Two-Dimensional ^{1}H and ^{13}C Nuclear Magnetic Resonance Studies of Poly(vinyl alcohol)

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ABSTRACT: The ^{1}H and ^{13}C nuclear magnetic resonance spectra of atactic poly(vinyl alcohol) in D_2O at a temperature of 353 K were analyzed by various two-dimensional NMR (2D NMR) methods including ^{1}H *J*-resolved spectroscopy, ^{1}H F_1-axis broad-band decoupled correlation spectroscopy, ^{1}H broad-band decoupled ^{13}C–^{1}H chemical shift correlation spectroscopy, and two-dimensional INADEQUATE spectroscopy. The combined use of these two-dimensional NMR methods provided absolute assignments of ^{1}H and ^{13}C spectra at triad–tetrad and pentad–hexad levels, respectively. The polymerization of PVA follows Bernoullian statistics with $P_m = 0.47$ at the triad–tetrad level, but does not follow any statistics at the pentad–hexad level.
    KEY WORDS   Poly(vinyl alcohol) / ^{1}H NMR / ^{13}C NMR Tacticity / Two-Dimensional NMR /

It has been well established that nuclear magnetic resonance (NMR) is a powerful tool for characterizing the microstructure of synthetic polymers.[1-4] Since the two most important NMR parameters, chemical shift and coupling constant, markedly depend on the local environment of nuclei and the relative orientation of chemical bonds, configurational and/or conformational characteristics of polymers are reflected upon NMR spectra.

^{13}C spectra are in most cases used for characterization, because ^{13}C spectra appear in a much wider range of chemical shifts than ^{1}H spectra and usually exhibit only chemical shifts.[2-4] The ^{13}C spectra of poly(vinyl alcohol) (PVA) have been reported by a number of workers.[5-11] Ovenall reported the ^{13}C NMR spectra of atactic PVA dissolved in D_2O at 100 MHz.[10] The spectra were resolved at the pentad–hexad level. He assigned spectra by comparing various samples which were synthesized under different polymerization conditions. Tonelli calculated chemical shifts at

the pentad-hexad level taking into account the γ-*gauche* effect.[11] His results were in disagreement with those obtained by Ovenall. Thus, the assignment of resonance lines to specific configurations is the most fundamental step for characterization.

Recently, two-dimensional (2D) NMR methods[12] have been used for the configurational assignment of ^{1}H and ^{13}C spectra of synthetic polymers.[13-26] Gippert and Brown applied *J*-resolved 2D spectroscopy and shift correlation spectroscopy (COSY) to assign the ^{1}H spectra of PVA.[15] Bovey *et al.* reported that the 2D NOE spectroscopy (NOESY) is quite useful for the assignment of poly-(methyl methacrylate).[19] The ^{13}C–^{1}H shift correlation 2D spectroscopy (CHCOSY) has been also applied to several polymers.[21-27] 2D NMR methods are quite good because one can assign spectra absolutely from the relationship between cross peaks in 2D spectra without comparison of various samples.

In this work we conducted various 2D

NMR spectroscopies including J-resolved 2D, COSY, CHCOSY, and 2D INADEQUATE in order to assign ^{13}C spectra of PVA.

EXPERIMENTAL

The PVA sample was obtained from Nippon Gosei Kagaku Co., Ltd. (a commercial product, NL-05, molecular weight <4400, the degree of saponification $>98.5\%$). PVA was dissolved at 10% (w/v) in D_2O for ^{1}H NMR measurements, and at 15% and 40% (w/v) in a mixture of D_2O–H_2O (50:50) for broad-band decoupled ^{13}C–^{1}H correlation spectroscopy and INADEQUATE measurements, respectively. In order to suppress a large residual water signal in ^{1}H spectra, the OH groups of PVA were replaced with OD by repeated lyophilization from D_2O solution.

All NMR experiments were performed at a temperature of 353 K on a JEOL JNM-GX500 spectrometer at a frequency of 500 MHz for ^{1}H and 125 MHz for ^{13}C, respectively.

