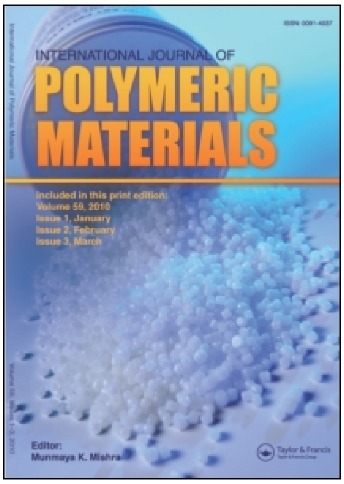

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Preparation and Molecular Structure of Poly(Vinyl Alcohol) by Low Temperature Bulk Polymerization of Vinyl Acetate and Saponification

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Vinyl acetate (VAc) was bulk-polymerized at 30, 40 and 50°C using a low temperature initiator, 2,2′-azobis(2,4-dimethylvaleronitrile) (ADMVN), and 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 saponifying it with sodium hydroxide. Low polymerization temperature and low conversion by adopting ADMVN proved to be successful in obtaining PVA of high molecular weight. PVAc having number-average degree of polymerization (P_n) of 6,800-10,100 was obtained, whose degree of branching for acetyl group of 0.6-0.7 at 30°C, 0.8-1.1 at 40°C, and 1.0-1.9 at 50°C at conversion of below 40%. Saponifying so prepared PVAc yielded PVA having P_n of 3,100-6,200, and syndiotactic diad (S-diad) content of 51-53%. The whiteness, S-diad content, and crystal melting temperature were higher with PVA prepared from PVAc polymerized at lower temperatures.

Keywords: Vinyl acetate; bulk-polymerization; low temperature; 2,2′-azobis(2,4-dimethylvaleronitrile); degree of branching; high molecular weight PVA

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INTRODUCTION

Recently, much attention has been paid to the high modulus/high strength organic fibers which can replace the carcinogenic asbestos fiber in construction materials. The poly(vinyl alcohol) (PVA) fiber is recognized as the best candidate because of its good mechanical properties together with excellent resistance to alkalis [1,2]. To obtain desirable fiber properties, it is essential to prepare PVA of high molecular weight (HMW) with little branched structures. Some researchers have tried to adopt new polymerization methods [3–9], and some have attempted to prepare new precursors such as poly(vinyl pivalate) [10–19].

Nikolaev *et al.* [3] synthesized linear HMW poly(vinyl acetate) (PVAc) by using a manganese chelate as an initiator in low temperature redox emulsion polymerization. Lanthier [4] obtained PVA having number-average degree of polymerization (P_n) of 12,000 by gamma ray radiation polymerization of VAc at -15°C. Rosenberg *et al.* [5] prepared PVA which have P_n of 3,200–5,000 by gamma ray radiation polymerization of vinyl acetate (VAc) in an emulsion system. Wu and West [6] synthesized ultrahigh molecular weight PVA having P_n of over 10,000 by low temperature-ultraviolet ray radiation polymerization of VAc in a bulk system. Yamamoto *et al.* [8] synthesized UHMW PVA having P_n of 12,800 by UV-initiated polymerization of VAc at 0°C in an emulsion system. These polymerization methods, however, inevitably require very complex and expensive radiation procedures, special polymerization initiator, and lower polymerization temperature.

The free radical polymerization of VAc is prone to bring about chain transfer (branching) reaction. However, a proper choice of polymerization conditions may suppress the branch formation reaction. As is well known, the polymerization temperature, type and concentration of initiator have a notable effect on the molecular weight of polymer.

In this study, a low-temperature initiator, 2,2′-azobis(2,4-dimethylvaleronitrile) (ADMVN), was selected in polymerization of VAc to obtain HMW PVAc with less branches. The effect of polymerization temperature and initiator concentration on the polymerization behavior of VAc and molecular structure of PVA obtained from the PVAc precursor 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. Other extra-pure grade reagents were used without further purification.

Bulk Polymerization of VAc

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 measuring the weight of the polymer. Conversions were averages of five determinations. The detailed polymerization conditions are listed in Table I.

