Proton and Carbon-13 Nuclear Magnetic Resonance Studies of Poly(vinyl alcohol)

Ting Kai Wu[*1a] **and Derick W. Ovenall**[1b]

Plastics Department and Central Research Department, E. I. du Pont de Nemours and Company, Experimental Station, Wilmington, Delaware 19898. *Received March 28, 1973*

ABSTRACT: Proton resonance spectra (220 MHz) and carbon-13 Fourier transform noise-decoupled spectra (22.6 MHz) of poly(vinyl alcohol) (PVA) were obtained. By examining the hydroxyl proton spectra in dimethyl sulfoxide solution, we have deduced triad tacticity of PVA. Moreover, the stereochemical sequence distributions in terms of triads and tetrads were determined from the methine and methylene carbon spectra, respectively. It was found that stereoregularity of radical-initiated polymerization of vinyl acetate is independent of the polymerization conditions but can be described by Bernoullian statistics.

High-resolution proton spectroscopy has been extensively applied to investigate the stereochemistry of poly(vinyl alcohol) (PVA). However, due to the complexity of the methylene and methine proton spectra, the spin-decoupling technique has to be used for quantitative determination of triad tacticity.[2a] Alternatively stereoregularity of PVA was measured from the acetyl methyl proton resonances of the derived poly(vinyl acetate).[2a] Only recently have two reports demonstrated that these tacticity measurements can be obtained directly by examining the hydroxyl proton spectra of PVA dissolved in perdeuterated dimethyl sulfoxide (Me_2SO-d_6).[2b,3] During the last year or so, solutions to many polymer structure problems became possible, primarily because of the development of the Fourier transform carbon-13 nmr method. In particular, the examples reported by Schaefer[4] clearly illustrated the versatility of the carbon-13 technique. This paper presents our studies on the Fourier transform carbon-13 spectra and the 220-MHz proton spectra of PVA. From the observed spectra we have determined the stereoregularity of vinyl acetate polymerization in terms of triad and tetrad distributions.

Experimental Section

The following PVA samples were used in this study. Sample A was the hydrolysis product of radical polymerized poly(vinyl acetate)[5] and sample B, which was obtained from cationic polymerization of vinyltrimethylsilyl ether in toluene at 96°, was kindly given to us by Professors Murahasi and Nozakura of Osaka University, Japan. We have estimated the stereoregularity of these samples by using the infrared method[2a] which involves measuring the ratio of absorbances at 916 and 850 cm^{-1}. The values of 0.38 and 0.04 were found for samples A and B, respectively, indicating that the former is atactic and the latter highly isotactic.

The carbon-13 nmr spectra were obtained using a Bruker HFX-90 nmr spectrometer, equipped with a Digilab NMR 3 Fourier transform accessory. The spectrometer was operated at 22.63 MHz with proton noise decoupling and a time-shared deuterium lock. Single-coil Fourier transform operation was used with exciting rf pulses of about 10 μsec. Samples were examined as 5% solutions (in Me_2SO-d_6, heavy water and hexafluoroisopropyl alcohol) in 10-mm tubes at 60°. The system was operated with an 8192 point data file and 5000-Hz bandwidth. Good spectra were generally obtained with 4000 pulses (data acquisition time, 55 min), except in the case of the aqueous solution of the isotactic sample, where low sample concentration necessitated an overnight run. All the carbon chemical shift values are reported with respect to tetramethylsilane.

For proton measurements, the nmr sample solutions were prepared to contain 0.5–10 wt % of PVA in Me_2SO-d_6. A small amount of hexamethyldisiloxane was added as the internal reference. Proton nmr spectra were recorded on a Varian HR-220 nmr spectrometer equipped with a variable-temperature probe. The spectra were calibrated by the audiomodulation technique and the peak intensities were determined by integration.

