

Preparation of High Molecular Weight Atactic Poly(vinyl alcohol) by Photo-induced Bulk Polymerization of Vinyl Acetate

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Abstract: Vinyl acetate was polymerized in ultraviolet-ray initiated bulk system at low temperatures using 2,2'-azobis(2,4-dimethylvaleronitrile) (ADMVN) or 2,2'-azobis(isobutyronitrile) (AIBN) as the photoinitiator, respectively. High molecular weight (HMW) poly(vinyl alcohol) (PVA) having number-average degree of polymerization (P_n) of 3,900-7,800 and syndiotactic diad (S-diad) content of 52.5-54.0% could be prepared by complete saponification of synthesized linear poly(vinyl acetate) (PVAc) having P_n of 5,900-9,400 obtained at conversion of below 30%. P_n of PVA using ADMVN was larger than that of PVA using AIBN. On the other hand, conversion of the former was smaller than that of the latter, and it was found that the initiation rate of the ADMVN was lower than that of AIBN. This could be explained by a fact that the rate of photolysis of AIBN is faster than that of ADMVN due to the higher quantum yield or dissociation rate constant of AIBN than that of ADMVN. The P_n , syndiotacticity, and whiteness of PVA from PVAc polymerized at lower temperatures were superior to those of PVA from PVAc polymerized at higher temperatures.

Keywords: VAc, Low temperature, HMW PVA, P_n , ADMVN, AIBN

Introduction

Poly(vinyl alcohol) (PVA) fibers and films have high tensile and impact strength, high tensile modulus, high abrasion resistance, excellent resistance to alkali, and oxygen barrier property which are superior to those of any known polymers[1-8]. To exhibit these properties, PVA should retain high molecular weight (HMW) and high syndiotacticity[1-12]. So it is necessary to improve polymerization methods of poly(vinyl acetate) (PVAc), precursor for PVA.

It has been known that HMW PVAc is hardly to obtain via conventional radical polymerization which is carried out at around 50°C or 60°C due to chain transfer to monomer and polymer, therefore, the molecular weight (MW) of PVAc is decreased due to the hydrolysis of branch chains during the saponification treatment to PVA and it has become also evident that only atactic polymer is obtained from the conventional radical polymerization.

Therefore various special polymerization methods have been attempted to raise MW of PVA[13-27]. Redox systems have been explored for the polymerization of vinyl acetate (VAc): Lyoo *et al.*[13] synthesized linear HMW PVAc by using a low temperature redox emulsion polymerization of VAc. The principal interest in redox systems has been to develop an initiator system that will function efficiently at low temperatures where HMW and more linear PVAc can be obtained. However, color formation or low polymerization efficiency are two common deficiencies of redox systems [14].

Initiation by radiation with gamma rays or ultraviolet (UV) has also been reported in the literature. These systems

were developed in attempts to produce linear HMW PVAc, once saponified, could be used for the production of HMW PVA. Rozenberg *et al.*[15] prepared PVA having number-average degree of polymerization (P_n) of 3,200-5,000 by gamma ray radiation polymerization of VAc in an emulsion system.

In this study, we utilized two types of azoinitiators which are superior to peroxide-type initiator in producing linear HMW precursor owing to relatively lower propagation rate of polymerization and less probability of termination reaction. To increase the MW and linearity and to minimize side reactions, VAc was polymerized in UV-ray initiated bulk system at low temperature using 2,2'-azobis(2,4-dimethylvaleronitrile) (ADMVN) or 2,2'-azobis(isobutyronitrile) (AIBN) as the photoinitiator, respectively. In the low temperature UV-ray initiated bulk polymerization of VAc, the effects of the AIBN and the ADMVN on the (MW)s of PVAc and PVA, conversion and degree of branching (DB) of this system were investigated. The tacticity and thermal properties of the PVA were also analyzed.

Experimental

Materials

VAc from Shin-Etsu was washed with aqueous solution of NaHSO₃ and water and dried over anhydrous CaCl₂, followed by distillation under reduced pressure of nitrogen. ADMVN and AIBN from Wako were dissolved in methanol and purified by crystallization. Other extra-pure grade reagents were used without further purification.

