Solid-State ^{13}C NMR and ^1H CRAMPS Investigations of the Hydration Process and Hydrogen Bonding for Poly(vinyl alcohol) Films

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ABSTRACT: The hydration process and resulting hydrogen bonding for atactic poly(vinyl alcohol) (A-PVA) films have been investigated by high-resolution solid-state NMR spectroscopy. In ^1H CRAMPS spectra for the A-PVA films which are dried after soaked in deuterated water for different periods, the prominent decrease in intensity is observed within 5 min for the resonance line assigned to the intermolecular hydrogen-bonded OH (OH_{inter}) groups while such an intensity reduction occurs over about 30 min for the line ascribed to the intramolecular hydrogen bonded-OH (OH_{intra}) groups. This fact indicates that the exchange between the OH protons and deuteriums of deuterated water is more preferably induced for the OH_{inter} groups compared to the case of the OH_{intra} groups in the noncrystalline region. In contrast, all OH protons in the crystalline region, including OH protons free from hydrogen bonding that are selectively allowed to exist in this region, are found to undergo the exchange with deuteriums at a much slower rate. It is also found by the ^{13}C spin-lattice relaxation analysis that there exist three components with different $T_{1\rho}$ values assigned to the crystalline, less mobile, and mobile components in the A-PVA films with the water content of 0.82 g-water/g-PVA. The line shape analysis of the CH resonance line for the crystalline component reveals that the probability of the formation of intra-molecular hydrogen bond in the *meso* sequence significantly increases by the addition of water. In the less mobile component the intra- and intermolecular hydrogen bonds are still kept irrespective of the enhanced molecular motion induced by the hydration but the *gauche* conformation markedly increases in mole fraction probably as a result of partial breaking of hydrogen bonding. In contrast, the mobile component is subjected to rapid exchanges among different conformations and hydrogen bonds, resulting in the appearance of the sharp triplet assignable to the CH carbons in the *mm*, *mr*, and *rr* sequences like the spectrum in solution. Finally the size of the crystallites is estimated to be about 26 nm by the analysis of the ^1H spin diffusion process from the water-swollen noncrystalline region to the crystalline region.

KEY WORDS Poly(vinyl alcohol) / Crystal Structure / Hydration / Hydrogen Bonding / Conformation / CP/MAS ^{13}C NMR / ^1H CRAMPS /

Poly(vinyl alcohol) (PVA) is a typical water-soluble/hydrophilic polymer and widely used as films and fibers for optical and other purposes.^{1,2} In addition, PVA has a potentiality as a material with high modulus and high tenacity because the tensile modulus along the molecular chain axis in the crystalline region is higher than that of polyethylene.^{3,4} However, such materials are not still developed probably because of the difficulty in controlling intra- and intermolecular hydrogen bonding during processing. Therefore, we conducted solid-state ^{13}C NMR^{5–10} and ^1H combined rotation and multiple pulse spectroscopy^{11–13} (CRAMPS) analyses to characterize the hydrogen bonds of the dried PVA films with different tacticities: The probabilities of the formation of intramolecular hydrogen bonding and the mole fractions of the *trans* conformation in the crystalline and noncrystalline components were successfully obtained by the detailed ^{13}C NMR line shape analysis for the CH resonance line and the statistical treatment for intensities of the constituent lines.¹⁰ The ^1H CRAMPS analysis also revealed the existence of three types of OH groups in the different hydrogen-bonded states at room temperature; intra- and intermolecular hydrogen bonded OH groups and OH groups free from hydrogen bonding.^{12,13} Moreover, ^1H - ^{13}C heteronuclear correlation (HETCOR) spectra indicated the evident correlations between the ^1H and ^{13}C corresponding constituent lines and supported

the assignments of the respective ^1H and ^{13}C resonance lines.¹³

As described above, the solid-state ^{13}C NMR and ^1H CRAMPS analyses are powerful for the characterization of hydrogen bonding of PVA in the solid state and our main interests were focused on the analysis for the dried PVA films. On the other hand, the characterization of hydrogen bonding in the hydrated state of PVA should be also very important, because PVA hydrogels are used for biomedical materials, absorbents, and other applications and their characteristic properties and functions may greatly depend on their hydrogen-bonded states.^{14–18}

In this paper, we apply similar solid-state ^{13}C NMR and ^1H CRAMPS analyses to the characterization of the hydration process and resulting hydrogen bonding for atactic PVA (A-PVA) films. ^1H CRAMPS analyses for the A-PVA films which are soaked in deuterated water for different periods reveal the breaking process of the intra- and intermolecular hydrogen bonds. As for the hydrated state of PVA, we separate three different regions by the difference in the penetration of water molecules and investigate hydrogen bonding and the chain conformation in each region. Furthermore, we evaluate the size of the crystallites by the ^1H spin diffusion method.

