

SHORT COMMUNICATIONS

 ^1H CRAMPS Measurements of Different Types of OH Groups in Poly(vinyl alcohol) Films

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(Received August 10, 1998)

KEY WORDS ^1H Combined Rotation and Multiple Pulse Spectroscopy / Hydrogen Bonding / Poly(vinyl alcohol) / Tacticity / Deuterated Poly(vinyl alcohol) / ^1H Chemical Shifts /

Many efforts to characterize hydrogen bonding in organic materials including polymer materials have been carried out by different methods such as X-ray diffractometry, NMR, IR, Raman spectroscopy, neutron diffractometry, theoretical calculations, and so on,^{1,2} because hydrogen bonding is one of the most important factors determining macroscopic material properties. We have also investigated intramolecular and intermolecular hydrogen bonding for poly(vinyl alcohol) (PVA) films and fibers in the different states by cross polarization/magic angle spinning (CP/MAS) ^{13}C NMR spectroscopy.^{3–7} In these investigations, prominent triplets observed for the CH resonance lines, which appear due to the formation of two, one, and no intramolecular hydrogen bond(s) for OH groups in the triad sequences, were evaluated in detail mainly for the crystalline component by considering the statistical formation of intramolecular and intermolecular hydrogen bonds in the sequences with the planar zigzag conformation. A similar analysis has been also successfully applied to the characterization of hydrogen bonding and the chain conformation for frozen PVA solutions by additionally considering effects of the formation of the *gauche* conformation along the chains.^{8,9}

High-resolution solid-state ^1H NMR spectra of PVA, obtained by combined rotation and multiple pulse spectroscopy (CRAMPS),^{10,11} also seems to provide important information about hydrogen bonding, because the resonance line assigned to OH protons is observed well separately from the lines for the CH and CH_2 protons.¹² In this communication, it is reported for the first time, on the basis of the lineshape analysis of ^1H CRAMPS spectra for PVA films at different temperatures, that there exist three types of OH groups in PVA films; hydrogen-bonded OH groups, OH groups free from hydrogen bonding, which preferentially exist in the crystalline region, and highly mobile OH groups in the noncrystalline region observed above T_g .

EXPERIMENTAL

Materials

Syndiotactic PVA (S-PVA), atactic PVA (A-PVA), and highly isotactic PVA (HI-PVA), which were provided by Kuraray Co., were used after complete saponifica-

tion.^{12,13} Films with a thickness of about $100\ \mu\text{m}$ were prepared by casting their aqueous solutions on a glass plate. After drying at 50°C for 2 days under vacuum, these films were subjected to annealing at 150 or 180°C for 10 min in an argon atmosphere. The triad tacticities determined by solution-state ^1H NMR spectroscopy are as follows: HI-PVA ($mm=0.79$, $mr=0.19$, $rr=0.02$), A-PVA ($mm=0.23$, $mr=0.50$, $rr=0.27$), S-PVA ($mm=0.19$, $mr=0.48$, $rr=0.33$). OH-group deuterated atactic PVA (A-PVA- d_1) and main-chain deuterated atactic PVA (A-PVA- d_3) were also used as films.

High-Resolution Solid-State ^1H NMR

^1H CRAMPS measurements were performed on a Chemagnetics CMX-400 spectrometer operating under a static magnetic field of 9.4 T. The multiple pulse sequence employed is BR-24,¹⁴ the $\pi/2$ pulse width and the pulse spacing being 1.3 and $3.0\ \mu\text{s}$, respectively. The rate of magic angle spinning was about 1.5 kHz throughout this work. ^1H 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 absorption isotherms of water on PVA samples separately obtained.¹² The contribution of such a low level of water was ignored in this work, because there was no detectable separate resonance line assigned to water.

