Preparation of High Molecular Weight Poly(vinyl Alcohol) With High Yield Using Low-Temperature Solution Polymerization of Vinyl Acetate

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ABSTRACT: Vinyl acetate (VAc) was solution-polymerized in tertiary butyl alcohol (TBA) and in dimethyl sulfoxide (DMSO) having low chain transfer constant at 30, 40, and 50°C, using a low temperature initiator, 2,2′-azobis(2,4-dimethylvaleronitrile) (ADMVN). The effects of polymerization temperature and initiator concentration were investigated in terms of polymerization behavior and molecular structures of poly(vinyl acetate) (PVAc) and corresponding poly(vinyl alcohol) (PVA) obtained by saponification with sodium hydroxide. The polymerization rates of VAc in TBA and in DMSO were proportional to the 0.49 and 0.72 powers of ADMVN concentration, respectively. For the same polymerization conditions, TBA was absolutely superior to DMSO in increasing the molecular weight of PVA. In contrast, TBA was inferior to DMSO in causing conversion to polymer, indicating that the initiation rate of VAc in TBA was lower than that in DMSO. These effects could be explained by a kinetic order of ADMVN concentration calculated using initial rate method and by an activation energy difference of polymerization obtained from the Arrhenius plot. Low-temperature solution polymerization of VAc in TBA or DMSO by adopting ADMVN proved successful in obtaining PVA of high molecular weight (number–average degree of polymerization (P_n): 4100–6100) and of high yield (ultimate conversion of VAc into PVAc: 55–80%) 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 and lightness were higher, and the degree of branching was lower with PVA prepared from PVAc polymerized at lower temperatures in TBA. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 80: 1003–1012, 2001

Key words: VAc; TBA; DMSO; low temperature; ADMVN; PVA; high molecular weight

INTRODUCTION

Poly(vinyl alcohol) (PVA) obtained by the saponification of poly(vinyl ester) or poly(vinyl ether) 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.[1–12] 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.[1,2,4–8] In particular, to increase molecular weight, which is a fundamental factor affecting physical properties of PVA, polymerization methods of vinyl acetate (VAc)[13–19] must be improved or other vinyl ester monomers such as vinyl pivalate[20–23] must be used.

In general, four polymerization methods of VAc—bulk, solution, emulsion, and suspension—are known. In bulk polymerization, high-molecular-weight (HMW) poly(vinyl acetate) (PVAc) can be obtained; the problem is that an increased polymerization rate has been produced by the higher polymerization heat,[24] causing side reactions; it is also difficult to control the viscosity of the reaction mixture. Thus, HMW PVAc with high conversion is rarely obtained at the same time.[17] To reduce the polymerization heat and the viscosity of the medium, solution polymerization of VAc was tried.[25,26] This solution polymerization method has advantages of easy control of polymerization exotherm and of higher conversion than those of bulk polymerization. These polymerizations, however, were conducted at temperatures above 45°C, using benzoyl peroxide (BPO) or azobisisobutyronitrile (AIBN) as initiators. Thus, 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 increased simultaneously by emulsion polymerization of VAc. However, because side-chain formation reactions due to a higher propagation rate of VAc[27] result in branched HMW PVAc, it is nearly impossible to produce HMW PVA from the precursor PVAc by a saponification reaction.[16] Until now, in the polymerization methods described above, HMW PVA can be prepared only by the use of ultraviolet (UV) ray or γ-ray radiation methods[14,28] and redox initiation methods[29] at polymerization temperatures of below 40°C. However, the radiation initiation polymerization processes inevitably require very complicated and expensive polymerization apparatus and special polymerization initiator, preventing commercialization. It has also been known that the redox initiation leads to serious discoloration and low polymerization efficiency.[30]

In this study, a low-temperature initiator, 2,2′-azobis(2,4-dimethylvaleronitrile) (ADMVN), which can reduce the polymerization temperature to room temperature,[17,22] was selected in solution polymerization of VAc to obtain HMW PVAc with higher conversions. This is expected to be a profitable precursor of a HMW PVA with high yield. Tertiary butyl alcohol (TBA) and dimethyl sulfoxide (DMSO) with low chain transfer constants were used as solvents. The effect of polymerization conditions on the polymerization behavior of VAc and molecular parameters of PVAc and PVA were examined.

EXPERIMENTAL

Materials

VAc (Shin-Etsu Co., 99.8%) was washed with an aqueous solution of $NaHSO_3$ and water and dried over anhydrous $CaCl_2$, and then distilled under reduced pressure of nitrogen. ADMVN (Wako Co., 99%) was recrystallized in methanol. Other extra-pure grade reagents were used without further purification.