TABLE I Results of bulk polymerization of VAc using ADMVN

ADMVN	*Temp.*	*Time*	*Conversion*	$P_n \times 10^{-4}$	
mol/mol of VAc	°*C*	*h*	%	*PVAc*	*PVA*
2×10^{-4}	50	1.0	37.1	0.90	0.31
1×10^{-4}	50	2.5	31.5	0.93	0.34
5×10^{-5}	50	2.5	27.4	0.92	0.36
4×10^{-5}	50	3.0	28.1	0.93	0.36
2×10^{-5}	50	4.0	24.9	0.89	0.38
2×10^{-4}	40	3.0	25.4	0.79	0.37
1×10^{-4}	40	4.0	22.1	0.76	0.38
5×10^{-5}	40	4.0	19.5	0.79	0.41
4×10^{-5}	40	6.0	21.1	0.84	0.44
2×10^{-5}	40	10.0	17.4	0.83	0.46
2×10^{-4}	30	6.0	19.2	0.87	0.51
1×10^{-4}	30	6.0	19.5	0.92	0.54
5×10^{-5}	30	8.0	17.5	0.94	0.56
4×10^{-5}	30	12.0	15.9	0.95	0.57
2×10^{-5}	30	14.0	14.8	1.01	0.62

Saponification of PVAc [8]

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. PVA produced was filtered and washed well with methanol.

Acetylation of PVA [8]

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. Then the mixture was poured into cold water to precipitate PVAc. 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) [20], respectively,

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

where $[\eta]$ is 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],

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

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.

Crystal melting temperature (T_m) of PVA was measured by differential scanning calorimeter (DSC) (Perkin-Elmer, DSC 7) with a sample weight of 10 mg and at a heating rate of 10°C/min.

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 onto 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).

RESULT AND DISCUSSION

Polymerization Behavior of VAc

In the free radical polymerization, the rate of polymerization (R_p) may be expressed by Eq. (3) [21]

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

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 15% conversion in the bulk polymerizations of VAc at 30°C using ADMVN. It was shown that the more the initiator concentration, the higher the polymerization rate in both cases. This tendency well agreed to the theoretical prediction in Eq. (3).

The dependence of polymerization rate on the initiator concentration can be determined from initial-rate method [22]. 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. From the calculation, it was found that the bulk polymerization rate of VAc were proportional to the exponent 0.58 of ADMVN concentrations, respectively. In accordance with the theoretical predic-

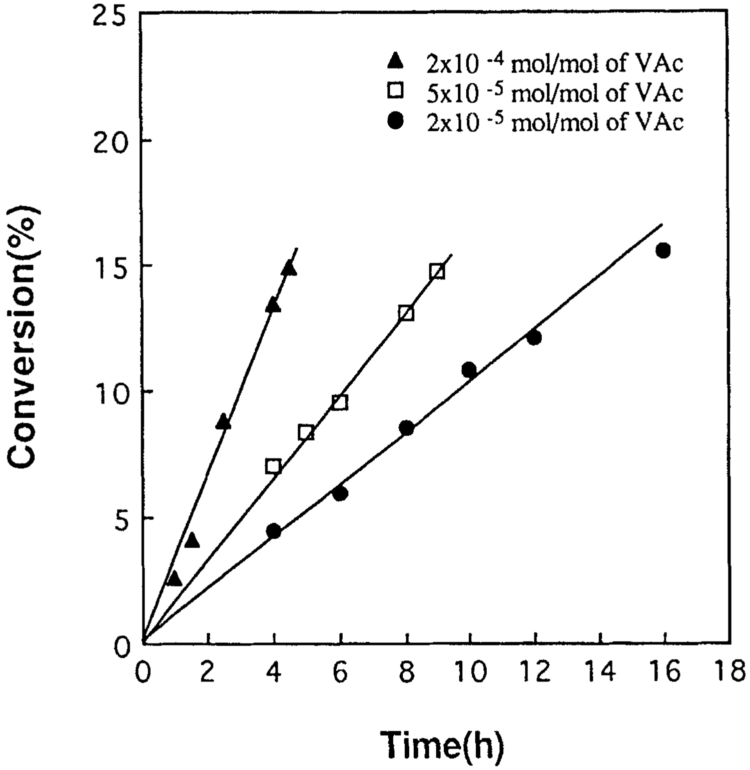

FIGURE 1 Initial conversion of VAc into PVAc bulk-polymerized at 30°C with polymerization time.

tions by Eq. (3), the bulk polymerization rate was proportional to $[\mathrm{ADMVN}]^{0.58}$.