Photo-bulk Polymerization

VAc was added in a pyrex tube, which was placed in a low

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Table 1. Parameters for photo-bulk polymerization of VAc

Type of photoinitiator	AIBN ADMVN
Amount of photoinitiator	2×10^{-4} mol/mol of VAc 1×10^{-4} mol/mol of VAc 5×10^{-5} mol/mol of VAc
Temperature	25°C, 20°C, 15°C, 10°C, 5°C, 0°C
Radiation type	ultraviolet ray
Radiation source	high pressure mercury lamp (500 watt)

temperature methanol bath and this was flushed with nitrogen for 3 h. After the polymerization temperature was fixed and AIBN or ADMVN was added, respectively, the mixture was irradiated with a high pressure 500 W mercury lamp. The polymer was purified by reprecipitation from acetone/n-hexane. After the elimination of monomer from polymerization product in a vacuum had been completed, conversion was calculated by measuring the weight of the polymer. Polymerization conditions are listed in Table 1.

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 by saponification. PVA produced was filtered and washed well with methanol.

Acetylation of PVA

1 g of PVA, 2 ml of pyridine, 20 ml of acetic anhydride and 20 ml of acetic acid were put into a three-necked flask, and mixture was stirred 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 MW of PVAc were calculated by using equation (1)[17,18],

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

where $[\eta]$ is intrinsic viscosity and P_n is number-average degree of polymerization of PVAc.

On the other hand, MW of PVA was determined from that of PVAc produced by acetylating PVA using equation (1).

DB for acetyl group of PVAc is calculated by equation (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, saponified from PVAc.

Syndiotactic triad and diad contents of PVA were determined by using proton-nuclear magnetic resonance (¹H-NMR) spectrometer (Varian, Sun Unity 300). 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 ¹H-NMR spectrum.

A homogeneous 1.0 g/dl solutions of three (PVA)s of similar (P_n)s obtained at polymerization temperatures of 0, 10, and 25°C, respectively, in dimethyl sulfoxide were poured onto stainless steel tray and dried at 40°C to produce films. The lightness of the PVA film was measured by Color eye (I.D.I., model C).

Results and Discussion

Photo-bulk Polymerization

It has been known that radiation-initiated bulk polymerization might be used for production of HMW PVA with little branching. This method has the following advantages: The radiation initiation rate is temperature-independent. Since the process can be carried out at low temperatures, undesirable side reactions are avoided. The initiation rate can be easily changed. Therefore, the polymerization rate and MW can be controlled. General photoinitiators using for radical polymerization of vinyl monomers are azo, benzoin, and benzophenone types. Azo and benzoin types are cleavage-type photoinitiators. On the other hand, benzophenone is hydrogen abstraction type, and it was known that its initiation rate is slower and its initiation mechanism is more complex than those of cleavage-type photoinitiators[28].

In this study, to identify the effect of photoinitiator on the MW and conversion of the resultant polymer, we used two different azo compounds of the formula R-N=N-R which are decomposed into free radicals by UV ray. The ADMVN has relatively larger side groups in comparison with the AIBN. Recently, we found that the AIBN could initiate VAc polymerization at over 50°C effectively, on the other hand, the ADMVN could initiate VAc polymerization even below 30°C effectively without radiation source[17,18].

In the radiation-initiated radical polymerization, the rate of polymerization (R_p) may be expressed by equation (3)[29],

$$R_p = k_p (I_0 \phi I \epsilon / k_t)^{0.5} [M][I]^{0.5} \quad (3)$$

where I_0 is the incident light intensity, ϕ is a quantum yield, l is a path length, ϵ is an extinction coefficient of photoinitiator, $[I]$ and $[M]$ are the concentrations of photoinitiator and monomer, and k_p and k_t are reaction rate constants of propagation and termination, respectively. This expression implies that the rate of polymerization is increased with increasing the concentration of photoinitiator. The conversion in the bulk polymerization of VAc using different AIBN and ADMVN concentrations at 0°C is plotted against time in Figure 1a and 1b, respectively. It was shown that the greater the initiator concentration, the higher the polymerization rate, in agreement with equation (3). The conversion rate of the ADMVN system was lower than that of the AIBN

