Saponification of High Molecular Weight Poly(vinyl pivalate)

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ABSTRACT: The saponification of high molecular weight poly(vinyl pivalate) (PVP) was examined in several solvents, and PVA of $P_n = 18000$ and 99%DS (degree of saponification) were obtained by saponification in the absence of oxygen with KOH (6 equivalents per monomer unit) in tetrahydrofuran at 60°C for 15 min. In acetone, dioxane and methyl ethyl ketone, saponification was performed but marked degradation was observed. Saponification in benzene and dimethyl sulfoxide did not take place. NaOH was not useful because it cause marked degradation in any solvent.

KEY WORDS Saponification / High Molecular Weight / Poly(vinyl pivalate)
/ Poly(vinyl alcohol) / Solvent Effect /

Poly(vinyl pivalate) (PVP) having larger P_n (average degree of polymerization) than 2×10^4 was obtained as described previously,¹ and was expected to afford high molecular weight poly(vinyl alcohol) (PVA). Although a few studies have been reported on the saponification of PVP,² it is very difficult to saponify PVP by these methods. New methods of saponification were examined and a good one was found as described in the present paper.

EXPERIMENTAL

Poly(vinyl pivalate)

In a 300 ml Pyrex Kjeldahl flask 100 ml of vinyl pivalate (VP), 10 ml of LWZ (polyoxyethylene nonyl phenyl ether sodium sulfate, Kao Co.), 200 ml of water and a teflon stirring bar were combined. The mixture was degased and the flask was sealed under vacuum. Then the flask was placed in a water-ethylene glycol bath at 0°C, and with stirring the mixture was

irradiated with a high pressure mercury lamp. After 70 h of irradiation, the mixture was poured into methanol and PVP precipitated. After filtration, the PVP was reprecipitated from methyl ethyl ketone and water, and was dried under vacuum at 60°C.

Saponification of PVP

In a 300 ml separable flask equipped with a reflux condenser and a dropping funnel 2.0 g of PVP was dissolved in 200 ml of each solvent. The solution and 20 ml of 25% KOH (or 18% NaOH) methanol solution in a dropping funnel were flushed with nitrogen. With stirring, the KOH solution was added slowly to the PVP solution and the mixture was kept at a fixed temperature (Table I) under nitrogen. The first precipitate appeared within 10 min, and after a fixed time (Table I) the precipitate was filtered, washed with methanol and dried under vacuum.

Table I. Results of saponification of poly(vinyl pivalate)

Run	Solvent	Base ^a	Reaction temp/°C	Reaction time/min	DS/% ^b		P_n^c	
					I ^e	II ^d		
1	Acetone	NaOH	60	15	87	87.8	2010 ^f	
2				30	99		2200 ^f	
3		KOH		15	94		9240 ^f	
4				30	100		8350 ^f	
5	Benzene	KOH	60	15	—	2.0	—	
6	Dimethyl sulfoxide	KOH	60	15	0	97.8	—	
7	Dioxane	KOH	60	15	97		4100	
8	Methyl ethyl ketone	KOH	60	15	99		99.7	8200
9	Tetrahydrofuran	KOH	60	10	97	99.0	17800	
10				15	99		10600 ^f	
11				15	99		18000	
12				20	99		17000	
13				30	99		10600 ^f	
14			50	10	80		83.0	18100
15				20	92		18700	
16				30	99		15800	
17				40	99		13200	
18			40	30	93		13300	
19				40	96		13500	
20				50	98		14800	
21				60	99		13500	
22		NaOH	60	30	83		14500 ^f	
23				60	95		9900 ^f	
24				90	95		8850 ^f	
25				120	94		8490 ^f	

^a Base amount: 6 equivalent per monomer unit mole.^b Degree of saponification.^c Determined from weight loss.^d Determined from ¹H NMR spectrum.^e Estimated from $[\eta]$ of acetylated (saponified PVP).^f P_n of PVP is 25800, and that of the others is 28300.

Acetylation of PVA

One 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 were added to a three-necked flask and with stirring, the mixture was kept at 100°C for 72 h. The mixture was poured into cool water and PVAc was precipitated. The PVAc was filtered, reprecipitated from methanol and water, and dried under vacuum at 60°C.

