High Molecular Weight Poly(vinyl alcohol) through Photo-Emulsion Polymerizations of Vinyl Acetate

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ABSTRACT: A mixture of vinyl acetate, water and polyoxyethylene nonyl phenyl ether sodium sulfate (LWZ; Kao Co.) was irradiated with a high pressure mercury lamp in the absence of initiator at 0°C and high molecular weight poly(vinyl acetate) (PVAc) which gave poly(vinyl alcohol) (PVA) of P_n (average degree of polymerization) = 12800 after hydrolysis was obtained in good yield. Initiation by a radical from LWZ decomposed by photoirradiation was deduced. The characteristics of the PVA were similar to those of usual PVA.

KEY WORDS High Molecular Weight / Poly(vinyl alcohol) / Photo-Emulsion Polymerization / Vinyl Acetate / Non-Initiator /

Poly(vinyl alcohol) (PVA) fiber spun from high molecular weight PVA gel is expected to have high modulus and high strength.¹ However, it is very difficult to obtain PVA of high molecular weight, because chain transfer reactions control the molecular weight of polymers in radical polymerization of vinyl acetate (VAc), which are precursors for PVA. Moreover, degradation occurs by hydrolysis of branched poly(vinyl acetate) (PVAc) formed by chain transfer reaction.²

In order to obtain a high molecular weight polymer, emulsion polymerizations of VAc were examined at low temperature. In the course of study it was found that some of them gave PVA of which P_n (average degree of polymerization) was over 1×10^4 after hydrolysis of PVAc. A part of the results has been reported³⁾ and further detailed results are shown in the present paper.

EXPERIMENTAL

Materials

VAc was washed with aqueous solution of NaHSO₃ and water, dried over anhydrous CaCl₂ and distilled under reduced pressure of nitrogen. Distilled water was used as a medium. Poxoxyethylene nonyl phenyl ether sodium sulfate (LWZ; Kao Co.) and sodium dodecyl sulfate (SDS) were used as emulsifiers without further purification. Potassium persulfate (KPS) and 2,2-azobis(2-amidinopropane)-hydrochloride (AAPH) were purified by recrystallization and used as initiators.

Polymerizations

In a 30 ml Pyrex Kjeldahl flask were placed 5 ml of VAc, a fixed amount of emulsifier, 10 ml of water and a teflon stirring bar. In some cases small amounts of initiator were added. The mixture was degassed and the flask was sealed under vacuum. The flask was placed in a water-ethylene glycol bath ($-5 \sim 5^\circ\text{C}$), and the

mixture was stirred and irradiated with a high pressure mercury lamp (300, 313, and 365 nm) for 10 h. Then the mixture was poured into 150 ml of water, and with stirring Na_2SO_4 was added gradually until the emulsion broke and polymer precipitated. After filtration the PVAc was washed with water and dried under vacuum at 60°C.

Saponification of PVAc

To a solution of 2 g of PVAc in 100 ml of methanol was added 2.5 ml of 40% NaOH aqueous solution, and the mixture was stirred for 5 h at room temperature to yield PVA by saponification. The PVA was filtered, washed well with methanol and dried under vacuum at 60°C.

Acetylation of PVA

In a three necked flask were placed 1 g of PVA, 2 ml (25 mmol) of pyridine, 20 ml (0.2 mol) of acetic anhydride, and 20 ml (0.35 mol) of acetic acid. The mixture was stirred at 100°C for 24 h under nitrogen to afford PVAc. Then the mixture was poured into cool water and PVAc precipitated. The polymer was filtered, purified to repeat reprecipitation with methanol and water and dried under vacuum at 60°C.

Determination of P_n

P_n of PVAc was determined from the intrinsic viscosity ($[\eta]$) in benzene at 30°C according to eq 1. P_n of PVA was determined to be equal to that of acetylated PVA.

$$\log P_n = 3.31 + 1.61 \log [\eta] \quad (1)^4$$

$^1\text{H-NMR}$ Spectroscopy

The ^1H NMR spectra of PVA were measured by using a JEOL JNM GX-500. The triad tacticity, 1,2-glycol sequences and degree of saponification were determined from the spectra.