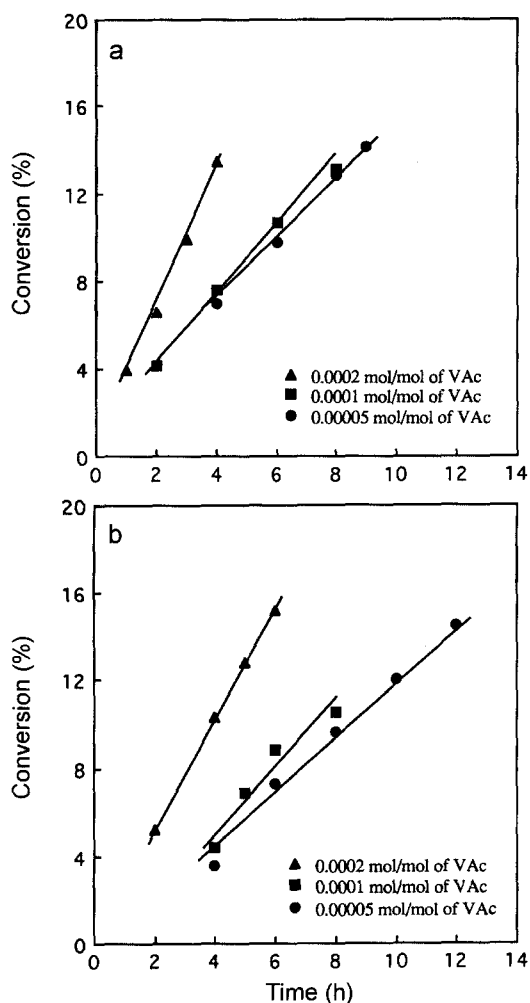


Figure 1. Conversions of VAc into PVAc in early stage of polymerization initiated by AIBN (a) and by ADMVN (b) at 0°C versus polymerization times.

system in which range of the photoinitiator concentrations investigated, which may be due to the structural difference between AIBN and ADMVN.

The dependence of polymerization rate on photoinitiator concentration can be determined by a kinetic study called initial-rate method[30]. Polymerization rate can be expressed by the exponential forms of reaction reagents. In early stage of polymerization, reaction rate is coincided with the slope of conversion-time relation. For small changes in initial concentration of one reagent with the other held constant, the ratio of polymerization rate can be related to the corresponding ratio of increments. If a measurement is made at two different initial concentrations of one component, the order with respect to that component can be simply determined by using equations (4)-(10):

