight and polymerization rate were increased simultaneously by emulsion polymerization of VAc. However, because side chain formation reactions due to a higher propagation rate of VAc [24] result in branched HMW PVAc, it is nearly impossible to produce HMW PVA from the precursor PVAc by saponification reaction [25]. Till now, in these polymerization methods described above, HMW PVA can be prepared only by the use of ultraviolet ray or γ-ray radiation methods accompanied by a complicated polymerization apparatus [6–8, 10]. In bulk polymerization, it is so difficult to increase the conversion of the precursor of PVA that the resultant HMW PVA with high yield is hardly prepared. Although relatively higher conversion of VAc into PVAc is attained in the case of solution polymerization than bulk polymerization, it is very difficult to obtain HMW PVAc with the conversion of over 60–70% owing to the high viscosity of the reaction solution.

The mechanism of suspension polymerization in the droplet is basically identical to that of bulk polymerization [26] and water used as a reaction medium minimizes exotherm and viscosity enhancement generated during polymerization [21]. Owing to these advantages, suspension polymerization of VAc has a possibility of producing HMW PVAc with high conversion which is a precursor of HMW PVA.

As is well known, molecular weight of polymer prepared by the suspension polymerization method is controlled by the type and amount of initiator and suspending agent, the polymerization temperature, the monomer-to-water ratio, and the agitation speed. It was known that the higher the agitation speed, the higher the molecular weight and the conversion [21, 27, 28]. There have been many researches on the suspension polymerization of VAc because it is possible to reach higher conversion that other polymerization methods [29–31]. Bravar et al. [32] synthesized PVAc with molecular weight of over 1 500 000 by using sodium salt of styrene/maleic acid copolymer as a suspending agent. Gunesch and Schneider [33] reported that molecular weight of PVAc was increased at lower content of initiator and at higher rate of agitation, which was concluded by determining polymerization heat and polymerization rate calculated by measuring the heat absorbed in water during suspension polymerization of VAc. Collins [34] prepared PVAc with 50% conversion polymerized at 80 °C using tragacanth gum and benzoyl peroxide (BPO) as a suspension agent and initiator, respectively. Wilson [35] utilized arabic gum as a suspension agent and $FeCl_3 \cdot 6H_2O$ and hydrogen peroxide as initiators at polymerization temperature of 85–95 °C to reach conversion of 54–55%. Schouteden and Tristmans [36] polymerized VAc at 50–90 °C using methyl ether cellulose and BPO as a suspending agent and as an initiator, respectively.

These polymerizations, however, were conducted at polymerization temperature of over 50 °C. In these cases, branch formation in PVAc results in molecular weight decrease of the resulting PVA due to a higher polymerization temperature of over 50 °C. Moreover, polymerization at lower temperature of below 40 °C was only possible by the use of ultraviolet or γ-ray radiation methods accompanied by a complicated polymerization apparatus [20]. Redox systems have been explored in the low-temperature polymerization of VAc to produce HMW PVA [5, 37, 38]. However, discoloration and low polymerization efficiency are two common deficiencies of redox systems.

In this study, a low-temperature initiator, 2,2′-azobis-(2,4-dimethylvaleronitrile) (ADMVN), which can lower the polymerization temperature down to room temperature [11] was selected in suspension polymerization of VAc to obtain HMW PVAc with higher conversions, which is expected to be a profitable precursor of HMW PVA. The effects of polymerization conditions on the polymerization behavior of VAc and molecular parameters of PVAc and PVA were examined.

Experimental

Materials

VAc purchased from Shin–Etsu was washed with an aqueous solution of $NaHSO_3$ and water and dried over anhydrous $CaCl_2$, followed by distillation under reduced pressure of nitrogen. The initiator ADMVN (Wako Co., 99%) was recrystallized twice from absolute methanol before use. PVA with number-average molecular weight of 127 000 and degree of saponification of 88% (Aldrich Co.) was used as a suspending agent. Other extra-pure grade reagents were used without further purification. Water used for all the procedures was deionized.

Suspension polymerization of VAc

In a typical reaction, suspension agent was dissolved in water under nitrogen atmosphere and constant stirring in a 250 ml reactor fitted with a condenser. After degassing, VAc monomer along with the ADMVN were added all at once at a fixed polymerization temperature. After predetermined times, the reaction mixture was cooled and kept for 1 day to effectively separate and to sink spherical PVAc particles. To eliminate residual VAc and suspension agent, PVAc polymerized was filtered and washed with warm water. Conversion was calculated by measuring the weight of the polymer. Conversions were averages of five determinations. The detailed polymerization conditions are listed in Table 1.