Figure 2 illustrates conversion-time histories of bulk polymerization for temperature levels of 30, 40 and 50°C. The rate of conversion was increased with increasing polymerization temperature.

Effect of Polymerization Conditions on the P_n

The results of bulk polymerization of VAc are listed in Table I. HMW (PVA)s having various (P_n) of 3,100–6,200 were prepared by saponifying HMW (PVAc)s having (P_n) of 9,000–10,100. To obtain polymers which have excellent linearity, conversion in this system was

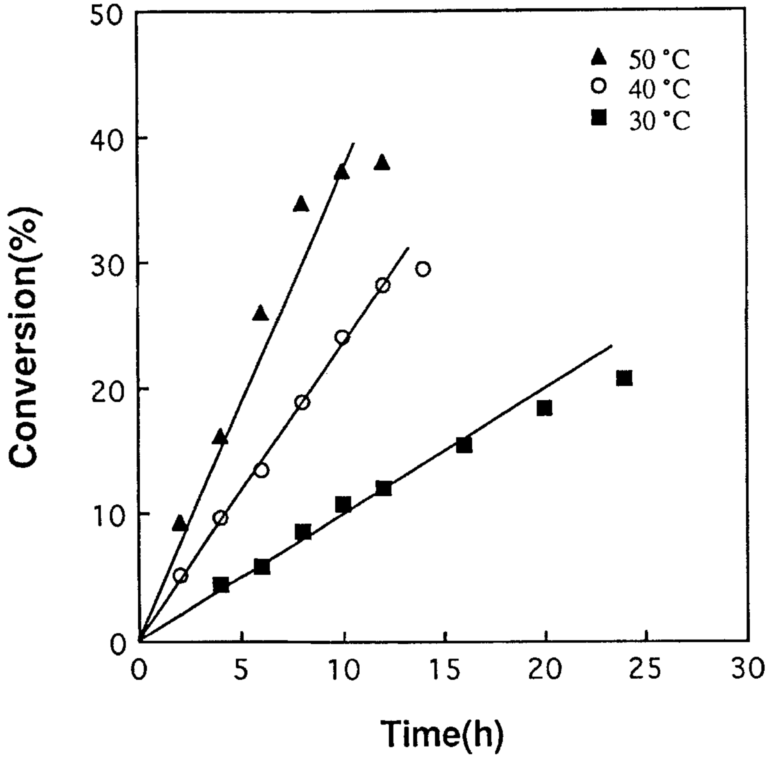

FIGURE 2 Conversion of VAc into PVAc bulk-polymerized using ADMVN concentration of 2 × 10^{-5} mol/mol of VAc with polymerization time.

controlled with the range of about 15–40%. PVA having maximum P_n of 6,200 at polymerization temperature of 30°C could be prepared at minimum ADMVN concentration of 2×10^{-5} mol/mol of VAc. From the results of polymerization, it was found that as ADMVN concentration decreased, HMW PVA was obtained. Furthermore, molecular weight increased at 30°C than 40 or 50°C and the time exhibiting similar conversion lengthened at 30°C.

In a free radical polymerization process, the kinetic chain length, ν, is expressed by Eq. (4) [21],

$$\nu = K_p[M]/2(fk_dk_t[I])^{1/2} \tag{4}$$

Referring to Eq. (4), the degree of polymerization may be decreased as the efficiency and concentration of initiator are increased. Figure 3