$$-(d[M]_1/dt) = (R_p)_1 = k[M]_1^{n_1}[I]_1^{n_2} \quad (4)$$

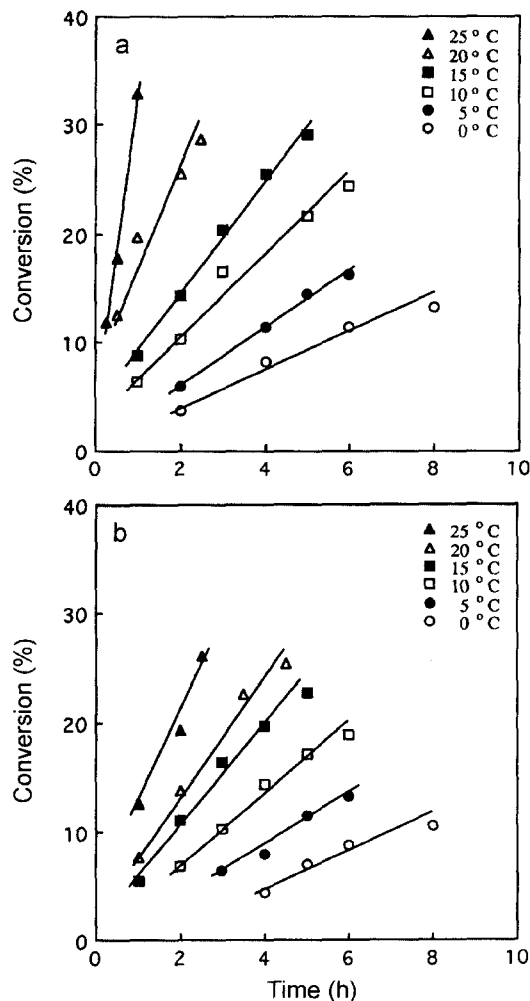


Figure 2. Conversions of VAc into PVAc obtained by photo-bulk polymerization of VAc using AIBN (a) and ADMVN (b) at six different polymerization temperatures versus polymerization times.

$$-(d[M]_2/dt) = (R_p)_2 = k[M]_2^{n_2}[I]_2^{n_2} \quad (5)$$

$$-(d[M]_3/dt) = (R_p)_3 = k[M]_3^{n_3}[I]_3^{n_3} \quad (6)$$

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

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

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

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

This procedure can be used to determine all exponents like n_1 , n_2 , and n_3 . From the calculation, it was found that the photo-bulk polymerization rate of VAc was proportional to the 0.60 powers of AIBN concentration and the 0.46 powers of ADMVN concentration, respectively. That is, the

polymerization rate of VAc by AIBN was higher than that by ADMVN.

The conversion in the photo-bulk polymerization of VAc using AIBN and ADMVN concentration of 1×10^{-4} mol/mol of VAc at six different polymerization temperatures is plotted against time in Figure 2a and 2b, respectively. Two things are worth noting in the figures. Firstly, the conversion rate was increased as the polymerization temperature was increased. Secondly, the conversion rate of ADMVN-system was lower than that of AIBN-system in all polymerization temperatures.

Molecular Weight and Degree of Branching

In the radiation-initiated radical polymerization, the kinetic chain length, ν , is related to the concentration of photoinitiator by equation (11)[29]:

$$\nu = (k_p/k_t^{0.5})([M]/I_0\phi I\epsilon [I])^{0.5} \quad (11)$$

Referring the equation (11), the molecular weight of polymer is largely determined by the number of free radicals at the initial stage. The molecular weight of polymer is predicted to decrease as the photoinitiator concentration increases because of increase in number of radicals. The results of photo-bulk polymerization of VAc are listed in Table 2. HMW (PVA)s having various (P_n)s of 3,900-7,800 could be prepared by saponifying HMW (PVAc)s having (P_n)s of 5,900-9,400. To obtain polymers, which have excellent linearity, conversion in this system was controlled with the range of about 10-30%. PVA having maximum P_n of 7,200 at 0°C in the presence of AIBN and 7,800 at 0°C in the presence of ADMVN could be prepared at photoinitiator concentration of 5×10^{-5} mol/mol of VAc. From the results of polymerization, it was found that as photoinitiator concentration decreased, PVA having higher MW was obtained, in accordance with the theoretical predictions by