Bulk polymerization of VAc [11]

VAc was poured into a 250 ml three-necked round bottom flask and flushed with nitrogen for 3 h. At the predetermined polymerization temperature ADMVN was added to the monomer. After predetermined times, the unreacted monomer was distilled out. PVAc was purified by reprecipitation from acetone/*n*-hexane. Conversion was calculated by using the same method adopted in the suspension polymerization.

Saponification of PVAc [10]

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.

Table 1 Suspension polymerization conditions of VAc

Type of initiator	ADMVN
Type of suspending agent	PVA
Initiator concentration	0.00002 mol/mol of VAc 0.00005 mol/mol of VAc 0.0001 mol/mol of VAc 0.0002 mol/mol of VAc
Suspending agent concentration	0.5 g/dl of water 1.5 g/dl of water 2.5 g/dl of water 4.5 g/dl of water 9.0 g/dl of water
VAc/water	0.250 l/l 0.333 l/l 0.500 l/l 0.750 l/l 1.000 l/l
Rpm	100, 300, 500, 1000, 1500
Temperature	30 °C, 40 °C, 50 °C

Acetylation of PVA [10]

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 flasks at 100 °C for 24 h under an atmosphere of nitrogen. Then the mixture was poured into cold water to precipitate PVAc. The PVAc thus produced was filtered and purified by repeating the reprecipitation from methanol and water.

Characterization

The molecular weight of PVAc was calculated by using Eq. (1) [39], respectively,

$$[\eta] = 8.91\times10^{-3}[P_n]^{0.62} \quad \text{(in benzene at 30 °C)} , \qquad (1)$$

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 PVA was determined from that of PVAc produced by acetylation of PVA using Eq. (1).

The degree of branching for the acetyl group (DB) of PVAc is calculated by Eq. (2) [2],

$$\mathrm{DB} = (\mathrm{DP}_1/\mathrm{DP}_2) - 1 , \qquad (2)$$

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

Syndiotactic triad contents of PVA were determined by using a proton–nuclear magnetic resonance (^{1}H-NMR) spectrometer (Varian, Sun Unity 300). Degree of saponification of PVA was determined by weight loss after saponification and by the ratio of methyl and methylene proton peaks in the ^{1}H-NMR spectrum.

A homogeneous 1.0 g/dl solutions of (PVA)s in DMSO which were obtained at polymerization temperatures of 30, 40, and 50 °C were poured into stainless-steel tray and dried at room temperature to produce films. The lightness of the PVA film was measured by Color eye (I.D.I., model C).

Results and discussion

Efficiency of ADMVN on the conversion

In the free radical polymerization, the rate of polymerization (R_p) may be expressed by Eq. (3) [40]

$$R_p = k_p[M][I]^{1/2}(fk_d/k_t)^{1/2} , \qquad (3)$$

where f is the initiator efficiency, [M] and [I] are the concentrations of monomer and initiator, and k_d, k_p and k_t are reaction rate constants of initiator decomposition, propagation, and termination, respectively. This expression predicts that the rate of polymerization is increased as the efficiency and concentration of initiator are increased. The dependence of polymerization rate on the initiator concentration can be determined from the initial-rate method [41]. For small changes in initiator concentration, the polymerization rate 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 using Eqs. (3)–(9).

$$-(\mathrm{d}[\mathrm{M}]_1/\mathrm{d}t) = (R_p)_1 = k[\mathrm{M}]_1^{n_1}[\mathrm{I}]_1^{n_2} , \tag{4}$$

$$-(\mathrm{d}[\mathrm{M}]_2/\mathrm{d}t) = (R_p)_2 = k[\mathrm{M}]_2^{n_1}[\mathrm{I}]_2^{n_2} , \tag{5}$$

$$-(\mathrm{d}[\mathrm{M}]_3/\mathrm{d}t) = (R_p)_3 = k[\mathrm{M}]_3^{n_1}[\mathrm{I}]_3^{n_2} , \tag{6}$$

