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Microstructure of Poly(vinyl alcohol) by 100-MHz Carbon-13 NMR†

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ABSTRACT: The microstructure of atactic and highly isotactic poly(vinyl alcohol) samples has been studied by 100-MHz carbon-13 NMR spectroscopy. Resolution-enhanced spectra show sensitivity to heptad and hexad tactic sequences. The highly isotactic sample obeys first-order Markov statistics while the atactic sample is Bernoullian. Spectra taken in Me_2SO-d_6 and in D_2O as solvents show marked differences, which may be due to conformation changes. Weak features, arising from reversed monomer sequences and other structural irregularities, have been identified in the spectrum of the atactic sample. A spin-echo NMR experiment with gated decoupling was used in the assignment of these weak features.

Introduction

Poly(vinyl alcohol) has been studied extensively by both proton and carbon-13 NMR, the objectives being the determination of tacticity and the detection and identification of structural irregularities such as end groups, branches, and reversed monomer sequences.

In the proton spectra, spin–spin splittings complicate the methine and methylene proton resonances and make tacticity determinations difficult. However, a number of workers showed that, when dimethyl-d_6 sulfoxide is used as a solvent, exchange of the hydroxyl protons is suppressed and three distinct hydroxyl proton resonances can be observed, corresponding to monomer units at the centers of isotactic, heterotactic, and syndiotactic triad sequences.[1–3]

Carbon-13 NMR spectra of poly(vinyl alcohol) samples taken at 25.14 MHz in D_2O solution were reported by Inoue et al.[4] Similar spectra, taken at 22.63 MHz in D_2O and dimethyl-d_6 sulfoxide solutions, were reported by Wu and Ovenall.[3] Both groups found that the methine carbon atom resonances were sensitive to triad tacticity, while structure visible in the methylene carbon atom resonances was interpreted in terms of partially overlapping tetrads. In later work at 22.63 and 67.9 MHz by Wu and Sheer,[5] additional fine structure was observed in the methine carbon atom resonances of poly(vinyl alcohol) samples dissolved in dimethyl-d_6 sulfoxide, and this was interpreted in terms of pentads.

The possibility of detecting 1,2-glycol units in poly(vinyl alcohol) by carbon-13 NMR was investigated by Inoue et al.[4] These can arise from occasional monomer inversion during the polymerization of vinyl acetate to give poly(vinyl acetate), from which the poly(vinyl alcohol) is prepared by hydrolysis. A model polymer prepared by the hydrolysis of poly(vinyl carbonate) and containing 17 1,2-glycol units per 100 monomer units was examined by these authors. A distinctive methylene carbon atom resonance attributed to 1,2-glycol units was observed, but the sensitivity was too low for the detection of 1,2-glycol units in normal poly(vinyl alcohol) samples, which would typically be an order of magnitude lower in concentration.

Adelman and Ferguson,[6] using 220-MHz proton NMR, studied structural irregularities in poly(vinyl alcohol) but were unable to detect 1,2-glycol units directly.

Recently, Amiya and Uetsuki have reported an investigation into the microstructure of poly(vinyl alcohol-*co*-crotonic acid) by proton and carbon-13 NMR.[7] Weak peaks in the 50.15-MHz carbon-13 NMR spectrum of a poly(vinyl alcohol) sample were assigned to carbon atoms in 1,2-glycol structures.

In the present work, carbon-13 NMR spectra of isotactic and atactic poly(vinyl alcohol) samples have been obtained with a spectrometer operating at 100.6 MHz. The high resolution and sensitivity of this instrument have been utilized in obtaining detailed information on tacticity and irregular structures.

Experimental Section

The highly isotactic sample had been studied previously.[3,5] The atactic sample was a commercial product, prepared by hydrolysis of a free radical initiated poly(vinyl acetate).

Carbon-13 NMR spectra were obtained at 100.6 MHz, using a Bruker WM-400 high-resolution NMR spectrometer. The samples were examined as solutions in dimethyl-d_6 sulfoxide (Me_2SO-d_6) and in D_2O in 10-mm NMR tubes. Sample temperatures were regulated at 50 °C, using the standard Bruker variable-temperature unit. Broad-band proton decoupling resulted in some dielectric heating of the solutions. To ensure that this did not vary from one sample to another, all samples were made up to a standard height of 3 cm (approximately 2 mL) and vortex plugs were used. Sample temperatures were measured by using similar NMR tubes containing 10% (w/v) solutions of the atactic polymer, into which a thermocouple was inserted through the hole in the vortex plug. These were allowed to come to equilibrium under the particular data collection sequence being used, i.e., with gated or continuous broad-band proton decoupling. The temperature inside the NMR tube was then adjusted to 50 °C by

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Table I
Spin-Lattice Relaxation Times for Methine Carbon Atom Resonances[a]

sequence	T_1, s
rmmr	0.30
rmmm	0.29
mmmm	0.29
mr features	0.32
	0.32
	0.31
	0.31
	0.31
	0.31
	0.32
rrrr	0.30
mrrr	0.31
mrrm	0.31

[a] 10% (w/v) atactic poly(vinyl alcohol) in Me_2SO-d_6 at 50 °C.

Table II
Spin-Lattice Relaxation Times for Methylene Carbon Atom Resonances[a]

sequence	T_1, s
rrr	0.18
rmr + mrr	0.17
mrm + mmr	0.17
mmm	0.17

[a] 10% (w/v) atactic poly(vinyl alcohol) in Me_2SO-d_6 at 50 °C.

resetting the variable-temperature unit. To avoid spurious readings caused by radio-frequency pickup on the thermocouple, the broad-band proton decoupler was turned off immediately before the temperature was read. Separate temperature adjustments were made for the two different solvents.