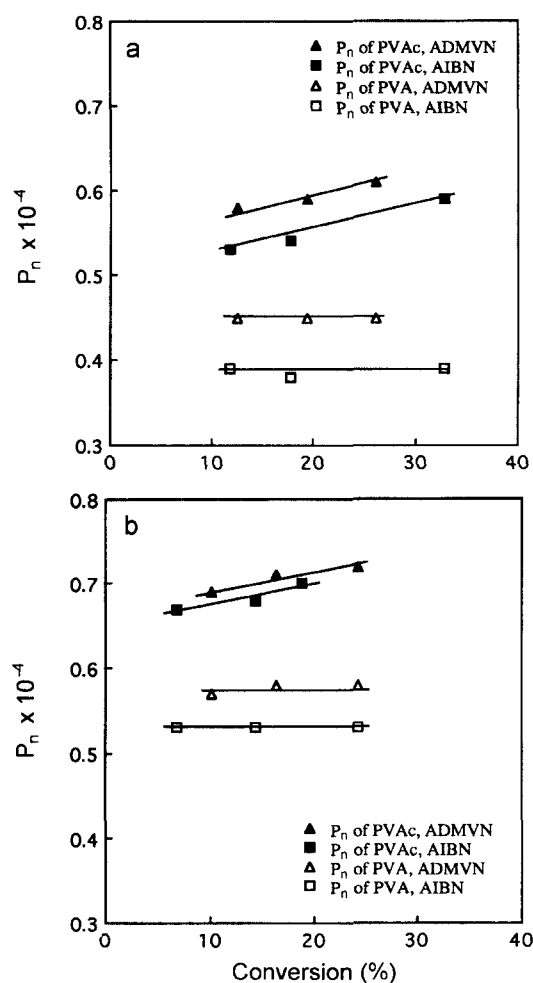


Figure 3. (P_n)s of PVAc, obtained by photo-bulk polymerization of VAc at 25°C (a) and 10°C (b) using photoinitiator concentrations of 1×10^{-4} mol/mol of VAc and resulting PVA versus conversions.

Table 2. Results of photo-bulk polymerization of VAc

Photoinitiator		Temp. $^\circ\text{C}$	Time h	Conversion %	$P_n \times 10^{-4}$	
Type	mol/mol of VAc				PVAc	PVA
AIBN	1×10^{-4}	25	1.0	32.8	0.59	0.39
ADMVN	1×10^{-4}	25	2.5	26.1	0.61	0.45
AIBN	1×10^{-4}	20	2.5	28.7	0.64	0.45
ADMVN	1×10^{-4}	20	4.5	25.4	0.63	0.48
AIBN	1×10^{-4}	15	5.0	29.1	0.67	0.49
ADMVN	1×10^{-4}	15	5.0	22.7	0.66	0.52
AIBN	1×10^{-4}	10	6.0	24.3	0.70	0.53
ADMVN	1×10^{-4}	10	6.0	18.9	0.72	0.58
AIBN	1×10^{-4}	5	6.0	16.2	0.71	0.56
ADMVN	1×10^{-4}	5	6.0	13.3	0.74	0.61
AIBN	5×10^{-5}	5	8.0	18.8	0.75	0.60
ADMVN	5×10^{-5}	5	8.0	14.5	0.79	0.65
AIBN	1×10^{-4}	0	8.0	13.1	0.80	0.66
ADMVN	1×10^{-4}	0	8.0	10.4	0.87	0.73
AIBN	5×10^{-5}	0	10.0	18.8	0.88	0.72
ADMVN	5×10^{-5}	0	12.0	14.5	0.94	0.78

equation (11). Moreover, MW increased at lower temperatures than higher temperatures although the longer reaction time is required for obtaining similar conversion.

(P_n) s of (PVAc)s obtained in photo-bulk polymerization carried out at 10 and 25°C using photoinitiator concentration of 1×10^{-4} mol/mol of VAc and corresponding (PVA)s obtained by saponifying PVAc are plotted against conversion in Figures 3a and 3b. It is interesting to see that P_n of PVA remains almost constant and nearly independent of P_n of PVAc. In Figure 3, (P_n) s of PVAc and PVA obtained by using ADMVN were larger than those obtained by AIBN. This could be explained by a fact that the rate of photolysis of AIBN is faster than that of ADMVN due to the higher quantum yield or dissociation rate constant of AIBN than that of ADMVN. The higher radical concentration in the early stage of the polymerization is the reason to result in higher rate of polymerization and lower molecular weight of the resultant polymer. Figure 4 exhibits plots of (P_n) s of PVAc obtained at similar conversion of about 20% using photoinitiator concentration of 1×10^{-4} mol/mol of VAc and corresponding PVA against polymerization temperature. The (P_n) s of both PVAc and PVA increased with a decrease in the polymerization temperature. However, it should be noted that the (P_n) s of both PVAc and PVA were greater when the ADMVN was used.