RESULTS AND DISCUSSION

Polymerization by Using KPS

Emulsion polymerizations of VAc were carried out at 5°C using KPS as an initiator by photo irradiation with a high mercury pressure lamp in a bath. As shown in Table I (1–4), polymers of $P_n = 7900$ –15600 were obtained in good yields. By saponification of the polymers, PVAs of $P_n = 4900$ –6300 were obtained.

Polymerization without Initiator

As shown in Table I(1–4), PVAc of smaller P_n was obtained at higher concentration of LWZ. Since it was considered that LWZ worked as an photo-initiator, emulsion polymerizations of VAc in the absence of initiator were examined at 5°C. As shown in Table I(5), PVAc was obtained in good yields, but P_n was not large. Then polymerization was examined at 5°C by irradiation with a lamp outside of the bath to decrease the illumination intensity. The yield decreased but P_n increased (Table I(6)).

In order to get PVAc of higher P_n , polymerization temperature should be lowered to decrease chain transfer reaction. Emulsion polymerizations by irradiation from outside of the bath were examined at 0°C without initiator. The results are listed in Table I(7–12), and showed that the yield increased with increasing LWZ amount up to 0.5 ml and reached to about 80% with more than 0.5 ml of LWZ. P_n of PVAc was 26300 at 0.1 ml of LWZ and decreased gradually with increasing LWZ amount. P_n of PVA was 12800 below the amount of LWZ of 0.1 ml and decreased gradually with increasing LWZ amount.

Dependence on Temperature

In order to decrease chain transfer reaction and to increase P_n of PVA, emulsion polymerization was carried out at –5°C. In this case, 2 g of NaCl was added in the emulsion to prevent freezing. By irradiation for 10 h, yield was 30% and P_n of PVAc and PVA were

Table I. Results of photo-emulsion polymerizations of VAc

Run	Initiator		Emulsifier		NaCl	Temp	Time	Yield	$P_n \times 10^{-4}$	
	Type	mol l ⁻¹	Type	ml	g	°C	h	%	PVAc	PVA
1 ^a	KPS	1.8×10^{-3}	LWZ	0.6	2	5	4	94.0	1.56	0.63
2 ^a	KPS	1.8×10^{-3}	LWZ	1.5	2	5	4	92.0	1.05	0.54
3 ^a	KPS	1.8×10^{-3}	LWZ	2.0	2	5	4	80.0	0.81	0.49
4 ^a	KPS	1.8×10^{-3}	LWZ	2.5	2	5	4	97.0	0.79	0.50
5 ^a	—	—	LWZ	1.5	0	5	4	96.0	0.91	0.58
6	—	—	LWZ	1.5	0	5	4	73.0	1.30	0.88
7	—	—	LWZ	0.05	0	0	10	34.5	2.10	1.28
8	—	—	LWZ	0.1	0	0	10	69.0	2.63	1.28
9	—	—	LWZ	0.3	0	0	10	65.3	2.10	1.24
10	—	—	LWZ	0.5	0	0	10	82.0	2.15	1.24
11	—	—	LWZ	0.7	0	0	10	82.3	1.88	1.04
12	—	—	LWZ	0.9	0	0	10	83.8	2.00	1.01
13	—	—	LWZ	0.1	2	0	10	17.3	0.87	0.78
14	—	—	LWZ	0.3	2	0	10	50.0	1.36	1.21
15	—	—	LWZ	0.5	2	0	10	70.0	1.51	0.99
16	—	—	LWZ	0.7	2	0	10	76.4	1.47	0.97
17	—	—	LWZ	0.9	2	0	10	71.2	1.83	0.94
18	—	—	LWZ	0.5	2	-5	10	30.8	1.37	1.28
19	—	—	SDS	0.05	0	0	10	0.0	—	—
20	—	—	LWZ	0.05	—	—	—	—	—	—
			+SDS	0.1	0	0	10	77.0	2.56	1.24
21 ^b	—	—	LWZ	1.5	2	0	10	0.0	—	—
22 ^b	AAPH	1.0×10^{-3}	LWZ	0.5	0	0	10	84.0	2.67	1.24
23 ^b	AAPH	1.0×10^{-3}	LWZ	0.5	2	0	10	74.1	2.36	1.10

^a Irradiated with a lamp inside of the bath, in the other cases irradiated with a lamp outside of the bath.^b Irradiated with 365 nm light through UV-DIB filter, in the other cases irradiated with 300, 313, and 365 nm light without filter.

