Imidazolymethylation of Poly(vinyl alcohol) by Chloromethylimidazole

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Recently, imidazole-containing polymers have been investigated as functional polymers. Synthesis of such polymers by introducing imidazole groups to the side chains of host polymers may be preferable to the procedure of copolymerization of imidazole-containing monomers. This is because it is possible to obtain polymers of various imidazole contents without altering the degree of polymerization. It was tried to introduce an imidazole group into the neutral water-soluble polymer poly(vinyl alcohol) (PVA), although the Williamson reaction of 4(5)-chloromethylimidazole with sodium alkoxide was reported not to be successful.¹ This paper describes the method to obtain imidazolymethylated PVA as follows. 4(5)-chloromethylimidazole was allowed to react with PVA in the aprotic polar solvent *N,N*-dimethylformamide (DMF).

EXPERIMENTAL

Materials

PVA (DP 2000) and PVA (DP 500) were purchased from Wako Pure Chemical Industries, Ltd., and from Nakarai Chemicals, Ltd., respectively. Their molecular weights, measured by the viscometric method,² were 85,300 and 22,600. 4(5)-Chloromethylimidazole hydrochloride was prepared according to the method of Turner, *et al.*¹

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4(5)-Imidazolymethylation of PVA

PVA was dissolved in DMF at the concentration of 1% with the aid of heat. 4(5)-Chloromethylimidazole hydrochloride was added to the solution; the molar ratios of this to the hydroxyl group of PVA ranged from 0.5 to 5. The mixture was heated at 85°C in a sealed tube under N_2 . The reaction product was poured into a Visking cellulose tube (size 24/32) and dialyzed against water for 48 hr. From the clear solution, a white or pale yellow spongy product was obtained by freeze-drying. The extent of substitution was calculated from the nitrogen content measured by a Yanaco CHN-corder (type MT-2).

Measurement of ^{13}C -NMR Spectra

^{13}C -NMR spectra were acquired on a Japan Electron Optics Laboratory JNM-FX 60 spectrometer, which is of Fourier transform type, operating at 15.04 MHz. The spectra was measured by $\pi/4$ pulses with complete proton decoupling; free induction decay signals of the repeating pulses were accumulated and Fourier transformed by the built-in computer (JEC-980A).

RESULTS AND DISCUSSION

4(5)-Imidazolymethylation of PVA

Table I shows the extent of substitution when PVA and 4(5)-chloromethylimidazole hydrochloride were heated at 85°C for 1 to 5 days in DMF. It was reported that an attempt to prepare ethers by treating the 4(5)-chloromethyl-

Figure 1. Schematic representation of imidazolymethylation of PVA.

Table I. Extent of imidazolymethylation^a

Sample no.	DP	Moles of chloromethyl-imidazole added, per OH of PVA	Reaction time, day	Extent of substitution, %
1	2000	1	1	19.0
2	2000	1	2	28.2
3	2000	1	3	31.9
4	2000	1	4	36.4
5	2000	1	5	37.7
6	2000	0.5	5	18.3
7	2000	5	5	51.4
8	500	1	1	21.5
9	500	5	5	37.0

^a The concentration of PVA in DMF was 1 % and the reaction temperature was 85°C.

imidazole hydrochloride with sodium alkoxides was not successful and only resinous substances resulted.¹ In our experiment, it seems that an ether bond was formed with the aid of DMF functioning as a weak base, as shown in Figure 1. When a similar aprotic polar solvent, dimethyl sulfoxide, was used, a dark brown precipitate was obtained; this was insoluble in water and in every organic solvent tested.

¹³C NMR Spectroscopy

¹³C NMR spectra of 4(5)-imidazolymethyl PVA, PVA and 4(5)-hydroxymethylimidazole hydrochloride are shown in Figure 2; the assignment of each signal is indicated in the figure. In the case of 4(5)-hydroxymethylimidazole (A), the signal at 54.6 ppm was assigned to the methylene carbon and signals at 117.7, 133.5, and 135.0 ppm were assigned to the carbons of imidazole ring. The methylene carbon of PVA shows a broad peak at 45.4 ppm. The signals assigned to the methine carbon of PVA were

Figure 2. ¹³C NMR spectra of imidazolymethylated PVA and related compounds. Samples were as follows: (A) hydroxymethylimidazole hydrochloride, 20 %; (B) PVA (DP 500), 25 %; (C) imidazolymethyl PVA (Sample No. 9 in Table I), 10 % (each was in D₂O). Numbers of pulses accumulated were 4,000 (A), 3,000 (B), and 15,000 (C).

split into three peaks (69.1, 67.5, 66.2 ppm) owing to microtacticity; these peaks were assigned by Inoue, *et al.*,³ to *mm*, *mr*, and *rr* triads with increasing field strength. The signal corresponding to methyl carbon (22.0 ppm) is probably due to an unsaponified acetyl group; the ratio of its peak area to that of methylene carbon was about 13%. Even though, in the case of ¹³C NMR spectra, the peak area is not accurately proportional to the number of the atoms, this value coincides with the saponification value specified by the maker (84–89%). The signal corresponding to the carbonyl carbon will appear at about 170 ppm, which is out of the measured range. Judging from the spectra of poly(vinyl acetate),³ the signals attributed to the methine carbons of unsaponified and saponified parts overlapped, and the trailing of the peak of methylene carbon at about 41–43 ppm is probably due to the methylene carbon of the unsaponified part. In the spectrum of the reaction product (C), the signals corresponding to the carbons of imidazole ring (118.4, 131.4, 135.2 ppm), and similar peaks corresponding to the signals of PVA (45.5, 65.7, 66.9, 68.3 ppm) are seen. In addition to these signals, three

peaks at 74.9, 61.2, and 42.3 ppm appeared. By the empirical rule that the δ value of ethereal α -carbon is higher by about 5 ppm compared with that of corresponding alcoholic α -carbon and the δ value of ethereal β -carbon is lower by about 4 ppm,⁴ these signals were assigned as follows. The signal at 61.2 ppm corresponded to the methylene carbon connecting the oxygen atom and the imidazole ring. The signals at 74.9 and 42.3 ppm were assigned to the methine carbon adjacent to ethereal oxygen and to the neighboring methylene carbons, respectively. These assignments are consistent with the structure assumed in Figure 1.

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