As a rule, difference between (P_n) s of PVAc and PVA is mostly obliged 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 5 shows variation of DB for acetyl group of PVAc polymerized at three different temperatures using photoinitiator concen-

tration of 1×10^{-4} mol/mol of VAc with conversion. DB was increased with increasing conversion for all the cases. The (DB)s for acetyl group of (PVAc)s were about 0.35-0.50 by AIBN at 25°C, 0.30-0.35 by ADMVN at 25°C, 0.26-0.32 by AIBN at 10°C, 0.21-0.24 by ADMVN at 10°C, 0.20-0.22 by AIBN at 0°C, and 0.18-0.20 by ADMVN at 0°C, respectively. It was found that DB for acetyl group of PVAc with ADMVN was lower than that with AIBN. DB for acetyl group of PVAc obtained at similar conversion of about 20% using photoinitiator concentration of 1×10^{-4} mol/mol of VAc

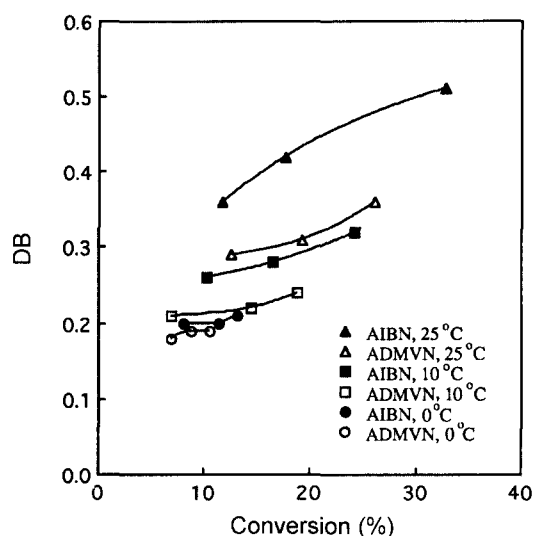


Figure 5. DB for acetyl group of PVAc, obtained by photo-bulk polymerization of VAc at three different temperatures using photoinitiator concentration of 1×10^{-4} mol/mol versus conversion.

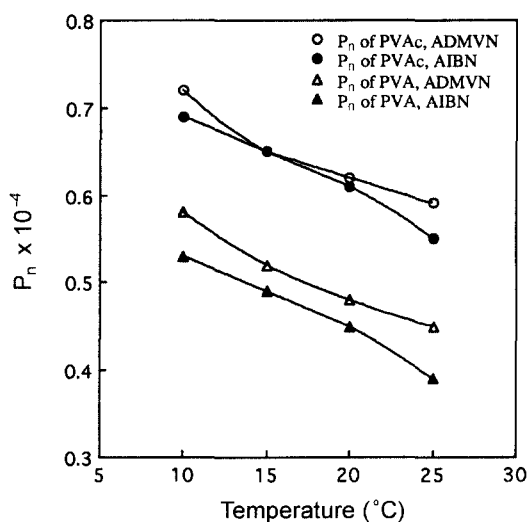


Figure 4. (P_n) s of PVAc, obtained by photo-bulk polymerization of VAc with photoinitiator concentration of 1×10^{-4} mol/mol at similar conversion of about 20% and resulting PVA versus polymerization temperatures.

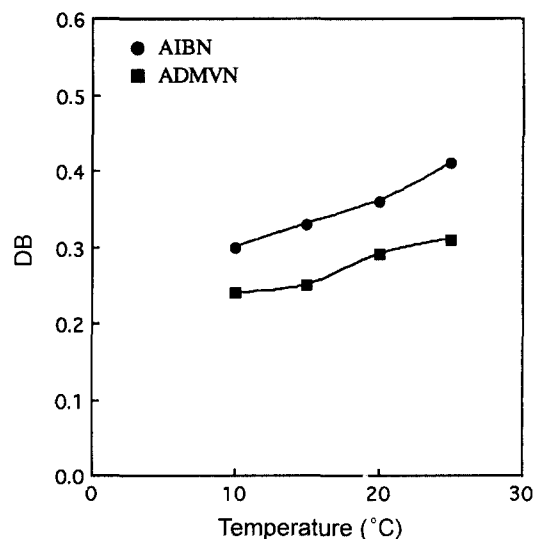


Figure 6. DB for acetyl group of PVAc, obtained by photo-bulk polymerization of VAc with photoinitiator concentration of 1×10^{-4} mol/mol versus polymerization temperature.

