High-Resolution Solid-State ^{13}C NMR of Poly(vinyl alcohol): Enhancement of Tacticity Splitting by Intramolecular Hydrogen Bonds

Takehiko Terao,* Shiro Maeda, and A. Saika

Department of Chemistry, Faculty of Science, Kyoto University, Kyoto 606, Japan.

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ABSTRACT: High-resolution ^{13}C NMR spectra of solid isotactic, atactic, and syndiotactic poly(vinyl alcohol) have been observed, exhibiting a splitting of the methine carbon resonance into three peaks as in solution. The splitting is amplified toward the downfield side by about 3.4 times that in Me_2SO-d_6 solution. The relative intensities of the three peaks reflect the tacticity of the sample, which is, however, in contradiction with the triad tacticity obtained in solution. It is shown that the fixation of the intramolecular hydrogen bonds in solids produces a large downfield shift, and partial formation of the intermolecular hydrogen bonds brings about the discrepancy in the relative intensities.

Introduction

^{13}C NMR spectroscopy in solution has been used as a powerful experimental means to determine the stereoconfiguration in vinyl polymers.[1] Recently, high-resolution ^{13}C NMR spectra in solids have become readily measurable by using the combined techniques (CP/MAS)[2] of high-power proton decoupling,[3] cross polarization,[4] and magic-angle sample spinning.[5] In solid polymers, however, line broadening due to anisotropic bulk magnetic susceptibility and chemical shift dispersion[6] smears out the splitting resulting from differences in tacticity. Consequently, observation of such splitting in solid polymers has not been reported so far.

In this paper we are concerned with ^{13}C NMR spectra of solid poly(vinyl alcohol) (PVA). PVA is known as a crystalline polymer even in atactic form. Many authors[7-10] made X-ray crystal analyses for atactic PVA, referring to intermolecular hydrogen bonds. Although Mooney[7] maintained that no intramolecular hydrogen bond exists, her model was pointed out to be wrong.[11] Others do not refer to intramolecular hydrogen bonds, while IR studies[12-14] suggest their existence. The splitting due to differences in tacticity, which was observed for the first time in the methine carbon resonance of solid PVA, is ascribed to enhanced downfield shifts by formation of intramolecular hydrogen bonds.

Experimental Section

PVA-A, -B, and -C were prepared by cationic polymerization of vinyl *tert*-butyl ether in toluene, radical polymerization of vinyl acetate in methanol, and cationic polymerization of vinyl formate in nitrobenzene, respectively. PVA-D (Kuraray) and poly(vinyl acetate) (Sekisui Chemical) are commercially available atactic samples. PVA-A, -B, and -C were dried under vacuum for 24 h at 338 K and placed in a desiccator until measurements were performed.

Solid-state ^{13}C NMR spectra were obtained on a home-built spectrometer operating at 15 MHz for ^{13}C by using the normal single-pulse method (SP) or the cross-polarization technique (CP)[4] with high-power proton decoupling,[3] and with or without magic-angle sample spinning (MAS).[5] A matched Hartmann-Hahn condition was established by using radio-frequency fields of 15 G for ^{1}H and 60 G for ^{13}C. A contact time of 0.85 ms and a repetition period of 2.0 s were used unless otherwise stated. CP/MAS spectra were obtained at room temperature, using a bullet-type spinner[15] with a spinning frequency of 2.4 kHz. ^{13}C NMR spectra (50 MHz) in Me_2SO-d_6 solution at 353 K were obtained on a JEOL FX-200 spectrometer, using proton noise decoupling with a repetition period of 2.0 s. ^{13}C chemical shifts are reported in parts per million (ppm) relative to Me_4Si. Chemical shifts of MAS spectra were originally obtained with respect to the methylene carbon resonance of solid adamantane measured before and/or after each measurement. The methylene carbon resonance of solid adamantane was observed at 89.79 ± 0.02 ppm upfield from the position of the MAS spectrum for liquid benzene. With the literature chemical shift value of 128.5 ppm[16] relative to Me_4Si for benzene, the chemical shift of the methylene carbon resonance of solid adamantane was determined to be 38.7 ppm with respect to Me_4Si. With this value as reference, chemical shifts of MAS spectra were converted to the value relative to Me_4Si.