The amount of isotactic polymer available was sufficient only to make up an approximately 5% (w/v) solution in Me_2SO-d_6. The atactic polymer was examined as both 5% (w/v) and 10% (w/v) solutions in Me_2SO-d_6 and as a 10% (w/v) solution in D_2O. The spectra of the 5% (w/v) and 10% (w/v) solutions of the atactic polymer in Me_2SO-d_6 were essentially identical, and the spectrum of the 10% (w/v) solution was used for quantitative work.

So that data collection parameters could be chosen to ensure quantitative results, spin-lattice relaxation times were determined for the 10% (w/v) solution of the atactic polymer in Me_2SO-d_6. The standard inversion-recovery technique was used in an overnight run with delay time cycling. Continuous broad-band proton decoupling was used, and the sample temperature was adjusted to 50 °C as described above. Spin-lattice relaxation times for the methine carbon atom features are listed in Table I, and spin-lattice relaxation times of the methylene carbon atom features are listed in Table II. Line broadening of 2 Hz was used during data processing to improve signal-to-noise ratios. Owing to the lower resolution, it was not possible under these conditions for T_1 values to be determined for carbon atoms in all the tactic sequences resolved when resolution enhancement was used. The variations in T_1 values observed, 0.29–0.32 s for the methine carbon atoms and 0.17–0.18 s for the methylene carbon atoms, are probably within experimental error.

To ensure that peak areas would be accurately proportional to the numbers of contributing nuclei, spectra of the Me_2SO-d_6 solutions of the two polymers were obtained with a 90° pulse, a spectral width of 10 kHz, and 32K data files, to give an acquisition time of 1.64 s. An additional delay of 1.8 s between the end of one acquisition and the start of the next, during which the decoupler was gating off, was used to provide complete relaxation and suppression of Overhauser effects.

Peak area ratios obtained from these spectra and used in determining polymer tacticity probabilities were, within 1%, identical with the same ratios determined from spectra obtained from similar runs, in which a 45° pulse was used, with no added relaxation delay and with continuous broad-band proton decoupling. This indicates that, considering the methine and methylene carbon atom resonances separately, the Overhauser effects for resonances within each set are very similar.

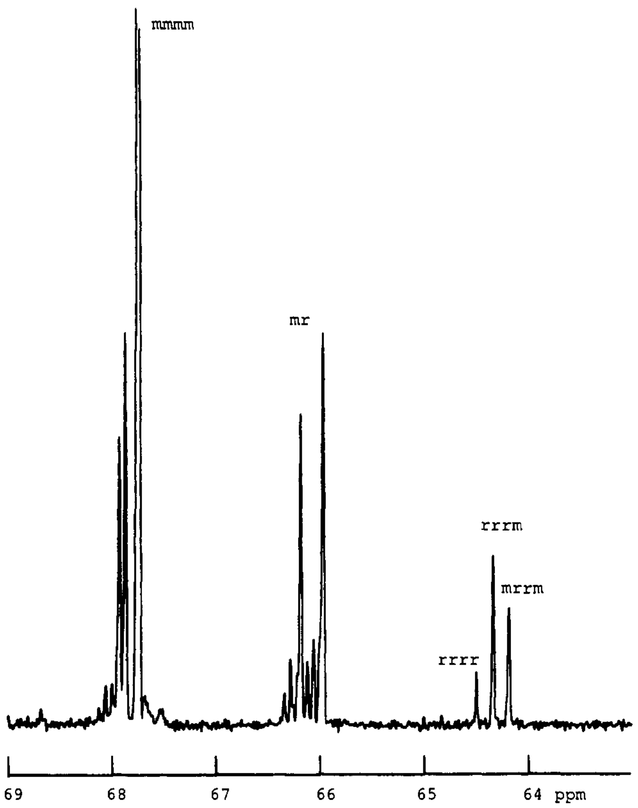


Figure 1. Methine carbon atom region of resolution-enhanced 100.6-MHz carbon-13 NMR spectrum of isotactic poly(vinyl alcohol) sample in Me_2SO-d_6 solution.

Data were collected for 15 h from the 10% (w/v) solutions of the atactic polymer and for 60 h for the weaker solution of the isotactic polymer to give good signal-to-noise ratios for accurate peak area measurements and to permit Lorentzian-to-Gaussian resolution enhancement[8] to be used during data processing. Numerical data were derived from the runs using the added relaxation delay and gated proton decoupling. The spectra shown in the figures, for which resolution enhancement was used, were obtained from the runs using continuous proton decoupling, since these gave better signal-to-noise ratios.

Results and Discussion

The methine carbon atom resonances of the highly isotactic sample are shown in Figure 1, which was obtained with resolution enhancement. Chemical shifts were referred to tetramethylsilane as zero by taking the central peak of the solvent multiplet as 39.5 ppm. As in the earlier studies, the methine carbon atom resonances appear as three distinct features assigned to the three possible triads: mm, mr, and rr, in order of decreasing frequency, i.e., from left to right.

