Studies on Different Types of Hydrogen Bonds in Poly(vinyl alcohol) Films by ^1H CRAMPS and Solid-State Two-Dimensional ^1H – ^{13}C Heteronuclear Correlation Analyses

Kenji MASUDA, Hironori KAJI, and Fumitaka HORII[†]

*Institute for Chemical Research, Kyoto University,
Uji, Kyoto 611-0011, Japan*

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ABSTRACT: Different hydrogen-bonded states of OH groups in poly(vinyl alcohol) (PVA) films with different tacticities have been characterized by ^1H combined rotation and multiple pulse spectroscopy (CRAMPS), solid-state ^{13}C NMR and two-dimensional (2D) ^1H – ^{13}C heteronuclear correlation (HETCOR) analyses. The newly developed line shape analysis for the ^1H CRAMPS spectra reveals the existence of three types of OH groups in different hydrogen-bonded states below T_g ; intramolecular and intermolecular hydrogen bonded OH (OH_{intra} , OH_{inter}) groups and OH (OH_f) groups free from hydrogen bonding. Above T_g , another resonance line which can be assigned to highly mobile OH (OH_f) groups in the non-crystalline region appears as a result of the reduction in mole fractions of the OH_{intra} and OH_{inter} groups, in good accord with the confirmation of the rubbery component by the solid-state ^{13}C NMR line shape analysis. In contrast, the mole fraction of the OH_f groups stays constant at -60 – 160°C , indicating that these OH groups are preferentially distributed in the crystalline region. In order to examine the correlations of the results obtained by ^1H CRAMPS and solid-state ^{13}C NMR analyses, 2D ^1H – ^{13}C HETCOR spectra have been also measured at room temperature for atactic and main-chain deuterated atactic PVA films. As a result, evident correlations between ^1H OH and ^{13}C CH constituent lines are observed at a cross polarization (CP) contact time of 120 μs , indicating the validity of the assignments for the ^1H OH and ^{13}C CH resonance lines made previously as well as in this work.

KEY WORDS Hydrogen Bonding / Chain Conformation / Poly(vinyl alcohol) / Crystal Structure / Cross Polarization-Magic Angle Spinning ^{13}C NMR / ^1H Combined Rotation and Multiple Pulse Spectroscopy / ^1H – ^{13}C Heteronuclear Correlation spectroscopy /

In previous papers,^{1,2} we reported that ^1H combined rotation and multiple pulse spectroscopy^{3,4} (CRAMPS) spectra obtained at room temperature for poly(vinyl alcohol) (PVA) films with different tacticities were resolved into four constituent lines assignable to hydrogen-bonded OH protons, CH protons, OH protons free from hydrogen bonding, and CH_2 protons in the order of increasing field. Here, the chemical shift and line width of the hydrogen-bonded OH line significantly depended on the tacticity, suggesting the concomitant change in fractions of the intramolecular and intermolecular hydrogen bonds. It was also found that another resonance line for OH protons appeared above about 80°C and this line could be assigned to the OH groups that undergo the enhanced molecular motion in the non-crystalline region above T_g (70 or 85°C ⁵). However, the mole fraction for the OH groups free from hydrogen bonding, which was found to be preferentially distributed in the crystalline region, was estimated to be as extraordinarily high as 0.47 in this region for atactic PVA (A-PVA) films. Since this may be due to the overestimation of the contribution from the OH groups free from hydrogen bonding, the development of a more detailed line shape analysis should be necessary by separately considering the contributions from the intramolecular and intermolecular hydrogen bonded protons.

On the other hand, it is well known that the CH resonance lines of cross polarization / magic angle spinning (CP/MAS) ^{13}C NMR spectra for PVA solid samples split into a triplet, lines I, II, and III in the order of increasing

field.^{8–14} Such a split, at least for the crystalline component in which each PVA chain has the planar zigzag conformation,^{6,7} is considered to be due to the formation of different types of intramolecular hydrogen bonds in the triad sequences although other interpretations^{15–17} were proposed. As shown in Figure 1, line I is assigned to the CH carbons bonded to OH groups which form two intramolecular hydrogen bonds with the vicinal OH groups in the *mm* sequence. In contrast, lines II and III are ascribed to the CH carbons bonded to OH groups that form one and no intramolecular hydrogen bond irrespective of the formation of intermolecular hydrogen bonding, respectively. On the basis of these assignments, we successfully clarified the dependencies of the formation of intramolecular hydrogen bonding mainly in the crystalline region on the tacticity, crystallization condition, temperature, water content, draw ratio, etc.^{9–14}

