

SHORT COMMUNICATIONS

Preparation and Saponification of High Molecular Weight Poly(vinyl pivalate)

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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 frequent chain transfer reaction occurs in the radical polymerization of vinyl acetate (VAc) as the precursor of PVA. By suppressing the chain transfer reaction of VAc, *i.e.* by a photo-emulsion polymerization at 0°C, we could obtain high molecular weight PVAc which afforded PVA of \bar{P}_n (average degree of polymerization) higher than 1×10^4 after saponification.² In the present study, the same low temperature polymerization, but of more stable monomer for the chain transfer has been investigated.

Vinyl pivalate (VP) was used as a monomer to reduce chain transfer reaction, and carried out photo-emulsion polymerization of VP in the absence of any added initiator as following. In a 30 ml Pyrex Kjeldahl flask were placed 5 ml of VP, a fixed amount of emulsifier, 10 ml of water and a teflon stirring bar. LWZ (polyoxyethylene nonyl phenyl ether sodium sulfate, Kao Co.) was used as an emulsifier. The mixture was degassed and the flask was sealed under vacuum. Then the flask was placed in a water-ethylene glycol bath at

0°C, and the mixture was being kept stirring and irradiated with a high pressure mercury lamp for 10 h. The emulsion was stable throughout. Then the mixture was poured into 150 ml methanol and PVP (poly vinyl pivalate) precipitated. After filtration, the PVP was reprecipitated from methyl ethyl ketone and water, and was dried under vacuum at 60°C.

The values of monomer conversion are listed in Table I. Monomer conversion increased

Table I. Results of photo-emulsion polymerizations^a of vinyl pivalate without addition of initiator at 60°C

LWZ ^b	Conversion	$\bar{P}_n \times 10^{-4}$
ml	%	
0.1	16.1	3.07
0.2	23.6	2.88
0.3	32.8	3.25
0.4	27.5	3.29
0.5	55.5	3.46
0.6	43.3	3.48
0.7	26.8	2.98
0.8	19.8	2.87
0.9	32.6	2.51
1.0	23.8	2.44

^a Vinyl pivalate, 5 ml; H₂O, 10 ml; irradiation, 10 h.

^b 35% aqueous solution.

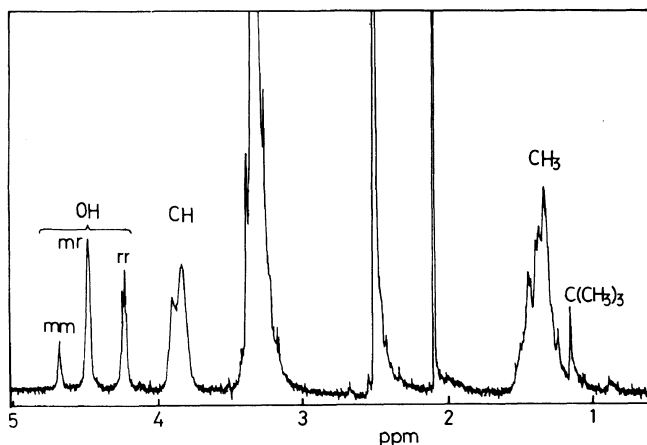


Figure 1. ^1H NMR spectrum of PVA obtained from PVP by saponification.

with increasing LWZ up to 0.5 ml and decreased gradually with increasing LWZ.

\bar{P}_n of PVP was determined from the intrinsic viscosity ($[\eta]$) measured in acetone at 25°C and the values were listed in Table I. \bar{P}_n increased with increasing LWZ up to 0.6 ml and decreased with increasing LWZ. PVP of $\bar{P}_n = 34800$ is expected to afford PVA of higher \bar{P}_n than that derived from PVAc.

A few studies have been reported on saponification of PVP.³ However, it is very difficult to saponify the PVP by these methods. Some new methods of saponification were examined and a good one was found as follows. In a 300 ml separable flask were placed 2.0 g of PVP ($\bar{P}_n = 25800$) and 200 ml of tetrahydrofuran, and PVP was dissolved. Then the solution and 20 ml of 25% KOH methanol solution in a dropping funnel were flushed with nitrogen. With stirring, the KOH solution was added to the polymer solution gradually and the mixture was stirred at 60°C for 15 min under nitrogen atmosphere. In the first 10 min precipitate appeared. The precipitate was filtered, washed with methanol and dried under vacuum.

^1H NMR spectrum of the polymer is shown in Figure 1. The degree of saponification was found to be about 99% from the figure and the weight loss by saponification. From the triplet

peaks of OH proton, the ratios of isotactic, heterotactic, and syndiotactic triad of the polymer were determined to be 11.3, 49.4, and 39.3%, respectively. The syndiotactic triad is higher than that (30%) of PVA prepared from PVAc.

The PVA was acetylated by the same manner described in the previous paper² and $[\eta]$ of acetylated PVA (PVAc) was determined in benzene at 30°C . \bar{P}_n of the PVAc thus obtained was 12580. A more detailed description will be presented in the future.

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