^{1}H CRAMPS Spectra of Poly(vinyl alcohol) Films with Different Tacticities

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Conventionally available poly(vinyl alcohol) (PVA) is a crystalline polymer with a melting temperature as high as about 250 °C, although it is produced in the almost atactic form in tacticity. The main chain has a planar zigzag conformation in the crystalline region as in the case of polyethylene (PE), and thus the Young's modulus along the molecular chain axis in the crystalline region is the highest among different sorts of polymers: 250 GPa for PVA[1] and 235 GPa for PE.[2] However, it is still very difficult to prepare high-modulus and high-tenacity films or fibers for PVA, probably due to the difficulty in controlling hydrogen bonding during processing.

We have therefore been studying the intramolecular and intermolecular hydrogen bonds of different PVA samples in detail by using high-resolution solid-state ^{13}C NMR spectroscopy.[3−6] We have found through these investigations that the probability for the formation of the intramolecular or intermolecular hydrogen bond in the *meso* sequence greatly depends on the tacticity, crystallization conditions, crystalline and noncrystalline states, water content, draw ratio, etc.

In this communication, we report the first results of solid-state high-resolution ^{1}H spectra measured for different PVA films with different tacticities by combined rotation and multiple pulse spectroscopy (CRAMPS).[7,8] This new sophisticated technique will provide us further information about the detailed structure of hydrogen bonding of solid PVA, because the ^{1}H nucleus is directly associated with hydrogen bonding.

Four sorts of PVA films with a thickness of about 100 μm, which were cast from aqueous or dimethyl sulfoxide solutions, were employed. Those films were dried at 50 °C for 2 days under vacuum just before NMR measurements. The triad tacticities determined by solution-state ^{1}H spectroscopy are as follows: HI-PVA (mm = 0.79, mr = 0.19, rr = 0.02),[9] I-PVA (0.57, 0.35, 0.08),[3] A-PVA (0.23, 0.50, 0.27),[3] S-PVA (0.19, 0.48, 0.33).[3] A fully main-chain deuterated atactic PVA (A-PVA-d_3) was also used as a film for comparison.

^{1}H CRAMPS measurements were performed on a Chemagnetics CMX-300 spectrometer operating under a static magnetic field of 7.05 T. The multiple pulse sequence employed is BR-24,[10] the $\pi/2$ pulse width and the pulse duration being 1.3 and 3.0 μs, respectively. The rate of magic angle spinning was about 1.5 kHz throughout this work. ^{1}H chemical shifts were expressed as values relative to the methyl proton of poly(dimethylsiloxane) inserted in each sample as an internal reference. During NMR measurements the absorption of moisture by the samples could not be avoided but the amount of hydrated water may be less than 1 wt % in each sample judging from the adsorption isotherms of water on PVA samples separately obtained.

Figure 1 shows 300 MHz ^{1}H CRAMPS spectra of different PVA samples measured at room temperature. From the downfield side, resonance lines assignable to OH, CH, and CH$_2$ protons can be clearly observed, although the OH lines are rather broad and superposed on the neighboring CH lines. To discriminate well between the contributions of OH and CH protons, these superposed lines were resolved into their respective contributions, as shown in Figure 1. In this analysis, each line was assumed as a Gaussian curve, and the validity of this assumption was confirmed by the good fitting for A-PVA-d_3.

The chemical shifts and line widths thus obtained for OH resonance lines are plotted against the mm fraction in Figure 2. The chemical shift significantly increases from 4.25 to 5.35 ppm with increasing mm fraction, while the line width becomes markedly narrower from 1.76 to 0.66 ppm with the increase in isotacticity. According to previous ^{13}C NMR results,[3,4,11] the fraction of intramolecular hydrogen bonds increases with increasing mm fraction. Since the oxygen−oxygen distance is much shorter for the intramolecular hydrogen bond (∼2.5 Å[12,13]) than for the intermolecular hydrogen bonds (2.7−2.9 Å[12,13]) in PVA, the deshielding effect may induce the significant increase of the chemical shift for higher isotactic samples.

On the other hand, the line width will possibly reflect the diversity of the structure of the intermolecular hydrogen bonding: the existence of the distribution in oxygen−oxygen distance, the oxygen−hydrogen−oxygen angle, and the number of hydrogens associated with one oxygen atoms (*e.g.*, see the case in the bifurcated hydrogen bonding). In contrast to such complexity of the intermolecular hydrogen bonding, the structure of the intramolecular hydrogen bonding seems very simple and homogeneous as suggested by the proposed structural model.[4,6] Accordingly, the dependence of the line width on the isotacticity will also stem from the change in the fractions of the intramolecular and intermolecular hydrogen bonds.