As for the characterization of the noncrystalline component, we developed a new line shape analysis for the CH carbon lines by considering downfield shifts due to the formation of the intramolecular hydrogen bonding for appropriate vicinal OH groups and upfield shifts owing to the γ -gauche effect^{18,19} induced by the introduction of the gauche conformation. In fact, CP/MAS ^{13}C NMR spectra of frozen PVA solutions were well resolved into several constituent lines reflecting these upfield and downfield shifts, and the statistical analysis of intensities of the constituent lines made it possible to determine two sorts of probabilities for the distribution of the trans conformation and for the formation of intramolecular hydrogen bonding for appropriate vicinal OH

[†]To whom correspondence should be addressed.

Table I. Degrees of polymerization (DP) and tacticities for different PVA samples

Sample	DP	Triad tacticity			Diad tacticity ^a	
		<i>mm</i>	<i>mr</i>	<i>rr</i>	<i>M</i>	<i>r</i>
S-PVA	1590	0.19	0.48	0.33	0.43	0.57
A-PVA	1700	0.23	0.50	0.27	0.48	0.52
A-PVA- <i>d</i> ₃	1150	0.22	0.50	0.28	0.46	0.54
LI-PVA	^b	0.50	0.39	0.11	0.70	0.30
MI-PVA	1130	0.66	0.28	0.06	0.81	0.19
HI-PVA	9100	0.79	0.19	0.02	0.88	0.12

^a Calculated by the least-squares method assuming Bernoullian statistics. ^b Not measured.

Figure 1. Schematic diagram for different types of hydrogen bondings in the crystalline region of PVA. Two neighboring planar zigzag chains are depicted on the basis of the crystal structure models proposed by Sakurada *et al.*⁶ and Bunn.⁷

groups.²⁰ This analytical method was also successfully applied to the characterization of hydrogen bonding and the chain conformation for the crystalline and noncrystalline components of PVA films prepared under different conditions.²¹

As described above, we characterized hydrogen bonding in PVA films by ¹H CRAMPS and solid-state ¹³C NMR analyses separately. To further confirm the assignments of the respective resonance lines in each spectrum, it must be better to apply two-dimensional (2D) ¹H–¹³C heteronuclear correlation (HETCOR) spectroscopy^{22–24} to our PVA systems. In this paper, we first develop a new line shape analytical method for ¹H CRAMPS spectra for PVA films with different tacticities by considering the separate contributions from the intramolecular and intermolecular hydrogen bonded OH groups. We next apply this method to the characterization of the different types of hydrogen bonds in PVA films as a function of temperature. In this case solid-state ¹³C NMR analysis is also carried out for A-PVA films to characterize the changes in hydrogen bonding and chain conformation above *T*_g. Finally, 2D ¹H–¹³C

HETCOR spectra are measured to examine the correlations between the ¹H OH constituent lines and the ¹³C CH constituent lines and to confirm the assignments of these resonance lines.

EXPERIMENTAL

Materials

Six PVA samples with different tacticities, which were provided by Kuraray Co., Ltd. were used after complete saponification. Table I shows viscosity-average degrees of polymerization (DP) and triad and diad tacticities determined at 50°C in deuterated dimethyl sulfoxide (DMSO-*d*₆) by gated scalar decoupling ¹³C NMR spectroscopy. A solution-state ¹H NMR measurement revealed that 94.5% of aliphatic protons were deuterated for the main-chain deuterated A-PVA (A-PVA-*d*₃) sample. All films with a thickness of about 100 μm were prepared by casting their 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.

Side-chain deuterated A-PVA (A-PVA-*d*₁) films were prepared by dissolving A-PVA in 99.9% deuterated water and then by casting the solution on a glass plate. The films thus obtained were further soaked into deuterated water since O²H deuterons on the surface of the PVA films tend to exchange to protons in an atmosphere during the casting process. The same drying and annealing processes described above were also applied to these side-chain deuterated films. The solution-state ¹H NMR measurements revealed that 89.4% OH protons were deuterated for A-PVA-*d*₁ films.