Results and Discussion

In the 100-MHz proton spectra of PVA, DeMember *et al.*[2b] and Moritani *et al.*[3] showed that the three hydroxyl resonance lines in the region of 4.1–4.6 ppm can be assigned to the isotactic, heterotactic, and syndiotactic triad placements, from low to high field. Figure 1 depicts the Me_2SO-d_6 solution spectra of PVA recorded at 220 MHz. For quantitative measurements of tacticities, all spectra were obtained at 22°, because the hydroxyl proton peaks move upfield to overlap the methine proton resonances at higher temperature.

Table I summarizes the tacticity data determined from the hydroxyl proton resonances. It is seen that sample A is almost ideally atactic, while sample B is highly isotactic. Moreover, the tacticity measurements on sample A agree, within the experimental error of ±3%, with those of Moritani and coworkers on their PVA which was derived from a radical-polymerized poly(vinyl acetate).[3] Even though the exact synthesis condition of their sample is not known, these results strongly support the conclusion of Kador and Mehnert that the stereoregularity of the radical-initiated polymerization of vinyl acetate is independent of the polymerization conditions.[6] We have also confirmed that the isotactic and heterotactic hydroxyl proton lines can be further split into doublets, as previously observed,[2b,3] by reducing the viscosity of the nmr sample solution. This was accomplished by using either a dilute solution (less than 2 wt %) or a solution temperature higher than 40°.

In Figure 2 are depicted the 22.6-MHz Fourier transform noise-decoupled carbon-13 spectra of the PVA samples dissolved in heavy water (D_2O) and in Me_2SO-d_6. The carbon resonance lines of the polymer are reasonably sharp and a splitting of about 4 Hz can be readily resolved. In this study, we have utilized the heptet resonances due to the deuterated methyl carbons of Me_2SO-d_6 at 39.65 ppm as an additional reference for the chemical shift measurements and as an indicator of the instrumental resolution as well.

Broadly speaking, the carbon spectra of PVA contain two groups of lines separated by approximately 21 ppm. Based on the reported spectra of poly(vinyl methyl ether)[7]

---

[1] (a) Plastics Department; (b) Central Research Department.

[2] (a) K. Fujii, *J. Polym. Sci., Part D,* **5**, 431 (1971), and the references therein. (b) J. R. DeMember, H. C. Haas, and R. L. MacDonald, *J. Polym. Sci., Part B,* **10**, 385 (1972).

[3] T. Moritani, I. Kuruma, K. Shibatani, and Y. Fujiwara, *Macromolecules,* **5**, 577 (1972).

[4] J. Schaefer, *Macromolecules,* **5**, 427 (1972), and the references therein.

[5] A. Beresniewicz, *J. Polym. Sci.,* **35**, 321 (1959).

[6] U. Kador and P. Mehnert, *Makromol. Chem.,* **144**, 29 (1971).

[7] L. F. Johnson, F. Heatley, and F. A. Bovey, *Macromolecules,* **3**, 175 (1970).

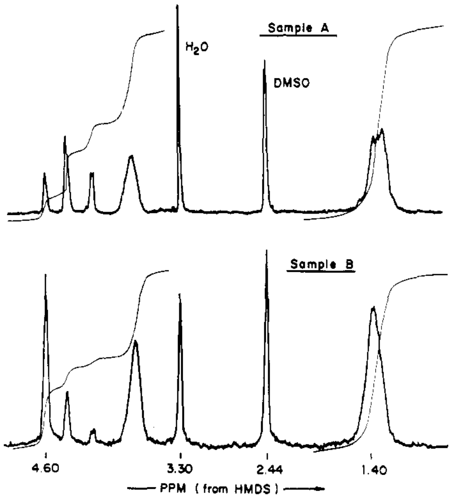

Figure 1. 220-MHz proton nmr spectra of poly(vinyl alcohol) dissolved in Me_2SO-d_6.