$$(R_p)_1/(R_p)_2 = ([\mathrm{I}]_1/[\mathrm{I}]_2)^{n_{2a}} , \tag{7}$$

$$(R_p)_2/(R_p)_3 = ([\mathrm{I}]_2/[\mathrm{I}]_3)^{n_{2b}} , \tag{8}$$

$$(R_p)_3/(R_p)_1 = ([\mathrm{I}]_3/[\mathrm{I}]_1)^{n_{2c}} , \tag{9}$$

$$n_2 = (n_{2a} + n_{2b} + n_{2c})/3 . \tag{10}$$

This procedure can be used to determine all exponents like n_1, n_2, n_3. Thus, in this study, from the calculation using the kinetic parameters obtained from the plots of conversion of up to 15% with polymerization time in Table 2, it was found that the suspension and bulk polymerization rates of VAc were proportional to the exponent 0.93 and 0.58 of ADMVN concentrations, respectively. That is, the suspension polymerization rate of VAc was higher than that by bulk polymerization. In accordance with the theoretical predictions by Eq. (3), the bulk polymerization rate was proportional to $[\mathrm{ADMVN}]^{0.58}$. In contrast, in the case of suspension polymerization, some discrepancy appeared between theoretical (0.5) and experimental (0.93) values. This anomaly with respect to normal kinetic behavior is generally accounted for by assuming that the precipitation of the growing polymers severely restrains bimolecular chain termination and hence that the radicals do not reach a stationary concentration. Further, some of the growing chains become buried in the dead polymer, an effect which corresponds kinetically to monomolecular chain termination [42, 43]. Therefore, the higher order of ADMVN concentration of suspension polymerization (0.93) in this study might be considered to cause monomolecular termination by occlusion of growing chains due to heterogeneous polymerization of VAc.

Table 2 Kinetic parameters used for the calculation of the initiator exponent at a polymerization temperature of 30 °C

	Suspension	Bulk
$(R_p)_1$ (% h^{-1})	8.215	3.568
$(R_p)_2$ (% h^{-1})	3.916	1.543
$(R_p)_3$ (% h^{-1})	1.112	0.936
$[\mathrm{I}]_1$ (mol/mol of VAc)	0.0002	0.0002
$[\mathrm{I}]_2$ (mol/mol of VAc)	0.00005	0.00005
$[\mathrm{I}]_3$ (mol/mol of VAc)	0.00002	0.00002
$(R_p)_1/(R_p)_2$	2.098	2.312
$(R_p)_2/(R_p)_3$	3.522	1.649
$(R_p)_3/(R_p)_1$	0.135	0.262
$[\mathrm{I}]_1/[\mathrm{I}]_2$	4.0	4.0
$[\mathrm{I}]_2/[\mathrm{I}]_3$	2.5	2.5
$[\mathrm{I}]_3/[\mathrm{I}]_1$	0.1	0.1
n_{2a}	0.535	0.605
n_{2b}	1.374	0.546
n_{2c}	0.869	0.582
n_2	0.926	0.578

Figure 1 illustrates conversion–time histories of suspension (A) and bulk (B) polymerizations for temperature levels of 30, 40, and 50 °C. The rate of conversion was increased with increasing polymerization temperature and the conversion rates of suspension polymerization were higher than those of bulk polymerization at all polymerization temperatures. In the case of bulk-polymerization (Fig. 1B), the conversion–time curves had the characteristic sigmoidal shape showing the acceleration in the rate of polymerization with conversion at the higher polymerization temperatures of 50 and 40 °C. That is, the rate of conversion was high at the early stage of polymerization at 50 and 40 °C but the ultimate conversion was lower. Increase in conversion with time was abruptly diminished during polymerization, probably due to the inefficient transfer and diffusion of heat because of the formation of PVAc at the early stage of polymerization. These features were clearly observed in BPO- or azobisisobutyronitrile (AIBN)-initiated free-radical polymerization of VAc above 45 °C. It might be though that the acceleration in rate is a consequence of diffusion-controlled termination reactions in these polymerizations. On the other hand, at 30 °C, the conversion was linearly increased without any abrupt changes in the slope. This might be explained by diminishing heat generated during polymerization at lower polymerization temperature by ADMVN. But the ultimate conversion (ca. 20%) was very low due to a viscosity increase by forming HMW PVAc molecules. In contrast, in the case of suspension polymerization (Fig. 1A), the conversions at 30 °C increased linearly up to