Polymerization

VAc was placed in a three-necked round bottom flask and flushed with dry nitrogen. The TBA or DMSO was added into a flask to dissolve the solid monomer and flushed with nitrogen for 3 h to eliminate oxygen. At the predetermined polymerization temperature, ADMVN 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. 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 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.

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 24 h under an atmosphere of nitrogen. The mixture was then poured into cold water to precipitate

Table I Parameters for Solution Polymerization of Vinyl Acetate

Type of initiator
  ADMVN
Type of solvent
  TBA
  DMSO
Initiator concentration
  0.00003 mol/mol of VAc
  0.00005 mol/mol of VAc
  0.0001 mol/mol of VAc
  0.0002 mol/mol of VAc
  0.0005 mol/mol of VAc
Monomer concentration
  1 mol/mol of solvent
  2 mol/mol of solvent
  4 mol/mol of solvent
Temperature
  30°C
  40°C
  50°C

ADMVN, azobisdimethylvaleronitrile; TBA, tertiary butyl alcohol; DMSO, dimethyl sulfoxide; VAc, vinyl acetate.

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 using eq. 1[31]:

$$[\eta] \, (dL/g) = 8.91 \times 10^{-3}[P_n]^{0.62}$$

$$\text{(in benzene at 30°C)} \quad (1)$$

where $[\eta]$ is intrinsic viscosity and P_n is a number–average degree of polymerization of PVAc. In contrast, the 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]:

$$DB = (DP_1/DP_2) - 1 \quad (2)$$

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

The syndiotactic diad (S-diad) contents of PVA were determined using a proton-nuclear magnetic resonance (^{1}H-NMR) spectrometer (Varian, Sun Unity 300). The degree of saponification of PVA was determined by weight loss after saponifica-

tion and by the ratio of methyl and methylene proton peaks in the ^{1}H-NMR spectrum.

Homogeneous 1.0 g/dL solutions of (PVA)s in DMSO, obtained at polymerization temperatures of 30, 40, and 50°C, were poured onto a 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

In a free radical polymerization, the rate of polymerization (R_p) may be expressed by eq. 3[32]:

$$R_p = k_p[M][I]^{0.5}(fk_d/k_t)^{0.5} \quad (3)$$

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. Figure 1 presents the initial conversion rate measured within 12% conversion in the solution polymerization of VAc in TBA [Fig. 1(a)] and in DMSO [Fig. 1(b)] at 30°C using ADMVN. It was shown that the greater the initiator concentration, the higher the polymerization rate, in agreement with eq. 3.

The dependence of polymerization rate on initiator concentration can be determined by the initial rate method.[33] 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 determined simply by using eqs. 4–10:
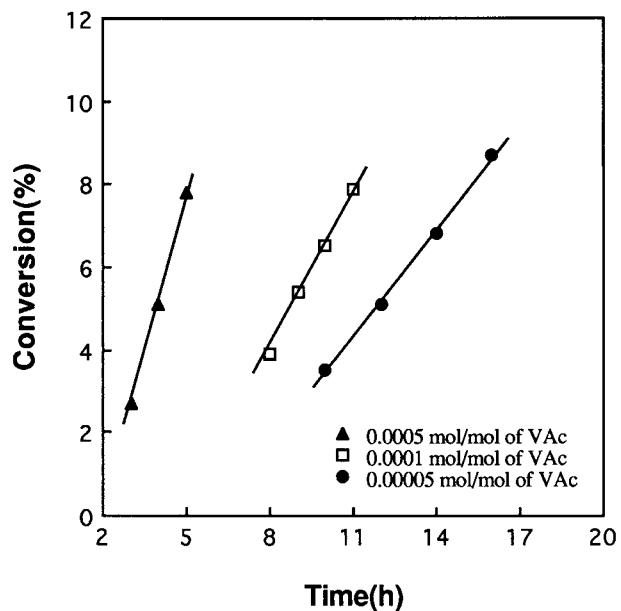
$$-(d[M]_1/dt) = (R_p)_1 = k[M]_1 n_1[I]_1 n_2[S]_1 n_3 \quad (4)$$