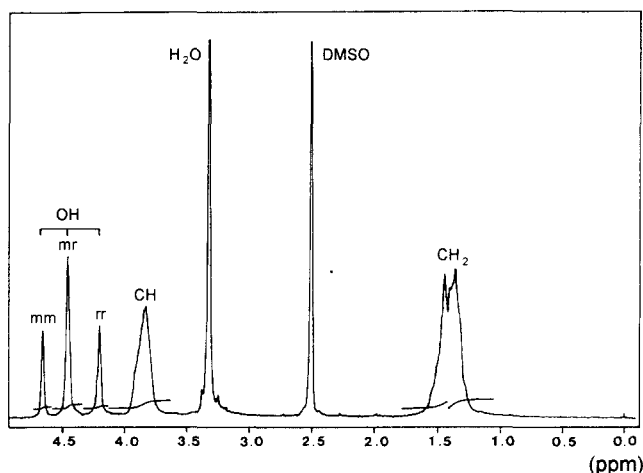


Figure 7. $^1\text{H-NMR}$ spectrum of completely saponified PVA having P_n of 7,300 and S-diad content of 54.2% from PVAc, obtained by photo-bulk polymerization of VAc at 0°C .

with photo-bulk polymerization temperature is shown in Figure 6. The *DB* was decreased as polymerization temperature 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.

Characteristics of PVA Saponified

To investigate the stereoregularity of PVA synthesized and to measure the degree of saponification of the resultant PVA after saponification, we used $^1\text{H-NMR}$ spectroscopic method, which was known as more correct method than FT-IR spectroscopic method in determining tacticity of PVA. Figure 7 shows the $^1\text{H-NMR}$ spectrum of the solution of PVA in dimethyl sulfoxide obtained from PVAc, polymerized at 0°C . The ratios of triad tacticities were estimated as 21.2, 49.2 and 29.6% for isotactic, heterotactic and syndiotactic triad, respectively, from the three peaks in the OH proton spectrum shown in Figure 8. It was shown that the intensity of *rr* peak at 4.22 ppm was larger than that of *mm* peak at 4.65 ppm. From this fact, it was concluded that the syndiotactic triad content of PVA was richer than the isotactic triad content. No acetyl proton peak at 2.0 ppm indicates that PVAc is completely saponified. The triad content of PVA from PVAc photo-bulk polymerized at three different temperatures using AIBN and ADMVN are shown in Figure 8a and 8b, respectively. As polymerization temperature is decreased, syndiotactic triad content is increased from 27.9% to 29.6%. But isotactic triad content is decreased from 22.6% to 21.2%. In contrast, heterotactic triad content remains nearly constant, about 50.0%, regardless of polymerization temperatures.

The end groups in PVA molecule seriously influence the color of the polymer, which are incorporated during