Solid-State NMR Measurements

All solid-state NMR measurements were performed on a Chemagnetics CMX-400 spectrometer operating under a static magnetic field of 9.4 T. A Chemagnetics 5 mm single resonance MAS probe was used to measure ¹H CRAMPS^{3,4} spectra at different temperatures. The multiple pulse sequence for ¹H CRAMPS was BR-24,²⁵ the $\pi/2$ pulse width and the pulse duration being 1.3 and 3.0 μs, respectively. The MAS rate was about 1.5 kHz for ¹H CRAMPS. CP/MAS ¹³C NMR measurements were conducted at different temperatures by using a Chemagnetics 7.0 mm MAS probe; the contact time was 500 μs and the ¹H and ¹³C field strengths $\gamma B_1/2\pi$ were 62.5 kHz. The MAS rate was set to about 5 kHz.

2D ¹H–¹³C HETCOR experiments were conducted by using a Doty double resonance 4.0 mm MAS probe; ¹H and ¹³C field strengths $\gamma B_1/2\pi$ were 100.0 kHz. In these

experiments, the frequency-switching Lee–Goldberg (FSLG)²⁶ pulse sequence was applied to suppress the ^1H – ^1H homonuclear dipolar interaction. Since OH protons are not directly bonded to carbons, the standard CP technique was used for the transfer of the polarization from protons to carbons. The CP contact time was 30–120 μs and the MAS rate was 7 kHz.

^1H chemical shifts for ^1H CRAMPS spectra were expressed as values relative to tetramethylsilane ($\text{Si}(\text{Me})_4$) by using the methyl proton line appearing at 0.0 ppm for poly(dimethylsiloxane) inserted in each sample as an internal reference. In the HETCOR experiments, the CH_3 resonance line of *para*-dimethoxybenzene crystals was used as an external reference, whose chemical shift value (3.22 ppm) was determined by ^1H CRAMPS. ^{13}C chemical shifts were expressed as values relative to Me_4Si by using the CH_3 line at 17.36 ppm for hexamethyl benzene crystals as an external reference.

RESULTS AND DISCUSSION

^1H CRAMPS Spectra at Room Temperature

Figure 2 shows 400 MHz ^1H CRAMPS spectra measured at 21°C for five undeuterated PVA films with different tacticities and one OH-group deuterated A-PVA (A-PVA- d_1) film. These spectra are found to be simply resolved into four Gaussian lines, as was already reported as a short communication in our previous paper.² According to the previous assignment, the respective lines are assigned to the OH protons (OH_h) associated with hydrogen bonding, CH protons, OH protons (OH_f) free from hydrogen bonding, and CH_2 protons in the order of decreasing chemical shift. As for A-PVA- d_1 , the significant decrease in intensity for the OH_f line compared to the case of A-PVA evidently confirms that the OH proton contribution also appears at about 2.9 ppm although it is not observed as a separated peak unlike the other resonance lines. The previous studies^{25–29} of ^1H chemical shifts for hydrogen-bonded protons also support these assignments for the OH_h and OH_f lines. Nevertheless, it was pointed out in the previous paper² that such a simple line shape analysis was not plausible to estimate the mole fraction of the OH_f protons. Namely the mole fraction thus obtained for the OH_f protons, which were preferentially distributed in the crystalline region, was found to be as extraordinarily high as about 0.47 in the crystalline region for A-PVA. Therefore, another line shape analysis has newly been developed in this work by considering the separated contributions from the OH groups associated with the intra- and intermolecular hydrogen bonds.