Wu and Sheer[5] found that tactic sequencing in this polymer did not follow Bernoullian statistics but could be described adequately by a first-order Markov model. In the present work, the first-order Markov probabilities, $P_{m/r}$ and $P_{r/m}$, where $P_{m/r}$ is the probability that a growing chain ending in a meso sequence will add a monomer unit to give a racemic sequence, were calculated by using equations given by Bovey:[9]

$$P_{m/r} = (mr)/[2(mm) + (mr)]$$

$$P_{r/m} = (mr)/[2(rr) + (mr)]$$

The fractional areas of the three triad features, (mm), (mr), and (rr), measured from the integrals of a spectrum obtained without smoothing or resolution enhancement, gave $P_{m/r} = 0.145$ and $P_{r/m} = 0.613$. Wu and Sheer[5] ob-

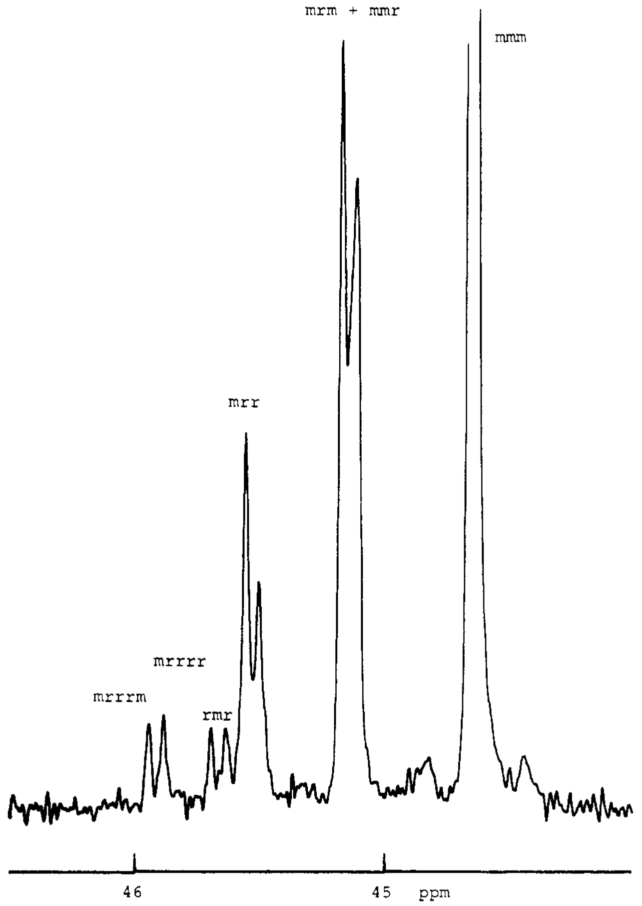


Figure 2. Methylene carbon atom region of resolution-enhanced 100.6-MHz carbon-13 NMR spectrum of isotactic poly(vinyl alcohol) sample in Me_2SO-d_6 solution.

tained $P_{m/r}$ = 0.158 and $P_{r/m}$ = 0.655 for this polymer. The differences between these two sets of values are probably due to the lower signal-to-noise ratios and resolution obtained by these authors. The sum of $P_{m/r}$ and $P_{r/m}$ differs significantly from unity and thus, as found by Wu and Sheer, sequencing in this polymer, which was prepared by hydrolysis of a cationically polymerized vinyl trimethylsilyl ether, does not follow Bernoullian statistics. The first-order Markov model can be fitted to triad intensities but requires longer sequence information for testing.

The methylene carbon atom resonances of this polymer are shown in Figure 2, in which the resolution has also been enhanced. In the earlier work,[3] the methylene carbon atom resonances appeared as four features from partially overlapping tetrads. In Figure 2, the four features are well resolved, and further partial splitting into hexads is visible. The fractional areas of the four main features of the methylene carbon atom resonances were measured from the integral of a spectrum obtained without smoothing or resolution enhancement. The fractional numbers of tetrads given by the first-order Markov model, with $P_{m/r}$ = 0.145 and $P_{r/m}$ = 0.613, were calculated from expressions given by Bovey,[9] and these two sets of data are compared in Table III. The two outer features are clearly due to the rrr and mmm tetrads, and the good agreement between the observed and theoretical intensities confirms the applicability of the first-order Markov model. The assignment of the two inner features to (rmr + mrr) and (mrm + mmr), respectively, provides the best fit to the observed areas. This differs from the assignments of ref 3, which may be in error, owing to peak overlap. The rrr tetrad is split into three peaks, which are assigned, in order, to the mrrrm, rrrrm, and rrrrr hexads, on the basis of their relative intensities. Further assignments could not be made unambiguously.

Table III
Tetrad Tacticity of Isotactic Poly(vinyl alcohol) Sample

tetrad	fraction		
	calcd[a]		obsd
rrr	0.029		0.032
rmr	0.017	0.108	0.124
mrr	0.091		
mrm	0.072	0.273	0.256
mmr	0.201		
mmm	0.591		0.588

[a] Using first-order Markov model with $P_{m/r}$ = 0.145 and $P_{r/m}$ = 0.613.

Table IV
Pentad Tacticity of Isotactic Poly(vinyl alcohol) Sample

pentad	fraction	
	calcd[a]	obsd
rrrr	0.011	0.013
mrrr	0.035	0.032
mrrm	0.028	0.028

[a] Using first-order Markov model with $P_{m/r}$ = 0.145 and $P_{r/m}$ = 0.613.

A further test of the model was made by using the methine carbon atom resonances. The rr triad feature is clearly split into the three possible pentads, rrrr, mrrr, and mrrm, while the mr and mm triad peaks show partial resolution into heptads. The resolution of the unenhanced spectrum was sufficient to give well-separated integrals for the three rr pentads, and in Table IV, the fractional areas of these are compared with theoretical values given by the first-order Markov model. The good agreement confirms the applicability of this model and permits unequivocal assignments of the rrrr, mrrr, and mrrm pentads to be made.