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EXPERIMENTAL

Samples

A-PVA with a viscosity-average degree of polymerization of 1700, which was provided by Kuraray Co., was used after complete saponification. The triad tacticities, which were determined at 50°C in deuterated dimethyl sulfoxide (DMSO- d_6) by gated decoupling ^{13}C NMR spectroscopy, are as follows: $mm = 0.23$, $mr = 0.50$, $rr = 0.27$. Films with a thickness of about 100 μm were prepared by casting the 10 wt% aqueous solution on a glass plate. After drying at 50°C for 2 days under vacuum, these films were subjected to annealing at 180°C for 10 min in an argon atmosphere. The A-PVA films to observe the hydration process by ^1H CRAMPS were prepared by soaking the annealed A-PVA films into 99.9% deuterated water at room temperature for different periods and then dried quickly under vacuum at room temperature for 2 days. Hydrated A-PVA films for ^{13}C NMR measurements were prepared by soaking annealed A-PVA films in normal water for 1 h, gently pressed with filter papers, and then packed in a MAS rotor with an O-ring seal^{6,7,9,19} or in a glass tube which was sealed by silicon adhesive to avoid the absorption or loss of water during NMR measurements. The water content for the hydrated A-PVA films was about 0.82 g-water/g-PVA.

Solid-State NMR Measurements

Solid-state ^{13}C NMR and ^1H CRAMPS measurements were performed at room temperature on a Chemagnetics CMX-400 spectrometer operating under a static magnetic field of 9.4 T. A JEOL GSX-200 spectrometer was also used for solid-state ^{13}C NMR measurements operating under a static magnetic field of 4.7 T. ^1H and ^{13}C radio frequency fields $\gamma B_1/2\pi$ were 62.5 kHz. The MAS rate was set to 5.0 kHz for the CMX-400 spectrometer and 3.5 kHz for the GSX-200 spectrometer to avoid overlapping of spinning side bands on other resonance lines. ^{13}C chemical shifts were expressed as values relative to tetramethylsilane (Me_4Si) by using the CH_3 line at 17.36 ppm for hexamethylbenzene crystals as an external reference. The saturation recovery method modified for solid-state measurement²⁰ was used for ^{13}C spin-lattice relaxation time ($T_{1\rho}$) measurements.

The multiple pulse sequence employed for ^1H CRAMPS^{21,22} measurements is BR-24,²³ the $\pi/2$ pulse width and the pulse spacing being 1.3 and 3.0 μs , respectively. The rate of magic angle spinning was about 1.5 kHz for ^1H CRAMPS measurements. ^1H chemical shifts were expressed as values relative to the CH_3 resonance line at 0.0 ppm of poly(dimethylsiloxane) inserted in each sample as an internal reference.

RESULTS AND DISCUSSION

Hydration Process for PVA Films

To investigate changes in hydrogen bonding during the hydration of PVA films, we have measured ^1H CRAMPS spectra for A-PVA films which were soaked in deuterated water for different periods and then quickly dried under vacuum as shown in Figure 1. These spectra provide us interesting information about the residual

Figure 1. 400 MHz ^1H CRAMPS spectra of dried A-PVA films after soaked in deuterated water for different periods.