Figure 3 shows the results obtained by the newly developed line shape analysis for the same ^1H CRAMPS spectra shown in Figure 2. Here, the elementary resonance line for the intramolecular hydrogen bonded OH (OH_{intra}) protons is assumed to be almost the same as the constituent resonance line for the hydrogen-bonded OH protons in HI-PVA films, because this sample contains mainly intramolecular hydrogen bonded OH groups as previously shown by CP/MAS ^{13}C NMR spectroscopy.^{9,10,13,14} In contrast, S-PVA films are composed of a larger amount of intermolecular hydrogen bonded OH (OH_{inter}) groups^{9,10,13,14} and the constituent OH_h line

Figure 2. 400 MHz ^1H CRAMPS spectra obtained at 21°C for PVA films with different tacticities. Here, line shape analyses have been made by assuming two different OH lines, OH_h , and OH_f , which are assigned to the hydrogen-bonded OH groups and OH groups free from hydrogen bonding, respectively.

for S-PVA may be therefore assumed to be similar to the elementary resonance line for OH_{inter} protons. Under these assumptions trial and error line shape analyses were repeatedly carried out by also considering the analytical results for other lines shown in Figure 2. Finally we could obtain the best fitting for each sample as shown in Figure 3. As a result, it is found that the respective constituent resonance lines including different OH lines have their own chemical shifts and line widths except for the CH_2 line as shown in Table II. For the CH_2 line the ^1H chemical shift value is slightly decreased with increasing isotacticity. These facts indicate that the CH_2 chemical shift depends on the tacticity of the two first neighboring OH groups whereas the CH and OH lines are insensitive to their tacticity because of the two-bond separated correlation. More importantly, the averaged chemical shift value and the line width for the intermolecular hydrogen bonded OH protons are found to be almost constant irrespective of the tacticity, although such facts are reasonably understood for the intramolecular hydrogen bonded OH protons because of their well-defined structure. The diversity of the intermolecular hydrogen bonding in PVA will be reflected on the broader line width for the OH_{inter} resonance line compared to other resonance lines.

The relative integrated intensities of the OH, CH, CH_2

Table II. ^1H Chemical shifts and half widths of the respective resonance lines of 400 MHz ^1H CRAMPS spectra for PVA films with different tacticities

Sample	OH			CH	CH_2
	OH_{intra}	OH_{inter}	OH_{f}		
Chemical shift/ppm	5.80 ± 0.05	4.70 ± 0.05	2.85 ± 0.05	4.20 ± 0.03	$1.40 - 1.60$
Half width/ppm	1.00 ± 0.05	1.55 ± 0.05	0.70 ± 0.02	0.50 ± 0.05	0.55 ± 0.03

Figure 3. 400 MHz ^1H CRAMPS spectra obtained at 21°C for PVA films with different tacticities. In these cases, line shape analyses have been made by assuming three different OH lines, OH_{intra} , OH_{inter} , and OH_{f} , which are assigned to the intramolecular and intermolecular hydrogen bonded OH groups and OH groups free from hydrogen bonding, respectively.

lines obtained by this line shape analysis are given in Table III. Here, the total intensity of the OH lines ($\text{OH}_{\text{intra}} + \text{OH}_{\text{inter}} + \text{OH}_{\text{f}}$) is set to 1.0 for each sample. It should be pointed out that the ratio of the intensities of the OH, CH, and CH_2 lines is in good agreement with the chemical compositional ratio of their protons for each PVA sample. This fact also indicates the validity of the line shape analysis newly developed for the samples shown in Figure 3 in this work.

The mole fractions of the OH_{intra} , OH_{inter} , and OH_{f} protons are plotted against the mm fraction in Figure 4. The mole fraction of the OH_{intra} protons significantly increases with the increase of the mm fraction, while the fraction of the OH_{inter} protons is reduced concomitantly. In contrast, the mole fraction of OH_{f} protons seems to

Table III. The relative intensities of respective resonance lines of different PVA samples

Sample	Relative intensity			CH	CH_2
	OH_{intra}	OH_{inter}	OH_{f}		
S-PVA	0.24	0.64	0.12	0.94	2.12
A-PVA	0.31	0.54	0.15	0.96	2.04
LI-PVA	0.38	0.46	0.14	0.97	2.00
MI-PVA	0.50	0.36	0.14	0.92	1.82
HI-PVA	0.65	0.22	0.13	1.04	2.04

Figure 4. Plots of the mole fractions of different OH protons for PVA films as a function of the mm fraction; OH_{intra} ($\circ$), OH_{inter} ($\triangle$), and OH_{f} ($\square$). $\blacksquare$ indicates the mole fraction of OH_{f} protons estimated in the crystalline region, which was obtained by multiplying the value shown by $\square$ by the degree of crystallinity for each sample.

