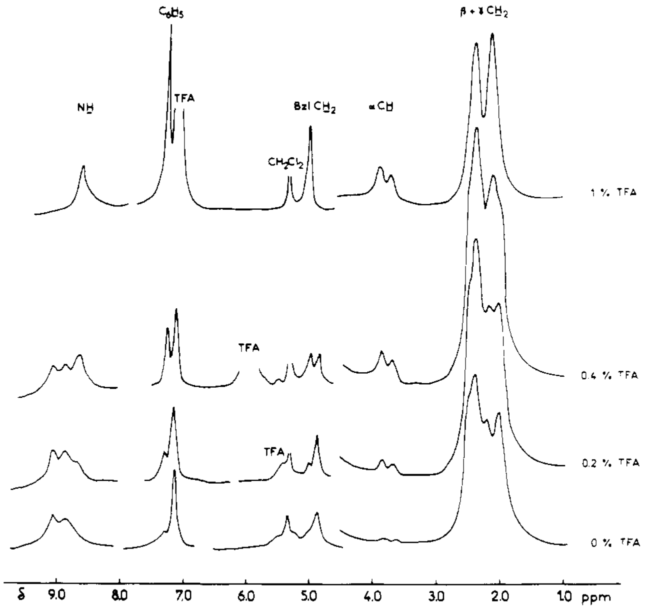

Figure 4. Spectra (270 MHz) at 20 °C of the double to single helical transconformation, $\pi\pi_{\mathrm{DL}}{}^{7.2} \rightarrow \alpha$, induced by TFA addition to PBD-LG in methylene chloride, c 7 mg/mL.

double helix α-CH peak (~5.3 ppm); likewise the double NH peak at ~9.0 ppm characteristic of the double helix is replaced by the single peak at ~8.6 ppm corresponding to the single helix. Since both the aromatic and benzyl-CH_2 side-chain proton resonances of the double helix are markedly upfield of their positions in the single helix, these two resonances both clearly show the occurrence of a transition. At the midpoint, "double peak" spectra are observed (i.e., simultaneous observation of both conformers) which probably originate from the polydispersity, but might also be due to a genuinely slow rate of conformational transition. Addition of TFA beyond 1% leads to breakdown of the α helix to random coil, as documented in ref 6.

Conclusions

The distinctive spectra presented for heat-treated PBD-LG dissolved in dioxane, chloroform, and methylene chloride suggest that the polymer conformation in these solvents is indeed that found in solid films cast from these solvents, i.e., the $\pi\pi_{\mathrm{DL}}{}^{7.2}$ and $\pi\pi_{\mathrm{DL}}{}^{9.0}$ double helices. This conclusion is strongly supported by the double helix–double helix and double helix–single helix transition observed in the NMR spectra. The main-chain NH and α-CH resonances of the double helices lie at unusually low field. These shift values may have their origin in the existence of a β-type structure and in side-chain effects, as suggested by the displacement of the aromatic and benzyl-CH_2 proton resonances.

Acknowledgments. Our thanks are due to Drs. G. Spach and E. M. Bradbury for helpful discussions and continuous interest in this work. P.D.C. and C.C.R. acknowledge the continuing support of the Science Research Council of Great Britain.

References and Notes

(1) (a) Centre de Biophysique Moléculaire; (b) Biophysics Laboratories.
(2) F. Heitz, B. Lotz, and G. Spach, *J. Mol. Biol.*, **92**, 1 (1975).
(3) F. Heitz, B. Lotz, and G. Spach, *C. R. Hebd, Seances Acad. Sci., Ser. C*:, **280**, 1509 (1975).
(4) B. Lotz, F. Colonna-Cesari, F. Heitz, and G. Spach, *J. Mol. Biol.*, **106**, 915 (1976).
(5) F. Heitz and G. Spach, *Macromolecules*, **8**, 740 (1975).
(6) F. Heitz, P. D. Cary, and C. Crane-Robinson, *Macromolecules*, **8**, 745 (1975).
(7) F. Heitz and G. Spach, *Macromolecules*, preceding paper in this issue.
(8) A. Caille, F. Heitz, and G. Spach, *J. Chem. Soc., Perkin Trans. 1*, 1001 (1973).
(9) I. D. Campbell, C. M. Dobson, R. J. P. Williams, and A. V. Xavier, *J. Magn. Reson.* **11**, 172 (1973).
(10) E. Dellacherie, J. Neel, and F. Colonna-Cesari, *Biopolymers*, **14**, 1447 (1975).