OH protons which are not exchanged with deuteriums during soaking in deuterated water. Figure 1 also shows the results of the line shape analysis previously developed^{12,13} for conventionally prepared and dried PVA films with different tacticities. Such a line shape analysis is found to be also successfully conducted for the partially OH-deuterated A-PVA samples. According to the results by this line shape analysis, the OH resonance lines are resolved into three contributions from the intra- and intermolecular hydrogen-bonded OH protons and OH protons free from hydrogen bonding, which are hereafter referred to as OH_{intra} , OH_{inter} , and OH_f protons, respectively. A prominent decrease in intensity of the OH_{inter} line is observed for the sample soaked for 5 min in deuterated water, whereas the intensity of the OH_{intra} line seems to stay almost unchanged in this sample. This fact indicates that rapid exchange first occurs within 5 min between intermolecular hydrogen-bonded OH protons and deuteriums of deuterated water probably in the noncrystalline region. There seems to be no occurrence of such exchange for the OH_{intra} protons during a shorter soaking period. However, a certain number of the OH_{intra} protons are also exchangeable with deuteriums for a longer soaking period, as clearly seen by the decrease in intensity of the OH_{intra} line for the sample soaked for 3 h.

The mole fractions of the OH_{intra} , OH_{inter} , and OH_f protons for the A-PVA films, which were determined as integrated fractions by the lineshape analysis shown in Figure 1, are plotted as a function of the soaking time in Figure 2. The closed circles designate the total mole fractions of the three OH protons. These fractions are in good accord with the mole fractions of the residual OH

Figure 2. Plots of the molar fractions of different OH groups against the soaking time for dried A-PVA films soaked in deuterated water for different periods. ●: Total mole fraction of the three OH groups; □: OH_{inter}; ○: OH_{intra}; △: OH_f.

groups after soaking in deuterated water for different soaking periods, which were separately estimated for the corresponding deuterated samples after dissolved in DMSO-*d*₆ by solution-state ¹H NMR spectroscopy. This fact indicates the validity of the ¹H CRAMPS line shape analysis used in this work.

It is found that the mole fraction of the OH_{inter} protons markedly decreases within 5 min, as also pointed out in Figure 1. In contrast, the fraction of the OH_{intra} protons is gradually reduced over the initial period of about 30 min. For longer-term soaking such decreases in mole fractions attain to extremely slow levels for both OH_{inter} and OH_{intra} protons. Almost the similar slow reduction in mole fraction is observed from the initial stage for the OH_f protons, which were confirmed to selectively exist in the crystalline region by the previous ¹H CRAMPS analysis.^{12,13} Moreover, the total mole fraction (0.42) of the three OH protons for the soaking time of 30 min is in good accord with the mole fraction (0.43) of the crystalline component determined at 160°C for the non-deuterated A-PVA films by the ¹H CRAMPS line shape analysis.^{12,13} It is, therefore, concluded that the OH protons in the noncrystalline region are preferentially exchanged with deuteriums within about 30 min and the exchange rate is much faster for OH_{inter} protons than for OH_{intra} protons. It should be also noted that the three kinds of OH protons in the crystalline region are also allowed to exchange with deuteriums at almost the same rates but their rates are found to be extremely slow at room temperature. According to the results shown in Figure 2, it will take more than 10⁶ h to exchange all OH protons with deuteriums of deuterated water in the crystalline region for A-PVA films. Such slow exchange rates in the crystalline region may be mainly due to the slow diffusion rate of water molecules in this region and the difference in proton-deuterium exchange rate cannot be detected for the OH groups differently associated with hydrogen bonding unlike the case in the noncrystalline region.

Hydrogen Bonding in the Hydrate State

Figure 3a shows a fully relaxed dipolar decoupling

Figure 3. High-resolution solid-state ¹³C NMR spectra of the hydrated A-PVA films with the water content of 0.82 g-H₂O/g-PVA: (a) Fully relaxed DD/MAS ¹³C NMR spectrum obtained by the $\pi/4$ single pulse sequence with a pulse delay time of 40 s. (b) CP/MAS ¹³C NMR spectrum measured at a CP contact time of 1.0 ms.