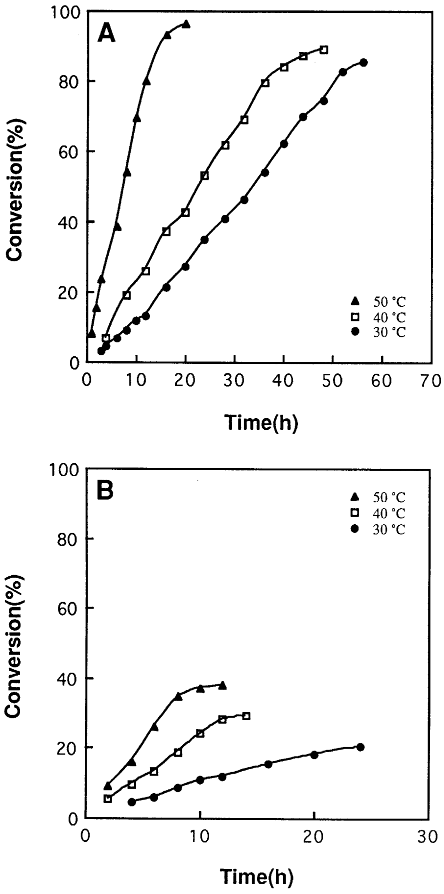

Fig. 1 Conversion of VAc into PVAc suspension polymerized using ADMVN concentration of 0.00002 mol/mol of VAc, suspending agent concentration of 1.5 g/dl of water, VAc/water of 0.5 l/l, and agitation speed of 300 rpm (A) and bulk polymerized using ADMVN concentration of 0.00002 mol/mol of VAc (B) with polymerization time

85% in spite of very low ADMVN concentration of 0.00002 mol/mol of VAc, which was absolutely impossible in bulk polymerization. This can be explained by an advantage of heterogeneous (suspension) polymerization of VAc. Furthermore, autoaccelaration described above seems not to be so noticeable in the suspension polymerization of VAc at 30 °C using ADMVN, as shown in Fig. 1A. This is an indication of suppression of irregular chain transfer reaction during polymerization. Below an ADMVN concentration of 0.00002 mol/mol of VAc, effective polymerization could not occur.

The rate of conversion is increased with an increase in the initiator concentration as depicted by Eq. (11) [40]

$$P_{\mathrm{eq}} = 1 - \exp(-2k_{\mathrm{p}}(f[\mathrm{I}]/k_{\mathrm{i}}k_{\mathrm{t}})^{1/2}) , \qquad (11)$$

where P_{eq} and k_{i} are conversion at the equilibrium of polymerization and reaction rate constants of initiation,

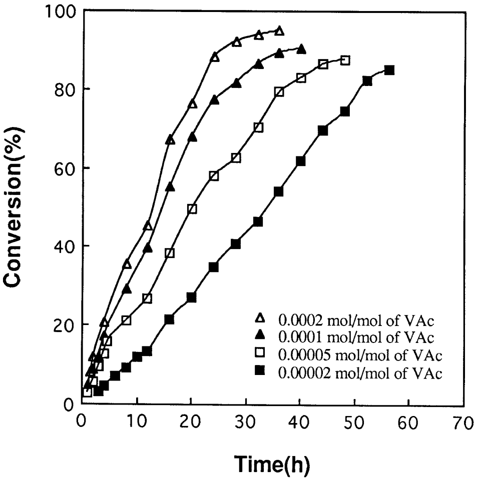

Fig. 2 Conversion of VAc into PVAc suspension polymerized at 30 °C using suspending agent concentration of 1.5 g/dl of water, VAc/water of 0.5 l/l, and agitation speed of 300 rpm with polymerization time

respectively. Effect of initiator concentration on the conversion of VAc into PVAc suspension-polymerized at 30 °C is shown in Fig. 2. The conversion rate increased as the ADMVN concentration was increased, which is well coincident with the theoretical predictions in Eq. (11). High ultimate conversions (85–95%) were obtained at all ADMVN concentrations. This explains the fact that suspension polymerization temperature of 30 °C by ADMVN is a useful one for producing PVAc with high yield.

As the polymerization rate does not remain constant it is necessary to select a certain type of rate for comparing experimental results. So, in the following we define “initial rates” arbitrarily measured up to 3% conversion on the linear log–log plots of conversion with polymerization time to obtain activation energy of polymerization. The activation energies calculated from the slopes of the two peaks in Arrhenius plots of initial rates were 31.4 kJ/mol for the suspension system and 37.3 kJ/mol for the bulk system, respectively. From the fact that the suspension system had a lower value of activation energy than bulk system, it was identified that polymerization rate of VAc by ADMVN in suspension was higher than that in the bulk.