The ^{1}H J-resolved 2D spectra were obtained in the F_1 frequency range of 100 Hz and F_2 frequency range of 2000 Hz. The time domain data were collected in a data matrix of 128×1024 points using the conventional pulse sequence of $90°–(t_1/2)–180°–(t_1/2)–acq(t_2)$.[27] A 5 mm sample tube containing of 0.6 ml solution was used. For each t_1 value, 32 transients were accumulated. The total measuring time was 3 h. The time domain data matrix was expanded to 256×2048 by zero-filling. A sine-bell window function was multiplied in both dimensions before the double Fourier transformation.

The F_1-axis broad-band decoupled proton COSY spectra were obtained in a frequency range of 2000 Hz in both dimensions. The time domain data were collected in a data matrix of 256×1024 points using the pulse sequence $90°–t_1/2–180°–(t_d–t_1/2)–45°–acq(t_2)$ proposed by Bax and Freeman.[28] The same sample as used in the J-resolved experiment was employed. For each t_1 value, 32 transients

were accumulated. The total data collection time was 5.5 h. The data matrix was zero-filled to 512×2048 and multiplied by sine-bell window function in both dimensions before the Fourier transformation.

The F_1-axis (^{1}H) broad-band decoupled ^{13}C–^{1}H chemical shift correlation (CHCOSY) spectra were observed in the F_1 (^{1}H) frequency range of 2000 Hz and the F_2 (^{13}C) frequency range of 4000 Hz. The time domain data matrix of 256×1024 points was obtained using the pulse sequence: $90°(^1H)–t_1/2–90°(^1H)–1/2J–180°(^1H)$, $180°(^{13}C)–1/2J–90°(^1H)–t_1/2–1/2J–90°(^1H)$, $90°(^{13}C)–0.3/J–acq$ (^{13}C with ^{1}H decoupled, t_2) proposed by Bax.[29] A 5 mm tube containing about 0.6 ml solution was used. For each t_1 value, 256 free induction decays were accumulated. The total accumulation time was 42.5 hr. The data matrix was zero-filled to 512×2048. A sine-bell window function was multiplied in both dimensions prior to the Fourier transformation.

2D INADEQUATE spectra were observed in the F_1 frequency range of 500 Hz and F_2 frequency range of 4000 Hz. The data were accumulated in a data matrix of 64×2048 using the pulse sequence: $90°–1/4J–180°–1/4J–90°–t_2–135°–acq(t_2)$ introduced by Mareci and Freeman.[30] A 10 mm sample tube containing about 2.5 ml of solution was used. For each t_1 value, 1344 transients were accumulated. The total accumulation time was 44 h. The data matrix was zero-filled to 256×4096 and multiplied by 4 Hz exponential line broadening in both t_1 and t_2 dimensions, respectively, before the Fourier transformation.

All 2D spectra are presented in absolute values. The ^{1}H chemical shifts were measured relative to the methylene *mmr* peak as 1.719 ppm, and the ^{13}C chemical shifts to methine *rrrr* peak as 65.53 ppm.