Characteristics

P_n s of PVP and PVAc(acetylated PVA) were determined from the intrinsic viscosity ($[\eta]$)

measured in acetone at 25°C and in benzene at 30°C, respectively.³

The degree of saponification (DS) was determined by weight loss after saponification and by the ratio of the *tert*-butyl proton and methylene proton peaks in the ¹H NMR spectrum of PVA (Figure 1).

RESULTS AND DISCUSSION

Degree of Saponification and P_n

The values of DS determined by weight loss are in good agreement with those determined by NMR (Table I), and these values are

Figure 1. ^1H NMR spectra of PVA from PVP: (a) saponified with NaOH in acetone for 15 min at 60°C and (b) saponified with KOH in tetrahydrofuran for 30 min at 60°C .

considered valid.

As the values of P_n were estimated as PVAc from $[\eta]$ of acetylated polymer. P_n s at low DS might not be valid, because the polymer had many pivalate groups. However, P_n s of well saponified PVA are considered valid.

Saponification in Acetone

P_n s of PVPs used for saponification were 25800 and 28300. Initially, we tried to saponify PVP according to Nozakura's method [2], but the mixture became dark brown and marked degradation occurred, i.e. after one week reaction, P_n decreased from 25800 to 2000. Moreover complete saponification could not be attained. Then we tried the method of Imai *et al.*,⁴ but PVP saponified was low. The reduction of PVP with LiAlH_4 was possible but difficult to remove the Li and Al compounds.

The above saponification was carried out in the presence of oxygen. Saponification in the absence of oxygen was examined by flushing the system with nitrogen gas. Initially, the

saponification of PVP was carried out in acetone under nitrogen by using NaOH as a base at 60°C , and 99% DS was attained in 30 min without discoloration. However, P_n of the PVA obtained decreased to 2200 (Table I, 2). Using KOH as a base, saponification was almost complete, and P_n of PVA was high (Table I, 4).

Solvent Effect

To obtain PVA with higher P_n , other solvents were examined. Saponification was poor in benzene and dimethyl sulfoxide under nitrogen with KOH at 60°C (Table I, 5, 6). Although high DS was attained in methyl ethyl ketone and dioxane in 15 min, degradation occurred (Table I, 7, 8). When tetrahydrofuran was the solvent, high DS and high P_n were found.

Saponification in Tetrahydrofuran

In tetrahydrofuran, 99% DS was attained in 15 min under nitrogen with KOH at 60°C , and P_n of PVA was 18000 (Table I, 11). Although degradation after completion of saponification was not as high as in acetone, some was observed (Table I, 12). Thus, it is better to stop the reaction quickly.

Shiraishi *et al.*⁵⁾ reported oxidative scission of the main chain of PVA in base. In these experiments, we propose that residual oxygen also causes degradation. To decrease oxygen that causes degradation, saponification at lower temperature was examined. However, it took 30 and 60 min to attain 99% DS at 50 and 40°C , respectively, and PVA of higher P_n could not be obtained (Table I, 16, 21). These results show that low activation energy for degradation, high reaction temperature, and short reaction time are favorable.

Base Type and Concentration

Saponification with NaOH in tetrahydrofuran at 60°C was unsatisfactory, because DS was only 95% even after 120 min and degradation occurred (Table I, 22–25).

Saponification with 1, 2, 3 or 6 equivalents

Table II. Dependence of saponification of PVP^a on KOH concentration in tetrahydrofuran at 60°C

KOH equivalent	DS/% ^b	P_n
1.0	21	—
2.0	50	—
3.0	95	16060
6.0	99	18000

^a P_n of feed PVP is 28300.^b Determined from weight loss in 15 min.

of KOH was examined to determine the effect on degradation (Table II).

Saponification with 1 and 2 equivalents was very slow, 3 equivalents were better but P_n was lower than that with 6 equivalents.

CONCLUSION

Saponification of high molecular weight PVP was performed at 60°C in 15 min with 6 equivalent of KOH per monomer unit in tetrahydrofuran in the absence of oxygen and

PVA with $P_n = 18000$ was obtained. The main problem is oxidation which prevents complete saponification and causes degradation.

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