stay almost constant irrespective of the tacticity. As shown in the case of A-PVA- d_3 films later, the OH_{f} groups are preferentially distributed in the crystalline region. This fact suggests that all OH groups are associated with intramolecular or intermolecular hydrogen bonding in the noncrystalline region. Probably such hydrogen bonding will be generally produced during the process of the sample preparation. It should be, therefore, reasonable to discuss the results for the OH_{f} protons shown in Figure 4 as results obtained for the crystalline component in these PVA samples. The degrees of crystallinity for S-PVA, A-PVA, and HI-PVA were estimated to be 0.48, 0.45, and 0.58 by solid-state ^{13}C NMR spectroscopy, respectively.^{9,10,13,14,21} It should be, therefore, pointed out that the mole fraction of the OH_{f} protons in the crystalline region seems to be significantly decreased with increasing isotacticity or syndiotacticity as indicated by the broken line in Figure 4. Intramolecular or intermolecular hydrogen bonding must be more regularly formed in the crystalline region for more isotactic or syndiotactic PVA samples, whereas it is pro-

duced statistically at random in an atactic PVA sample and thus the OH_f groups are more frequently formed there.

Dynamics of OH Groups

Figure 5 shows CP/MAS ¹³C NMR spectra of the crystalline and noncrystalline components of A-PVA films at 21 and 120 °C. These spectra for the crystalline and noncrystalline components are separately obtained by using the difference in ¹³C spin-lattice relaxation time as described in our previous papers.^{9–14,21} The line shape analysis previously developed^{20,21} has been applied to these spectra, in which 9 constituent lines are introduced by considering downfield shifts due to the formation of intramolecular hydrogen bonding for the appropriate vicinal OH groups and upfield shifts caused by the γ -gauche effect^{18,19} induced by the introduction of the gauche conformation along the PVA chain with the planar zigzag conformation. As for the crystalline component, the CH resonance line is well resolved into lines 1, 3, and 6, which respectively correspond to lines I, II, and III, at 21 and 120 °C by the line shape analysis previously developed.^{20,21} This result indicates that there is almost no change in intra- and intermolecular hydrogen bonding in the crystalline region in A-PVA films at 120 °C compared to the state at room temperature.

In contrast, the CH resonance line of the noncrystalline component is well resolved into 6 constituent lines at 21 °C, although this line seemingly splits into three peaks because of enhanced intensities for lines 1(I), 3(II), and 6(III). Additional three lines should be mainly due to the existence of the gauche conformations in the noncrystalline region, as reported in our previous paper.^{20,21} Moreover, a somewhat broader line is newly introduced at 120 °C at about 69 ppm. Since the $T_{1\rho}$ of this component is found to be as short as 0.8 s compared to the values of 5–10 s for other noncrystalline lines, this component should be assigned to the rubbery component which undergoes rapid exchanges in conformation and hydrogen bonding above T_g in the noncrystalline region. The changes in relative intensities of other constituent lines for the noncrystalline component at 120 °C also indicate that more gauche conformations are produced in the less mobile noncrystalline component with $T_{1\rho}$ = 5–10 s at 120 °C compared to the case at 21 °C.

Figure 6 shows ¹H CRAMPS spectra of A-PVA-*d*₁ films at different temperatures. It is found that the chemical shifts of the CH and CH₂ resonance lines stay almost constant at different temperatures, although the chain conformation is evidently changed in the noncrystalline region above T_g as shown above by solid-state ¹³C NMR spectroscopy. Such a temperature independence for these lines simplifies the following line shape analyses for the OH resonance lines of A-PVA-*d*₃ at different temperatures. The chemical shift values of 4.2 and 1.45 ppm respectively obtained here for the CH and CH₂ lines are used as fixed parameters below.

Figure 7 shows ¹H CRAMPS spectra of main-chain deuterated A-PVA-*d*₃ films measured at different temperatures. Below T_g , the overall lineshape is almost the same at each temperature, but a significant lineshape change is observed above 80 °C as a result of the appearance of a new resonance line at about 4.65 ppm. By con-

Figure 5. Line shape analyses for CP/MAS ¹³C NMR spectra of different components in A-PVA films: the crystalline component at 120 (a) and 21 °C (b); the noncrystalline component at 120 (c) and 21 °C (d).