Carbon-13 NMR Determination of Pentad Tacticity of Poly(vinyl alcohol)

Ting Kai Wu* and M. Lana Sheer

Plastic Products and Resins Department, E. I. duPont de Nemours and Company, Experimental Station, Wilmington, Delaware 19898. Received September 30, 1976

ABSTRACT: Carbon-13 Fourier transform spectra (22.6 and 67.9 MHz) of poly(vinyl alcohol), PVA, were obtained. By using the appropriate experimental conditions, we were able to resolve the methine carbon resonances into a triplet of triplets which are readily assignable to pentad tacticity. Quantitative analysis of the methine carbon spectra provided further support to the previous conclusion that stereoregularity of radical-initiated polymerization of vinyl acetate is almost ideally atactic. In addition, we found that the stereochemical sequence distribution in the isotactic PVA derived from cationic polymerization of vinyl trimethyl silylether conforms to first-order Markov statistics.

Previous work has clearly demonstrated the utility of high-resolution NMR spectroscopy for determining the stereochemistry of vinyl acetate polymerization.[1-5] Examination of the perdeuterated dimethyl sulfoxide (DMSO-d_6) solution of the derived poly(vinyl alcohol), PVA, revealed that both the hydroxyl proton[1,4] and methine carbon resonances[4] can be used for quantitative measurements of triad tacticity. In fact, the methylenes carbon spectra are attributable to tetrad sequence placements.[2,4] Moreover, the 220-MHz acetoxy methyl proton spectra of the corresponding poly(vinyl acetate) dissolved in nitromethane are resolved into six lines and provide a partial analysis of pentad tacticity.[5] From these results, we concluded that the configuration sequence distribution of radical polymerization of vinyl acetate is independent of polymerization conditions but describable by a Bernoulli-trial process.[4,5] Recently we further investigated the carbon-13 spectra of PVA; a method for quantitative analysis of pentad tacticity is reported in this paper.

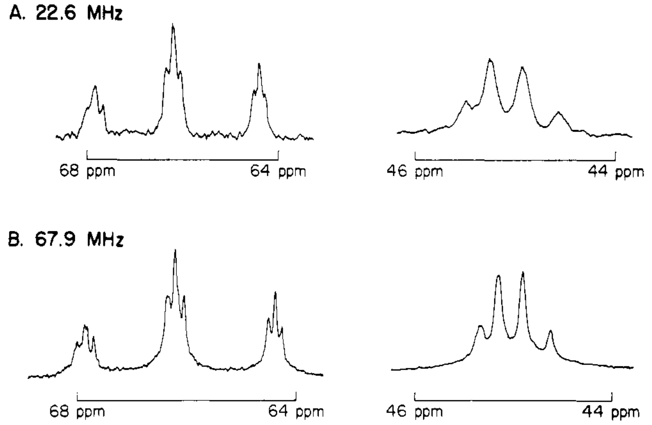

Figure 1. High-resolution carbon-13 NMR spectra (22.6 MHz and 67.9 MHz) of an atactic poly(vinyl alcohol) dissolved in DMSO-d_6 at 80 °C.

Experimental Section

The two PVA samples used in this work were those reported previously, i.e., an atactic and highly isotactic polymer.[4] NMR sample solutions were prepared to contain about 10 wt % of the former and 5 wt % of the latter in DMSO-d_6.

The 22.6-MHz Fourier transform carbon-13 spectra were obtained on a Bruker WH-90 NMR spectrometer. Field/frequency stabilization was attained with a PFP deuterium lock on the solvent resonance. All samples were ^{1}H broad band decoupled and run in the single coil PAPS Fourier mode using 10 μs pulses (45° tilt). A sweep width of 1000 Hz and a data file of 8192 points were employed. We examined the effects of apodization parameters on the spectrum and found the optimum line broadening value to be 0.2 Hz. All the spectra were the result of 13 000 or 56 000 pulses. The carbon-13 chemical shifts are reported with respect to tetramethylsilane (TMS). Peak intensities were obtained by digital integration, planimetry, and peak height measurements.

The 67.9-MHz proton-decoupled Fourier transform carbon-13 spectra on the atactic sample were recorded on a Bruker HX-270 spectrometer.

Results and Discussion

Figure 1A depicts a high-resolution 22.6-MHz carbon-13 spectrum of the atactic PVA dissolved in DMSO-d_6 at about 80 °C. In comparison with an earlier 22.6-MHz scan reported in our previous paper,[4] this spectrum exhibits significantly improved resolution. For example, the upfield methylene quartet, which was just recognizable then, is very well resolved now and can be accordingly assigned to the tetrads of rrr, rrm + mrm, mmr + rmr, and mmm from low to high field.[4] More interestingly, in the region of 64 to 68 ppm additional fine structure was observed in the methine carbon resonances, i.e., the previously observed triplet pattern is in fact a triplet of triplets. Therefore, the shielding of the methine carbon in PVA is dependent on its pentad sequence placement.