It should be noted here that HI-PVA[9] has a somewhat different crystal structure compared to the crystal structure[12,13] assumed for other PVA samples with lower mm fractions. Judging from the results shown in Figures 1 and 2, there seems to be no significant discontinuous difference in chemical shift and line width for the respective resonance lines between HI-PVA and other PVA samples.

Figure 3 shows 300 MHz ^{1}H CRAMPS spectra for A-PVA-d_3 measured at temperatures ranging from room temperature to 150 °C. Similar spectra were also obtained for A-PVA, but the change in line shape was not clearly observed because of the severe overlap of the OH and CH resonance lines, especially at higher temperatures. At temperatures below T_g (70 or 85 °C[14]), the OH resonance line has almost the same line shape described as a single Gaussian, indicating no significant difference in the contributions from the crystalline and noncrystalline regions. Our previous ^{13}C NMR study[3,4] also revealed that the local structure reflected on the ^{13}C chemical shift is almost the same below T_g, and only the fraction of the intramolecular hydrogen bonds is considerably higher in the noncrystalline region. Above T_g, in contrast, the contribution from the noncrystalline

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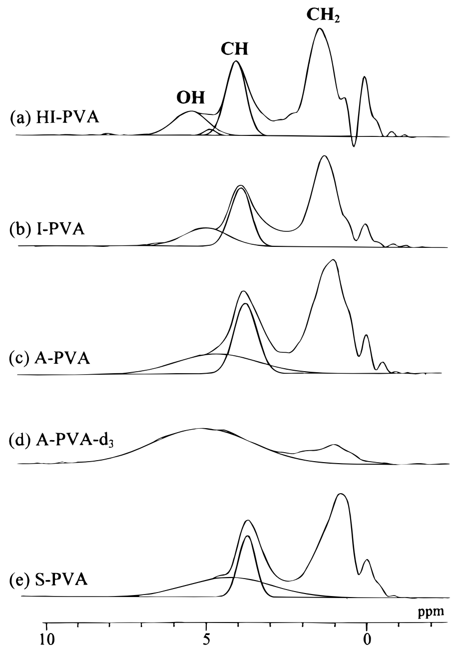

Figure 1. 300 MHz ^{1}H CRAMPS spectra of PVA films with different tacticities measured at room temperature.

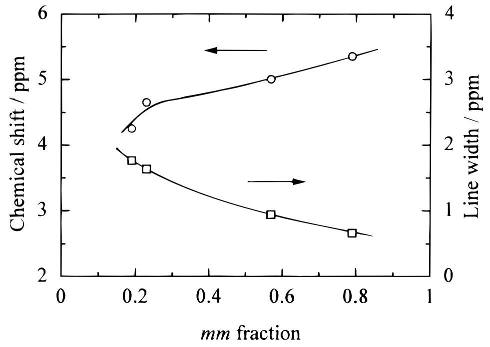

Figure 2. Plots of the chemical shifts and line widths of OH resonance lines for different PVA samples as a function of the *mm* fraction.

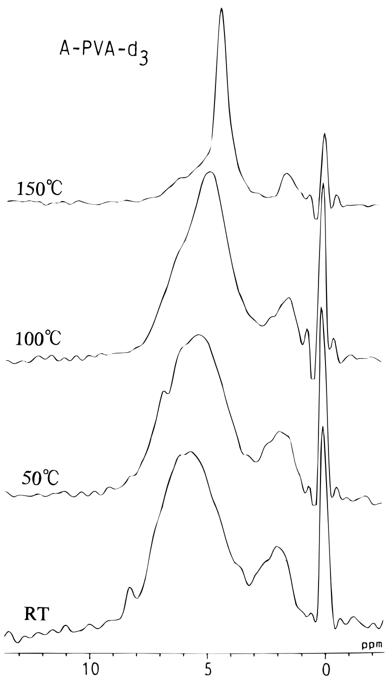

Figure 3. 300 MHz ^{1}H CRAMPS spectra of A-PVA-d_3 at different temperatures.

region becomes narrower in line width and the resonance center concomitantly shifts upfield, resulting in better observation of those two components at 150 °C. Rapid exchanges among different conformations and different hydrogen-bonding states may induce the decrease in chemical shift and narrowing in line width for the noncrystalline component. More detailed analyses and discussion will be made after the measurements of two-dimensional ^{13}C−^{1}H heteronuclear correlation spectra for different PVA samples.

In summary, ^{1}H CRAMPS spectra have successfully been measured for PVA films with different tacticities. The OH resonance line is well resolved by the curve fitting method, although it is considerably superposed on the adjacent CH resonance line. The chemical shift and the line width thus obtained for the OH line significantly depend on the *mm* fraction, suggesting the concomitant change in fractions of intramolecular and intermolecular hydrogen bonds. Although the contributions from the crystalline and noncrystalline regions cannot be separately observed below T_g, those resonance lines are well resolved above T_g due to the upfield shift and line narrowing for the noncrystalline component.

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