Figure 6. 400 MHz ¹H CRAMPS spectra of A-PVA-*d*₁ films, measured at different temperatures.

sidering this new line, similar lineshape analyses have been conducted for all the spectra shown in Figure 7. Here, each constituent line is assumed to be described by a Gaussian curve. The chemical shift values of the

Figure 7. Line shape analyses of ^1H CRAMPS spectra measured for A-PVA- d_3 films at different temperatures.

OH_{intra} , OH_{inter} , OH_f , CH, and CH_2 protons, which are listed in Table III, are used as fixed parameters. Moreover, the ratio of the relative integrated intensities for the residual CH and CH_2 protons is assumed to be 1/2 in each spectrum. The respective constituent lines thus obtained are shown as thin lines. Broken lines, which are linear combinations of the respective thin lines, are in good accord with the experimental spectra. The relative intensity of the OH ($\text{OH}_{\text{intra}} + \text{OH}_{\text{inter}} + \text{OH}_f + \text{OH}_r$), CH, and CH_2 lines in each spectrum is found to be of the order of 1.0/0.06/0.12, which is in good accordance with that obtained by solution-state ^1H NMR spectroscopy.

The OH_r line significantly becomes narrower with a slight upfield shift with increasing temperature. This fact indicates that the OH groups undergo exchange motion among different hydrogen-bonded states including the state free from hydrogen bonding above T_g and the exchange rate may become faster with increasing temperature. The chemical shift of the OH_r resonance line at 140 °C or 160 °C (not shown) is almost in accord with the average chemical shift of three OH lines associated with the *mm*, *mr*, and *rr* sequences for A-PVA in DMSO- d_6 solution. As revealed in Table II, no significant effect of the chain conformation appears on the ^1H chemical shifts of the different types of OH protons within the resolution of ^1H CRAMPS spectra unlike the case of the CH carbon resonance lines shown in Figure 5. It is, therefore, plausible to employ the three-site or two-site exchange model³¹ among the OH_{intra} , OH_{inter} , and OH_f protons to evaluate the ^1H chemical shift of the OH_r line.

Figure 8. Plots of the mole fractions of different OH protons for A-PVA- d_3 films as a function of temperature.

As will be shown later, the mole fractions of the OH_{intra} , OH_{inter} , and OH_f protons are 0.33, 0.67, and 0 below T_g in the noncrystalline region, respectively. Accordingly, the chemical shift of the OH_r line is simply estimated to be 5.06 ppm by the two-site exchange model, when the exchange is assumed to selectively occur between the OH_{intra} and OH_{inter} groups with a rate higher than about 500 s^{-1} . This calculated value is much larger than the observed value (4.35 ppm) at 160 °C, suggesting that there is some contribution from the OH_f groups above T_g . When the mole ratio of the OH_{intra} and OH_{inter} protons is assumed not to be significantly changed above and below T_g as a first approximation, the mole fraction of the OH_f groups is estimated to be 0.32 at 160 °C in the noncrystalline region by using the three-site exchange model. This result suggests that about 1/3 of the OH groups may exist as OH groups free from hydrogen bonding during the exchange motion in the rubbery state of A-PVA.

The mole fractions obtained for the different OH protons in Figure 7 are plotted against the temperature in Figure 8. Below T_g , three types of OH protons, OH_{intra} , OH_{inter} , and OH_f protons are found to stay constant irrespective of temperature. In contrast, the mole fractions of the OH_{intra} and OH_{inter} protons markedly decrease above T_g as a result of the rapid increase in the fraction of the OH_r protons. Such remarkable changes should be attributed to the onset of the exchange among the OH_{intra} , OH_{inter} , and OH_f groups in the noncrystalline region as described above. Above about 150 °C, the respective mole fractions are found to reach to constant values.

