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Assignment of finely resolved ^{13}C NMR spectra of poly(vinyl alcohol)

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Abstract

^{13}C NMR spectra of three poly(vinyl alcohol)s differing in the stereoregularity (atactic, syndiotactic-rich and isotactic-rich) were determined in DMSO-d_6 and D_2O. The methylene and methine carbon absorptions including so far unassigned ones (mmmr heptad signals in mm-centered region and all heptad signals in mr-centered region) were completely assigned with hexads and heptads, respectively, and the assignments were quantitatively confirmed for atactic and syndiotactic-rich poly(vinyl alcohol)s. The isotactic-rich polymer showed a discrepancy between the observed and the calculated intensities, assuming the first-order Markov statistics, due to difficulty in determining its polymerization mechanism. © 2001 Published by Elsevier Science Ltd.

Keywords: Poly(vinyl alcohol); ^{13}C NMR assignment; Polymerization statistics

1. Introduction

The ^{13}C NMR spectra of most of the vinyl polymers have been determined and assigned as summarized by Matsuzaki et al. [1]. However, those of even simple vinyl polymers are not fully assigned and needs reinvestigations using spectrometers of very high resolution such as 500–600 MHz, and new NMR techniques such as HETCOR-TOCSY (heteronuclear chemical shift correlation-total correlation spectroscopy) and INADEQUATE spectroscopy. In our previous articles, finely resolved ^{13}C NMR spectra of poly(vinyl acetate)s [2] and polyacrylonitriles [3] differing in their tacticities were reinvestigated and new assignments were proposed.

The ^{13}C NMR spectra of poly(vinyl alcohol) (PVA) have been investigated by several investigators [4–9]. Among them, Ovenall [7] qualitatively assigned enhanced methine and methylene carbon spectra of atactic and isotactic poly(vinyl alcohol)s (PVAs) with heptads and hexads, respectively. However, mmmr heptad signals composed of four sharp absorptions and all of mr-centered heptad signals (heterotactic absorptions) were left unassigned, probably due to their complexity. Quantitative confirmation has not been carried out except for several absorptions of isotactic PVA. Tonelli [8] calculated ^{13}C NMR chemical shifts using γ-gauche effect method and proposed a little different order of chemical shifts for methylene carbon signals. Hikichi et al. [9] assigned a finely resolved spectra of a radically obtained PVA using HETCOR (^{1}H–^{13}C COSY) and 2D INADEQUATE technique. The results are the same as those of Ovenall. In this article, absorptions including so-far unassigned ones are completely assigned and quantitatively confirmed, using three PVA samples with different tacticities and different polymerization mechanisms.

2. Experimental

2.1. Samples

An almost atactic PVA (m diad, 0.46)(A-PVA) was prepared from radically obtained poly(vinyl acetate). Poly(vinyl alcohol) was then treated with sodium periodate to cleave 1,2-glycol units in the polymer. DP = 100. A syndiotactic-rich PVA (m diad, 0.39)(S-PVA) was obtained by deesterification of poly(vinyl pivalate) which was prepared by radical polymerization of the monomer with 2,2-azobisisobutyronitrile as catalyst in methanol at 60°C. The deesterification of poly(vinyl pivalate) to PVA was carried out with KOH in THF at 60°C.

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Table 1
Configuration parameters of poly(vinyl alcohol)s

		A-PVA	S-PVA	I-PVA
Triad	mm	0.218	0.148	0.699
	mr	0.492	0.493	0.252
	rr	0.290	0.359	0.048
Parameters	P_{mr}	0.530	0.625	0.153
	P_{rm}	0.459	0.407	0.724
	$P_{mr} + P_{rm}$	0.989	1.032	0.877

An isotactic-rich PVA (m diad, 0.92)(I-PVA) was obtained from poly(*tert*-butyl vinyl ether) which was prepared from the monomer by cationic polymerization with BF_3OEt as catalyst at −78°C in toluene. The polymer was deetherified with hydrogen bromide [10].

2.2. ^{13}C NMR measurement

^{13}C NMR measurements were carried out with a JEOL LA 500 spectrometer at 125 MHz in D_2O at 80°C or in DMSO-d_6 at 80°C. Both S-PVA and I-PVA did not dissolve in D_2O. The intensity of the peaks was determined from integration curves. The error of the determination is ±0.002.