At high sensitivity, the mm triad resonance first shows (in order of decreasing frequencies) three very weak peaks, which are assigned to the three possible heptads from the rmmr pentad. The fractional intensities of these three heptads were calculated from the first-order Markov model, using extensions of the expressions given by Bovey.[9] From their relative intensities, these three peaks were assigned, in order, to the rrmmrr, rrmmrm, and mrmmrm heptads. Next are two intermediate peaks, arising from partial overlap of the four heptads derived from the rmmm pentad. Unequivocal assignment of these two peaks is not possible. Finally, there is a very strong peak from the mmmm pentad.

The mr triad appears as eight partially overlapping peaks. Since four pentads and sixteen heptads contribute to this feature, no further assignments within this triad could be made unequivocally.

The fractional numbers of tactic sequences up to hexads, calculated analytically with the first-order Markov model, were checked against the output of a computer program, which gives tactic sequences up to hexads for the Bernoullian and first- and second-order Markov models. This program was kindly supplied by Professor H. J. Harwood of the University of Akron and was modified by Dr. R. C. Ferguson of these laboratories.

The methine carbon atom region of the resolution-enhanced spectrum of the 10% (w/v) solution of the atactic poly(vinyl alcohol) in Me_2SO-d_6 is shown in Figure 3. Assignments are based on the analysis of the spectrum of the isotactic polymer. As shown more clearly in Figure 4, the mm triad resonance is split into the ten possible heptad

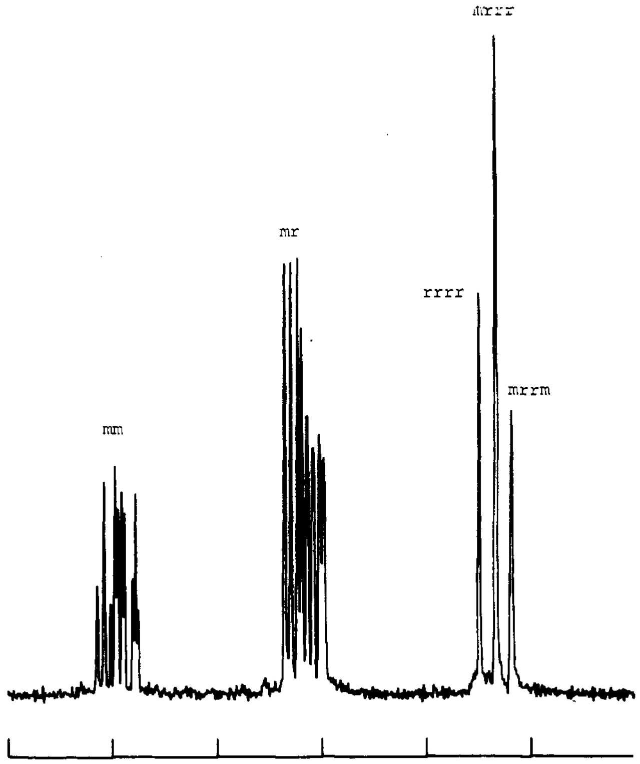


Figure 3. Methine carbon atom region of resolution-enhanced 100.6-MHz carbon-13 NMR spectrum of atactic poly(vinyl alcohol) sample in Me$_2$SO-d_6 solution.

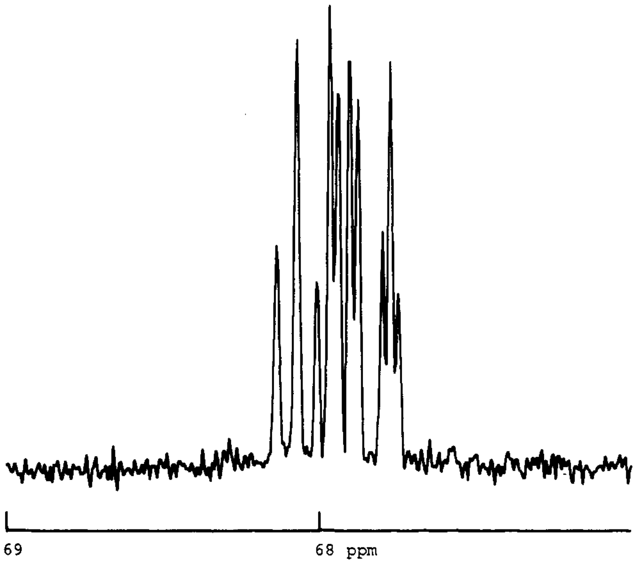


Figure 4. Expansion of methine carbon atom region of resolution-enhanced 100.6-MHz carbon-13 NMR spectrum of atactic poly(vinyl alcohol) sample in Me$_2$SO-d_6 solution, showing mm triad resonance split into heptads.

resonances. The first three peaks are assigned to the rrmmrr, rrmmrm, and mrmmrm sequences. Four peaks at the center of the mm triad arise from the four possible mmmr-centered heptads. The remaining three peaks are assigned to the three mmmm-centered heptads in the order rmmmr, mmmmmr, and mmmmmm. In Figure 3, the central mr triad, which comprises four pentads and sixteen heptads, is split into eight peaks, while the rr triad is split only into the rrrr, mrrr, and mrrm pentads. The chemical shifts of the methine carbon atom features in the spectrum of the atactic polymer are listed in Table V. The chemical shifts of corresponding features in the spectrum of the isotactic sample are very similar.