The sum of the constant values obtained for the OH_{intra} , OH_{inter} , and OH_f protons above 150 °C is 0.43 and this value is in good accord with the degree of crystallinity for conventional annealed A-PVA samples.⁵ This result implies that the OH_f groups preferentially exist in the crystalline region where the hydrogen bonds and the conformation are kept unaltered even at higher temperatures. The localization of the OH_f groups may be also reflected on the temperature independence of the mole fraction on the OH_f protons shown in Figure 8. On the other hand, all OH groups in the noncrystalline region become the OH_r groups at 160 °C and thus the

OH_{inter}, OH_{intra}, and OH_f groups at 160°C can be regarded as those existing in the crystalline region. Therefore, the mole fractions of the respective OH groups in the crystalline region can be determined as follows; OH_{intra} = 0.24, OH_{inter} = 0.59, and OH_f = 0.17. The previous molecular dynamics calculations indicated that the mole fraction of the OH protons forming intramolecular hydrogen bonding was 0.17–0.4³² or about 0.4³³ in the crystalline region. Our value obtained here roughly agrees with these calculated values. Furthermore, this value obtained by ¹H CRAMPS is in good accord with the mole fraction (0.27) of the CH I carbons associated with the two intramolecular hydrogen bonds obtained in Figure 5 by the solid-state ¹³C NMR analysis. This fact indicates that the hydrogen of the OH group bonded to the CH I carbon always forms intramolecular hydrogen bonding with the vicinal OH group as shown in Figure 1.

The mole fractions of the respective OH groups in the rigid noncrystalline region can be calculated by subtracting their values at 160°C from those at each temperature. The mole fractions thus obtained below *T_g* is OH_{intra} = 0.33, OH_{inter} = 0.67, and OH_f = 0. Here, the mole fraction of the OH_{intra} groups is also in good accord with that value (0.35) of the CH I carbon obtained for the noncrystalline component at 21°C by the solid-state ¹³C NMR analysis shown in Figure 5.

2D ¹H–¹³C HETCOR Spectra

As described above, ¹H CRAMPS and CP/MAS ¹³C NMR analyses give quantitative and consistent information about the different hydrogen bonded states in PVA films. Here, we further apply the 2D ¹H–¹³C HETCOR technique to PVA films to directly confirm the correlations of the results obtained by these two NMR analyses. This technique will also confirm the assignments of the resonance lines in the respective spectra.

Figure 9 shows 2D ¹H–¹³C HETCOR spectra of A-PVA films measured at 24°C with CP contact times of 30 and 120 μs. The corresponding 1D ¹H and ¹³C projection spectra are also displayed along the appropriate axes. The line widths of the ¹H resonance lines are too broad to separately discriminate among them compared to the ¹H CRAMPS spectra shown in Figures 2 and 3. Such low resolution may be due to the imperfect ¹H–¹H dipolar decoupling mainly stemming from the employment of the 4 mmφ CP/MAS probe. As clearly seen in Figure 9a, enhanced correlations are observed for CH II, CH III, and CH₂ lines although the correlation peak is much smaller for the CH I line probably due to the less intensity of this line. The ¹H chemical shifts of the correlation peaks for the CH I, II, and III lines agree with each other as indicated by the dotted line in Figure 9a. Since this averaged chemical shift is almost in good accord with the value for the CH protons in Table III obtained by ¹H CRAMPS, each one-bond C–H correlation should be selectively observed at a contact time of 30 μs. In contrast, significant differences in ¹H chemical shifts for these correlation peaks appear at a contact time of 120 μs as shown in Figure 9b: The peak tops of the slices of the respective correlation peaks shown at the bottom of the figure evidently shift downfield in the order of correlation peaks for the CH I, II, and III. This fact indicates that more contributions from intramolecular hydrogen bonding

Figure 9. 2D ¹H–¹³C HETCOR spectra of the A-PVA films measured at 24°C with CP contact times of 30 (a) and 120 μs (b). The top and left spectra are projection spectra. The spectra shown at the bottom are the slices for different CH resonance lines.

may appear in the order of the CH I, II, and III in good accord with the assignments for the CP/MAS ¹³C and ¹H CRAMPS spectra. It is also found that the two-bond C–H correlations can be observed at a contact time of 120 μs but the one-bond C–H contributions seem to be still too large.