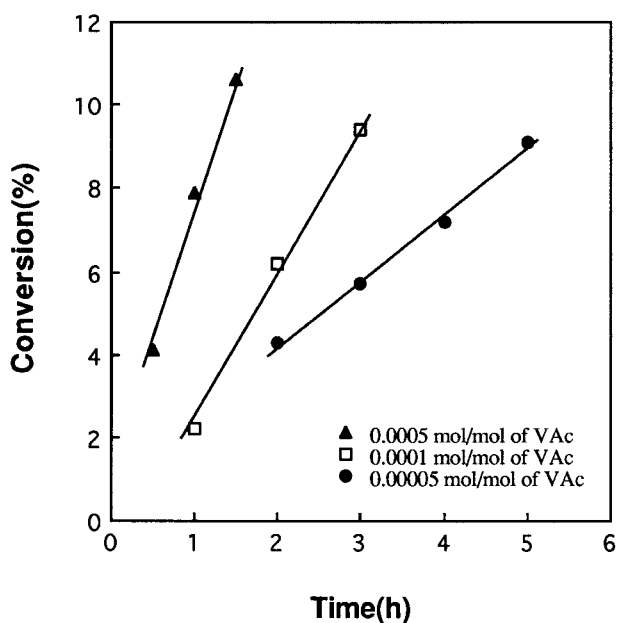$$-(d[M]_2/dt) = (R_p)_2 = k[M]_2 n_1[I]_2 n_2[S]_2 n_3 \quad (5)$$

$$-(d[M]_3/dt) = (R_p)_3 = k[M]_3 n_1[I]_3 n_2[S]_3 n_3 \quad (6)$$

$$(R_p)_1/(R_p)_2 = ([I]_1/[I]_2)n_{2a} \quad (7)$$

$$(R_p)_2/(R_p)_3 = ([I]_2/[I]_3)n_{2b} \quad (8)$$

Figure 1 Conversion of VAc into PVAc in early stage of polymerization in TBA (a) and in DMSO (b) at 30°C using VAc concentration of 4 mol/mol of solvent with polymerization time.

$$(R_p)_3/(R_p)_1 = ([I]_3/[I]_1)n_{2c} \qquad (9)$$

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

where [s] is the concentration of solvent.

This procedure can be used to determine all exponents, such as n_1, n_2, n_3. From the calculation, it was found that the polymerization rates of VAc in TBA and in DMSO were proportional to the 0.49 and 0.72 powers of ADMVN concentrations, respectively. That is, the polymerization rate of VAc in DMSO was higher than that in TBA. In satisfactory agreement with eq. 3, the polymerization rate in TBA was proportional to $[ADMVN]^{0.49}$. In contrast, in the case of DMSO, there is considerable discrepancy between theoretical (0.5) and experimental (0.72) 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, preventing the radicals from attaining stationary concentration. Further, some of the growing chains become buried in the dead polymer, an effect that corresponds kinetically to monomolecular chain termination.[34,35] Therefore, the higher order with respect to ADMVN in the DMSO system (0.72) in this study might be attributed to monomolecular termination involving occlusion of growing chains due to heterogeneous nature of the polymerization of VAc.

Figure 2 shows the effect of monomer concentration on the conversion of VAc into PVAc polymerized in TBA and in DMSO at 30°C, using ADMVN at 0.0001 mol/mol of VAc. In all condi-
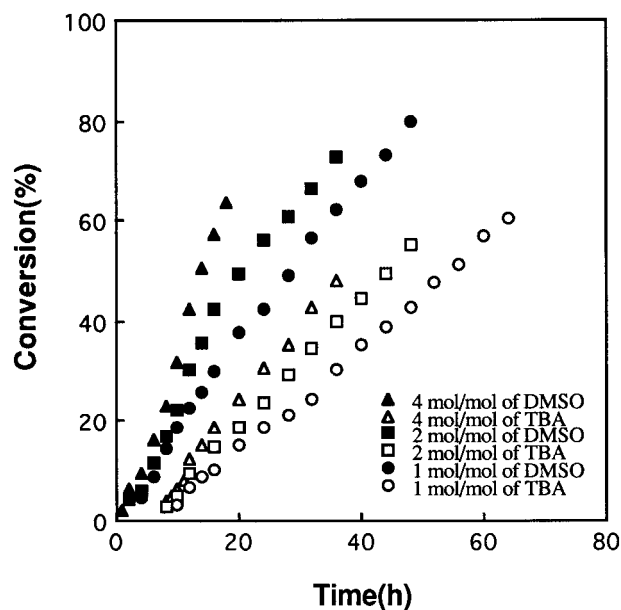