(DD)/MAS ¹³C NMR spectrum measured for the hydrated A-PVA films with the water content of 0.82 g-H₂O/g-PVA by the $\pi/4$ single pulse sequence. Here, the pulse delay time was set to 40 s because the *T*_{1C} of the crystalline component is 10.3 s as shown in Figure 5 later. A sharp triplet is clearly observed for the CH resonance line and the constituent lines are assigned to the CH carbons in the *mm*, *mr*, and *rr* triad sequences in the order of decreasing chemical shift.²⁴ These lines may appear as a highly mobile component which is produced in the noncrystalline region by the addition of water. Even in the hydrated state, the CH I and II resonance lines seem to also appear though the CH III line may be superposed on the contribution from the mobile CH carbons. Here, the CH I, II, and III lines are assigned to the CH carbons which are associated with two, one, and no intramolecular hydrogen bond(s) in the triad sequence with the planar zigzag conformation, respectively.^{5-10,25-28}

For comparison, CP/MAS ¹³C NMR spectrum for the same hydrated A-PVA films is shown in Figure 3b. Here, the CP contact time was set to 1 ms. The CH I, II, and III lines are clearly observed in this spectrum probably due to less molecular mobility of the corresponding CH carbons. In contrast, the *mm*, *mr*, and *rr* triplet is suppressed to the noise level because of the less CP efficiency of the corresponding carbons with higher mobility. Only the *mr* contribution is barely detected as indicated by an arrow in Figure 3b. From these spectra it is found that there are at least two components with different molecular mobilities. To obtain more detailed information about the components including the hydrated A-PVA films, *T*_{1C} relaxation behavior has been measured for this sample at room temperature by the saturation recovery pulse sequence modified for solid-state measurements.²⁰

Figure 4 shows the partially relaxed ¹³C NMR spectra of the hydrated A-PVA films measured by the saturation recovery method²⁰ with different *T*_{1C} delay times (τ). As

Figure 4. Partially relaxed ^{13}C NMR spectra of the hydrated PVA films measured at room temperature by the saturation recovery method modified for solid-state measurements.

Figure 5. The saturation recovery process of the integrated intensity for the CH resonance line shown in Figure 5 as a function of the T_{1C} delay time (τ).

is clearly seen for the spectra obtained for $\tau < 0.5$ s, there exist three sharp CH lines corresponding to the highly mobile component in the noncrystalline region. As the τ value further increases, the CH I and II lines appear and their intensities are significantly increased. To examine the existence of the components with different mobilities, the integrated intensities of the whole CH line over the region from 55 to 85 ppm are plotted against τ in Figure 5. It is clearly found by the computer-aided least-squares method that the saturation recovery curve, indicated as closed circles, can be resolved into three components with different T_{1C} values, as shown in Figure 5. The component with the longest T_{1C} value (10.3 s) should be assigned to the crystalline component, because a longer T_{1C} value implies less molecular mobility under

Figure 6. High-resolution solid-state ^{13}C NMR spectra of the different components measured for the hydrated A-PVA films at room temperature: (a) crystalline; (b) less mobile; (c) mobile.

the present experimental condition. The component with the shortest T_{1C} value (0.04 s) can be readily assigned to the mobile component in the noncrystalline region because this component corresponds to the sharp CH triplet appearing for $\tau < 0.5$ s as seen in Figure 4. In contrast, the assignment of the component with the medium T_{1C} value (1.0 s) seems not to be straightforward and this component is simply referred to as the less mobile component hereafter.

The very short T_{1C} value of the mobile component may imply the occurrence of the rapid exchange among the hydrogen-bonded and free OH groups induced by the hydration in the noncrystalline region. It should be also noted that the T_{1C} value of the crystalline component greatly decreases to 10.3 s compared with the case of the dried sample with $T_{1C} \sim 60$ s.⁵⁻¹⁰ This fact also suggests the increase in molecular mobility in the crystalline region by the hydration, but it does not indicate the break and exchange of hydrogen bonding because the CH I, II, and III lines are observed even in the hydrated sample as shown later in Figure 6b.