In order to obtain more evident correlations, main-chain deuterated A-PVA-*d*₃ films have been employed to suppress the contributions from the CH and CH₂ protons. Figure 10 shows a 2D ¹H–¹³C HETCOR spectrum of this sample measured at 24°C at a CP contact time of 120 μs. As expected, a much enhanced correlation peak can be observed for the CH I line and all correlation peaks seem to shift downward as a result of the suppression of the contributions from the CH and CH₂ protons. In fact, the ¹H chemical shifts of the slice spectra for the CH I, II, and III lines, which are shown at the bottom of Figure 10, are 5.9, 5.0, and 4.7 ppm, respectively. The ¹H

Figure 10. 2D ^1H - ^{13}C HETCOR spectrum of the A-PVA- d_3 films measured at 24°C with a contact time of 120 μs . The top and left spectra are projection spectra. The spectra shown at the bottom are the slices for different CH resonance lines.

chemical shift values thus obtained for the CH I and III lines are almost in agreement with those of OH_{intra} and OH_{inter} protons shown in Table III, respectively. This fact indicates that the CH I and III lines are mainly attributed to the CH carbons bonded to OH groups forming the intra- and intermolecular hydrogen bonds, respectively. In contrast, the value of 5.0 ppm obtained for the CH II line is the intermediate value of the chemical shifts for the OH_{inter} and OH_{intra} protons. This result may imply that the CH II line is ascribed to the CH carbons bonded to the OH groups forming intra- or intermolecular hydrogen bonding as shown in Figure 1.

As for the OH_f line, it is very difficult to find correlations with particular CH carbon resonance line, because of the less intensity of this contribution. Nevertheless, broad upfield tailing of the slice spectra for the CH II and III lines may be due to the contribution from the OH protons free from hydrogen bonding. It should be, therefore, concluded that the results obtained by the 2D ^{13}C - ^1H HETCOR experiments are well consistent with the results separately obtained by solid-state ^{13}C NMR and ^1H CRAMPS analyses. This conclusion also leads to the confirmation for the previous assignments^{8-14,20,21} of the CH I, II, and III lines that these lines should be respectively assigned to the CH carbons associated with two, one, and no intramolecular hydrogen bond(s) for the planar zigzag PVA chain as shown in Figure 1.

CONCLUSION

^1H CRAMPS, solid-state ^{13}C NMR, and 2D ^1H - ^{13}C HETCOR analyses have been applied to the PVA films with different tacticities including some partially deuterated samples and the following conclusions have been

obtained:

- (1) It is found by ^1H CRAMPS analyses below T_g that there exist three types of OH groups, OH_{intra} , OH_{inter} , and OH_f , which are respectively assigned to the OH groups associated with intra- and intermolecular hydrogen bonding and OH groups free from any hydrogen bonding. These lines have their inherent ^1H chemical shift values irrespective of the triad tacticity, conformation, and temperature.
- (2) Above T_g , a new resonance line referred to OH_r appears at about 4.5 ppm and this OH_r line can be assigned to the OH groups which undergo rapid exchanges among different types of hydrogen bonds in the noncrystalline region. When the mole ratio of OH_{intra} and OH_{inter} groups is assumed to be the same as that below T_g , the mole fraction of OH_f groups is estimated to be 0.32 at 160°C in the rubbery noncrystalline region by analyzing the ^1H chemical shift value of the OH_r groups in terms of the three-site exchange model. In good accord with the appearance of the OH_r line, the CH resonance line assignable to the rubbery component is found to appear above T_g by solid-state ^{13}C NMR line shape analysis.
- (3) The mole fraction of the OH_f groups stays constant irrespective of temperature, whereas the mole fractions of the OH_{intra} and OH_{inter} groups are markedly decreased above T_g with increasing temperature as a result of the appearance of the OH_r groups. The former fact suggests that the OH_f groups are preferentially distributed in the crystalline region probably because of the rigid crystal structure even at higher temperatures. In fact, the sum of the mole fractions of the OH_{intra} , OH_{inter} , and OH_f groups at 160°C, where two former fractions also level off, well agrees with the degree of the crystallinity for conventional annealed A-PVA samples.
- (4) 2D ^1H - ^{13}C HETCOR spectra for A-PVA films reveal that two-bond separated correlations between OH protons and CH carbons are successfully observed at a CP contact time of 120 μs but the contributions from the CH and CH_2 protons are still seriously overlapped. The employment of main-chain deuterated A-PVA- d_3 films improves such a situation and more evident correlations are detected between the ^1H OH lines and ^{13}C CH lines. These results confirm the validity of the assignments described above for the resonance lines in ^1H CRAMPS and CP/MAS ^{13}C NMR spectra of PVA samples with different tacticities.

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