Results and Discussion

Figure 1 shows the 50-MHz ^{13}C NMR spectrum of PVA-B in Me_2SO-d_6 solution at 353 K. The four lines about 46 ppm and the three lines about 67 ppm are assigned to the methylene and the methine carbons, respectively, and the heptet resonances about 40 ppm are due to the deuterated methyl carbons of Me_2SO-d_6. The three lines for the methine carbons are assigned to isotactic (mm), heterotactic (mr), and syndiotactic (rr) triads in the order of increasing magnetic field.[17] The triad tacticities determined from the methine carbon resonances for PVA-A, -B, and -C, and tabulated in Table I with the values calculated from the Bernoulli statistics,[18] indicate that PVA-A is fairly isotactic, PVA-B is atactic, and PVA-C is slightly syndiotactic. Consistent with the results of Inoue et al.[19] and Wu and Ovenall,[17] the triad tacticities of PVA-B and -C are described by the Bernoulli process within a probable experimental error, while that of PVA-A is not. Therefore, at least PVA-B and -C are not stereoblock polymers having alternating chain segments of considerable length but are polymers in which the meso and the racemic arrangements are distributed according to the Bernoulli statistics.

CP/MAS spectra of PVA-A, -B, and -C are shown in Figure 2. The bars schematically represent the spectra in Me_2SO-d_6 solution at 353 K; in each spectrum, the bars corresponding to the methine carbon resonance indicate the individual chemical shifts and the triad tacticity, and the bars for the methylene carbon resonance the average chemical shift of the four lines. Noteworthily the methine carbon resonance is split into three peaks in the CP/MAS spectra. We designate these three peaks peak 1, peak 2, and peak 3 in order of increasing magnetic field. The relative intensities of peaks 1, 2, and 3 derived by deconvolution are 0.32, 0.39, and 0.29 for PVA-A, 0.14, 0.44, and 0.42 for PVA-B, and 0.09, 0.43, and 0.48 for PVA-C, respectively. The chemical shifts of the methine and the methylene carbon resonance in solution and in the CP/MAS spectra are contrasted in Table II.

The chemical shifts of the three peaks in the methine carbon resonances are about 77, 71, and 65 ppm regardless of tacticity. The intensity of peak 1 is strongest in isotactic PVA-A and weakest in syndiotactic PVA-C. On the contrary, the intensity of peak 3 is strongest in PVA-C and

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Table I
Triad Tacticity of Poly(vinyl alcohol)

	PVA-A		PVA-B		PVA-C	
triad	obsd[a]	Bernoulli trial $P_m = 0.742$[b]	obsd	Bernoulli trial $P_m = 0.464$	obsd	Bernoulli trial $P_m = 0.437$
mm	0.570	0.550	0.219	0.215	0.188	0.191
mr	0.343	0.383	0.490	0.497	0.497	0.492
rr	0.087	0.067	0.291	0.287	0.315	0.318

[a] Obtained from the methine carbon resonance in Me_2SO-d_6 solution at 353 K. [b] The probability of generating a meso sequence when a new monomer unit is formed at the end of a growing chain.

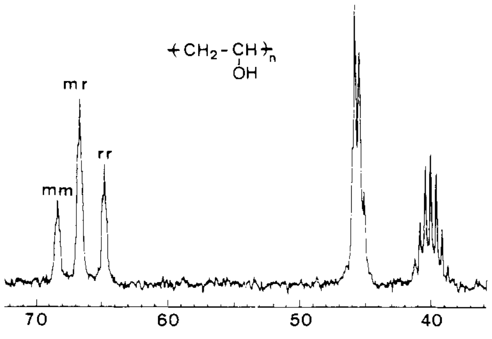

Figure 1. ^{13}C NMR spectrum of PVA-B (7.8% (w/w) solution in Me_2SO-d_6 at 353 K).

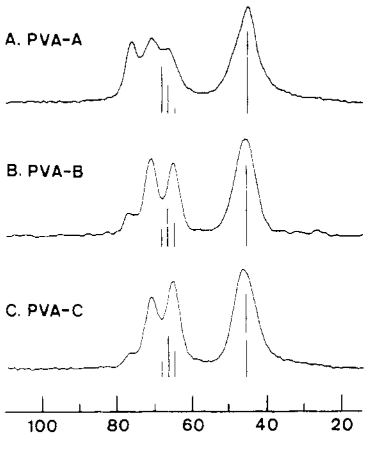

Figure 2. ^{13}C CP/MAS spectra of poly(vinyl alcohol) at room temperature: (A) PVA-A; (B) PVA-B; (C) PVA-C. Line spectra represent the ^{13}C spectra in Me_2SO-d_6 solution at 353 K.