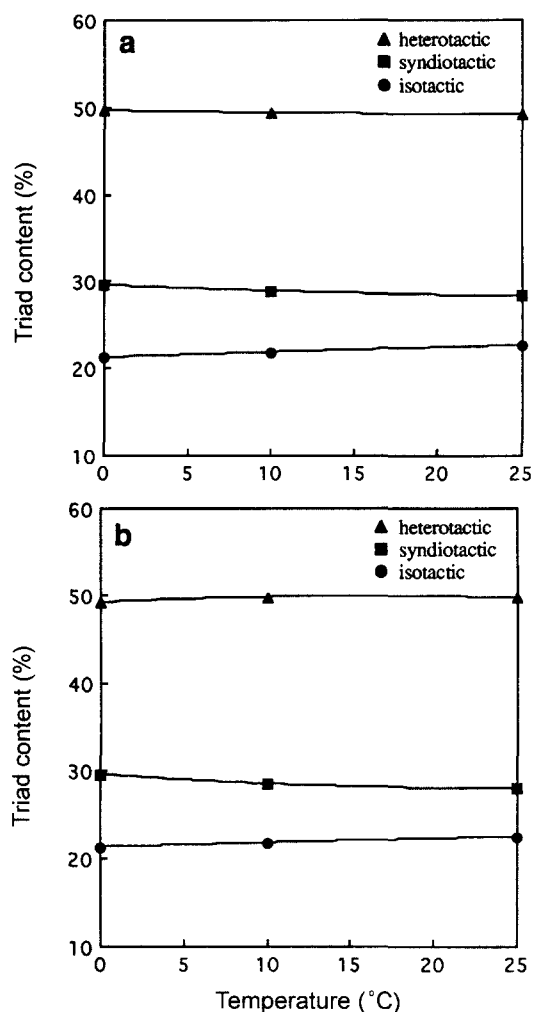


Figure 8. Triad tacticities of PVA from PVAc obtained by photo-bulk polymerization of VAc using AIBN (a) and ADMVN (b) concentrations of 1×10^{-4} mol/mol at three different polymerization temperatures.

polymerization by one of the following reactions: chain transfer, initiation, or termination. Especially, termination by disproportionation is known to introduce aldehyde end groups, leads to 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[2]. Methods for preventing formation of ketone end group have been focused on either minimizing formation of acetaldehyde during polymerization [31,32] or eliminating of aldehydes once formed through oxidation[33], reduction[34,35], and blocking[36]. Figure 9 shows effect of 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 was higher than that at higher temperature. This may be explained by the fact that polymerization of VAc is largely

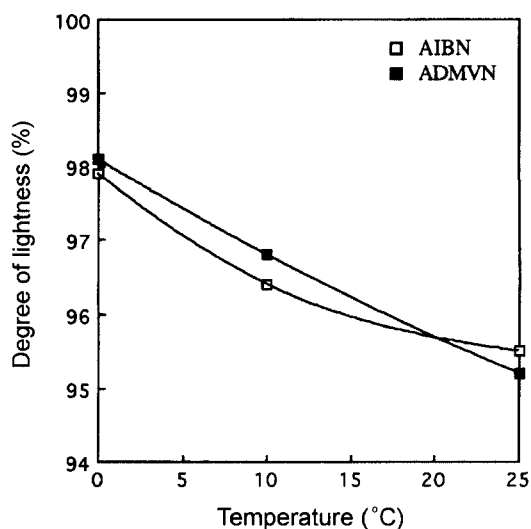


Figure 9. Degree of lightness of the films of PVA from PVAc, obtained at three different photo-bulk polymerization temperatures.

terminated by recombination rather than by disproportionation at lower temperature. As a consequence, low content of unsaturated end groups of PVA is resulted, which is formed during saponification of PVAc polymerized in lower temperature[34].

Conclusion

Considering the effect of various polymerization parameters on the conversion, linearity, and MW of PVAc and the resulting PVA and tacticity of PVA, we could conclude as below: Through a series of calculation using initial-rate method, it was found that the photo-bulk polymerization rate of VAc was proportional to the 0.60 powers of AIBN concentration and the 0.46 powers of ADMVN concentration, respectively. That is, the polymerization rate of VAc by AIBN was higher than that by ADMVN. At the same concentration of photoinitiator, ADMVN was superior to AIBN in increasing P_n of PVA, on the other hand, ADMVN was inferior to AIBN in increasing conversion. This could be explained by a fact that the rate of photolysis of AIBN is faster than that of ADMVN due to the higher quantum yield or dissociation rate constant of AIBN than that of ADMVN. The higher radical concentration in the early stage of the polymerization is the reason to result in higher rate of polymerization and lower molecular weight of the resultant polymer. To all the synthesized products, it was found that P_n of PVA was constant and independent of the increase of P_n of PVAc according to the increase of conversion. The *DB* for acetyl group was about 0.25-0.40. And the syndiotacticity and whiteness increases as the polymerization temperature is lowered.

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