On the basis of the T_{1C} measurement shown in Figures 4 and 5, the spectra of the respective components can be separately recorded. The spectrum of the crystalline component is readily obtained by the CPT1 pulse sequence²⁹ by setting the T_{1C} delay time to 5 s, where the contributions from shorter T_{1C} components are fully suppressed. In contrast, separate recording of the less mobile and mobile components is not straightforward as described below: When the saturation recovery method is applied to the hydrated A-PVA films with three T_{1C} values (T_{1C}^c , T_{1C}^{lm} , and T_{1C}^m), the magnetization $M(t)$ at time t should be expressed as follows;

$$M(t) = M_{c0}[1 - \exp(-t/T_{1C}^c)] + M_{lm0}[1 - \exp(-t/T_{1C}^{lm})] + M_{m0}[1 - \exp(-t/T_{1C}^m)] \quad (1)$$

where M_{c0} , M_{lm0} , and M_{m0} are the equilibrium magnetizations of the crystalline, less mobile, and mobile components, respectively. According to eq 1, the magnetization at time t_a is expressed as the following equation when t_a is much shorter than T_{1C}^c and then the first term can be assumed to be 0:

$$M(t_a) = M_{lm0}[1 - \exp(-t_a/T_{1C}^{lm})] + M_{m0}[1 - \exp(-t_a/T_{1C}^m)] \quad (2)$$

Then,

$$AM(t_a) = BM_{lm0} + M_{m0} \quad (3)$$

where

$$A = 1/[1 - \exp(-t_a/T_{1C}^m)] \\ B = [1 - \exp(-t_a/T_{1C}^{lm})]/[1 - \exp(-t_a/T_{1C}^m)] \quad (4)$$

By subtracting $AM(t_a)$ and M_{c0} from the total equilibrium magnetization M_{t0} , M_{lm0} is obtained as:

$$M_{t0} - AM(t_a) - M_{c0} = (1 - B)M_{lm0} \quad (5)$$

Here, M_{t0} and M_{c0} correspond to the fully relaxed ^{13}C NMR spectrum and the spectrum of the crystalline component, respectively. Accordingly, the spectrum (M_{lm}) of the less mobile component is obtained by subtracting the spectrum of the crystalline component and the spectrum ($AM(t_a)$) obtained at $t_a = 0.05$ s from the fully relaxed spectrum (Figure 3a). On the other hand, the spectrum (M_{m0}) of the mobile component is obtained by subtracting the spectrum (BM_{lm}) of the less mobile component from the spectrum ($AM(t_a)$) obtained at $t_a = 0.05$ s as is clearly seen by eq 3.

Figure 6 shows the CH resonance lines for the crystalline, less mobile, and mobile components in the hydrated A-PVA films, separately recorded by the methods described above. As shown in Figure 6a, lines I, II, and III, which are well described as Gaussian curves, are clearly observed for the crystalline component, although a minor Gaussian contribution referred to as III_f should be introduced most upfield for better fitting. From the intensity analysis of lines I, II, and III including III_f by the method previously reported,^{10,27} the probability (f_a) for the formation of intramolecular hydrogen bonding is found to be 0.84. Table I files the f_a value thus obtained

for the crystalline component of the hydrated A-PVA films together with the integrated fractions of the constituent lines. For comparison, the results for the dried A-PVA films⁹ are shown in this table. It is clearly found that the f_a value is as large as 0.84 for the hydrated sample compared to the value (0.67) for the dried sample. This simply suggests that some intermolecular hydrogen bonds in the *mm* and *mr* sequences are changed to the intramolecular hydrogen bonds by the addition of water. Such changes in hydrogen bonding will be induced together with the enhanced molecular motion that is indicated by the decrease in T_{1C} for the hydrated PVA films as shown in Figure 5. Some small amount of water may rapidly diffuse in the crystalline region probably through structural defects and promote the changes in hydrogen bonding and molecular mobility.

On the other hand, line III_f should be assigned to the CH carbons combined to the OH groups free from hydrogen bonding, as already done for the hydrated PVA films in the previous work.^{5,7} This assignment may be supported by the existence of the OH_f protons free from hydrogen bonding in the crystalline region as was already described in Figures 1 and 2. Moreover, a small amount of water penetrating in the crystalline region may induce the downfield shift for the III_f line, which must be overlapped on line III in the dried state. The same III_f component was also directly observed in the crystalline component for the dried PVA fibers and the mole fraction was found to increase with increasing draw ratio.²⁸