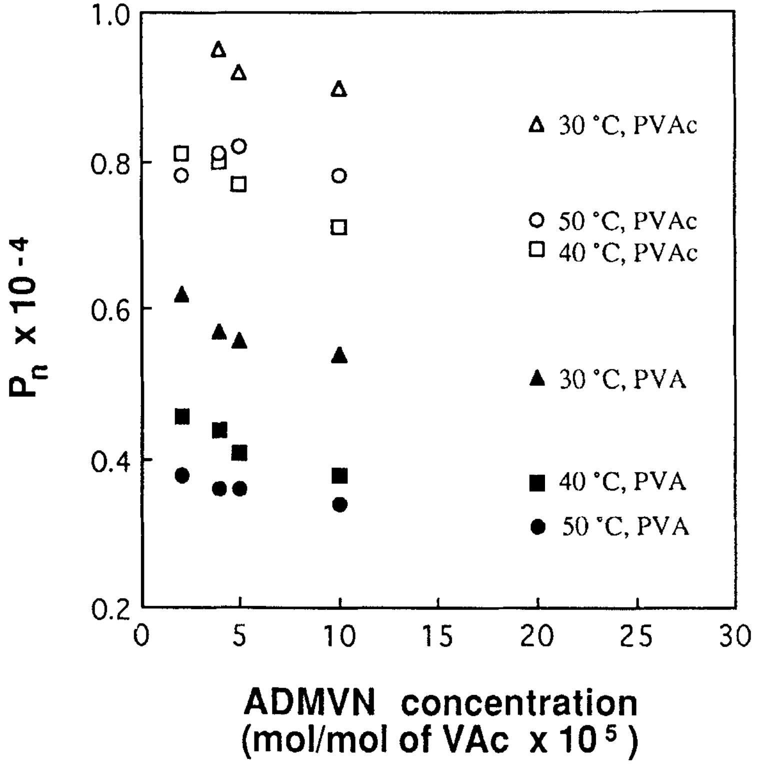

FIGURE 3 Plots of (P_n)s of PVAc obtained at three different polymerization temperatures at similar conversion of about 15% and resulting PVA *vs.* ADMVN concentrations.

exhibits plots of (P_n)s of PVAc and corresponding PVA against ADMVN concentration. PVAc was sampled at three different polymerization temperatures at similar conversion of about 15% to clarify effects of ADMVN concentration and polymerization temperature. Difference between (P_n)s of PVAc and PVA is mostly obliged to branched structures, which may be broken down when saponified. In accordance with the theoretical predictions by Eq. (4), (P_n)s of PVAc and PVA were increased as polymerization temperature or initiator concentration was decreased.

(P_n)s of PVAc obtained at ADMVN concentration of 1×10^{-4} mol/mol of VAc and corresponding PVA obtained by saponifying PVAc with conversions are listed in Table II. It is interesting to see that P_n of

TABLE II (P_n)s of PVAc obtained at three different polymerization temperatures at the ADMVN concentration of 1×10^{-4} mol/mol of VAc and resulting PVA with conversions

Conversion	P_n *of PVAc* $\times 10^{-4}$			P_n *of PVA* $\times 10^{-4}$		
	at 50°*C*	*at* 40°*C*	*at* 30°*C*	*at* 50°*C*	*at* 40°*C*	*at* 30°*C*
About 5%	0.68	0.65	0.85	0.33	0.37	0.53
About 10%	0.70	0.69	0.88	0.33	0.38	0.54
About 15%	0.78	0.71	0.90	0.34	0.38	0.54
About 20%	0.81	0.73	0.92	0.33	0.38	0.54

PVA remains almost constant and nearly independent of P_n of PVAc. However, polymerization temperature in bulk polymerization of VAc has a notable effect on P_n of resultant PVA.

DB and Tacticity

As a rule, difference between (P_n)s of PVAc and PVA is due to a branched structure. In this study, the effects of ADMVN concentration, polymerization temperature, and conversion on the *DB* of PVAc were investigated. Figure 4 shows variation of *DB* for acetyl group of PVAc polymerized at three different temperatures with conversion. *DB* was increased with increasing conversion for all the cases. In addition, the rate of increasing *DB* with conversion was decreased as polymerization temperature was lowered. *DB* for acetyl group of PVAc obtained at similar conversion of about 15% and at three different polymerization temperatures is listed with ADMVN concentration in Table III. On the whole, *DB* was increasing with increasing ADMVN concentration at polymerization temperatures of 40 and 50°C. On the other hand, at 30°C, *DB* was nearly constant irrespective of ADMVN concentration. Over the range of ADMVN concentrations observed, the extent of increasing *DB* was more prominent at higher polymerization temperature.