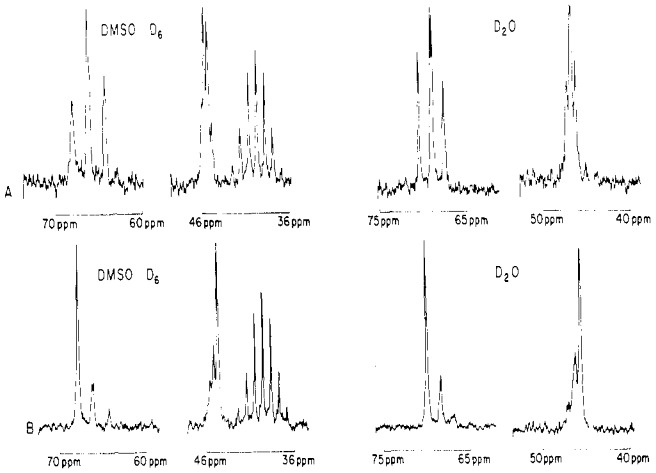

Figure 2. 22.6-MHz carbon-13 Fourier transform nmr spectra of poly(vinyl alcohol).

and the calculated chemical shift values,[8] we have assigned the resonance lines at low and high field to the methine and methylene carbons, respectively. The positions of these peaks are summarized in Table II.

As illustrated in Figure 2, the spectral features of the carbon nuclei of PVA are dependent on the solvents. For example, in the aqueous solution spectrum of sample A additional fine structure of the central methine carbon line can be resolved, while the methylene carbons of this sample in Me_2SO-d_6 solution give rise to a quartet pattern. Moreover, only a broad peak is observed for the methylene carbons of PVA dissolved in hexafluoroisopropyl alcohol.[9] Therefore, we have determined the stereoregularity of PVA in terms of triad and longer sequence placements by examining the spectra obtained in the appropriate solvents.

Table I
Triad Tacticity Determinations of Poly(vinyl alcohol)

	Triad Tacticity[b]					
	Sample A			Sample B		
Method[a]	mm	mr	rr	mm	mr	rr
Proton	0.207	0.498	0.296	0.702	0.225	0.073
Carbon-13						
Me_2SO-d_6	0.23	0.52	0.25	0.67	0.25	0.08
D_2O	0.20	0.55	0.24	0.72	0.22	0.06

[a] Proton measurements were obtained from the hydroxyl proton lines. Carbon-13 measurements were derived from the methine carbon resonances. [b] mm, mr, and rr represent, respectively, isotactic, heterotactic, and syndiotactic triads.

Table II
Carbon-13 Chemical Shifts of Poly(vinyl alcohol)

Carbons	Chemical Shifts (ppm from Me_4Si)[a]			
Methylene				
Me_2SO	45.8	45.6	45.2	44.8
D_2O	47.1	46.4	46.1	45.5
Methine				
Me_2SO	67.8	66.2		64.3
D_2O	70.4	69.0, 68.8		67.5

[a] The chemical shifts were obtained in Me_2SO-d_6 solutions and D_2O solutions. The reproducibilities of our measurements were within ±0.1 ppm.

In a systematic study of carbon-13 nuclear Overhauser effect in polymer solution, Schaefer and Natusch[10] concluded that the Overhauser enhancements for many synthetic polymers such as polystyrene, poly(vinyl chloride), and poly(methyl methacrylate), are independent of tacticity and are the same for different types of carbons in or near the polymer main chain. The practical consequence of their work is that the integrated intensities in the carbon-13 nmr spectrum of a polymer solution can be used to count the number of carbons contributing to the resonance signal. From our spectra, the total integrated intensities of the methine carbons of PVA were found to be, within experimental error, equal to those of the methylene carbons. We have, therefore, utilized the carbon-13 integral spectra to obtain quantitative structural information of PVA.