Effect of polymerization conditions on molecular weight

In a free radical polymerization process, the kinetic chain length, ν, is expressed by Eq. (12) [40],

$$\nu = K_{\mathrm{p}}[\mathrm{M}]/2(fk_{\mathrm{d}}k_{\mathrm{t}}[\mathrm{I}])^{1/2} . \qquad (12)$$

Referring to Eq. (12), the degree of polymerization may be decreased as the efficiency and the concentration of initiator are increased. (P_n)s of PVAc prepared by suspension and bulk polymerizations and corresponding PVA obtained by saponifying PVAc with conversions are shown in Fig. 3. Difference between (P_n)s of PVAc and PVA is mostly obliged to branched structures, which may be broken down when saponified. It is interesting to see that P_n of PVA remained almost constant up to ca. 40–50% conversion and nearly independent of P_n of PVAc, and then P_n of PVA slightly decreased at higher conversions of over 40–50%. This was attributed by 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 ones. In accordance with theoretical prediction, (P_n)s of PVAc and PVA were increased with a decrease in the ADMVN concentration in Fig. 3. HMW (PVA) s having various (P_n)s of 4200–6000 could be prepared by saponifying HMW (PVAc)s having (P_n)s of 7600–14 100 polymerized in suspension. It should be noted that PVA with P_n of up to 5500 could be prepared from PVAc suspension-polymerized at conversion of ca. 85% using minimum ADMVN concentration of 0.00002 mol/mol of VAc, which is comparable to P_n of PVA (6200) from PVAc by bulk polymerization using same polymerization conditions (conversion: ca. 20%). Therefore, it can be concluded that the suspension polymerization of VAc using the low temperature initiator ADMVN is an effective method to increase both yield and molecular weight at the same time.

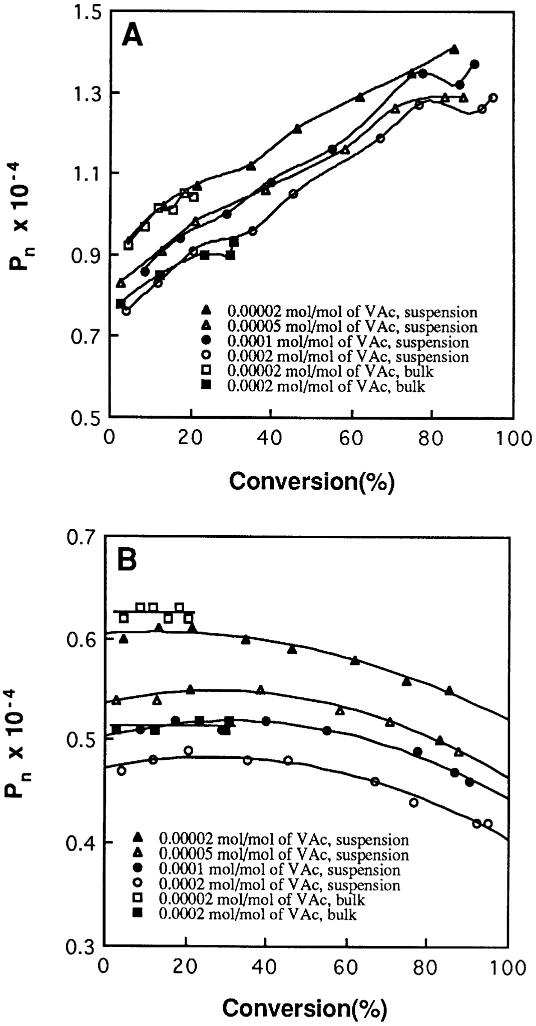

Fig. 3 Plots (P_n) s of PVAc obtained by suspension polymerization at 30 °C using suspending agent concentration of 1.5 g/dl of water, VAc/water of 0.5 l/l, and agitation speed of 300 rpm and by bulk polymerization at 30 °C (A) and resulting PVA (B) vs. conversion