Table V
^{13}C Chemical Shifts of Methine Carbon Atom Features of Atactic Poly(vinyl alcohol) in Me$_2$SO-d_6

sequence	shift, ppm	sequence	shift, ppm
rrmmrr	68.14	mr triad	66.35
rrmmrm	68.07		66.29
mrmmrm	68.01		66.22
			66.18
mmmr heptads	67.97		66.13
	67.94		66.07
	67.91		66.02
	67.88		65.97
rmmmmr	67.80	rrrr	64.48
rmmmmm	67.78	mrrr	64.33
mmmmmm	67.75	mrrm	64.18

Table VI
^{13}C Chemical Shifts of Methylene Carbon Atom Features of Atactic Poly(vinyl alcohol) in Me$_2$SO-d_6

sequence	shift, ppm	sequence	shift, ppm
mrrrm	45.92	rrmrr + mrr	45.55
rrrrm	45.86		45.53
rrrrr	45.81		45.50
			45.47
mrmrm	45.66	mrm + mmr	45.16
mrmrr	45.61		45.12
		mmm	44.66

Table VII
^{13}C Chemical Shifts of Methine Carbon Atom Features of Atactic Poly(vinyl alcohol) in D$_2$O

sequence	shift, ppm	sequence	shift, ppm	sequence	shift, ppm
mm	68.26	mr	66.86	rrrr	65.53
	68.22		66.83	rrrm	65.37
	68.18		66.67	mrrm	65.21
			66.64		

The fractional areas of the three triads, obtained from the integral of a spectrum without smoothing or resolution enhancement, showed that the sequence distribution was Bernoullian with $P_m = 0.46 \pm 0.01$. The error limit was chosen on the basis of the fractional area of the methine carbon atom resonances from weak features, such as reversed monomer units. These can be seen clearly in the unenhanced spectrum at high sensitivity.

The methylene carbon atom region of the resolution-enhanced spectrum of the Me$_2$SO-d_6 solution of the atactic sample is shown in Figure 5. Partial splitting into hexads is visible. Chemical shifts and tentative assignments based on the analysis of the isotactic sample are given in Table VI. The chemical shifts of the corresponding features in the spectrum of the isotactic sample are very close to these values.

The methine and methylene carbon atom regions of the resolution-enhanced spectrum of the 10% (w/v) D$_2$O solution of the atactic polymer are shown in Figures 6 and 7. Chemical shift calibration was obtained from a run in which a small amount of acetone was added to the solution and the chemical shift of its methyl carbon atom resonance taken as 30.6 ppm. The spectrum of the D$_2$O solution differs considerably from that of the Me$_2$SO-d_6 solution.

The methine carbon atom resonances are split into the three triad features as before. Further splittings are also observed, but only those of the rr triad, which splits into the three possible pentads, are readily interpretable. The mm and mr triads are split into three and four features, respectively, but the relative intensities of these features are not in the ratios expected for pentads or heptads. The

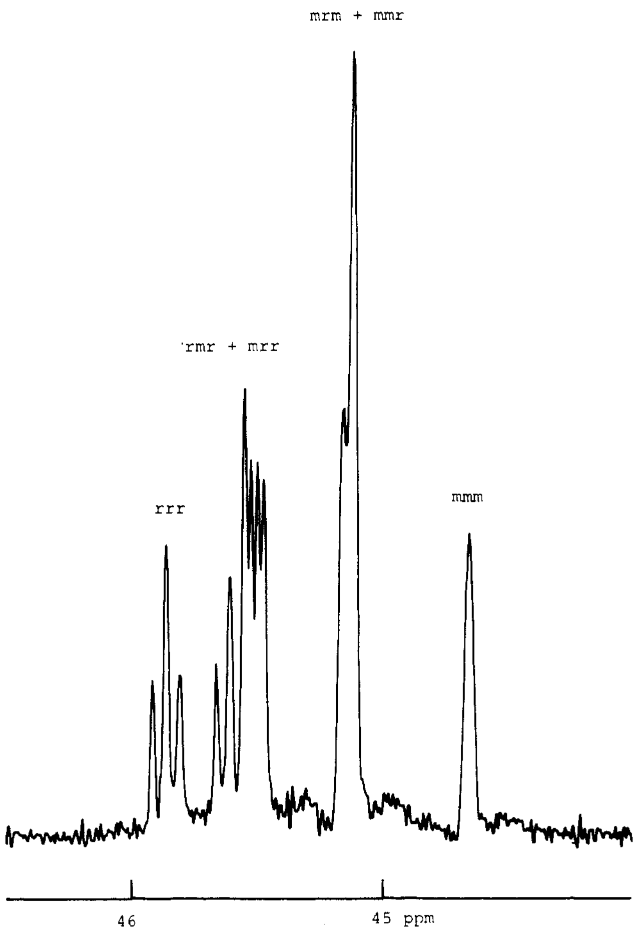


Figure 5. Methylene carbon atom region of resolution-enhanced 100.6-MHz carbon-13 NMR spectrum of atactic poly(vinyl alcohol) sample in Me_2SO-d_6 solution.