Figure 2 Conversion of VAc into PVAc polymerized at 30°C using ADMVN concentration of 0.0001 mol/mol of VAc with polymerization time.
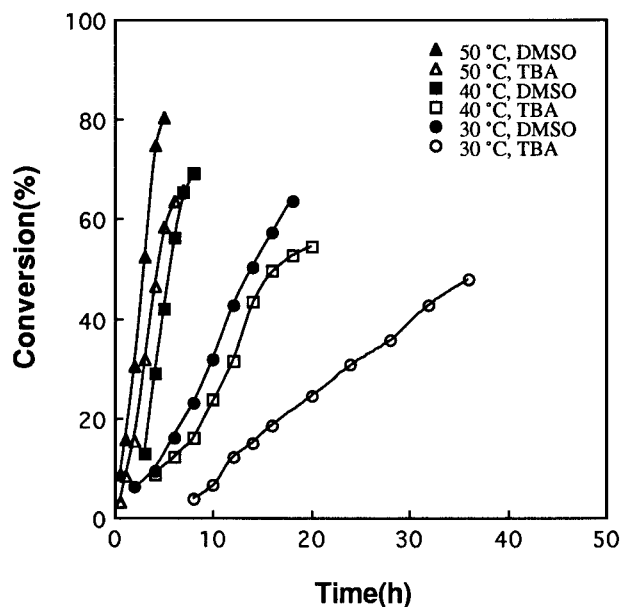
Figure 3 Conversion of VAc into PVAc using VAc concentration of 4 mol/mol of solvent and ADMVN concentration of 0.0001 mol/mol of VAc with polymerization time.

tions, the conversion of the DMSO system was higher than that of the TBA system. At higher monomer concentration, the radicals generated from the initiator largely attack the double bonds of monomer molecules, which possess high electron density. Conclusively, a higher rate of polymerization results. In the case of solution polymerization of VAc, it is very difficult to control the process if the monomer concentration is high because the excessive polymerization exotherm accelerates the polymerization. This indicates that autoacceleration may lead to excessive chain transfer during polymerization if the monomer concentration is high. However, Figure 2 shows that such autoacceleration does not appear to be so noticeable during the low-temperature polymerization of VAc in TBA and in DMSO using ADMVN. This is indicative of suppression of irregular chain transfer reaction during polymerization. In contrast, the rate of polymerization may be decreased at lower monomer concentrations.

Figure 3 illustrates conversion–time plots for temperatures of 30, 40, and 50°C at monomer concentration of 4 mol/mol of solvent and initiator concentration of 0.0001 mol/mol of VAc. The rate of conversion was increased with increasing polymerization temperature and the rates using TBA were much lower than those using DMSO at all

temperatures. At the higher polymerization temperatures of 50 and 40°C, the conversion–time curves had the characteristic sigmoidal shape showing the increase in rate of polymerization with conversion. 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. These features were clearly observed in BPO- or AIBN-initiated free-radical polymerization of VAc above 45°C. It might be thought that the increase in rate is a consequence of diffusion controlled termination reactions in solution polymerizations of VAc. In contrast, at 30°C, conversion of the TBA system 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. High ultimate conversions (55–80%) were obtained at all ADMVN concentrations, compared with the case of bulk polymerization of VAc using ADMVN at 30°C (20–30%).[17] This explains why a solution polymerization temperature of 30°C by ADMVN is useful for producing PVAc of high yield.

As the polymerization rate does not remain constant, a specific type of rate must be selected with which to compare experimental results. The following discussion defines "initial rates" as measured up to 3% conversion on the linear log–log plots of conversion with time to obtain activation energy of polymerization. Figure 4 shows Arrhenius plots of these rates. The activation energies calculated from the slopes of the two plots were 43.8 kJ/mol for the TBA system and 39.2 kJ/mol for the DMSO system. Because the TBA system had a higher activation energy than the DMSO system, polymerization rate of the DMSO system was identified as being higher than that of TBA system.