The P_n, triad and diad contents, and T_m of PVA from PVAc polymerized at three different polymerization temperatures are summarized in Table IV. As polymerization temperature was decreased, syndiotactic triad content was increased. But isotactic triad content was decreased. On the other hand, heterotactic triad content remained

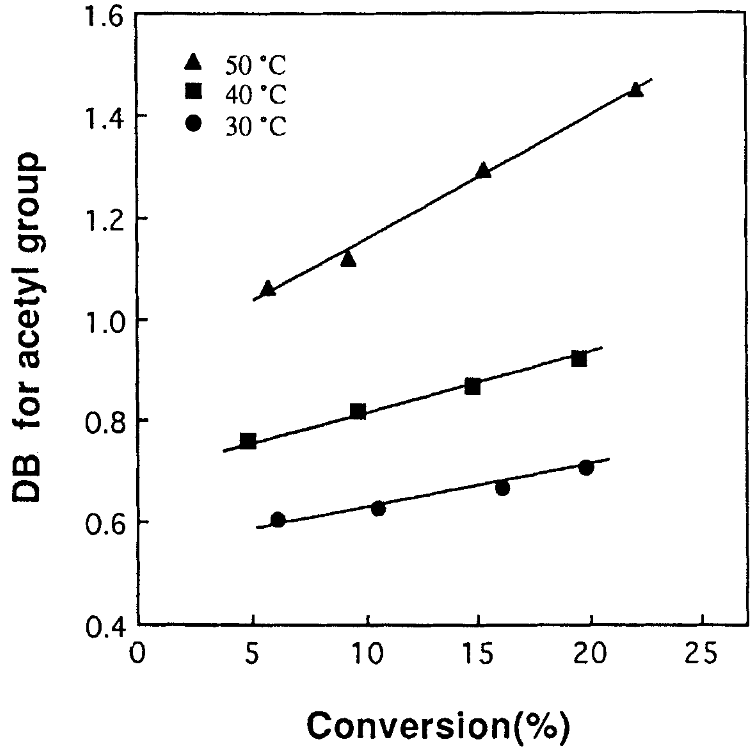

FIGURE 4 *DB* for acetyl group of PVAc obtained at three different polymerization temperatures at the ADMVN concentration of 1×10^{-4} mol/mol of VAc with conversion.

TABLE III *DB* for acetyl group of PVAc obtained at different polymerization temperatures at similar conversion of 15% with ADMVN concentration

ADMVN concentration	*DB*		
mol/mol of VAc	*at* 50°*C*	*at* 40°*C*	*at* 30°*C*
2×10^{-4}	1.32	0.84	0.67
1×10^{-4}	1.29	0.87	0.67
5×10^{-5}	1.28	0.88	0.64
4×10^{-5}	1.25	0.82	0.67
2×10^{-5}	1.05	0.76	0.66

nearly constant, 50%, regardless of polymerization temperature. *S*-diad content of PVA appeared to be independent of P_n of polymer, and slightly increased with lowering polymerization temperature. In general, PVA with *S*-diad contents exceed 53–54% (about the

TABLE IV Molecular parameters of PVA synthesized

Polymerization temperature (°C)	P_n	DS^a (%)	mm^a (%)	mr^a (%)	rr^a (%)	m^a (%)	r^a (%)	T_m (°C)
30	6,200	99.9	22.3	49.8	27.9	47.2	52.8	233.2
30	5,700	99.9	22.5	49.5	28.0	47.4	52.6	233.0
30	5,600	99.9	22.1	50.2	27.7	47.2	52.8	233.4
30	5,400	99.9	22.5	49.9	27.6	47.5	52.5	232.8
30	5,100	99.9	22.4	49.7	28.0	47.3	52.5	232.6
40	4,600	99.9	23.1	49.6	27.3	47.9	52.1	231.1
40	4,400	99.9	22.6	50.4	27.0	47.4	52.2	231.5
40	3,800	99.9	23.0	49.8	27.2	47.2	52.1	230.9
40	3,700	99.9	22.8	49.7	27.5	47.5	52.3	231.4
50	3,800	99.9	23.6	49.9	26.5	48.5	51.5	230.3
50	3,600	99.9	23.9	49.8	26.3	48.8	51.2	229.8
50	3,400	99.9	23.6	50.2	26.2	48.3	51.7	230.4
50	3,100	99.9	23.8	50.0	26.2	48.8	51.2	229.7

[a] DS, mm, mr, rr, m, and r are, respectively, degree of saponification, isotactic triad, heterotactic triad, syndiotactic triad, isotactic diad, syndiotactic diad contents determined by using ^{1}H-NMR spectroscopy.

maximum value obtained in VAc polymerization) are described as "syndiotacticity-rich". Thus, it was found that PVA was prepared in this study was a typically atactic. T_m of PVA is independent of P_n of polymer and increased with lowering polymerization temperature, which well agrees with tacticity data described above. A negligible effect of molecular weight on T_m of PVA suggests that the shape and size of the crystal are almost same over the molecular weight range observed.

