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A Convenient Method for the Preparation of Poly(Vinyl Alcohol) from Poly(*t*-Butyl Vinyl Ether)

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t-Butyl vinyl ether, like benzyl vinyl ether and trimethylsilyl vinyl ether, is known as a starting monomer for the synthesis of isotactic poly(vinyl alcohol). Poly(*t*-butyl vinyl ether) has been converted into poly(vinyl alcohol) by two methods. Fujii *et al.* converted poly(*t*-butyl vinyl ether) into ploly(vinyl acetate) by direct acetylation reaction with acetic anhydride and Lewis acid; they then saponified the resultant poly(vinyl acetate) to poly(vinyl alcohol).[1] Okamura *et al.* converted poly(*t*-butyl vinyl ether) into poly(vinyl alcohol) by the cleavage reaction of the ether bond with dry hydrogen bromide[2] in a manner similar to that used in the case of poly(benzyl vinyl ether).[3] However, since the reaction conditions are rather drastic, more or less colored poly(vinyl alcohol) specimens are usually obtained.

The present authors wish to report a more convenient method for the preparation of poly(vinyl alcohol) from poly(*t*-butyl vinyl ether) using a 46% aqueous solution of hydrogen fluoride. By this method, the procedure can be extremely simplified and colorless poly(vinyl alcohol) can be obtained.

t-Butyl vinyl ether was polymerized with $BF_3 \cdot O(C_2H_5)_2$ as an initiator in toluene at −78°C under a nitrogen atmosphere. ($[M]_0=20$ vol%, $[Cat]=2\times10^{-3}$ mol/*l*). These reaction conditions are known to yield an isotactic poly(*t*-butyl vinyl ether). The resultant polymer was purified by reprecipitation into methanol from a toluene solution. The polymer thus obtained had an intrinsic viscosity $[\eta]$ of 0.356 (d*l*/g) in benzene at 30.4°C.

Found: C, 71.97; H, 12.03%. Calcd for $C_6H_{12}O$: C, 71.94; H, 12.08%.

The cleavage reaction of the polymer into poly(vinyl alcohol) was carried out in a polyethylene beaker. To 0.355 g of poly(*t*-butyl vinyl ether), 5 m*l* of a 46% aqueous solution of hydrogen fluoride was added. The reaction mixture was kept standing at room temperature and shaken occasionally. After 1 hr, the reaction mixture became homogeneous; it was kept standing for 2 more hours. The solution was then subjected to dialysis using a cellophane membrane. The dialyzate was freeze-dried to give 0.123 g of colorless poly(vinyl alcohol).

The poly(vinyl alcohol) obtained had a specific viscosity, η_{sp}, of 0.515 for a 0.905 g/d*l* aqueous solution at 30.0°C.

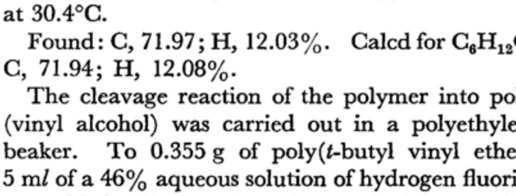

Fig. 1. Infrared spectra of isotactic (a) and atactic (b) poly (vinyl alcohol) prepared from poly(*t*-butyl vinyl ether).

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[1] K. Fujii and R. Mochizuki, *Kobunshi Kagaku* (*Chem. High Polymers, Japan*), **19**, 124 (1962).

[2] S. Okamura, T. Kodama and T. Higashimura, *Makromol. Chem.*, **53**, 180 (1962).

[3] S. Murahashi, H. Yuki, T. Sano, U. Yonemura, H. Tadokoro and Y. Chatani, *J. Polymer Sci.*, **62**, 77 (1962).

Found: C, 54.26; H, 9.14%. Calcd for C_2H_4O: C, 54.53; H, 9.15%. The results of elementary analysis make it clear that pure poly(vinyl alcohol) was obtained by this method. The infrared spectrum of a film prepared from an aqueous solution of the resultant poly(vinyl alcohol) showed that the conversion was complete; it coincided with that of the isotactic poly(vinyl alcohol) obtained previously.[4]

Atactic poly(vinyl alcohol) was similarly obtained from atactic poly(*t*-butyl vinyl ether), which had itself been obtained with $BF_3 \cdot O(C_2H_5)_2$ in methylene chloride at $-78°C$ ($[M]_0 = 20$ vol%, $[Cat] = 2 \times 10^{-3}$ mol/*l*).

The infrared spectra of the isotactic and atactic poly(vinyl alcohol) thus obtained are shown in Fig. 1.

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[4] S. Murahashi, S. Nozakura and M. Sumi, *J. Polymer Sci.*, *B*, **3**, 245 (1965).