By comparing the carbon spectra of samples A and B, we were able to assign the three methine carbon resonance lines to the isotactic, heterotactic, and syndiotactic triads, with increasing field strength. The fractions of triad tacticity of PVA, which were calculated from the integrated methine carbon spectra, are summarized in Table I. The good agreement between the proton and carbon nmr data presented in this table indicates that the Overhauser enhancements are indeed independent of the tacticity of PVA. The splitting of the central methine carbon line in D_2O solution probably arises from the pentad effect. However, since ideally there are ten distinguishable pentad placements, unambiguous assignments cannot be made for out spectra at the present time.

Dyad statistics predict that sample A should give rise to two methylene carbon lines of roughly equal intensities corresponding to meso (m) and racemic (r) dyads. However, a quartet pattern is observed in the Me_2SO-d_6 solution spectrum. Our spectral assignment for methylene

---

(8) From the chemical shift data of alkanes and aliphatic alcohols, reported by L. P. Lindemann and J. Q. Adams [*Anal. Chem.*, 43, 1245 (1971)] and J. D. Roberts, F. J. Weigert, J. L. Kroschwitz, and H. J. Reich [*J. Amer. Chem. Soc.*, **92**, 1338 (1970)], the contribution of a hydroxyl group to α (methine) carbon chemical shift was found to be 41.9 ppm. The β, γ, and δ carbons experience shifts of 8.3, −3.2, and 0.7 ppm, respectively. By ignoring the effects of solvents and tacticity, we have used these constants to calculate the chemical shifts of PVA, *i.e.*, with respect to Me_4Si, 47.6 ppm for methylene carbon and 65.1 ppm for methine carbon.

(9) In hexafluoroisopropyl alcohol solution the methylene carbons of PVA give rise to a broad and unresolved peak centered at 45.1 ppm, while the methine carbon resonances are masked by the solvent peak.

(10) J. Schaefer and D. F. S. Natusch, *Macromolecules*, 5, 416 (1972).

Table III
Spectral Assignment of Methylene Carbon Resonances of Atactic Poly(vinyl alcohol)

Methylene Carbon Shift	Tetrad Assignments	Methylene Carbon Peak Intensities[a]	
		Calcd	Obsd
45.8	rrr	0.161	0.17
45.6	rrm + mrm	0.383	0.37
45.2	mmr + rmr	0.361	0.35
44.8	mmm	0.095	0.11

[a] Obtained from the carbon-13 spectrum of sample A dissolved in Me_2SO-d_6.

Table IV
Tetrad Tacticity Determinations of Poly(vinyl alcohol)

Sample	Tetrads[a]					
	rrr	rrm	mrm	rmr	mmr	mmm
A	0.17	0.25	0.12	0.16	0.19	0.11
B	0.04	0.06	0.08	0	0.25	0.57

[a] The tetrads were calculated from the triad data of Table I and the methylene carbon data of Table III.

carbon resonances of PVA is based on the following observations. From the triad data of sample A in Table I, it can be shown that only a single parameter is required to describe the configurational sequence of this sample. Or, in other words, the stereoregularity of the radical-polymerized poly(vinyl acetate), from which this sample is derived, obeys Bernoullian statistics.[11] This parameter, P_{m}, is defined as the probability that a growing polymer chain will form an m sequence. For sample A, $P_{\mathrm{m}} = (\mathrm{mm})^{1/2} = 1 - (\mathrm{rr})^{1/2} = 0.456$, where mm and rr are, respectively, the fractions of isotactic and syndiotactic triads. Then the various tetrad placements in sample A can be readily calculated from P_{m};[11] *i.e.*, $\mathrm{mmm} = P_{\mathrm{m}}^3$, $\mathrm{mmr} = 2P_{\mathrm{m}}^2(1 - P_{\mathrm{m}})$, $\mathrm{rmr} = P_{\mathrm{m}}(1 - P_{\mathrm{m}})^2$, $\mathrm{mrm} = P_{\mathrm{m}}^2(1 - P_{\mathrm{m}})$, $\mathrm{rrm} = 2P_{\mathrm{m}}(1 - P_{\mathrm{m}})^2$, $\mathrm{rrr} = (1 - P_{\mathrm{m}})^3$. The calculated concentrations of the six tetrads can be made consistent with the observed methylene carbon peak intensities as shown in Table III; *i.e.*, the four lines of the methylene quartet were ascribed to the tetrads of rrr, rrm + mrm, mmr + rmr, and mmm from low to high field. It is noteworthy that these assignments are qualitatively confirmed by the peak positions and intensities of the corresponding spectrum of the highly isotactic sample B. The fact that the tetrad placements in sample A can be accounted for by the Bernoullian trial process indicates that the stereochemistry of the free-radical polymerization of vinyl acetate is independent of the configuration of the ultimate unit, the penultimate unit, as well as the pen-penultimate unit of the growing polymer chain.