The (P_n) values of PVAc polymerized in TBA and in DMSO and corresponding PVA obtained by saponifying PVAc with conversions are shown in Figures 5 and 6. Figure 5 shows the temperature effect and Figure 6 shows the monomer concentration effect. The difference between the (P_n) values of PVAc and PVA is attributed mainly 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 ~40–50%
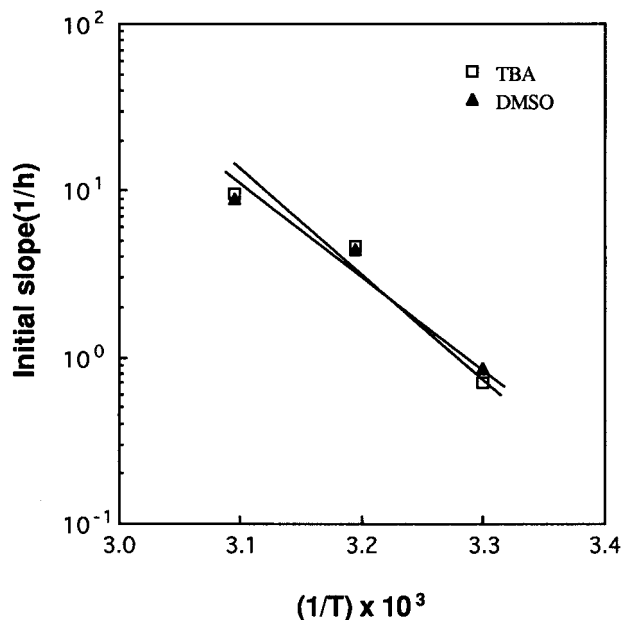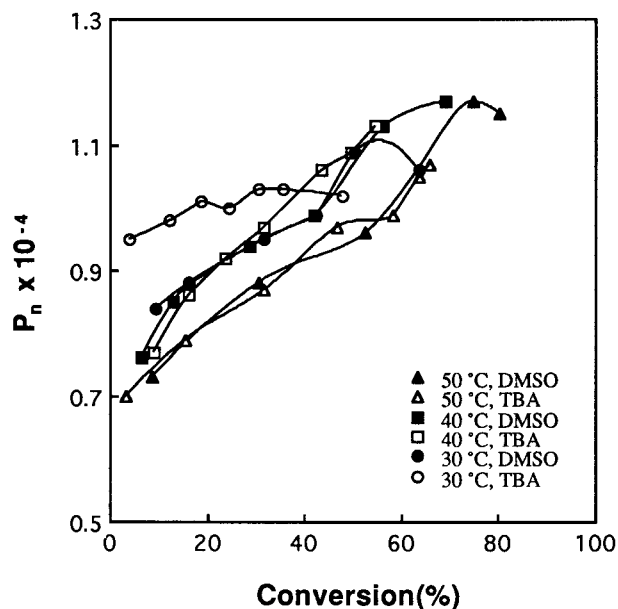
Figure 4 Arrhenius plot for the solution polymerization of VAc using VAc concentration of 4 mol/mol of solvent and ADMVN concentration of 0.0001 mol/mol of VAc.
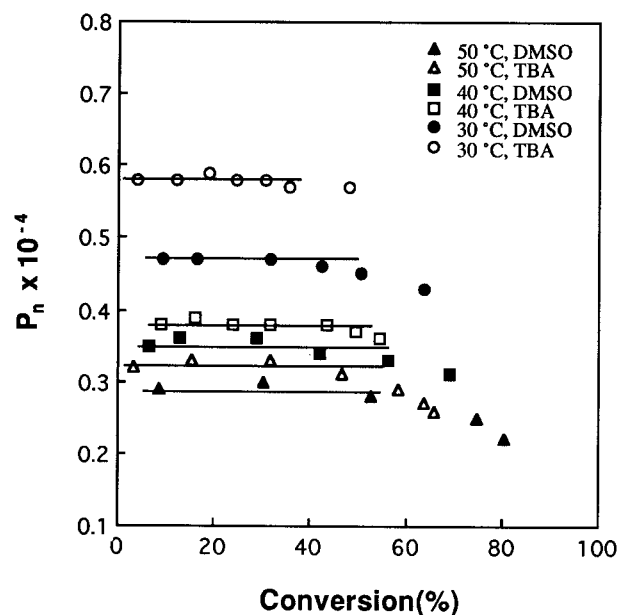
4100–6100 could be prepared by saponifying HMW (PVAc)s. It should be noted that PVA with P_n of ≤5700 could be prepared from PVAc solution polymerized in TBA at 30°C at conversion of ~50%, using an ADMVN concentration of 0.0001 mol/mol of VAc. This is comparable to P_n of PVA
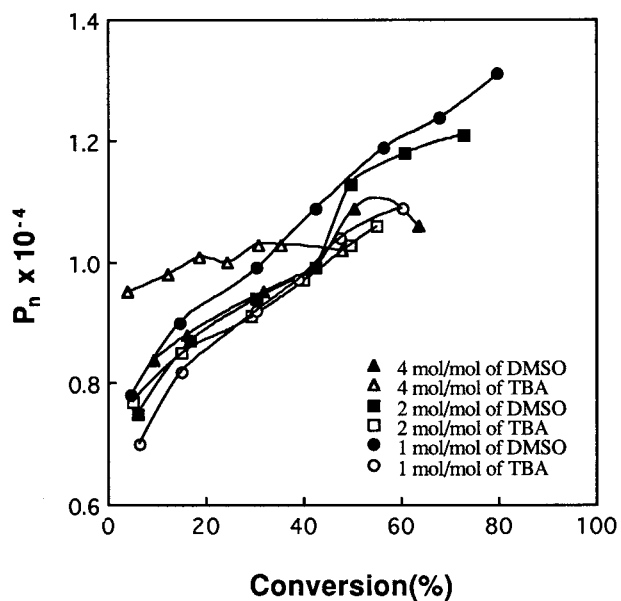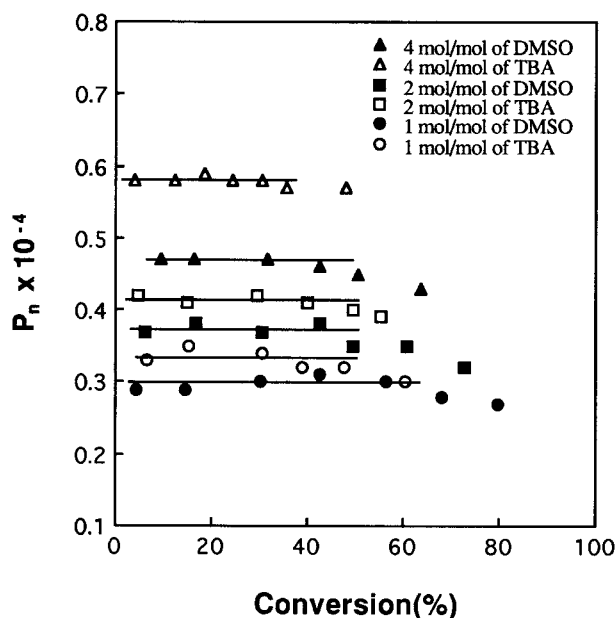