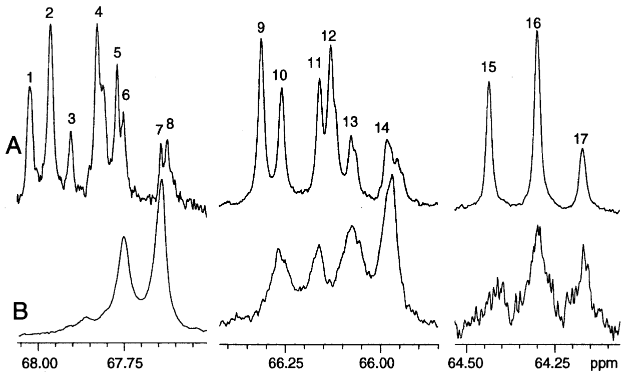

Fig. 1. ^{13}C NMR spectra of methine carbon of poly(vinyl alcohol)s measured in DMSO-d_6: (A) S-PVA; (B) I-PVA.

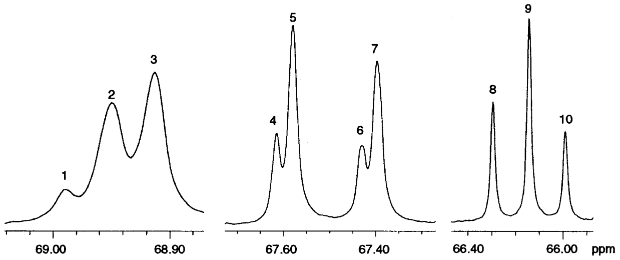

Fig. 2. ^{13}C NMR spectra of methine carbon of atactic poly(vinyl alcohol) measured in D_2O.

Table 2
Assignment for methine carbon spectra of poly(vinyl alcohol)s measured in DMSO-d_6 at 100°C

Peak no.	Chemical shift (ppm)	Assignment	A-PVA ($r = 0.54$)		S-PVA ($r = 0.61$)		I-PVA ($r = 0.18$)	
			Observed	Calculated[a]	Observed	Calculated[b]	Observed	Calculated[c]
1	68.09	rrmmrr	0.020	0.018	0.021	0.020	0.064	0.016
2	68.04	mrmmrr	0.030	0.030	0.029	0.028		
3	67.98	mrmmrm	0.018	0.013	0.013	0.010		
4	67.92	rmmmrr + mmmmrr	0.055	0.059	0.037	0.041	0.270	0.181
5	67.86	rmmmrm	0.024	0.026	0.016	0.018		
6	67.85	mmmmrm	0.026	0.023	0.013	0.011		
7	67.75	rmmmmr	0.016	0.014	0.007	0.008	0.365	0.502
8	67.74	mmmmmr + mmmmmm	0.030	0.035	0.011	0.013		
9	66.40	rrmrrr + rrmrrm	0.075	0.076	0.105	0.108	–	–
10	66.35	mrmrrr + mrmrrm	0.066	0.065	0.080	0.074	0.067	0.013
11	66.26	rrmrmr + rrmrmm	0.066	0.065	0.068	0.074	0.039	0.044
12	66.24	mrmrmr + mrmrmm + rmmrrr + mmmrrr	0.115	0.122	0.108	0.116	–	–
13	66.17	rmmrrm + mmmrrm	0.062	0.057	0.056	0.045	0.065	0.043
14	66.08	mmrm	0.107	0.106	0.078	0.075	0.081	0.155
15	64.57	rrrr	0.086	0.085	0.123	0.126	0.012	0.004
16	64.43	mrrr	0.141	0.144	0.170	0.173	0.023	0.019
17	64.30	mrrm	0.063	0.061	0.065	0.060	0.014	0.025

[a] Assuming Bernoullian statistics for $P_m = 0.46$.
[b] Assuming Bernoullian statistics for $P_m = 0.39$.
[c] Assuming first-order Markov statistics for $P_{mr} = 0.15$ and $P_{mr} = 0.72$.