Figures 4, 5 and 6 present the effect of various suspension polymerization conditions of VAc on the molecular weights of PVAc and PVA, respectively. PVAc was sampled at similar conversion of about 80% to precisely clarify the effect of the polymerization conditions. Figure 4A and B shows the effect of concentration of the suspending agent. At a concentration of 1.5 g/dl of water, maximum (P_n)s of PVAc (13 500) and PVA (5600) were obtained and this tendency was nearly same irrespective of ADMVN concentration. Below this concentration, suspension agent could not cause stable dispersion required for effective suspension polymerization owing to an insufficient concentration. In contrast, at a higher concentration of 9.0 g/dl of water, significant increase of viscosity of polymerization medium made it difficult to agitate the system. From these results, it was found that optimum concentration of suspending agent is about 1.5 g/dl of water in this polymerization of VAc at 30 °C. Figure 5A and B are plots of (P_n)s of PVAc and PVA vs VAc/water ratio, which show that the lower the value, the higher the molecular weight (maximum P_n of PVA: 5700). This might be explained by the fact that the lowered polymerization, termination, and chain transfer rates by enlarged ability of water to effectively spread the high exotherm of VAc generated during polymerization and to cool the medium increased the linearity of PVAc and the molecular weight of PVA. The effect of agitation speed is shown in Fig. 6A and B. Molecular weight of both PVAc and PVA increased with an increase in the agitation speed, which well coincided with the results of Gunesch and Schneider [33]. But, over 1000 rpm there was no difference in molecular weight and the highest P_n of PVA was 5800 at this rpm.

Molecular structure of PVAc and PVA

As a rule, difference between (P_n)s of PVAc and PVA is due to a branched structure. In this study, the effect of

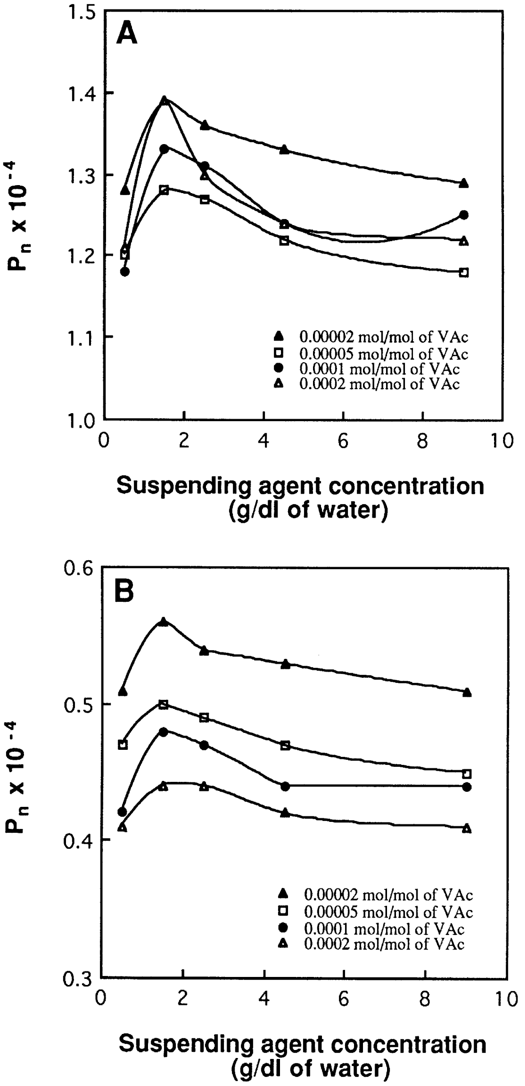

Fig. 4 Dependence of suspending agent concentration on the (P_n)s of PVAc polymerized at 30 °C using VAc/water of 0.5 l/l and agitation speed of 300 rpm (A) and resulting PVA (B)

