Determination of 1,2-Glycol Linkages in Poly(vinyl alcohol) by 400 MHz ^1H -NMR and ^{13}C -NMR

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The determination of 1,2-glycol linkages in poly(vinyl alcohol), PVA, is important because such an irregular bonding produces serious undesirable effects on the properties of PVA. The chemical assay method¹ has usually been adopted for this determination, but some new method of nondestructive determination has long been sought. NMR is one of the potential methods of nondestructive analysis, but the 200 MHz spectrometer has been found insufficient for the purpose. This report will show that 400 MHz ^1H - and 100 MHz ^{13}C -NMR are useful for the determination of the concentration of 1,2-glycol linkages.

Three types of PVA samples were used for the present work. Sample A was an alkali-hydrolysis product of poly(vinyl acetate), PVAc, which has been polymerized at 60°C, and is commercially available from Kuraray Co., Ltd.. Samples B and C were derivatives of PVAc synthesized from vinyl acetate, VAc, in an alcohol solution. Sample B was obtained in methanol at -78°C in the presence of an initiator of triethyl borane, and Sample C in ethanol at 200°C without an initiator. In any analysis by NMR, it is essential to have appropriate reference compounds. In the present investigation, model compounds of 2,3-hexandiol, 1,3-4(threo)-hexanetriol, 1,3-4(erythro)-hexanetriol and 2,5-hexanediol were used as the references. They were synthesized in our laboratory or were purchased, if available.

The PVA samples were dissolved in dimethyl sulfoxide- d_6 (DMSO- d_6). Their ^1H -NMR spectra were obtained at 60°C on a JEOL GX-400 NMR spectrometer operating at 400 MHz. Solutions of PVA in deuterium oxide, D_2O , were used as the samples for the measurements of 100 MHz ^{13}C -NMR, which were carried out at 80°C. The concentration of PVA was set at 5 wt/vol.% for the DMSO- d_6 solutions and at 20 wt/vol.% for the D_2O solutions. Tetramethyl silane, TMS, was added as the internal standard to the DMSO- d_6 solution and sodium 3-trimethyl silylpropionate, TSP, to the D_2O solution. The NMR spectra were measured under the following conditions: data points, 32K; spectral width, 8K for ^1H and 10K for ^{13}C ; flip angle, 45°; pulse interval, 3 s; number of scans, 32 for ^1H and 20000-40000 for ^{13}C .

The 400 MHz ^1H -NMR spectrum of PVA-A dis-

solved in DMSO- d_6 is shown in Fig. 1, where the hydroxyl proton signals were removed from the observable range by adding a few drops of trifluoroacetic acid(TFA) to the solution. Since the signals related to the 1,2-glycol linkages, which appeared in the chemical shift regions 0.8-1.3 and 3.0-3.8 ppm, were very small, the partly expanded spectra are also shown in the figure.

The 100 MHz ^{13}C -NMR signals corresponding

Fig. 1 400 MHz ^1H -NMR spectra of PVA and its model compounds of irregular structure in PVA.

Fig. 2 100 MHz ^{13}C -NMR spectrum of PVA-C in D_2O , increased amplitude showing only 1,2-glycol linkage.

Table 1 Contents of the 1,2-glycol units per 100 monomer units

Sample	Terminal	Inner positions	Total
A	1.53	0.17	1.70
B	0.67	0.11	0.78
C	2.60	0.50	3.10

to the 1,2-glycol linkages are small in intensity for all samples. The latter signals were enhanced as shown in Fig. 2 for sample C. Signal assignment was made according to the data of the previous papers.^{2,3} Splitting of the carbon signals in the figure may suggest the presence of some configuration effect which is produced by the surrounding atoms on the 1,2-glycol linkage. By the signal intensity

measurements, the contents of the 1,2-glycol units located at the terminal and the inner positions of a polymer chain were evaluated and are listed in Table 1. The sum of the values for sample A approximately agrees with the total value of the 1,2-glycol linkage determined by the chemical assay method of periodic acid titration. More details will be reported later.

References

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