Table 3
Assignment for methine carbon spectra of ataactic poly(vinyl alcohol) in D_2O at 100°C

Peak no.	Chemical shift (ppm)	Assignment	A-PVA ($r = 0.54$)	
			Observed	Calculated[a]
1	68.99	rrmmrr	0.025	0.018
2	68.95	mrmmrr + rmmmrr+ rmmmrm	0.084	0.088
3	68.91	mrmmrm + mmmmrr + mmmmrm + mmmm	0.109	0.112
4	67.62	rrmrrr + rrmrrm	0.076	0.076
5	67.58	mrmrrr + mrmrrm+ rmrm	0.190	0.184
6	67.43	rmmrrr + mmmrrr	0.072	0.068
7	67.40	rmmrrm + mmmrrm+ mmrm	0.154	0.164
8	66.30	rrrr	0.081	0.085
9	66.15	mrrr	0.144	0.144
10	65.99	mrrm	0.066	0.061

[a] Assuming Bernoullian statistics for $P_m = 0.46$.

3. Results and discussion

3.1. Methine carbon spectra

Fig. 1 shows methine carbon spectra of PVAs measured in DMSO-d_6. The spectra were largely divided into three parts, mm (peaks 1–8), mr (peaks 9–14) and rr (peaks 15–17) in the order of increasing magnetic field. The triad fractions are obtained from the spectra as shown in Table 1. It has been known that the polymerization mechanism of radically obtained polymers usually obeys Bernoullian statistics. The ads were calculated assuming Bernoullian statistics for A-PVA and S-PVA. For I-PVA, the ads were calculated assuming the first-order Markov statistics for the polymerization mechanism. The peaks 1–14 were assigned with heptads as shown in Table 2. The peaks 4–6 and 9–14 were assigned for the first time. It is seen that the calculated

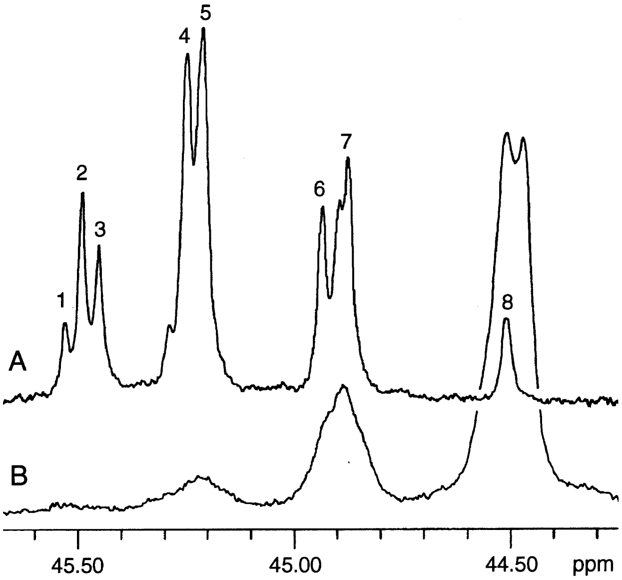

Fig. 3. ^{13}C NMR spectra of methylene carbon of poly(vinyl alcohol)s measured in DMSO-d_6: (A) S-PVA; (B) I-PVA.

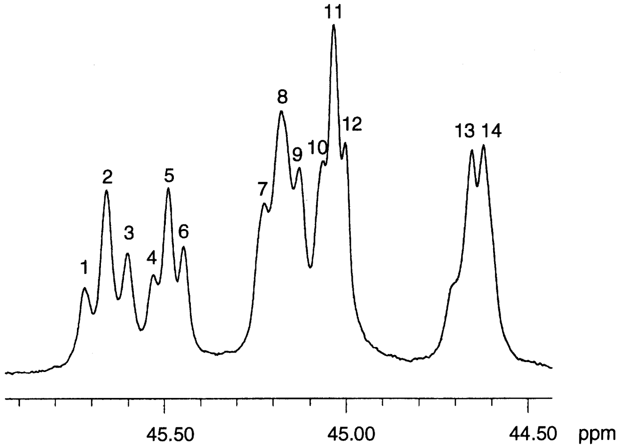

Fig. 4. ^{13}C NMR spectra of methylene carbon of atactic poly(vinyl alcohol) measured in D_2O.