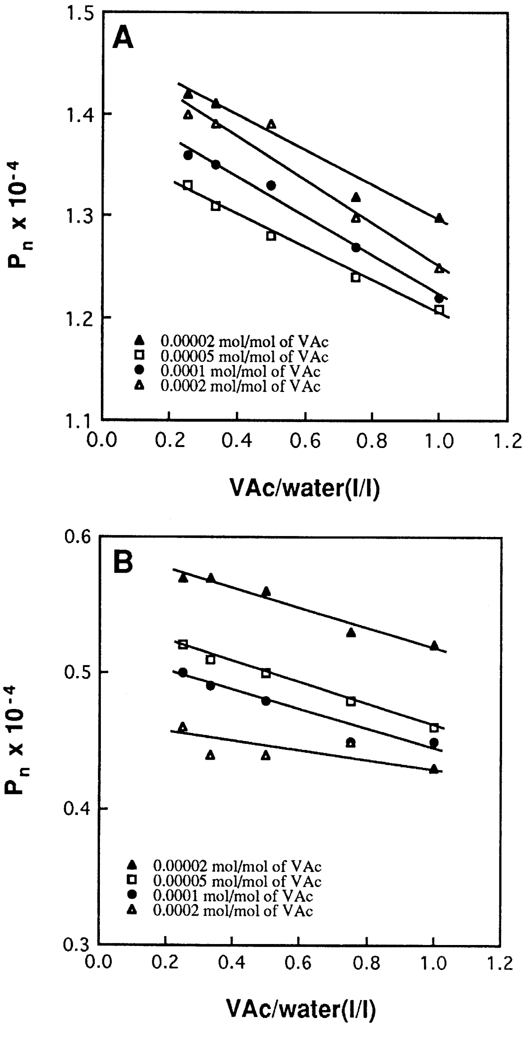

Fig. 5 Dependence of VAc/water ratio on the (P_n)s of PVAc polymerized at 30 °C using suspending agent concentration of 1.5 g/dl of water and agitation speed of 300 rpm (A) and resulting PVA (B)

ADMVN concentration and conversion on the DB of PVAc was investigated. Figure 7 shows variation of DB for acetyl group of PVAc polymerized at 30 °C using four different ADMVN concentrations with conversion. As might be imagined, DB was increased with increasing conversion for all the cases. Further, the rate of increasing DB with conversion was decreased as ADMVN concentration was lowered. This may be ascribed to the fact that at higher polymerization temperatures, the accelerated polymerization reaction may bring about a chain transfer (branching) reaction more easily.

As polymerization temperature was decreased, syndiotactic triad content was increased from 26 to 28%. But isotactic triad content was decreased from 24% to 22%. On the other hand, heterotactic triad content remained nearly constant, 50%, regardless of polymerization temperature. That is, syndiotacticity of PVA slightly increased with lowering polymerization temperature.

The end groups in PVA molecule seriously influence the color of the polymer, which are incorporated during polymerization by one of the following reactions: chain transfer, initiation, or termination [2]. Especially, termination by disproportionation is known to introduce aldehyde end groups, which leads to a saturated and unsaturated end groups. The unsaturated group, when saponified, yields an aldehyde group. Also, the presence of

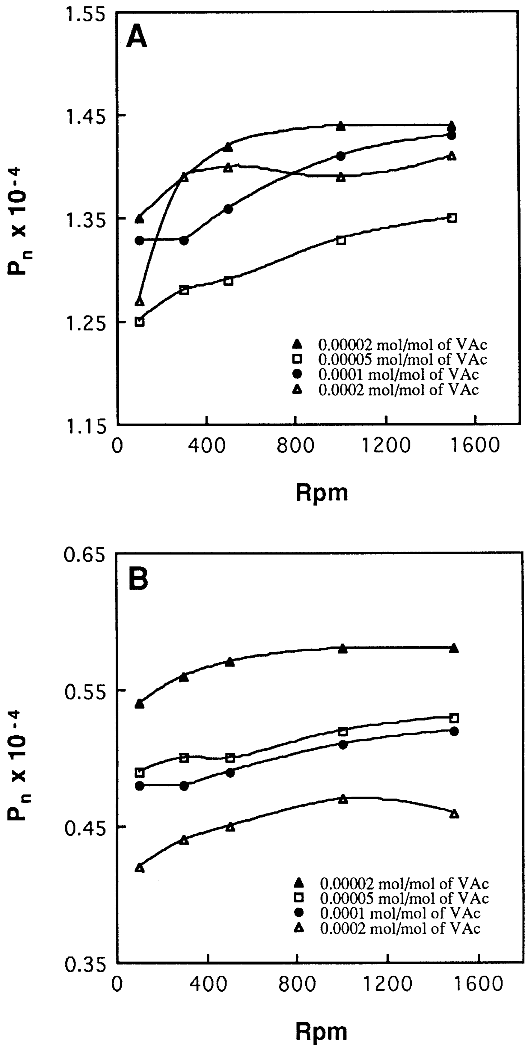

Fig. 6 Dependence of agitation speed on the (P_n)s of PVAc polymerized at 30 °C using suspending agent concentration of 1.5 g/dl of water and VAc/water of 0.5 l/l (A) and resulting PVA (B)

