High Resolution NMR Spectra of Stereoregulated Polyvinyl Alcohol

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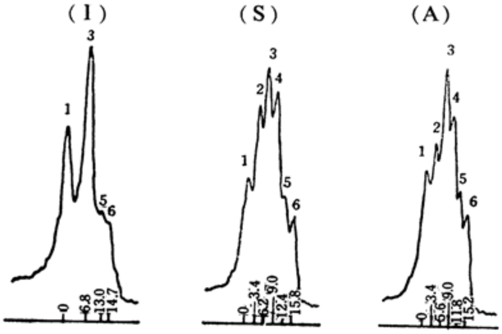
In order to study the stereoregulated structure of polyvinyl alcohol (PVA), the high resolution NMR spectra of PVA dissolved in heavy water (about 3% PVA in weight) were examined. The samples used in the present work were isotactic rich (I), syndiotactic rich (S) and atactic PVA (A). The sample I obtained from poly-*tert*-butyl ether, and S from polyvinyl formate which was polymerized from vinyl formate at −78°C. The sample A was prepared from thermally polymerized polyvinyl acetate. NMR measurements were made with a Varian V-4300-C spectrometer operating at 56.4 Mc.

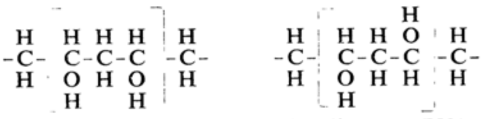
The spectra of PVA consist of three signals corresponding to the three nonequivallent proton groups, namely, methylene, methine and hydroxyl groups. Among them, the hydroxyl proton signal appears in the lowest magnetic field at room temperature, shifts remarkably to higher magnetic field with increasing sample temperature (about 0.6 p. p. m. over the temperature range from 24 to 110°C). This shift is believed to be assigned to breaking of hydrogen bond⁽¹⁾. The methine signal is seen in the magnetic field higher than that for hydroxyl signal at room temperature. However, its structure can not be resolved separately from hydroxyl signal in higher temperature, as the shift of hydroxyl signal results an overlapping on the methine signal. Finally, methylene signal appears in the highest magnetic field. Raising the temperature of sample makes the methylene signal narrower, and gives a hyperfine structure above 70°C. It is clear that the above narrowing is due to the more free segmental motion of PVA molecule at higher temperature.

The methylene signals obtained at 110°C show different patterns depending on the structures of the stereoregulated PVA molecules as shwon in Fig. 1. In this figure, the spectrum I, S and A stand for isotactic rich, syndiotactic rich and atactic PVA, respectively. In the isotactic rich PVA the peaks 1 and 3 are predominant, while in the syndiotactic rich PVA other peaks 2, 4 and 6 are also observed. The syndiotactic rich PVA used in the present work was so abundant in isotactic structure that the difference between the spectrum S and A was not so markedly.



Relative line positions measured from the lowest peak, c./sec.

Fig. 1. Spectra of methylene group of stereoregulated PVA at 110°C. The spectrum I, S and A stand for isotactic rich, syndiotactic rich and atactic PVA, respectively.



$$\begin{array}{ccccc} \mathrm{H} & \mathrm{H} & \mathrm{H} & \mathrm{H} & \mathrm{H} \\ -\mathrm{C}- & \mathrm{C}- & \mathrm{C}- & \mathrm{C} & -\mathrm{C}- \\ \mathrm{H} & \mathrm{O} & \mathrm{H} & \mathrm{O} & \mathrm{H} \\ & \mathrm{H} & & \mathrm{H} & \end{array} \qquad \begin{array}{ccccc} & & & \mathrm{H} & \\ \mathrm{H} & \mathrm{H} & \mathrm{H} & \mathrm{O} & \mathrm{H} \\ -\mathrm{C}- & \mathrm{C}- & \mathrm{C}- & \mathrm{C} & -\mathrm{C}- \\ \mathrm{H} & \mathrm{O} & \mathrm{H} & \mathrm{H} & \mathrm{H} \\ & \mathrm{H} & & & \end{array}$$

Isotactic PVA Syndiotactic PVA

Fig. 2. Structure of the ideal isotactic and syndiotactic PVA.

As shown in Fig. 2, cis- and trans-configurations of a proton and a hydroxyl group around -C-C- chain are most remarkable difference between the isotactic and the syndiotactic PVA molecule as far as ideal structures concern. In a PVA molecule, two protons of a given methylene group are affected both by the spin-spin interaction with the proton of the methine and by the magnetic anisotropic effect of the hydroxyl group⁽²⁾. Therefore, it is explained that the differences in both effects mentioned above bring about the difference in hyperfine structures observed. Details of the work will be published in the near future in this journal.

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1) J. A. Pople, W. G. Schneider and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance", McGraw-Hill Book Co., New York, (1959), p. 400.

2) M. Karplus, *J. Phys. Chem.*, **64**, 1793 (1961).