RESULTS AND DISCUSSION

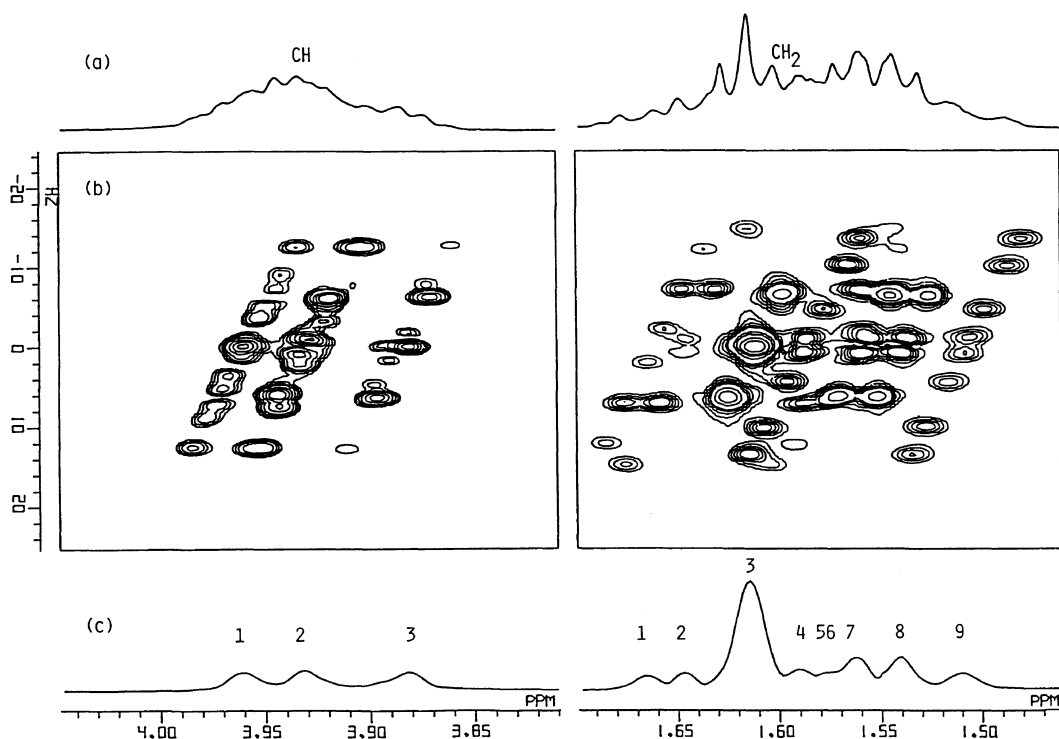Figure 1(a) shows the 500 MHz conventional one-dimensional ^{1}H NMR spectrum of

Figure 1. (a) One-dimensional 500 MHz ^{1}H NMR spectrum of 5% PVA in D_2O at 353 K. (b) 500 MHz ^{1}H J-resolved 2D NMR spectrum of PVA under the same conditions as (a). (c) The projection of (b) at an angle of 45° onto the F_2-axis.

PVA in D_2O at a temperature of 353 K. The spectrum consists of two groups of resonances, methines at low field and methylenes at high field. Each group further exhibits many overlapping resonances. This complexity arises from the fact that the resonances of methines and methylenes in various configurational states show different chemical shifts and are further split by ^{1}H–^{1}H scalar couplings among neighboring methine and methylene protons. The spectrum is too complex to be analyzed.

Figure 1(b) shows the ^{1}H J-resolved 2D NMR spectrum of PVA. As seen in the figure, this 2D spectrum gives the scalar coupling (J) and the chemical shift (δ) separately along the two different F_1 and F_2 axes, respectively. Figure 1(c) shows the projection of the 2D spectrum at an angle of 45° onto the F_2 axis, yielding the so-called proton broad-band decoupled spectrum. In the methine proton re-

gion, the projection shows three resonances, indicating that methines are assignable by triad sequences, *i.e.*, *mm*, *mr*, and *rr*. In the methylene proton region, nine resonances with different chemical shifts are discernable. Thus, methylenes can be assigned by tetrad sequences. In the 2D spectrum three multiplets of methylenes 3, 7, and 8 do not show the large splitting originating from the geminal coupling (~ -14 Hz). At the tetrad level, two protons of the central methylene in the *rrr* or *mrm* sequence are in the chemically equivalent environment. Thus, two of three methylenes of 3, 7, and 8 are assignable to *rrr* and *mrm*, and the remaining one accidentally has magnetically equivalent protons.