Table VIII
^{13}C Chemical Shifts of Methylene Carbon Atom Features of Atactic Poly(vinyl alcohol) in D_2O

sequence	shift, ppm	sequence	shift, ppm
mrrrm	45.07	mmmrm	44.36
rrrrm	45.01	rmmrm + mmmrr	44.33
rrrrr	44.95	rmmrr	44.29
mrmrm	44.86	mrm + mmm	43.99
mrmrr	44.82		43.93
rrmrr	44.77		43.89
mmrrm	44.55		
rmrrm + mmrrr	44.49		
rmrrr	44.44		

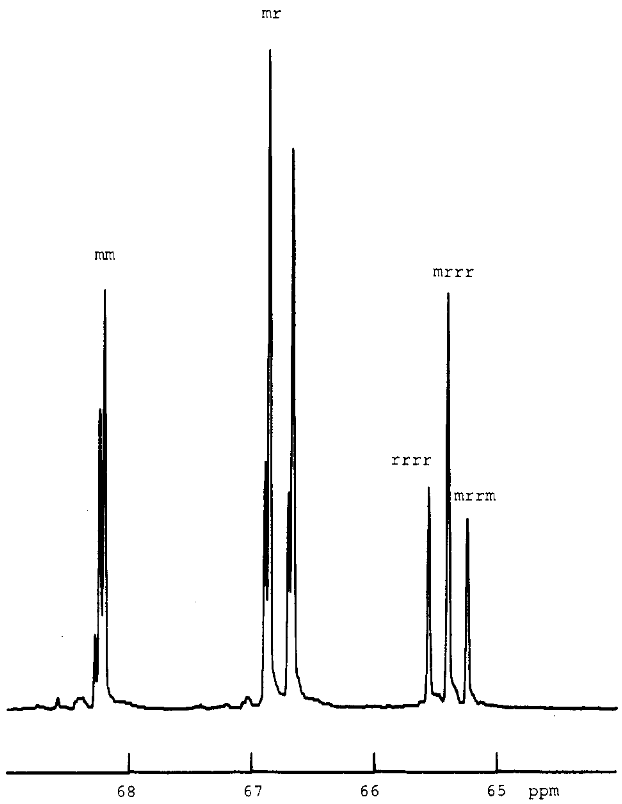


Figure 6. Methine carbon atom region of resolution-enhanced 100.6-MHz carbon-13 NMR spectrum of atactic poly(vinyl alcohol) sample in D_2O solution.

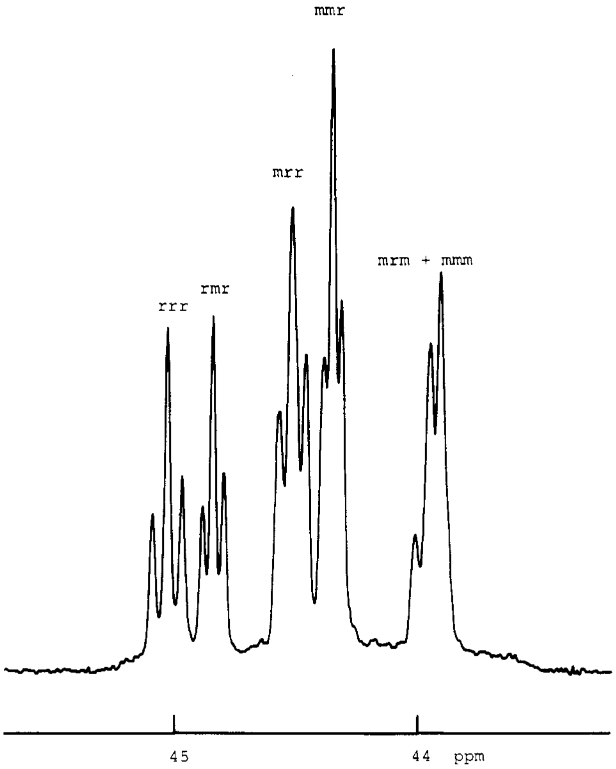


Figure 7. Methylene carbon atom region of resolution-enhanced 100.6-MHz carbon-13 NMR spectrum of atactic poly(vinyl alcohol) sample in D_2O solution.

methylene carbon atom resonances show rather better resolution into hexads than in the spectrum of the Me_2SO-d_6 solution. Chemical shifts and tentative assignments are given in Tables VII and VIII. Since the detailed assignments are based on relative peak heights, which can be distorted by resolution enhancement, some errors may be present.

The sensitivity of ^{13}C chemical shifts to polymer tacticity has been attributed by Tonelli and co-workers to the different numbers of non-hydrogen atom γ-gauche interactions experienced by carbon atoms in the various tactic sequences.[10] These result in upfield shifts of several ppm for each interacting non-hydrogen atom. A rotational isomeric state model was used to predict the number of γ-gauche interactions experienced by particular carbon atoms in different tactic sequences and hence to derive their relative chemical shifts. In this way, a good fit was obtained for the methyl carbon atom resonance pattern in atactic polypropylene, using heptads.

Tonelli and Schilling have observed solvent effects in the ^{13}C NMR spectrum of atactic poly(vinyl chloride).[10] Gradual addition of dimethyl sulfoxide to poly(vinyl chloride) dissolved in 1,2,4-trichlorobenzene resulted in

