

SHORT COMMUNICATIONS

Preparation of High Molecular Weight Poly(vinyl alcohol)

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Since Kevlar was produced by Du Pont, new polymer materials which will take its place have been developed. Polyethylene fiber spun from ultra-high molecular weight polyethylene gel was reported by Pennings¹ and Smith *et al.*² Poly(vinyl alcohol) (PVA) fiber spun from high molecular weight PVA gel is also expected to have a high modulus and high strength from Sakurada's results.³ 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 reactions.⁴

Emulsion polymerizations of VAc were carried out at low temperature to obtain high molecular weight polymer. In the course of study it was found that some of them gave PVA of larger P_n (average degree of polymerization) than 1×10^4 after hydrolysis of PVAc obtained. This method is simple and described below.

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. 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 stirred and irradiated at 313 nm from a high pressure mercury lamp for 10 h. The emulsion was very stable throughout. After polymerization, the mixture was poured into 150 ml of water and with stirring Na₂SO₄ was added gradually until the emulsion broke and PVAc precipitated. After filtration the PVAc was washed well with water and dried under vacuum at 60°C.

To 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. The PVA was filtered, washed well with methanol and dried under vacuum at 60°C.

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 give PVAc. The mixture was poured into cool water and PVAc precipitated. The PVAc was filtered, purified to repeat reprecipitation from methanol and water and dried under vacuum at 60°C.

Table I. Results of emulsion polymerization by photo-irradiation of the LWZ/VAc/H₂O system^a at 0°C

LWZ ^b (ml)	Conversion (%)	$P_n \times 10^{-4}$ (PVAc)	$P_n \times 10^{-4}$ (PVA)
0.05	34.5	2.10	1.28
0.3	65.3	2.10	1.24
0.5	82.0	2.15	1.24
0.7	82.3	1.88	1.04
0.9	83.8	2.00	1.01

^a VAc, 5 ml; H₂O, 10 ml.^b 35% aqueous solution.

The P_n of PVAc was determined from the intrinsic viscosity ($[\eta]$) in benzene at 30°C.⁵ P_n of PVA was determined to be equal that of acetylated PVA. These results are also listed in Table I.

As shown in Table I monomer conversion increased with increasing LWZ up to 0.5 ml and reached 80% with more than 0.5 ml of LWZ. P_n of PVAc was over 2×10^4 in these cases and decreased gradually with increasing LWZ. P_n of PVA was over 1.0×10^4 in these cases and decreased gradually from 1.28×10^4

with increasing LWZ.

High molecular weight PVA was obtained easily by 313 nm irradiation of the LWZ/VAc/H₂O system, but the mechanism of initiation is not clear. However, in an LWZ/VAc/methanol system (homogeneous system) no polymerization was observed by 313 nm irradiation for 10 h at 0°C and by heating at 60°C for 10 h. So it is considered that initiation by impurities in LWZ is not so important. A more detailed description will be presented in the future.

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