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Title	Solid-State 13C and 1H NMR Analyses of Hydrogen Bonding and the Conformation of Poly(vinyl alcohol) (FUNDAMENTAL MATERIAL PROPERTIES-Molecular Motion Analysis)
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Solid-State ^{13}C and ^{1}H NMR Analyses of Hydrogen Bonding and the Conformation of Poly(vinyl alcohol)

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CP/MAS ^{13}C NMR analyses have been made for different frozen solutions of poly(vinyl alcohol) (PVA) samples with different tacticities. The CH resonance lines of the frozen PVA solutions split in different ways significantly depending on the tacticities and the solvents. These CH resonance lines are well resolved into 9 constituent lines whose chemical shifts are estimated by assuming the downfield shifts due to intramolecular hydrogen bonding and the upfield shifts induced by the γ-*gauche* effect. Furthermore, the relative intensities of the lines for atactic PVA samples are successfully interpreted by the statistical treatment assuming the statistical formation of the intramolecular hydrogen bond and the random distribution of the *trans* and *gauche* conformations. Separate ^{1}H CRAMPS analyses have also revealed the existence of the OH groups free from hydrogen bonding together with hydrogen-bonded OH groups in PVA films.

Keywords: CP/MAS ^{13}C NMR / ^{1}H CRAMPS / Poly(vinyl alcohol) / Hydrogen bonding / Conformation

When hydrogen bonding with the oxgen-oxygen distance less than about 0.27 nm is formed, ^{13}C chemical shifts significantly shift downfield for carbons associated with such hydrogen bonding. For solid poly(vinyl alcohol) (PVA) samples with different tacticities, the CH resonance line splits into three lines (lines I, II, and III) in CP/MAS ^{13}C NMR spectra [1]. These lines are assigned to the CH carbons associated with the formation of two, one, and no intramolecular hydrogen bond(s) in the triad sequences at least for the crystalline component. By analyzing the relative intensities of the lines, we have already clarified features of hydrogen bonding for different PVA samples [1,2]. In this report, a similar analysis is applied to frozen PVA solutions, where conformational effects should be also considered. The first detection of the OH groups free from hydrogen bonding by ^{1}H

CRAMPS is also briefly reported for PVA films.

The triad tacticities of PVA samples used in this work are as follows: HI-PVA (*mm* = 0.79, *mr* = 0.19, *rr* = 0.02), MI-PVA (*mm* = 0.66, *mr* = 0.28, *rr* = 0.06), LI-PVA (*mm* = 0.50, *mr* = 0.39, *rr* = 0.11).

CP/MAS ^{13}C NMR spectra were measured on a JEOL GSX-200 spectrometer operating under 4.7 T. ^{1}H CRAMPS spectra were obtained on a Chemagnetics CMX-400 spectrometer operating under 9.4 T by using the BR-24 multiple pulse sequence [3].

Figure 1 shows CP/MAS ^{13}C NMR spectra of frozen DMSO-d_6 solutions of PVA samples with different tacticities, which were measured at -50˚C [4]. For reference, the spectrum of the crystalline component for A-PVA films prepared from 10 wt% DMSO solution is also shown in this figure. The broken lines indicate ^{13}C chemical shifts of lines I, II, and III in the crystalline state. In

the frozen A-PVA/DMSO-d_6 solution, the CH resonance line clearly splits into two lines and these two lines have the same chemical shifts as lines II and III. In the frozen LI-PVA solution, however, the CH resonance line does not split clearly. In the frozen MI-PVA and HI-PVA solutions appears only a single line whose chemical shift is in disagreement with that of either line II or III. It has also been found that CP/MAS ^{13}C NMR spectra of frozen PVA aqueous solutions are significantly different from the spectrum of the crystalline component of PVA films.