Table 4
Assignment of methylene carbon spectra of poly(vinyl alcohol)s in DMSO-d_6 at 100°C

Peak no.	Chemical shift (ppm)	Assignment	A-PVA ($r = 0.54$)		S-PVA ($r = 0.61$)		I-PVA ($r = 0.18$)	
			Observed	Calculated[a]	Observed	Calculated[b]	Observed	Calculated[c]
1	45.54	mrrrm	0.034	0.033	0.034	0.035	0.023	0.013
2	45.51	mrrrr	0.068	0.078	0.099	0.103		
3	45.46	rrrrr	0.059	0.046	0.072	0.075		
4	45.25	mrmrm + mrmrr + mmrrm + mmrrr	0.227	0.217	0.209	0.209	0.083	0.089
5	45.26	rrmrr + rmrrm + rmrrr	0.170	0.179	0.205	0.237		
6	44.95	mrm	0.342	0.344	0.096	0.100	0.226	0.305
7	44.89	mmr			0.206	0.185		
8	44.56	mmm	0.101	0.102	0.080	0.055	0.667	0.592

[a] Assuming Bernoullian statistics for $P_m = 0.46$.
[b] Assuming Bernoullian statistics for $P_m = 0.39$.
[c] Assuming first-order Markov statistics for $P_{mr} = 0.15$ and $P_{mr} = 0.72$

Table 5
Assignment of methylene carbon spectra of atactic poly(vinyl alcohol) in D_2O at 100°C

Peak no.	Chemical shift (ppm)	Assignment	A-PVA ($r = 0.54$)	
			Observed	Calculated[a]
1	45.72	mrrrm	0.038	0.033
2	45.66	mrrrr	0.070	0.078
3	45.60	rrrrr	0.041	0.046
4	45.53	mrmrm	0.029	0.028
5	45.49	mrmrr + rrmrm	0.059	0.065
6	45.45	rrmrr	0.051	0.038
7	45.23	mmrrm	0.075	0.057
8	45.18	mmrrr + rmrrm	0.118	0.133
9	45.13	rmrrr	0.066	0.076
10	45.07	mmmrm	0.058	0.050
11	45.04	rmmrm + mmmrr	0.107	0.115
12	45.01	rmmrr	0.079	0.066
13	44.56	mmrmm + mmrmr + mmmmm	0.101	0.104
14	44.53	rmrmr + mmmmr + rmmmr	0.109	0.111

[a] Assuming Bernoullian statistics for $P_m = 0.46$.

intensities agree well with the observed ones for both A-PVA and S-PVA. It is noted that a large substituent group in S-PVA does not affect the polymerization mechanism, i.e. the Bernoullian statistics.

^{13}C NMR spectra of I-PVA is broad except for mr region of methine absorptions. The check whether the first-order Markov statistics holds for the polymerization mechanism of I-PVA was carried out by comparing mmmm pentad signal (peaks 7 + 8 in Fig. 1) and mmm tetrad signal (peak 8 in Fig. 3) intensities with those calculated. As shown in Tables 2 and 4, there are considerable discrepancies indicating that the assumption does not hold good. Therefore, the calculated values are approximate. In Table 2, for rr region semi-quantitative agreement is observed. However, for mr region, no agreement especially in the case of peak 10, is seen.

Fig. 2 shows the methine carbon spectrum of A-PVA in D_20. The appearance of the spectrum is very different from those in DMSO-d_6 except for rr-centered pentads. It is known, however, that the spectra are fundamentally the same as those in DMSO-d_6 showing degeneration and overlapping of the signals. The assignments shown in Table 3 indicates a good agreement of the observed intensities with the calculated.

3.2. Methylene carbon spectra

Fig. 3 shows methylene carbon spectra of PVAs in DMSO-d_6. Table 4 shows the chemical shifts, intensities of peaks and the assignments previously reported (except mrm + mmr) by Ovenall [7]. The agreement of the calculated intensities with the observed is satisfactory for A-PVA and S-PVA. For I-PVA, semi-quantitative agreement was obtained. Fig. 4 shows methylene carbon spectrum of A-PVA in D_20. In contrast to the methine spectrum, the methylene carbon spectrum in D_2O is more finely resolved than in DMSO-d_6. All the signals were assigned with hexads as shown in Table 5. The observed intensities agree well with the calculated.

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