Figure 2(a) shows the F_1 axis broad-band decoupled ^{1}H–^{1}H correlation spectrum of PVA. Projections of this spectrum onto the F_1 and F_2 axes correspond to broad-band de-
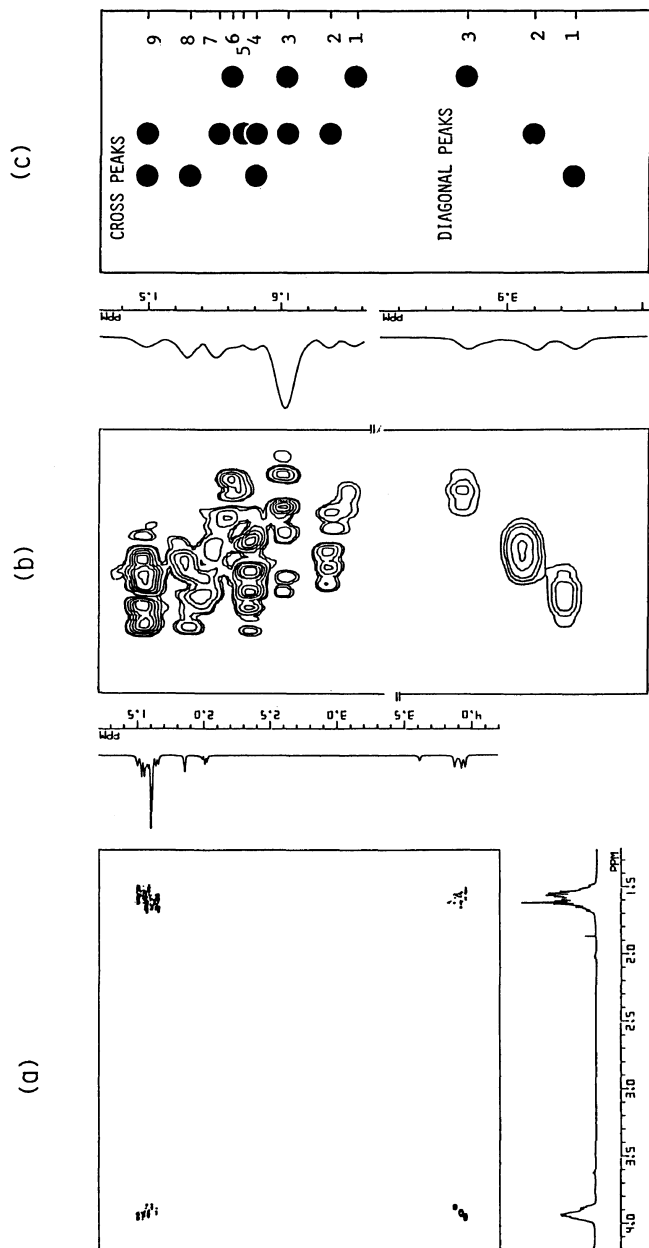
Figure 2. (a) $F_1(^1H)$-axis broad-band decoupled COSY spectrum of PVA under the same conditions as Figure 1(a). (b) The expanded view of cross peaks between methine and methylene protons and diagonal peaks of methines.

coupled and normal 1D spectra, respectively. Cross peaks indicate the existence of scalar coupling between non-equivalent protons. The broad-band decoupling in the F_1 axis greatly reduces overlapping resonances. Figure 2(b) is an expanded view of the cross peak region of methylenes and methines (upper left of Figure 2(a)), and diagonal peaks of methines (lower left of Figure 2(a)).

An examination of connectivity of methines and methylenes in various configurational states shows that *mm* methine has cross peaks with *mmm* and *mmr* methylenes, *rr* with *rrr* and *rrm*, and *mr* with *mrm*, *rrm*, *mmr* and *rmr*. Such a relationship is depicted in Figure 3. Taking into account this relationship as well as the existence of equivalent methylene protons other than methylene protons in the *rrr* and *mrm* sequences, four or three (in case methylene protons in the *mmm* or *mmr* sequence are equivalent) cross peaks will appear for *mm* methines, three or two (in case methylene protons in the *mrr* sequence are equivalent) for *rr*, and seven or six (in case methylene protons in any one of *mmr*, *mrr*, and *rmr* sequences are equivalent) for *mr*.

As seen in Figure 2(b), methine 2 has a larger number of cross peaks than other methines. Therefore, methine 2 can be assigned to *mr* methine. Figure 3 indicates that *rrr* and *mrm* methylenes having equivalent protons exhibit only one cross peak at *rr* and *mr* methines, respectively. Figure 2(b) shows that methylene 3 having equivalent protons ha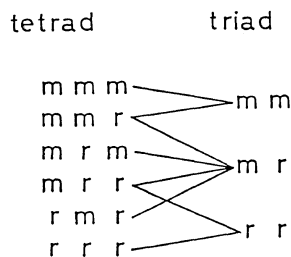s two cross peaks at *mr* and methine 3. This indicates that methylene 3 has accidentally equivalent protons. Methylene 7 having equivalent protons shows only one cross peak at *mr*, indicating that methylene 7 is assignable to *mrm*. Methylene 8 having inherently equivalent protons is assignable to *rrr*, and has only one cross peak at methine 1. Thus, we can assign methine 1 to *rr*, methine 3 to *mm*, and methylene 3 to *mmr*. Methylenes 4 and 9 have cross peaks at *rr* and *mr* methines, indicating that these two methylene protons are nonequivalent *mrr* methylene protons. Methylenes 1 and 6 have cross peaks at only *mm* methine. Thus, these two resonances are due to non-equivalent *mmm* methylene protons. Methylenes 2 and 5 have cross peaks at only *mr* methine, implying that these are assignable to non-equivalent *rmr* methylene protons. Assignments of methylenes 5 and 6 in Figure 2(b) are rather difficult. But these assignments are confirmed by a close inspection of the diagonal part of methylenes (the upper right of Figure 2(a)). The schematic drawing of predicted 2D spectrum based on this assignment is shown in Figure 2(c), which is comparable to Figure 2(b).