Degree of Lightness of PVA

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 group. The unsaturated group, when saponified, yields an aldehyde group. Also, the presence of ketone and aldehyde end groups leads to formation of conjugated double bond during saponification [2]. Conjugated double bond leads to yellowing and deteriorates thermal stability of the polymer, which are undesirable in applications of PVA. Methods for preventing formation of ketone end group have been focused on either minimizing formation of acetaldehyde during polymerization [23, 24] or eliminating of aldehydes once formed through oxidation [25], reduction [26] and blocking [27]. Figure 5 shows effect of polymerization temperature and conversion of VAc into PVAc on the degree of lightness of resulting PVA film. The lightness of the PVA film from PVAc polymerized at lower temperature and at lower 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 [28, 29]. In consequence the amount of saturated and unsaturated end groups is decreased with PVAc prepared at lower polymerization temperature during saponification [30].

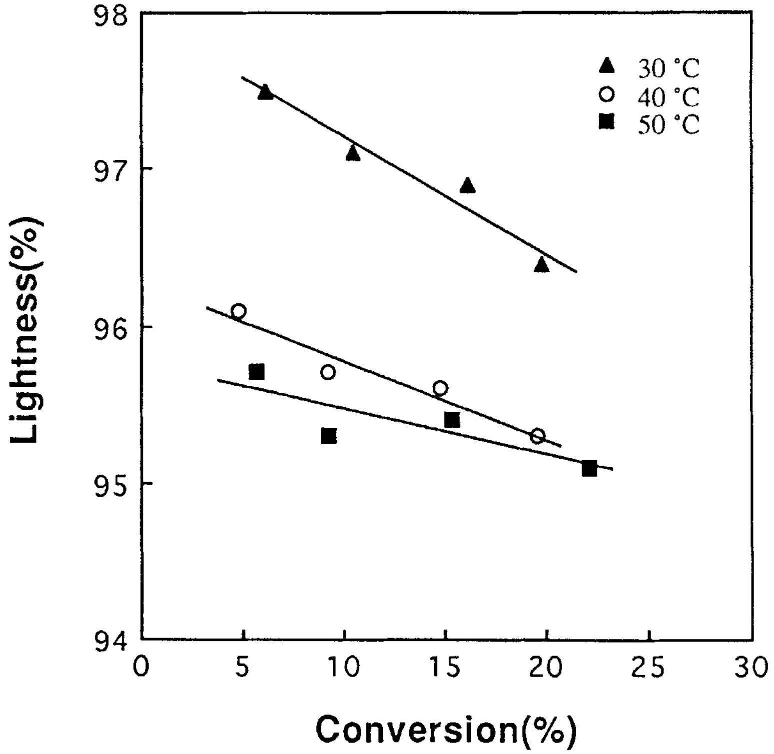

FIGURE 5 Lightness of the films of PVA from PVAc obtained at three different polymerization temperatures with conversion.

CONCLUSION

In bulk polymerization of VAc, a low-temperature initiator, ADMVN seemed to be advantageous in suppressing chain transfer (branching) reaction because it could lower polymerization temperature down to *ca.* 30°C. Hence, ADMVN was more effective in preparing HMW PVAc with less branches. Through a series of calculation using initial-rate method, it was found that the bulk polymerization rate of VAc at 30°C was proportional to the exponent 0.58 of ADMVN concentration. The degree of branching for acetyl group at 30°C was calculated to be 0.6–0.7.

Bulk polymerization of VAc at 307°C by ADMVN and saponification produced HMW PVA with P_n of 5,100–6,200. The P_n, lightness, and syndiotactic triad content were higher with PVA prepared from PVAc polymerized at lower temperatures. Conclusively, this bulk polymerization is expected to be an easy way of producing HMW PVA by simple chemical initiation without using special devices such as irradiation.

In a near future, we will report on the low-temperature solution polymerization of VAc in solvent having lower chain transfer constants by ADMVN to increase both conversion and molecular weight.

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