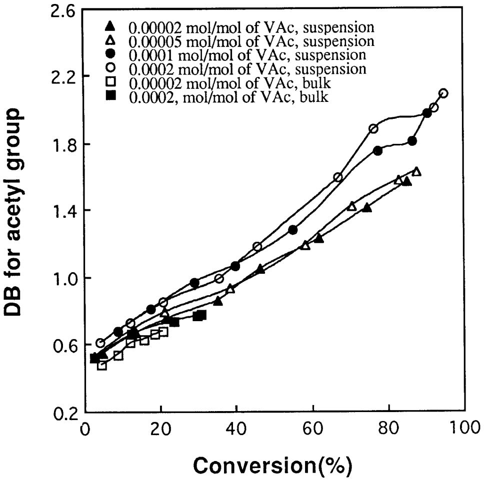

Fig. 7 DB for the acetyl group of PVAc obtained by the suspension polymerization at 30 °C using suspending agent concentration of 1.5 g/dl of water, VAc/water of 0.5 l/l, and agitation speed of 300 rpm

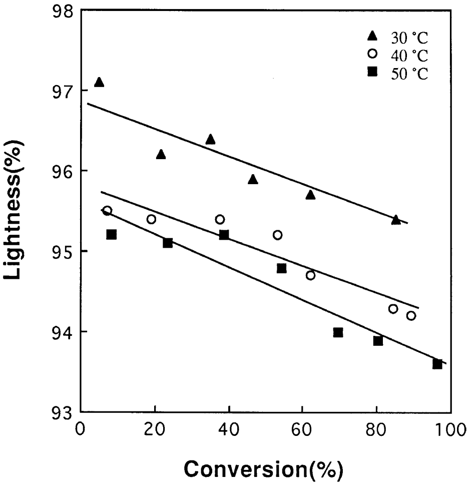

Fig. 8 Lightness of the films of PVA prepared by the saponification PVAc obtained at three different suspension polymerization temperatures with conversion

ketone and aldehyde end groups leads to the formation of conjugated double bond during saponification. Conjugated double bond leads to yellowing and deteriorates thermal stability of the polymer, which are undesirable in applications of PVA. Figure 8 shows the effects of conversion and suspension polymerization temperature of VAc on the degree of lightness of resulting PVA film. The lightness of the PVA film from PVAc polymerized at lower temperature and conversion was higher than that at higher ones. This may be explained by the fact that polymerization of VAc is largely terminated by recombination rather than by disproportionation at lower temperature [2, 3]. Consequently, the amount of saturated and unsaturated end groups is decreased with PVAc prepared at lower polymerization temperature during saponification [44].

Conclusion

As is well known, it is not an easy job to obtain HMV PVAc with high conversion, a precursor of HMW PVA, by free radical polymerization initiated with AIBN or BPO in bulk because of polymerization exotherm and chain branching during polymerization of VAc. However, a low-temperature initiator, ADMVN seems to be advantageous in suppressing the chain transfer reaction because it can lower the polymerization temperature down to ca. 30 °C. Hence, ADMVN is more effective in preparing HMW PVAc with less branches. Furthermore, suspension polymerization is a powerful method for enhancing conversion.

Through a series of calculations using the initial-rate method, it was found that the suspension and bulk polymerization rates of VAc at 30 °C were proportional to the exponent 0.93 and 0.58 of ADMVN concentrations, respectively. At the same polymerization conditions, the suspension method was absolutely superior to the bulk method in increasing conversion of PVAc. On the other hand, the suspension method was slightly inferior to the bulk method in increasing molecular weight of the polymer, which indicated that the bulk polymerization rate of VAc by ADMVN was slower than that in suspension. These effects could be explained by an activation energy difference of polymerization obtained from the Arrhenius plot. But the molecular weight difference between two methods were very small.

Suspension polymerization of VAc at 30 °C by ADMVN and saponification produced HMW PVA with P_n of 4200–5800 and with maximum conversion of VAc into PVAc of 85–95%. This compares well with the bulk polymerization of VAc at 30 °C using ADMVN with P_n of 5200–6200 and with the maximum conversion of about 20–30%. The P_n, lightness, and syndiotactic triad content were higher in PVA prepared from PVAc polymerized at lower temperatures. Conclusively, this suspension polymerization is expected to be an easy way of producing HMW PVA with high yield by simple chemical initiation without using special devices such as irradiation. Moreover, it has a merit that the separated spherical PVAc beads having HMW can be saponified directly as a heterogeneous state for preparing stable PVA particles for the drug delivery system and for cancer cell-killing embolic treatments according to the increased requirement for biomedical material [3, 4].

In the near future, we will report on the low-temperature suspension polymerization of other precursor monomer by ADMVN for producing stereoregular PVA to increase both syndiotacticity and molecular weight.

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