13700 and 12800, respectively (Table I(18)). The values of P_n (PVA)/ P_n (PVAc) at 5, 0 and -5°C were 0.404 (Table I(1)), 0.656 (Table I(15)), and 0.934 (Table I(18)), respectively. The high value at -5°C showed that the chain transfer reaction to polymer hardly took place at -5°C. However, P_n s of PVAc and PVA were similar to those obtained at 0°C. The result suggested the influence of NaCl on the emulsion polymerization.

Effect of NaCl

Initially it was expected that PVAc with larger P_n would be obtained because the addition of NaCl decreases concentration of VAc in water and polymerization in micell occurs predominantly. However, as shown in

Table I(13—17), NaCl did not improve yield and P_n but retarded them. The marked retardation at low LWZ concentration suggested that NaCl made micell unstable. So it was found that NaCl was of no use except for an antifreezing reagent.

Effect of SDS

As above mentioned, PVAc of large P_n was obtained at low LWZ concentration because of decreasing of initiation rate by LWZ. In order to decrease LWZ amount and to keep emulsion stable, SDS, which can not initiate the emulsion polymerization by photo-irradiation (Table I(19)), was added. As shown in Table I(7 and 20), the yield became twice by the addition of 0.1 ml of SDS, and P_n of PVAc

Figure 1. ^1H NMR spectra of PVA obtained through photo-emulsion polymerization measured in $\text{DMSO}-d_6$ (a) and in $\text{DMSO}-d_6$ in the presence of trifluoroacetic acid.

increased a little but P_n of PVA was not changed. (Table I(21–23)).

Dependence on Wavelength

Although PVAcS were obtained in good yield by irradiation with 365, 313, and 300 nm lights in the absence of an initiator, no polymerization occurred with 365 nm light through a filter (UV-DIB; Toshiba Co.). So 365 nm light is not effective in the photo-emulsion polymerization of VAc in the absence of initiator. However, when AAPH (water soluble azo-compound) was added, PVAcS of large P_n were obtained in good yield by irradiation with 365 nm light

Characteristics of PVA

The characteristics of the typical PVA obtained as above were analyzed as following. The ratios of triad tacticity were estimated as 22.1, 49.5 and 28.4% for isotactic, heterotactic and syndiotactic triad, respectively, from the three peaks in the OH proton spectrum shown in Figure 1(a). The ratio of 1,2-glycol structure was estimated to be about 1% from the ratio of the intensity of methine proton of the structure at 3.3 ppm to that of methylene proton at 1.5 ppm in Figure 1(b) observed in

Figure 2. UV-spectra of VAc, 1; Pyrex glass, 2; LWZ, 3; AAPH, 4.

the presence of trifluoroacetic acid. The degree of saponification was estimated to be 99.7% from the ratio of the intensity of acetyl proton at 2 ppm to that of methylene proton in Figure 1(b). These values of characteristics are similar to those of PVA obtained usually through radical polymerization of VAc.

On the Initiation Mechanism

As above described polymerization took place by irradiation with 313 and 300 nm lights in the absence of initiator, when LWZ was used as an emulsifier. But, when SDS was used as an emulsifier, polymerization did not take place. These facts indicated that vinyl acetate monomer did not initiate but LWZ initiated the photo-emulsion polymerization. So we considered the initiation mechanism as following: LWZ has a very low absorbance at 313

and 300 nm (Figure 2) and hardly decomposes by irradiation. However, once it decomposes, the hydrophilic part is pulled out into the aqueous phase, and another hydrophobic part is pulled into monomer phase in the micelle to initiate polymerization efficiently. Radicals are too few to terminate and P_n of PVAc is controlled mainly by chain transfer reaction. As the results, PVAc of large P_n is obtained, but the initiation mechanism has not been well clarified. We are investigating the initiation mechanism and will present it elsewhere.

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