The CH resonance line of the less mobile component obtained from eq 5 is shown in Figure 6b. Since the line shape is significantly different from that of the crystalline component, this resonance line is resolved into some constituent lines by the lineshape analysis^{10,27} previously developed. Here, 9 constituent lines with different chemical shifts are introduced by considering downfield shifts due to the formation of the intramolecular hydrogen bonding for appropriate vicinal OH groups and upfield shifts caused by the γ -*gauche* effect^{30,31} induced by the introduction of the *gauche* conformation along the all-*trans* conformation. In this case, 6 constituent lines are used to reproduce the observed spectrum. In Table I is also summarized the integrated intensity fractions of the respective constituent lines for the CH carbons for the less mobile component of the hydrated A-PVA films. For comparison, the corresponding fractions are also filed for the noncrystalline component of the dried A-PVA films.⁹ It is found that lines 1 and 3, which respectively correspond to lines I and II, are somewhat decreased in intensity by the hydration but their contribu-

Table I. Integrated Fractions of the Respective Constituent Lines for the CH Carbons and f_t and f_a Values for Different Components of Dried and Hydrated A-PVA Films

Samples	Line						f_t	f_a
	1(I)	2	3(II)	4	5	6(III)	7	
Dried A-PVA films ^a								
Crystalline	0.10		0.46			0.44	1.0	0.67
Noncrystalline	0.19	0.05	0.43	0.04	0.09	0.21	0.92	0.97
Hydrated A-PVA films ^b								
Crystalline	0.14		0.50			0.36	1.0	0.84
Less Mobile	0.08	0	0.30	0.36	0.18	0.04	0.04	— ^c

^a Ref 9; ^b this work; ^c not calculated because the previous statistical treatment^{10,27} is not suitable in this case.

tions are still kept at significant levels. In contrast, the intensity of line 6, which corresponds to line III, greatly decreases by the addition of water. Such decreases mainly contribute to the intensity increases for lines 4 and 5. Since lines 4 and 5 are assigned to the CH carbons associated with the *gauche* conformation, the non-crystalline PVA chains adopt more randomized conformations probably due to breaking of intra- and intermolecular hydrogen bonding by the addition of water. In fact, the *trans* fraction f_t is as high as 0.92 for the non-crystalline component for the dried PVA films as shown in Table I.⁹ Unfortunately, the real *trans* fraction f_t as well as the f_a value cannot be obtained for the less mobile component of the hydrated sample, because the previous statistical treatment^{10,27} is not successfully carried for the relative intensities of the constituent lines. The main cause of the difficulty may be the non-random distributions in conformation and hydrogen bonding in the less mobile component probably due to the location of this component as an interfacial component between the crystalline and the mobile amorphous components.

The spectrum of the mobile component is also obtained from eq 3 by using two types of spectra as shown in Figure 6c. Sharp three lines assignable to the CH carbons in the *mm*, *mr*, and *rr* sequences are clearly observed, suggesting that the conformation and hydrogen bonding are fully averaged out, like in solution, as a result of the enhanced molecular motion by the addition of water. Moreover, the relative integrated intensity of the *mm*, *mr*, and *rr* lines of the mobile component is found to 0.24/0.50/0.26, which is in good agreement with the relative mole fraction of the corresponding triad tacticity of the A-PVA sample. This fact indicates that the *mm*, *mr*, and *rr* units may be equally distributed in the crystalline and noncrystalline regions for the A-PVA films.

To estimate the crystallite size in the hydrate state, the ^1H spin diffusion process has been examined at room temperature by the pulse sequence shown in Figure 7. In this pulse sequence, ^1H magnetization for the mobile component and water included in this component is selectively left by setting the $T_{2\text{H}}$ delay time τ_t to 100 μs with use of their longer ^1H spin-spin relaxation times ($T_{2\text{H}}$).³² The ^1H spin diffusion is allowed to proceed during the τ_d period. In this period, the ^1H magnetization is set alternately along the $+z$ or $-z$ axis to reduce the effect of the ^1H spin-lattice relaxation. It should be, however, noted that the ^1H spin-lattice relaxation time of the hydrated PVA films is much longer than the τ_d values employed in this work and thus the effect of the ^1H spin-lattice relaxation is negligibly small in this system. After that period, the ^1H magnetization is transferred to the corresponding ^{13}C spin system by the CP technique and the ^1H spin diffusion process is detected as the change in ^{13}C magnetization as a function of τ_d .