weakest in PVA-A. Thus, the splitting of the methine carbon resonances appears to reflect the stereoregularity of the sample. However, peak 1, peak 2, and peak 3 cannot simply be assigned to the mm, mr, and rr triads, respectively: the relative intensities of the three peaks in the solid state are not consistent with the triad tacticity in solution. Moreover, peak 1 and peak 2 in solids are shifted significantly downfield compared with the mm and the mr line in solution, respectively. The relative intensities of the three peaks of the methine carbon resonance in the CP/MAS spectra showed no contact-time dependence over a range 0.05–5 ms. Therefore, the discrepancy between the relative intensities of the three peaks and the triad tacticity is not attributable to the difference in the cross-polarization efficiency and the ^{13}C spin–lattice relaxation time in the rotating frame among the three peaks. For assignment of peaks 1, 2, and 3, it is necessary to first trace the origins of the large downfield shifts and the discrepancy between the relative intensities and the triad tacticity.

Table II
^{13}C Chemical Shifts of Poly(vinyl alcohol)[a]

	solution[b]				solid			
	CH				CH			
	mm	mr	rr	CH_2	peak 1	peak 2	peak 3	CH_2
PVA-A	68.3	66.6	64.8	45.3	76.0	70.7	66.0	44.8
PVA-B	68.4	66.8	64.8	45.5	77.4	71.2	65.3	46.0
PVA-C	68.3	66.6	64.9	45.7	76.7	71.0	65.2	46.5

[a] In ppm with respect to Me_4Si. [b] Obtained in Me_2SO-d_6 solution at 353 K.

First, we will discuss the downfield shifts of the methine carbon resonance in the CP/MAS spectrum. We cannot attribute the splitting of the methine carbon resonance to a difference in conformation,[20] since the crystalline part of PVA takes the same zigzag planar conformation regardless of the tacticity.[13,21] In solution hydrogen bonds cause a downfield shift of the resonance of the carbon atom directly bonded to the hydrogen-bonded oxygen atom.[22,23] In solids this downfield shift is expected to be larger than that in solution because hydrogen bonds are usually fixed in solids. Recently, we observed appreciable hydrogen-bond shifts for enol forms of diketones in the solid state.[24] For dimedone (5,5-dimethyl-1,3-cyclohexanedione) the average chemical shift of the carbonyl and the enol carbon, which are equivalent in solution, moves downfield by 10.6 ppm compared with the corresponding shift in Me_2SO-d_6 solution, while for tropolone it differs only by 1.3 ppm from the corresponding shift in solution. This observation is attributable to the difference in strength of the hydrogen bonds between the two compounds: dimedone has a short O···O distance (2.594 Å) as compared with the distance (2.75 Å) in tropolone. In solid PVA, the O···O distance of 3.41 Å[25] between the two neighboring hydroxyl groups in the racemic arrangement is too long to make a hydrogen bond, while in the meso arrangement the distance of 2.52 Å[25] suggests the existence of a strong intramolecular hydrogen bond. On the other hand, the O···O distances of intermolecular hydrogen-bonded hydroxyl groups calculated from various models, each having two kinds of hydrogen bonds are 2.8 and 2.9 Å (Bunn[8]), 2.69 and 2.98 Å (Nitta et al.[9]), and 2.70 and 2.73 Å (Sakurada et al.[10]). Thus, the O···O distance of the intermolecular hydrogen bond is larger than that of the intramolecular one. Moreover, it is improbable that intermolecular hydrogen bonds corresponding to the individual tacticities are formed. Consequently, we consider that the downfield shifts of the methine carbon resonance are due to strong intramolecular hydrogen bonds, while the intermolecular hydrogen bonds may cause the line width of the resonance to broaden to some extent. In the case of poly(vinyl acetate) the downfield shift of the methine carbon resonance is not expected, because the oxygen atom bonded to the methine carbon atom cannot make a hydrogen bond. Figure 3 shows that its CP/MAS spectrum meets this