The tetrad distributions in the PVA samples can also be completely determined by using the following relationships of tetrads and traids: $\mathrm{mmr} = 2(\mathrm{mm} - \mathrm{mmm})$ and $\mathrm{mmr} = 2\ (\mathrm{rr} - \mathrm{rrr})$. The calculated results are presented in Table IV.

After this article had been submitted, a similar work was published by Inoue, Chûjô, and Nishioka.[12] They report the carbon-13 spectra of poly(vinyl alcohol) dissolved in D_2O.

---

(11) F. A. Bovey, "Polymer Conformation and Configuration," Academic Press, New York, New York, 1969, Chapters 1 and 2.

(12) Y. Inoue, R. Chûjô, and A. Nishioka, *J. Polym. Sci., Part A-2*, **11**, 393 (1973).

^{19}F Nuclear Magnetic Resonance Spectra of Tetrafluoroethylene–Propylene Copolymers

Kenkichi Ishigure,* Yoneho Tabata, and Keichi Oshima

Department of Nuclear Engineering, University of Tokyo, Tokyo, Japan. *Received January 3, 1973*

ABSTRACT: High-resolution ^{19}F nmr spectra were measured at 94 MHz. of three kinds of tetrafluoroethylene–propylene copolymers, *i.e.*, alternating, tetrafluoroethylene- and propylene-rich copolymers prepared by γ-ray irradiation. The spectra were found to be quite sensitive not only to the sequence distribution but also to the configurational structure of the copolymers, and are well interpreted in terms of tetrads. It was concluded from the analysis of the spectra that the copolymers prepared in the temperature range of −78 to 30° have random configurations. Spectral parameters, especially chemical shift differences between nonequivalent nuclei, were observed to show marked temperature dependences, which were inferred to be closely related to the conformational structures of the copolymers.

Nuclear magnetic resonance has been widely applied to the investigations of polymer and copolymer structures for the past decade. Most of the work, however, has been concerned with proton resonance. Fluorine resonance has found only limited applications in this field despite the advantage of large chemical shifts.

In the previous papers[1-3] the authors have shown that ^{19}F nmr is a very powerful tool to investigate the structures of fluorine-containing copolymers such as tetrafluoroethylene (C_2F_4)–isobutylene and chlorotrifluoroethylene (C_2ClF_3)–isobutylene copolymers. The ^{19}F spectra of these copolymers have been interpreted in terms of tetrads and have given useful information concerning the sequence distribution of the copolymers. In the present work ^{19}F nmr spectra were obtained for C_2F_4–propylene (C_3H_6) copolymers and investigated in relation to their structures. As will be seen, the spectra are somewhat complicated by spin-spin coupling and by the asymmetric structures of the polymers compared to the previous cases.

Experimental Section

All copolymer samples were prepared by the γ-ray-initiated copolymerizations of the monomer mixtures at various tempera-

---

(1) K. Ishigure and Y. Tabata, *Macromolecules*, **3**, 450 (1970).

(2) K. Ishigure, Y. Tabata, and K. Oshima, *Macromolecules*, **3**, 27 (1970).

(3) K. Ishigure, Y. Tabata, and K. Oshima, *Polym. J.*, **2**, 321 (1971).