Table I lists a complication of assignments of the ^{1}H spectrum of PVA in D_2O at 373 K. Our assignments made at 500 MHz are in agreement with the results of Gippert and

tetrad   triad

Figure 3. Connectivity of triad methines and tetrad methylenes.

Table I. Assignments of the ^{1}H spectra of PVA

	Peak No.	Configuration	Chemical shift/ppm
CH	1	*rr*	3.957
	2	*mr*	3.930
	3	*mm*	3.879
CH$_2$	1	*mmm*	1.660
	2	*rmr*	1.645
	3	*mmr*	1.614
	4	*mrr*	1.586
	5	*rmr*	1.574
	6	*mmm*	1.566
	7	*mrm*	1.558
	8	*rrr*	1.539
	9	*mrr*	1.508

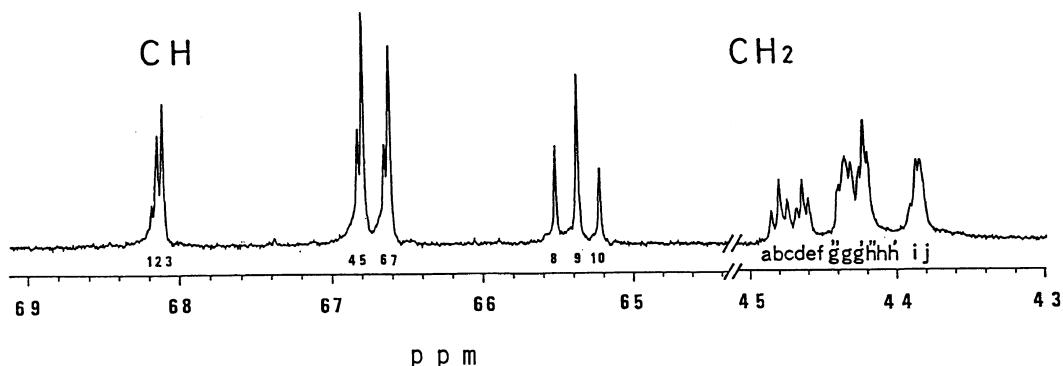**Figure 4.** 125 MHz ^{1}H noise-decoupled ^{13}C NMR spectrum of 15% PVA in a mixture of D_2O–H_2O (50 : 50) at 353 K.
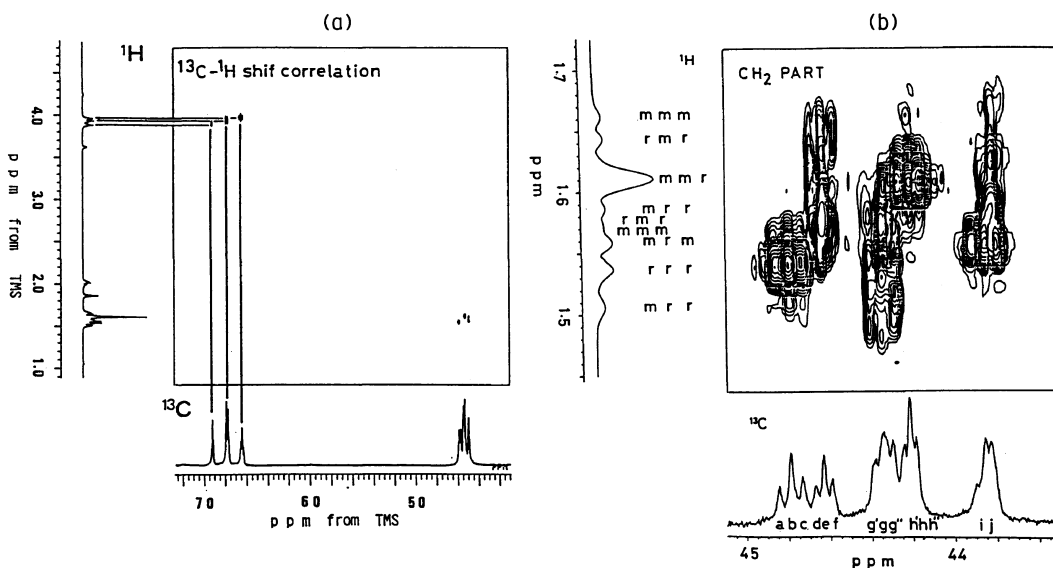