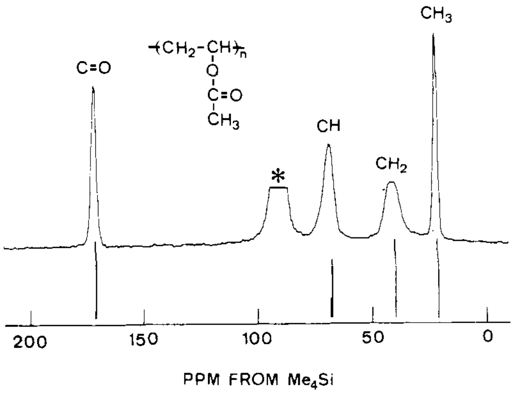

Figure 3. ^{13}C CP/MAS spectrum of poly(vinyl acetate) at room temperature. The spectrum was obtained with a contact time of 3 ms and a repetition period of 3.0 s. The line spectrum represents the spectrum in CDCl$_3$ solution.[31] The peak marked with an asterisk is the signal from a poly(oxymethylene) rotor.

expectation. This fact further supports our view that the downfield shifts of peaks 1 and 2 in PVA are due to intramolecular hydrogen bonds.

In the case of the mm or the mr triad, the oxygen atom bonded to the central methine carbon atom can make two or one intramolecular hydrogen bond(s), respectively. On the other hand, no intramolecular hydrogen bond is expected in the rr triad. Assuming that the line position shifts downfield by about 6 ppm per intramolecular hydrogen bond, we can assign peak 1, peak 2, and peak 3 to the methine carbon with two, one, and no intramolecular hydrogen bond(s), respectively. If intramolecular hydrogen bonds were formed to the full capacity, peaks 1, 2, and 3 should be assigned to the mm, mr, and rr triads, respectively. However, the observed relative intensities of the three peaks are not consistent with the triad tacticity. We believe that partial formation of intermolecular hydrogen bonds brings about the discrepancy in the relative intensity. If some of the hydroxyl groups in the meso arrangement form intermolecular hydrogen bonds, there result three cases in the mm triad where the number of the intramolecular hydrogen bond(s) is two, one, or zero, each resonance line belonging to peak 1, 2, or 3, respectively. Similarly, the resonance line of the mr triad belongs to peak 2 or peak 3 corresponding to whether the intramolecular hydrogen bond is formed or not, respectively. Accordingly, we assign peak 1 to the mm triad with two intramolecular hydrogen bonds, peak 2 to the mm and mr triads with one intramolecular hydrogen bond, and peak 3 to the mm, mr, and rr triads with no intramolecular hydrogen bond. Therefore, the relative intensities of the three peaks in the solid state are not consistent with those in solution: the relative intensity of peak 3 is larger than the rr triad and that of peak 1 is less than the mm triad. It is thus considered to be due to the enhancement of the tacticity splitting by intramolecular hydrogen bonds that splitting in the solid state could be first observed in solid PVA. Generally, the observation of the splitting may be almost impossible because of a broad line width in the solid state.

As for the methylene carbon resonance, line splitting is not observed, in contrast with the methine resonance. The line shape and the position at the maximum height, however, depend on the tacticity of each sample. Wu and Ovenall[17] assigned the four lines of the methylene carbon resonance in MeSO-d_6 solution to rrr, rrm + mrm, mmr + rmr, and mmm in order of increasing magnetic field, and Inoue et al.[19] assigned the three lines in D$_2$O solution to rrr + rmr, rrm + rmm, and mrm + mmm in the same order. Thus, when the line width is larger than the splitting, the line shape of the methylene carbon resonance is expected to be symmetric for atactic PVA-B, while it is expected to be asymmetric for isotactic PVA-A and syndiotactic PVA-C with a steeper slope on the upfield side and the downfield side, respectively. In addition, the position at the maximum height is in the order of PVA-C, -B, and -A with increasing magnetic field.

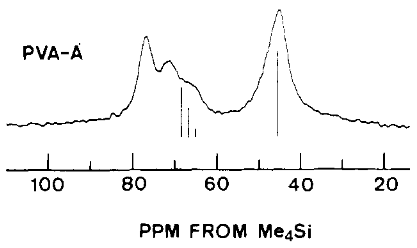

Figure 4. ^{13}C CP/MAS spectrum of PVA-A left in the air for 4 days. The line spectrum is the same as in Figure 2A.