(a)

(b)

Figure 5 (P_n)s of PVAc polymerized using VAc concentration of 4 mol/mol of solvent and ADMVN concentration of 0.0001 mol/mol of VAc (a) and resulting PVA (b) with conversion.

conversion and nearly independent of P_n of PVAc; the P_n of PVA slightly decreased at higher conversions of >40–50%. This was attributed to the frequent chain transfer reactions between polymers, resulting in termination and branch formation reactions at higher conversions, whereas chain transfer reactions between monomers were prevalent at lower conversions. The P_n of PVA was increased with a decrease in the polymerization temperature or of the solvent concentration. In addition, P_n of PVA by TBA system was much higher than that by DMSO system in Figures 5 and 6.

The effects of initiator concentration and polymerization temperature on the (P_n)s of PVAc produced at 30°C, using monomer concentration of 4 mol/mol of solvent and resulting PVA, respectively, are shown in Figure 7. PVAc was sampled at similar conversions of about 30%, to clarify the effects of initiator concentration and polymerization temperature. P_n of PVA was increased as ADMVN concentration or polymerization temperature was decreased. P_n of PVA using TBA was much higher than that using DMSO at all ADMVN concentrations. This was due to the lower polymerization rate of TBA system, as proved by activation energy difference in Figure 4. HMW (PVA)s having various (P_n)s values of

(a)

(b)

Figure 6 (P_n)s of PVAc polymerized at 30°C, using ADMVN concentration of 0.0001 mol/mol of VAc (a) and resulting PVA (b) with conversion.

(5700) from PVAc by bulk polymerization, using same polymerization conditions (conversion: ~25%). In the case of the DMSO system, PVA with P_n of ≤4500 could be prepared from PVAc solution polymerized in DMSO at 30°C, at a conversion of ~65%, using a minimum ADMVN concentration of 0.0001 mol/mol of VAc, It can be

concluded that the solution polymerization of VAc at 30°C, using low temperature initiator ADMVN and TBA having a low chain transfer constant, is a effective method to increase both yield and molecular weight at the same time.