Figure 5. (a) F_1(^{1}H)-axis broad-band decoupled CHCOSY spectrum of PVA under the same conditions as in Figure 3. (b) The expanded view of methylene region of (a).

Brown[15] made at 360 MHz except for the reverse of assignments of methylenes 5 and 6 in the crowded region.

Figure 4 shows the 125 MHz ^{1}H noise-decoupled ^{13}C spectrum of PVA, which displays two groups of resonances from methine and methylene as similarly as ^{1}H spectrum. Each group consists of a number of resolved peaks due to different configurations, suggesting that resonances are distinguishable at the pentad–hexad or higher level.

The ^{13}C–^{1}H chemical shift correlation two-dimensional spectroscopy (CHCOSY) can correlate ^{13}C resonances with proton resonances via direct-bond coupling J_{C-H}. Thus, if the proton spectrum is completely analyzed, CHCOSY immediately gives assignments of ^{13}C spectrum at the same level as a proton.

Figure 5(a) shows the F_1(^{1}H)-axis broad-band decoupled CHCOSY spectrum of PVA

Figure 6. (a) INADEQUATE 2D spectrum of 40% PVA in a mixture of D_2O–H_2O (50 : 50) at 353 K. (b) The expanded spectrum of (a).

in D_2O at a temperature of 353 K. Three groups of resonances in the methine region, (1, 2, 3), (4, 5, 6, 7), and (8, 9, 10) (see Figure 4) are assignable by reference of the proton assignment made above at the triad level to *mm*, *mr*, and *rr* methine carbons, respectively. Figure 5(b) shows an expanded view of the methylene region. As seen in the figure, peaks a, b, and c can be assigned to methylene carbons in *rrr*-centered hexads. However, it is not possible to make further assignment of methine and methylene carbon resonances at the pentad–hexad level by CHCOSY.

The 2D INADEQUATE spectrum is helpful to examine the connectivity of carbon atoms. This experiment detects double-doublet signals arising from ^{13}C–^{13}C pairs in natural abundance, suppressing 200 times stronger singlet signals originating from single carbons. Figure 6 shows the methine and methylene parts of the 2D INADEQUATE spectrum of PVA in D_2O at a temperature of 353 K. The F_2-axis represents the single quantum ^{13}C frequency and the F_1-axis corresponds to the double quantum frequency which is the sum of single quantum frequencies. The 2D spectrum manifests itself in a symmetrical way with respect to a straight line with a slope of -2 passing through the zero frequency. In Figure 6, this straight line is not shown because the central part of the spectrum is omitted and methine and methylene parts are shown.

This 2D spectrum tells us the connectivity of methine and methylene carbons. For example, we can see two cross peaks of 8-b, and 8-c methine 8; four cross peaks of 9-a, 9-b, 9-g, and 9-g'' at methine 9; and one cross peak of 10-g'' at methine 10. In the previous section, we assigned methines 8, 9, and 10 to *rr*-centered pentads and methylenes a, b, and c to *rrr*-centered hexads. With the help of the connectivity of methines and methylenes shown in Figure 7, one can find that *rrrr* methine has two cross peaks with hexad methylenes of *rrrrr* and *rrrrm*; *mrrm* methine has no cross peak with *rrr*-centered hexads, but two cross peaks