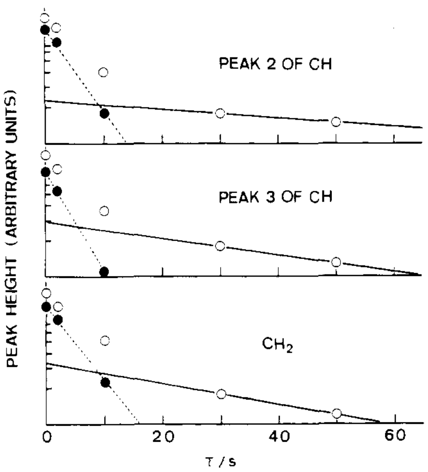

Figure 5. ^{13}C T_1 plots of PVA-B by the T1CP method at room temperature: open circles represent T_1 plots; closed circles are obtained by subtracting a component (solid line) with a longer T_1 value. Slopes of fitted lines yield the T_1 values of about 80 s (solid line) and about 6 s (dotted line) for each carbon.

Figure 4 shows the spectrum of PVA-A exposed in the air for 4 days. A significant change is seen in comparison with the spectrum of a dry sample (Figure 2A): the intensity of peak 1 increases and that of peak 3 decreases. This change is reversible by redrying the sample. We believe that water molecules occupy the space between molecules in isotactic PVA-A and stretch the intermolecular distance, causing some of the intermolecular hydrogen bonds to break and their hydroxyl groups to form new intramolecular hydrogen bonds. As for atactic PVA, it remains to be questioned whether water molecules penetrate the space between PVA molecules.[26-28] We observed no detectable change in the spectra of PVA-B and -C left in the air. Even a swollen PVA-B sample kept in water for 24 h at room temperature showed no change. For PVA-B and -C, however, the result is not in contradiction with the penetration of water molecules into PVA. A rise of the melting point and of the dissolving temperature resulting from a decrease of isotactic parts[29] indicates a stronger condensation force in PVA-B and -C than in PVA-A. Thus, the intermolecular hydrogen bonds may probably remain intact irrespective of water absorption, which explains their invariant spectra.

In Figure 5 are shown the results of ^{13}C spin–lattice relaxation time measurements by the T1CP method.[30] The recovery of magnetization obeys not a single exponential but two overlapping exponentials whose T_1 values are

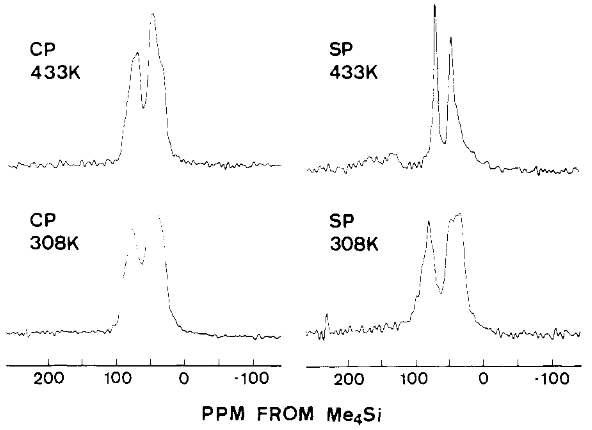

Figure 6. ^{13}C NMR spectra of PVA-D without MAS at 308 K and 433 K: CP spectra obtained with a contact time of 3 ms and a repetition period of 0.5 s (left-hand side); SP spectra obtained with a repetition period of 1.0 s (right-hand side).

about 80 and 6 s (peak 1 of the methine carbon resonance was omitted because of the poor S/N ratio). On the other hand, measurements by a saturating comb–τ–90° pulse sequence[32] show that another component with a T_1 value of about a few hundred milliseconds exists. Crystalline polymers like PVA consist of a crystalline, a medium, and an amorphous component. Only the components with T_1 values of 80 and 6 s assigned to the crystalline and the medium component, respectively, were detected in the CP/MAS spectra, while the mobile component was missed by the CP technique. Figure 6 shows the CP and the SP spectra of atactic PVA-D without MAS at 308 and 433 K; the SP spectra were obtained with a repetition period of 1.0 s. The CP spectra consisting of a crystalline and a medium component signal do not show any notable temperature dependence; in the SP spectra, which are due primarily to the amorphous component signal, the line width decreases with increasing temperature. Therefore, we conclude that in the amorphous component there exists fast micro-Brownian motion prevailing against the intra- and intermolecular hydrogen bonds at high temperatures, while in the crystalline and the medium component the hydrogen bond is still fixed even at 433 K. Splitting due to tacticity could not be observed in the SP spectrum at 433 K. On the other hand, we observed splitting in the SP/MAS spectrum with a repetition period of 1.0 s at room temperature. Variable-temperature SP/MAS experiments are in progress in our laboratory for investigating the details of the molecular motion and hydrogen bonds in PVA.

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