RESULTS AND DISCUSSION

Figure 1 shows 400 MHz ^1H CRAMPS spectra of PVA samples with different tacticities measured at room temperature. In a previous paper,¹² we have already assigned three main resonance lines appearing at 5.4, 4.2, and 1.4 ppm to OH, CH, and CH_2 protons, respectively. Here, the OH resonance line is referred to as OH_h line since these OH groups are associated with intramolecular and intermolecular hydrogen bonds as pointed out previously.¹² In fact, the linewidth and the chemical shifts of the OH_h line significantly depend on the tacticity, probably reflecting the wide distribution of intermolecular hydrogen bonding. However, the relative integrated intensities of OH_h , CH, and CH_2 lines are not in accord with the compositional ratio 1 : 1 : 2 for

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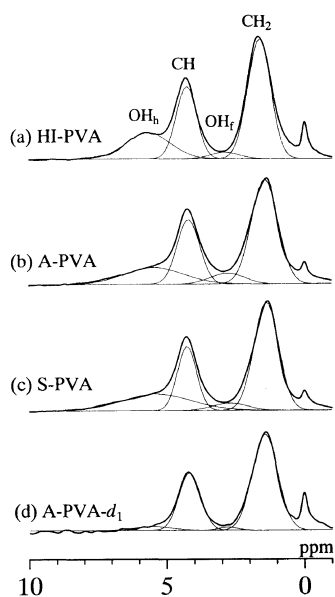


Figure 1. 400 MHz ^1H CRAMPS spectra of PVA films with different tacticities, measured at room temperature.

the respective protons because the OH_h line is significantly low in intensity.

In order to make the contribution of each line clear, a lineshape analysis has been conducted for each sample by assuming each line to be described as a Gaussian curve. An additional contribution, referred to as OH_f hereafter, is found to be reasonably introduced in the region between the CH and CH_2 lines to obtain good fitting for each sample. The relative integrated intensities of OH ($=\text{OH}_h + \text{OH}_f$), CH, and CH_2 lines obtained by the lineshape analysis are also in good agreement with the compositional ratio of their protons. Moreover, in the OH-group deuterated atactic PVA sample (A-PVA- d_1), the OH_f line is greatly reduced in intensity in accord with the decrease in intensity for the OH_h line. These results indicate that the OH_f line should be also ascribed to the OH protons. The chemical shift of the OH_f line is as low as 2.8 ppm compared to the value 5.4 ppm for the OH_h line. Since such a prominent upfield shift of the OH_f line will be induced by the liberation from hydrogen bonding, it is concluded that the OH_f line should be assigned to the OH protons free from hydrogen bonding. In addition, it should be simply pointed out here that the mole fraction of the OH_f groups determined from the integrated intensity is as high as 0.27 for A-PVA, while this value is less than 0.18 for HI-PVA and S-PVA. The cause of such a high value for A-PVA is not clear at present, but this fact may suggest the necessity to develop a better analytical method. Nevertheless, it seems reasonable to conclude that there exists some amount of the contribution of the OH groups free from hydrogen bonding at about 2.8 ppm.

Figure 2 shows the spectra of the main-chain deuterated atactic PVA (A-PVA- d_3) films measured at -60 – 160°C . Here, the intensities of the CH and CH_2 resonance lines are very weak because only a small number of residual protons exist in the main-chain. Although the lineshape is hardly changed below room temperature, a new line referred to as OH_r hereafter seems to appear at about 4.5 ppm at 110 and 160°C . In

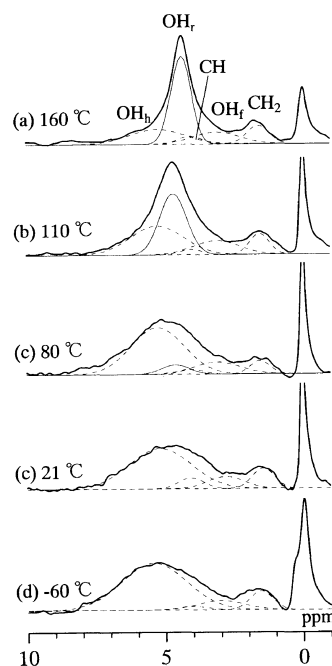


Figure 2. 400 MHz ^1H CRAMPS spectra of A-PVA- d_3 films, measured at different temperatures.