with *mrrmr* and *mrrmm*; and *mrrr* has four cross peaks with *mrrrm*, *mrrrr*, *mmrrr*, and *rmrrr*. Therefore, methine 8, 9 and 10 are assigned to *rrrr*, *mrrr*, and *mrrm* methines, respectively. Methylene a has one cross peak with *mrrr*, indicating that methylene a is assignable to *mrrrm*. Methylene b has two cross peaks with *rrrr* and *mrrr*. Thus, one can assign methylene b to *mrrrr*. The remaining methylene c has one cross peak with *rrrr*. Methylene c can be assigned to *rrrr*.
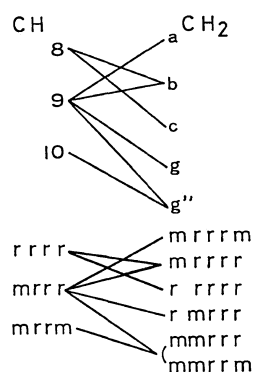

Figure 7. Connectivity of pentad methines and hexad methylenes.

Table II. Assignments of the ^{13}C spectra of PVA

	Peak No.	Configuration	Chemical shift/ppm
CH	1	*rmmr*	68.18
	2	*mmmr*	68.14
	3	*mmmm*	68.10
	4	*rmrr*	66.83
	5	*mmrr*	66.79
	6	*rmrm*	66.65
	7	*mmrm*	66.61
	8	*rrrr*	65.53
	9	*mrrr*	65.37
	10	*mrrm*	65.22
CH$_2$	a	*mrrrm*	44.85
	b	*mrrrr*	44.79
	c	*rrrrr*	44.74
	d	*mrmrm*	44.68
	e	*mrmrr*	44.64
	f	*rrmrr*	44.59
	g'',g,g'	*mrr*	44.38, 44.34, 44.30
	h'',h,h'	*mmr*	44.24, 44.22, 44.19
	i, j	*mmm,mrm*	43.86

Table III. Fractional areas of methine peaks

Peak No.	Configuration	Fraction	Bernoulli trial $P_m = 0.469$	1st-order Markov trial $P_{m/r} = 0.563, P_{r/m} = 0.498$	2nd-order Markov trial $\alpha = 0.496, \beta = 0.422$ $\gamma = 0.441, \delta = 0.466$
1	rmmr	0.021	0.062	0.047	0.054
2	mmmr	0.093	0.110	0.104	0.106
3	mmmm	0.115	0.048	0.059	0.052
		0.229	0.220	0.210	0.212
4	rmrr	0.075	0.140	0.100	0.054
5	mmrr	0.174	0.124	0.128	0.124
6	rmrm	0.070	0.124	0.164	0.131
7	mmrm	0.160	0.110	0.127	0.093
		0.479	0.498	0.519	0.402
8	rrrr	0.082	0.080	0.074	0.086
9	mrrr	0.150	0.140	0.147	0.150
10	mrrm	0.060	0.062	0.073	0.065
		0.292	0.282	0.284	0.301

Table II shows the results of assignments of ^{13}C spectrum of PVA. Our results are in agreement with the results obtained by Ovenall[10] at the triad–tetrad level, but in disagreement with the results calculated by Tonelli[11] at the pentad–hexad level.

As seen in Table III, fractions of triad methines and tetrad methylenes deduced from areas of the ^{13}C spectra show that this sample follows Bernoullian statistics with $P_m = 0.47$, where P_m means the probability that the monomer adds in meso-fashion to the chain end. Fractions of pentads and hexads, however, do not follow any Bernoullian, first or second Markovian statistics. Therefore, it is not possible to make assignment on the basis of propagation statistics at the pentad–hexad level. Ovenall[10] has stated that the relative intensities of three- and four-line features of mm and mr triads are not in the ratios expected for pentads or hexads. As a result, he could not assign methylene carbons at the pentad level. At present, the reason of disagreement is not known.

In conclusion, absolute configurational assignments were made at the triad-tetrad and pentad–hexad levels for ^{1}H and ^{13}C spectra of PVA, respectively. The combined use of various 2D NMR methods has been proved to be very useful for the configurational assignment of vinyl polymers.

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