Systematic investigation of the effects of solution temperature on the 22.6-MHz spectra of the atactic sample revealed that spectral resolution can be made similar to that obtainable at 67.9 MHz as shown in Figure 1B by heating the sample solution to a temperature equal to or greater than 60 °C. (See Figure 2A–C.) In Table I the triad tacticities determined from the methine carbon spectra of this work are compared with those reported in the previous paper. The agreements between the present carbon-13 and the previous proton measurements are usually within ±3.3% indicating that either the 220-MHz proton or 22.6-MHz carbon-13 NMR method can be used to obtain highly reliable tacticity determinations of PVA. These results are confirmed by the 67.9-MHz carbon-13 spectra.

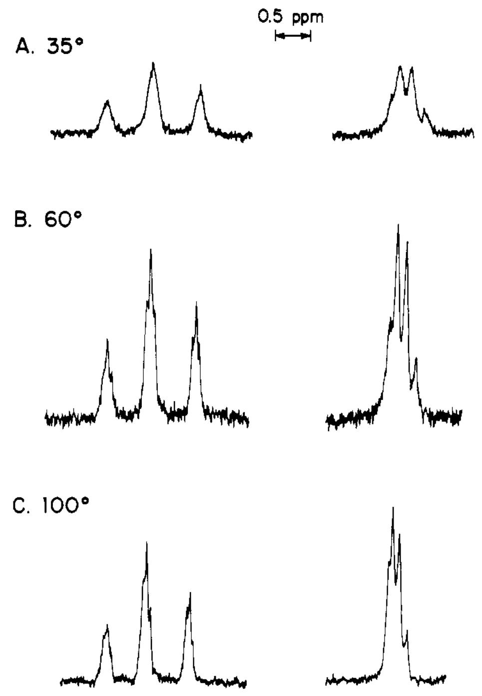

Figure 2. Temperature effects on 22.6-MHz carbon-13 spectra of poly(vinyl alcohol).

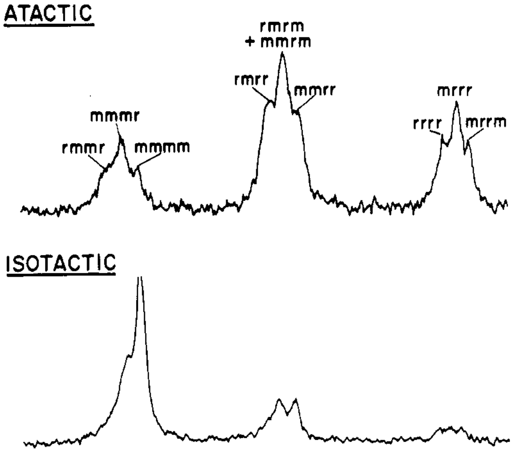

Figure 3. Methine carbon spectra (22.6 MHz) of poly(vinyl alcohol) in DMSO-d_6 solution.

Table I
Comparisons of NMR Measurements

Triad	Proton	Carbon	
	Ref 1	Ref 1	Present work
Atactic sample			
mm	0.207	0.23	0.220
mr	0.498	0.52	0.492
rr	0.296	0.25	0.289
Isotactic sample			
mm	0.702	0.67	0.711
mr	0.225	0.25	0.229
rr	0.073	0.08	0.060

Our previous results conclusively showed that radical polymerization of vinyl acetate is a Bernoullian process, i.e., the stereochemical configuration of the derived PVA can be described by a single parameter, $P_m = 0.456$ (P_m is the probability that a growing polymer chain will form an m sequence).[4,5] Then the various pentad sequences in this polymer can be calculated from P_m, e.g., mmmm = $P_m{}^4$, etc.[6] With the aid of the calculated pentad distribution we were able to make

Table II
Pentad Tacticity Determinations of Poly(vinyl alcohol)

Chemical[a] shift	Pentad assign	Atactic sample			Isotactic sample		
		Calcd[b]	Obsd[d]	(Obsd[d])	Calcd[c]	Obsd[d]	(Obsd[d])
68.01	rmmr	0.062	0.064	0.21	0.014	0.008	0.68
67.88	mmmr	0.103	0.091		0.170	0.189	
67.70	mmmm	0.043	0.053		0.527	0.484	
66.31	rmrr	0.147	0.139	0.26	0.011	0.052	0.11
66.20	mmrm	0.103	0.094		0.130	0.112	
66.20	mrmr	0.123	0.120	0.23	0.021	0	0.12
66.04	mmrr	0.123	0.125		0.068	0.093	
64.51	rrrr	0.088	0.097	0.10	0.007	0.025	0.03
64.38	mrrr	0.147	0.143	0.14	0.027	0.029	0.04
64.26	mrrm	0.061	0.073	0.06	0.025	0.027	0.02