As a rule, difference between (P_n)s of PVAc and PVA is attributable primarily to branched structures, which may be broken down when saponified. In this study, the effect of conversion, polymerization temperature, and type and amount of solvent on the *DB* for acetyl group of PVAc was investigated. Figure 8 shows variation of *DB* for the acetyl group of PVAc polymerized at three different temperatures with conversion. *DB* increased with an increasing conversion for all the cases. Furthermore, the rate of increasing *DB* with conversion was decreased as the polymerization temperature was lowered. At higher polymerization temperatures, the accelerated polymerization reaction may facilitate a chain transfer (branching) reaction. Also, the rate of increasing *DB* with conversion of TBA system was much lower than that of DMSO system. This might be ascribed by a polymerization rate difference between two solvents. Based on the fact that *DB* of PVAc polymerized at 30°C in TBA was a very low value of <1, the low-temperature solu-
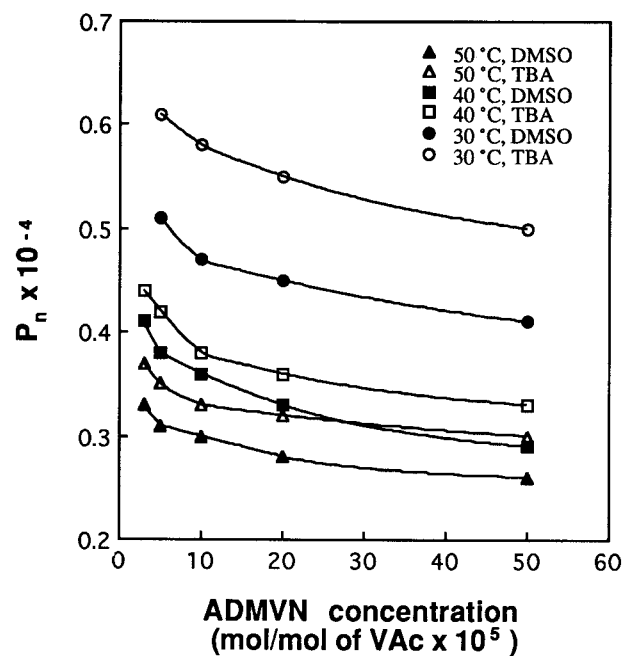

Figure 7 P_n of PVA from PVAc polymerized using VAc concentration of 4 mol/mol of solvent and ADMVN concentration of 0.0001 mol/mol of VAc with ADMVN concentration.
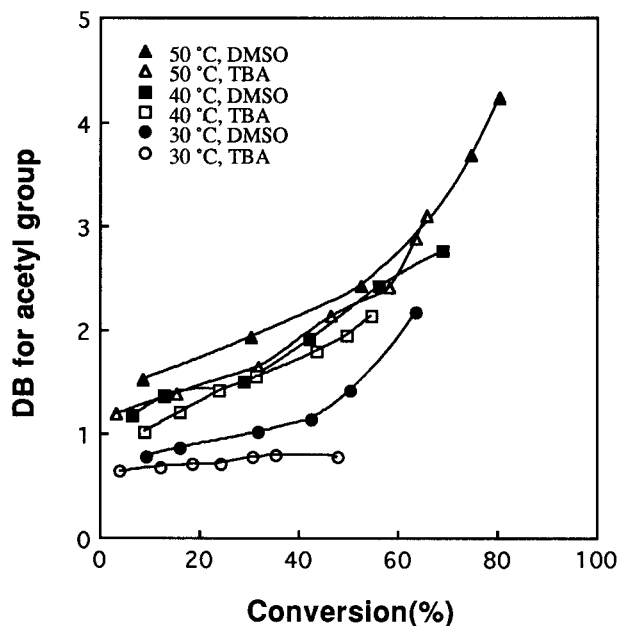
Figure 8 *DB* for the acetyl group of PVAc polymerized using VAc concentration of 4 mol/mol of solvent and ADMVN concentration of 0.0001 mol/mol of VAc with conversion.

tion polymerization of VAc using ADMVN and TBA was determined to produce PVAc with high linearity. Figure 9 presents monomer concentra-
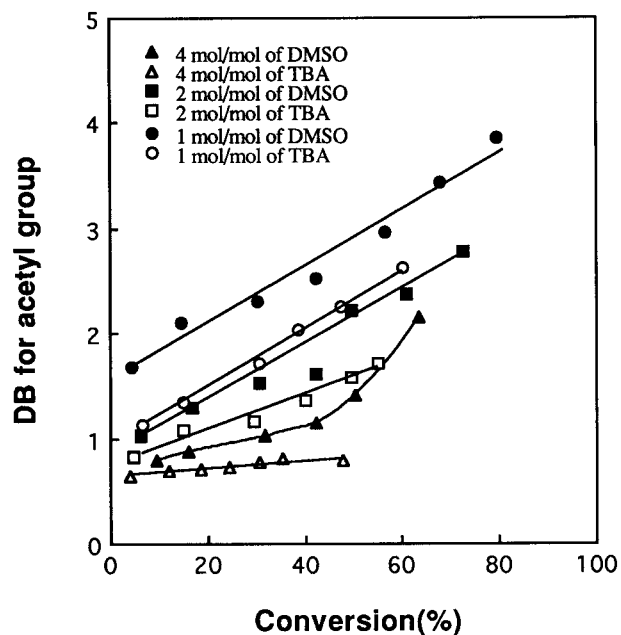