The CH resonance lines of frozen PVA solutions, whose line splitting greatly depends on the solvents and tacticities as described above, can be well resolved into 9 constituent lines. These lines have different chemical shifts estimated by assuming the downfield shifts due to intramolecular hydrogen bonding and the upfield shifts induced by the γ-*gauche* effect [5]. Furthermore, the relative intensities of the respective constituent lines are successfully interpreted by the statistical treatment assuming the statistical formation of the intramolecular hydrogen bonds for the two appropriately successive OH groups and the random distribution of the *trans* and *gauche* conformations along the PVA chains. The probabilities for the *trans* conformation and the intramolecular hydrogen bond are also determined through this analysis for the atactic PVA samples. In contrast, such a statistical analysis cannot be applied to the cases of frozen solutions for PVA samples with higher isotacticity, suggesting the preferable formation of some specific conformations.

Similar statistical analyses have been also conducted for the crystalline and noncrystalline components of A-PVA films. In particular, the contribution of the *gauche* conformation can be well considered for the non-crystalline component as in the cases of the frozen solutions. The features of the crystalline and non-crystalline states of different PVA samples will be interpreted in terms of the probabilities of the intramolecular hydrogen bond and the *trans* conformation.

Figure 2 shows ^{1}H CRAMPS spectra of three types of A-PVA films; (a) A-PVA films, (b) OH-group deuterated films (A-PVA-d_1), (c) main-chain deuterated A-PVA (A-PVA-d_3). We have already been assigned three main resonance lines to OH, CH, and CH$_2$ protons in the order of increasing field [6]. Here, the OH line is markedly broader than the other two lines, probably reflecting the wide distribution of hydrogen bonding. However, the relative integrated intensity of the OH, CH, and CH$_2$ lines is not in accord with the composition ratio 1:1:2, because the intensity of the OH line is much low. In this figure, the results obtained by the lineshape analysis are also shown, in which a Gaussian curve is assumed for each line. It is found that an additional contribution indicated as OH$_f$ should be introduced at 2.8 ppm to obtain best fitting. Moreover, the total intensity of the OH and OH$_f$ lines well agrees with that of the CH line. In sample A-PVA-d_1, the OH$_f$ line is greatly reduced in intensity together with the decrease of the OH line. From these experimental results, it is concluded that the OH$_f$ line should be
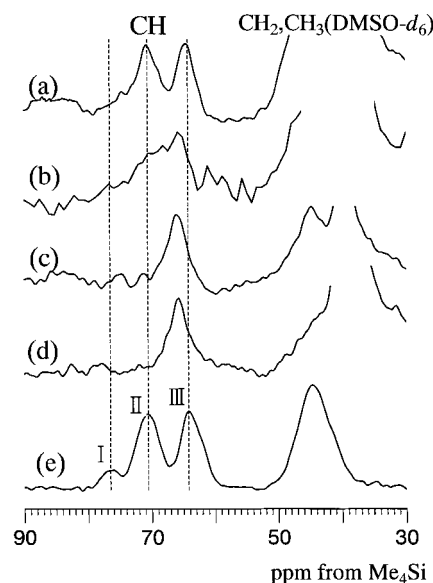

Figure 1. CP/MAS ^{13}C NMR spectra of frozen DMSO-d_6 solutions of PVA samples with different tacticities, measured at -50°C: (a) A-PVA, (b) LI-PVA, (c) MI-PVA, (d) HI-PVA, (e) crystalline component of A-PVA films.
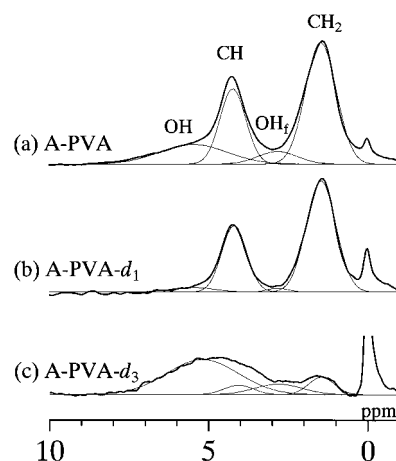

Figure 2. ^{1}H CRAMPS spectra of three types of A-PVA films, measured at room temperature.

assigned to the OH protons free from hydrogen bonding.

As is described above, solid-state ^{13}C and ^{1}H NMR spectroscopies are found to be useful in characterizing hydrogen bonding and the conformation in different states of PVA.

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