[a] Chemical shifts were measured in ppm with respect to TMS. [b] The pentads were calculated using the Bernoullian parameter, $P_{\mathrm{m}} = 0.456$. [c] The pentads were calculated from the first-order Markov statistics: $P_{\mathrm{m/r}} = 0.138$, $P_{\mathrm{r/m}} = 0.655$. [d] Obsd designates the observed relative methine carbon peak intensities. (Obsd) represents the pentads obtained from the acetoxy methylproton spectra of the corresponding PVAc (ref 2).

unambiguous assignments for the nine methine carbon peaks of the atactic sample. (See Figure 3.) The methine carbon spectrum of the isotatic PVA can be analyzed simply by examining the chemical shift data. In order to determine individually the rmrm and mmrm pentads which give rise to only a single methine carbon peak at 66.20 ppm, we used the following pentad–pentad relationship to determine the mmrm pentads.[6]

$$\mathrm{mmrm} = \mathrm{mmmr} + 2(\mathrm{rmmr}) - \mathrm{mmrr}$$

The concentration of rmrm pentads was then obtained by subtracting the concentration of mmrm pentads from the normalized intensity of this peak.

In Table II are summarized the complete determinations of pentad distribution in the two PVA samples along with the partial pentad analyses from the acetoxy proton spectra of the corresponding poly(vinyl acetate).[5] Also included for comparison is the calculated pentad distribution using $P_{\mathrm{m}} = 0.456$ for the atactic sample. Based on these results, we conclude that 22.6-MHz carbon-13 NMR spectroscopy can be used for quantitative analysis of the stereoregularity of PVA in pentad distribution and that the Bernoullian parameter $P_{\mathrm{m}} = 0.456$ can account for the stereochemistry of radical polymerization of vinyl acetate to at least pentad sequence placements.

We have also examined the chain statistics applicable to the isotactic polymer. Since its triad distribution does not satisfy, within experimental error, the relationship of $(\mathrm{mr})^2 = 4(\mathrm{mm})(\mathrm{rr})$, Bernoullian statistics should not be used to describe its stereochemical configuration. In accordance with the first-order Markov process we define two independent parameters: $P_{\mathrm{r/m}} = (\mathrm{mr})/2\mathrm{r}$ and $P_{\mathrm{m/r}} = (\mathrm{mr})/2\mathrm{m}$ (e.g., $P_{\mathrm{r/m}}$ represents the probability that a growing polymer chain ending in r sequence will add a monomer to form an m sequence). The various pentad sequence placements can then be calculated from these parameters; i.e., $\mathrm{mmmm} = (\mathrm{mm})(1 - P_{\mathrm{m/r}})^2$, $\mathrm{mrmr} = (\mathrm{mr})P_{\mathrm{r/m}}P_{\mathrm{m/r}}$, etc.[7] In Table II comparisons of the calculated and observed pentad data reveal that sequence distribution in the isotactic sample can be adequately accounted for by the first-order Markov statistics. The precursor of this PVA is a cationically polymerized vinyl trimethyl silylether. The stereochemistry of such a polymerization is, therefore, dependent on the configuration of the terminal monomer unit of the growing polymer chain.

Acknowledgment. The authors would like to acknowledge D. K. Nickerson for obtaining many of the carbon-13 spectra. Special thanks are due to Professor G. C. Levy of the Florida State University for making available his Bruker HX-270 NMR spectrometer.

References and Notes

(1) T. Moritani, I. Kurama, K. Shibatani, and Y. Fujiwara, *Macromolecules*, **5**, 577 (1972).
(2) Y. Inoue, R. Chujo, and A. Nishioka, *J. Polym. Sci., Polym. Phys. Ed.*, 11, 393 (1973).
(3) Y. Inoue, R. Chujo, A. Nishioka, S. Nozakura, and H. Iimuro, *Polym. J.*, **4**, 244 (1973).
(4) T. K. Wu and D. W. Ovenall, *Macromolecules*, **6**, 582 (1973), and references cited therein.
(5) T. K. Wu and D. W. Ovenall, *Macromolecules*, **7**, 776 (1974).
(6) F. A. Bovey, "High Resolution NMR of Macromolecules", Academic Press, New York, N.Y., 1972, Chapter 3.
(7) Reference 6, Chapter 8.