this figure, the results of the lineshape analysis is also shown. It is found that the OH_r resonance line, which is described as a solid line, really appears at temperatures above T_g (70°C or 85°C^{15}) and becomes narrower with increasing temperature. Moreover, the chemical shift of the OH_r line at 160°C is in good accord with the averaged chemical shift for three OH lines of A-PVA in dimethyl sulfoxide (DMSO)- d_6 solution, which are ascribed to OH groups in the *mm*, *mr*, and *rr* sequences.^{16,17} In contrast, the chemical shifts of the CH and CH_2 lines, which are almost the same as their corresponding averaged values obtained by solution-state ^1H NMR spectroscopy,^{16,17} stay constant in this temperature range, although rapid exchanges in conformations must occur above T_g in the noncrystalline region. This fact indicates that the conformational exchange may induce almost no appreciable effect on the chemical shifts for protons in the main chains and also in the side-groups for solid PVA. It is, therefore, concluded that the OH_r line can be assigned to the OH groups which undergo rapid changes in hydrogen bonding as a result of enhanced molecular motion above T_g in the noncrystalline region. If the exchange is assumed to simply occur between the OH_h and OH_f groups, the mole fraction of the OH_h groups is estimated to be about 0.60 at 160°C in the rubbery noncrystalline region by the simple two-site exchange model.¹⁸

The mole fractions of the OH_h , OH_f , and OH_r groups, determined as integrated fractions by the lineshape analysis for the spectra of A-PVA- d_3 shown in Figure 2, are plotted against the temperature in Figure 3. Above T_g , the mole fraction of the OH_r groups is markedly increased as a result of the reduction in the mole fraction of the OH_h groups, reflecting the onset of the rapid change in hydrogen bonding due to the enhanced molecular motion in the noncrystalline region as described above. Finally both mole fractions seem to approach to certain values above 160°C . In contrast,

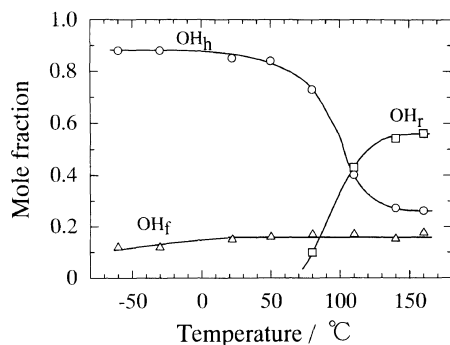


Figure 3. Plots of the mole fractions of different OH groups for A-PVA- d_3 films as a function of temperature.

the mole fraction of the OH_f groups stays almost constant above room temperature, although this fraction is slightly decreased below room temperature with decreasing temperature. Since the OH_f groups are not affected by the glass transition unlike the OH groups in the noncrystalline region described above, these OH_f groups should exist in the crystalline region. In fact, the total mole fraction of the OH_h and OH_f groups obtained at 160°C is almost the same value as the degree of crystallinity reported for conventional annealed PVA samples.¹⁵ Further detailed characterization of hydrogen bonding is in progress for different PVA samples.

In summary, we have successfully confirmed the existence of three types of OH groups, OH_h, OH_f, and OH_r groups, in PVA films with different tacticities by the ^1H CRAMPS analysis. Below T_g , the OH_h groups associated with hydrogen bonding and the OH_f groups free from hydrogen bonding are observed in ^1H CRAMPS spectra as separate resonance lines with different chemical shifts probably as a result of the difference in deshielding effect due to hydrogen bonding. In contrast, the OH_h groups in the noncrystalline

region undergo the rapid change in hydrogen bonding by enhanced molecular motion above T_g , resulting in the appearance of another resonance line ascribed to the OH_r groups. Further lineshape analyses of ^1H CRAMPS spectra at different temperatures have revealed that the OH_f groups are allowed to preferentially exist in the crystalline region and their mole fraction stays almost constant above room temperature.

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