Figure 8 shows the ^{13}C detected ^1H spin diffusion process for the hydrated A-PVA films as a function of τ_d . For shorter τ_d values only the sharp triplet line of the mobile component is observed for the CH resonance line, indicating that the ^1H magnetization of the mobile component including water is selectively left as expected. Lines I, II, and III of the crystalline component seem to appear at $\tau_d \sim 5$ ms as a result of the spin diffusion from the mobile component including water and their intensities

Figure 7. Pulse sequence for ^{13}C -detected ^1H spin diffusion measurements.

Figure 8. ^{13}C -detected ^1H spin diffusion process for the hydrated PVA films observed by the pulse sequence shown in Figure 7.

markedly increase with increasing τ_d value.

In Figure 9 the peak intensity of line II shown in Figure 8 is plotted as a function of $\tau_d^{1/2}$. It is found that the experimental points are well described as a straight line before leveling off due to the saturation of the ^1H spin diffusion from the mobile component to the crystalline component. When the saturation is assumed to occur at time τ_d^s , the diffusion length r is given by³³⁻³⁵

Figure 9. Plot of the peak intensity of the CH II line shown in Figure 8 as a function of the square root of the spin diffusion time τ_d .

$$r^2 = aD \tau_d^s \quad (6)$$

where D is the spin diffusion coefficient and a is the constant factor depending on the structural models for the spin diffusion. The τ_d^s value is estimated to be 59 ms from Figure 9 and D is assumed to be $0.5 \text{ nm}^2 \text{ ms}^{-1}$.³⁴ If it is assumed that the spherical crystalline phases are dispersed in the noncrystalline continuous phase for the A-PVA films, a should be equal to 6 in eq 6.^{33–35} Then, the averaged radius r of the crystallites is estimated to be 13 nm. This value seems somewhat too large as the crystallite size of A-PVA. The main cause of the overestimation may be the use of the large D value since the spin diffusion will be reduced by the enhanced molecular motion in the hydrated state. A separate experiment is in progress to determine the spin diffusion coefficient in the hydrated PVA films.

CONCLUSION

The hydration process and resulting hydrogen bonding for A-PVA films have been investigated by solid-state ^{13}C NMR and ^1H CRAMPS analyses and the following conclusions have been obtained:

- (1) ^1H CRAMPS analyses of the A-PVA films which are dried after soaked in deuterated water for different periods reveal that the mole fraction of intermolecular hydrogen-bonded OH groups markedly decreases by soaking for 5 min. In contrast, the intramolecular hydrogen-bonded OH groups is found to decrease in fraction over the soaking time of about 30 min. These results indicate that the exchange between OH protons and deuteriums occurs much more rapidly for the intermolecular hydrogen-bonded OH groups than for the intramolecular hydrogen-bonded OH groups in the noncrystalline region. On the other hand, such exchange in the crystalline region proceeds extremely slowly and the rate is almost of the same level for different OH groups including OH groups free from hydrogen bonding.
- (2) Solid-state ^{13}C NMR analyses for the hydrated A-PVA films reveal that there are three components with different $T_{1\rho}$ values; the crystalline, less mobile, and mobile components. In the crystalline component, the probability f_a of the formation of intra-

molecular hydrogen bonding is significantly increased by the addition of water and the OH groups free from hydrogen bonding is separately observed as a result of the downfield shift of the resonance line by the hydration. Two types of hydrogen bonds are found to still remain in the less mobile component even in the presence of water but the *gauche* fraction greatly increases compared to the case in the dried state probably due to breaking of hydrogen bonding by water. As for the mobile component, different types of OH groups are rapidly exchanged with each other by the enhanced molecular motion induced by the addition of water. Moreover, the mole fractions of the *mm*, *mr*, and *rr* sequences obtained for this component are in good accord with the total triad tacticities separately determined for this A-PVA sample. This fact indicates that the different triad structural units are equally distributed in the crystalline and noncrystalline regions.

- (3) The ^1H spin diffusion process from the water swollen noncrystalline region to the crystalline region is successfully measured by the pulse sequence prepared by the combination of the Goldman–Shen pulse sequence and the CP technique and this process is satisfactorily analyzed in terms of the structural model in which the spherical crystalline phases are distributed in the noncrystalline continuous phase. As a result, the averaged radius of the A-PVA crystallites is estimated to be 13 nm.

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