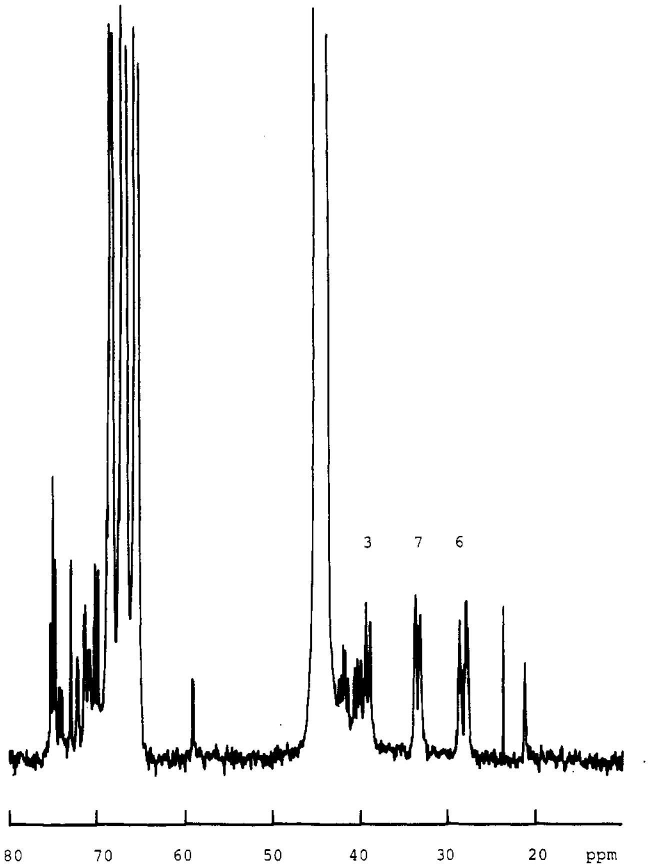


Figure 8. 100.6-MHz carbon-13 NMR spectrum of atactic poly(vinyl alcohol) sample in D_2O solution, showing weak peaks from reversed sequences and other minor structures.

Table IX
^{13}C Chemical Shift Additivity Factors for Aliphatic Alcohols

(a) Primary Alcohols
$R\text{-}^{\gamma}CH_2\text{-}^{\beta}CH_2\text{-}^{\alpha}CH_2OH$
$\alpha = 48.9$ ppm, $\beta = 10.3$ ppm, $\gamma = -5.8$ ppm
(b) Secondary Alcohols
$R\text{-}^{\gamma}CH_2\text{-}^{\beta}CH_2\text{-}^{\alpha}CHOH\text{-}^{\beta}CH_2\text{-}^{\gamma}CH_2\text{-}R'$
$\alpha = 40.8$ ppm, $\beta = 7.7$ ppm, $\gamma = -3.4$ ppm
$R\text{-}^{\gamma_1}CH_2\text{-}^{\beta_1}CH_2\text{-}^{\alpha_1}CHOH\text{-}^{\beta_2}CH_3$
$\alpha_1 = 44.9$ ppm, $\beta_1 = 7.5$ ppm, $\beta_2 = 9.8$ ppm, $\gamma_1 = -3.1$ ppm

appreciable changes in the methylene carbon atom resonances but had little effect on the methine carbon atom resonances. The authors concluded that, since only the methylene carbon atom resonance was altered, this must a specific, nonconformational effect.

In the case of atactic poly(vinyl alcohol), changing the solvent from $Me_2SO\text{-}d_6$ to D_2O results in marked changes in both the methylene and methine carbon atom resonances, and it seems likely that changes in the polymer conformation have occurred.

The spectrum of the atactic poly(vinyl alcohol) sample in D_2O solution is plotted at high sensitivity in Figure 8. Line broadening of 2 Hz was used. For the assignment of weak features, the carbon-13 chemical shift additivity factors, listed in Table IX, were derived from data for a number of primary and secondary alcohols.[11] These additivity factors were used to predict carbon-13 chemical shifts in possible minor structures by adding them to the carbon-13 chemical shifts of the parent alkane structures. The latter were calculated by using the Lindeman and Adams empirical formula.[12] In Table X, calculated carbon-13 chemical shifts for reversed sequences in poly(vinyl alcohol) are compared with the chemical shifts of some of the weak features seen in Figure 8. The chemical shifts of the normal repeat unit resonances are also included. Where multiplets due to tacticity effects are observed, average chemical shifts have been used.

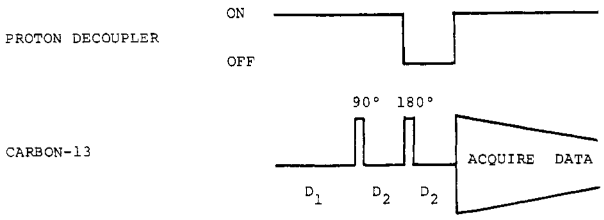
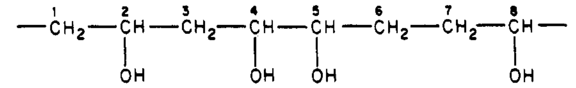


Figure 9. Pulse sequence for spin-echo experiment.

Table X
Predicted and Observed ^{13}C Chemical Shifts for Reversed Structures in Poly(vinyl alcohol)



$$-\overset{1}{C}H_2-\underset{OH}{\overset{2}{C}H}-\overset{3}{C}H_2-\underset{OH}{\overset{4}{C}H}-\underset{OH}{\overset{5}{C}H}-\overset{6}{C}H_2-\overset{7}{C}H_2-\underset{OH}{\overset{8}{C}H}-$$

carbon	shift, ppm pred	shift, ppm obsd
6	30.9	28.0
7	34.3	33.2
3	42.0	38.8
1	45.4	44.5[a]
2	64.0	66.4[a]
8	67.4	
4	75.1	see text
5	78.5	

[a] Normal repeat unit carbon atom resonances.

Resonances from methylene carbon atoms 6 and 7 are clearly identified and show sensitivity to dyad and higher tactic sequences. From the relative areas of these resonances and that of the main head-to-tail methylene carbon atom resonance, the number of reversals was found to be 1.9 per 100 monomer units. This is in the range found by chemical methods for similar poly(vinyl alcohol) samples.[6] Two weak resonances at 38.5 and 39 ppm are tentatively assigned to methylene carbon atom 3, with a predicted chemical shift of 42.0 ppm. Other weak, and as yet unidentified, resonances fall in the region 39–42 ppm.