Figure 9 *DB* for the acetyl group of PVAc polymerized at 30°C using ADMVN concentration of 0.0001 mol/mol of VAc with conversion.
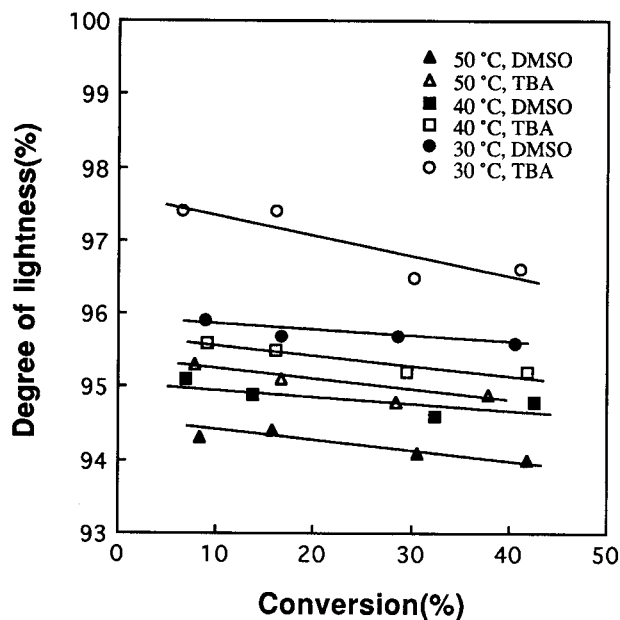

Figure 10 Degree of lightness of the films of PVA prepared by the saponification PVAc obtained at three different solution polymerization temperatures with conversion.

tion effect. As VAc concentration was increased, the *DB* was decreased in all cases. This is explained by increasing chain transfer reaction with an increase in the solvent concentration.

The end groups in the 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.[3] In particular, termination by disproportionation is known to introduce aldehyde end groups, leading to saturated and unsaturated end groups. The unsaturated group, when saponified, yields an aldehyde group. Also, the presence of ketone and aldehyde end groups leads to the formation of a conjugated double bond during saponification. A conjugated double bond leads to yellowing and deteriorates thermal stability of the polymer, which are undesirable in applications of PVA. Figure 10 presents effects of polymerization temperature, type of solvent, and conversion on the degree of lightness of PVA film. The lightness of the PVA film from PVAc polymerized at lower temperature and conversion was higher than that at higher temperatures and conversions. This may be explained by the fact that polymerization of VAc at lower temperature is largely terminated by recombination rather than by disproportionation.[2,3] Consequently, the quan-

tity of saturated and unsaturated end groups is decreased with PVAc prepared at lower polymerization temperature during saponification.[36] In addition, the lightness of the TBA system was higher than that of DMSO system. This was explained by the higher polymerization rate and faster termination rate of the DMSO system, which agreed well with the results presented in Figures 5 and 8.

CONCLUSIONS

To obtain HMW PVAc with high conversion and high linearity for a precursor of HMW PVA, VAc was solution polymerized using a low-temperature initiator, ADMVN, and low chain transfer constant solvents, TBA and DMSO. It is not an easy job to obtain HMW 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, ADMVN and TBA seem to be advantageous in lowering polymerization temperature down to ~30°C and in suppressing chain transfer reaction, respectively. That is, ADMVN is more effective in preparing HMW PVAc with fewer branches. Furthermore, solution polymerization is a powerful method for enhancing conversion.

Through a series of calculations using the initial-rate method, the solution polymerization rates of VAc at 30°C in TBA and in DMSO were found to be proportional to the exponent 0.49 and 0.72 of ADMVN concentrations, respectively. At the same polymerization conditions, TBA was clearly superior to DMSO in increasing P_n of PVA. By contrast, TBA was inferior to the bulk method in increasing the conversion of the polymer, indicating that the solution polymerization rate of VAc in TBA was slower than that in DMSO. These effects could be explained by an activation energy difference of polymerization obtained from the Arrhenius plot.

Solution polymerization of VAc at 30°C by ADMVN and saponification produced HMW PVA with P_n of 4100–6100 and with maximum conversion of VAc into PVAc of 55–80%. 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 and lightness were higher and DB was lower with PVA prepared from PVAc polymerized at lower temperatures in TBA (DB of below 1 at 30°C). Conclusively, this solution polymerization is expected to be an easy way of producing HMW PVA with high yield by simple chemical initiation without the need for special devices such as irradiation.

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

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