Resonances from the methine carbon atoms in reversed structures are less readily identified. The resonance of carbon 8, with a predicted chemical shift of 67.4 ppm, is probably masked by the mm triad methine carbon atom resonance of the main repeat units at 67.9 ppm. A number of weak peaks are present in the region 69–75 ppm and the resonances of carbons 4 and 5 may be part of these.

Also visible in Figure 8 are two weak peaks at 58.7 and 58.8 ppm. These are assigned to the ultimate carbon atom in end groups with structure $-CHOH-CH_2-CH_2OH$, the two peaks coming from essentially random dyad tacticity. This carbon atom is predicted to have a chemical shift of 59.5 ppm. The penultimate carbon atom in this end group has a predicted chemical shift of 40.6 ppm. There are several weak peaks in this region, while the resonance of the antepenultimate carbon atom is predicted to occur at 64.1 ppm and would be masked by the methine carbon atom resonances of the normal repeat unit.

A weak peak at 21 ppm is assigned to methyl carbon atoms in residual unhydrolyzed vinyl acetate units in the polymer. When plotted on an expanded scale, this peak shows partial splitting into a triplet due to tacticity.

For further confirmation of the assignments of the weak peaks visible in Figure 8, a spin-echo *J*-modulated experiment[13] was carried out. This makes use of the fact that single-bond carbon–proton couplings are all very similar (125–160 Hz), but the multiplets from carbon atoms with

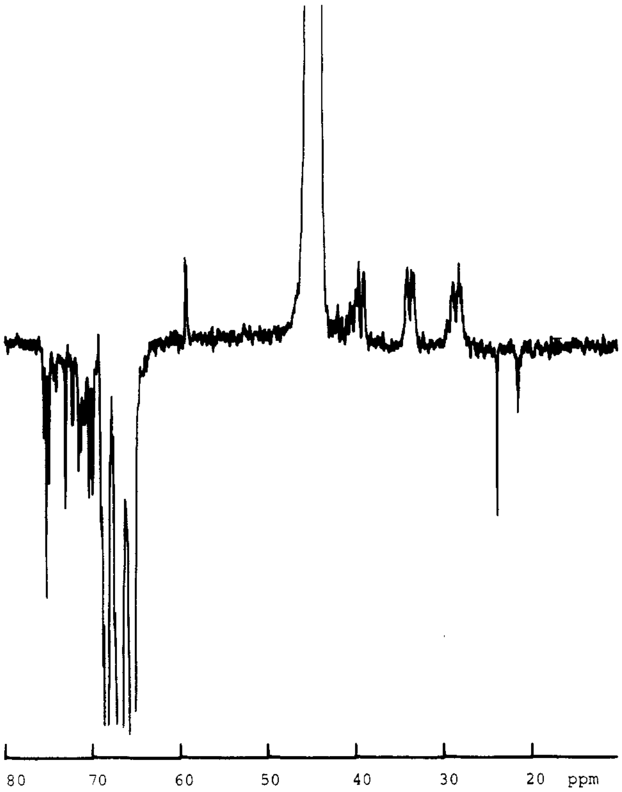


Figure 10. 100.6-MHz carbon-13 NMR spectrum of atactic poly(vinyl alcohol) sample in D_2O solution using spin-echo sequence with gated decoupling. The spectrum is plotted so that methylene carbon atom resonances are positive and the methine and methyl carbon atom resonances negative.

different numbers of attached hydrogen atoms have different symmetries. The pulse sequence used is shown in Figure 9. After a relaxation delay D_1, an echo is generated by a 90° pulse followed, after an interval D_2, by a 180° pulse, and the second half of the echo is then acquired. The proton decoupler is gated off during the refocusing period following the 180° pulse but remains on during the rest of the sequence. If D_2 is set to about $1/J(^{13}C–H)$, i.e., about 7 ms, precession of the individual spin components during the period that the proton decoupler is off results in the resonances of methylene and quaternary carbon atoms having the opposite sign from the resonances of methine and methyl carbon atoms. To avoid phase discrepancies due to imperfect pulses, a 16-phase cycle, based on the sequence described by Bodenhausen et al.[14] was used. The spin-echo spectrum of the D_2O solution of the atactic poly(vinyl alcohol) sample is shown in Figure 10. This has been plotted so that the methylene and possible quaternary carbon atom resonances are positive, while the methine and methyl carbon atom resonances are negative. The spectrum was obtained with a relaxation delay of 6 s. It confirms the above assignments and shows that the carbon atom giving rise to the sharp peak at 23.3 ppm carries an odd number of hydrogen atoms. This peak is tentatively identified from its chemical shift as arising from the methyl group in the structure $-CH_2-CHOH-CH_3$.

This technique promises to be particularly valuable in the identification of weak peaks in the carbon-13 NMR spectra of polymers. The traditional methods used in carbon-13 NMR to determine the number of hydrogen atoms bonded to the individual carbon atoms involve observing the proton-coupled spectrum, by gating off the decoupler during data acquisition, or the partially coupled spectrum, by using off-resonance CW proton decoupling. These methods are usually not effective when applied to synthetic polymers owing to loss of resolution and sensitivity.

Registry No. Isotactic poly(vinyl alcohol), 25067-41-8; atactic poly(vinyl alcohol), 9002-89-5.

References and Notes

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