suming that point dipoles exist at the midpoints of polar bonds. The C–Cl bond moment is 2.0 D.[18] The dielectric constant was assumed to be 4.0.[19]

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

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ABSTRACT: Two poly(vinyl alcohol) samples of known stereoregularity were converted to poly(vinyl acetate) by acetylation. The 220-MHz proton resonance spectra and 22.6-MHz carbon-13 Fourier transform noise-decoupled spectra of the acetylated products were obtained in a variety of solvents. By examining the acetoxy methyl proton spectra in nitromethane solution, we have deduced triad and pentad tacticity. The stereochemical sequence distributions in terms of triads and tetrads were determined from the methylene carbon spectra in perdeuterated 1,1,2,2-tetrachloroethane solution at 120°.

Poly(vinyl acetate), PVAc, was one of the first examples used by many authors to illustrate the utility of high resolution proton nmr method for tacticity determination.[2a] Bovey and coworkers reported that the resonances due to the acetoxy methyl protons in different stereoregular sequences of PVAc can be readily resolved.[2b] However, Ramey and Messick showed that the spectral features of these methyl protons are dependent on the solvents.[3] By carrying out a systematic study on model compounds, Fujii, *et al.*,[4] were able to make unambiguous spectral assignments for PVAc. Recently, Abe and Nishioka further demonstrated that the line widths of the acetoxy methyl proton peaks are not uniform and can vary significantly with different solvents.[5] In two recent papers the carbon-13 spectra of PVAc were reported but no detailed spectral analysis was given.[6,7]

In this work, two poly(vinyl alcohol) samples, PVA, of known stereoregularity were converted to PVAc by acetylation. The 220-MHz proton and 22.6-MHz noise-decoupled Fourier transform carbon-13 spectra of the derived acetylated products were obtained in a variety of solvents. From the observed spectra we have deduced the tacticities of the PVAc samples in terms of triad, tetrad, and pentad placements.

Experimental Section

The PVA samples used in this work were those reported previously, *i.e*, an atactic and a highly isotactic polymer.[8] These samples were converted into PVAc by acetylation in pyridine with acetic anhydride.[9] Infrared absorption of hydroxyl groups (~3400 cm^{-1}) was used to monitor the extent of acetylation. The derived products were found to have degrees of esterification in excess of 99.5% in both cases.

For proton measurements the nmr sample solutions were prepared to contain 5 wt % of PVAc. A small amount of hexamethyldisiloxane (HMDS) was added as internal reference. Proton spectra were recorded on a Varian HR-220 nmr spectrometer equipped with a variable temperature probe. The spectra were calibrated by the audiomodulation technique.

The carbon-13 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. Our spectral measurement procedure was in accordance with that described in the previous papers.[7,8] In this study samples were examined as 10% solutions in 10-mm tubes at elevated temperatures. All the carbon chemical shift values were reported with respect to the internal reference HMDS.

Peak areas were determined by using (i) integration, (ii) a Du Pont 310 Curve Resolver, and (iii) a planimeter.

Results and Discussion

I. Proton Resonance Spectra. From the 100-MHz spectra of an atactic PVAc in deuterated chloroform (CDCl$_3$) and carbon tetrachloride (CCL$_4$) solutions, Abe and Nishioka showed that the line widths of the triplet acetoxy methyl proton resonances are not constant.[5] More surprisingly, these methyl protons in nitromethane solution were found to exhibit a six-line spectrum. They attributed these observations to the pentad tacticity effects but did not attempt a detailed analysis of the nitromethane solution spectrum.[5] In the present study we have examined the 220-MHz spectra of the PVAc samples dissolved in a variety of solvents. Some examples are depicted in Figure 1 and the proton chemical shifts are summarized in Table I. Generally speaking, the spectral feature of the acetoxy methyl protons of the atactic polymer can be described by (i) a relatively broad singlet (in benzene, chlorobenzenes, 1-chloronaphthalene, and hexafluoroacetone deuterate), (ii) a triplet (in most of the other solvents), and (iii) a triplet with fine structures (in nitromethane and nitroethane). From the singlet acetoxy proton spectra, it is seen that the solvent shielding increases from hexafluoroacetone deuterate < 1-chloronaphthalene < *o*-dichlorobenzene < benzene. With the exception of the fluorinated solvent, the observed diamagnetic shielding effect appears to be inversely related to the molecular size of the solvent. On the other hand the shielding of the triplet acetoxy methyl protons increases from nitrobenzene < methanol, CDCl$_3$ < perdeuterated 1,1,2,2-tetrachloroethane (CDCl$_2$CDCl$_2$), methylene chloride < CCl$_4$ < perdeuterated dimethyl sulfoxide (DMSO-d_6). In this case the observed trends cannot be simply correlated with the polarity or with the size of the solvent molecule.

Since more than three peaks were observed for the acetoxy protons in the nitromethane solution spectra, we have attempted to analyze these lines in terms of configurational sequences longer than triad placements. In Figure 2 the

Table I
Chemical Shifts of Acetoxy Methyl Protons of Poly(vinyl acetate)

	Chemical shift, ppm from HMDS[a]		
Solvent (Temp, °C)	mm	mr	rr
CCl_4 (69)	1.946	1.918	1.891
$CDCl_3$ (90)	1.971	1.954	1.932
$CDCl_2CDCl_2$ (116)	1.950	1.936	1.914
CH_2Cl_2 (23)	1.955	1.932	1.909
Benzene (30)	1.800	1.800	1.800
(60)	1.810	1.810	1.810
o-Dichlorobenzene (125)	1.896	1.896	1.896
1-Chloronaphthalene (22)	1.945	1.945	1.945
(102)	1.918	1.918	1.918
Methanol (22)	1.971	1.955	1.927
Hexafluoroisopropyl alcohol (22)	1.964	1.964	1.941
Hexafluoroacetone deuterate (80)	2.000	2.000	2.000
DMSO-d_6 (90)	1.923	1.895	1.877
Nitroethane (22)	1.945	1.918	1.884, 1.891, 1.898
(80)	1.927	1.909	1.872, 1.884, 1.889
Nitromethane (65)	1.932	1.909	1.882, 1.891, 1.898
(100)	1.932	1.905, 1.914	1.886, 1.891, 1.900
Nitrobenzene (22)	2.051	2.032	2.005
(102)	2.009	1.989	1.973

[a] mm, mr, and rr represent respectively isotactic, heterotactic, and syndiotactic triads.

Table II
Triad Tacticity Determinations of Poly(vinyl acetate)

	Triad tacticity[a]					
	Atactic sample			Isotactic sample		
Method	mm	mr	rr	mm	mr	rr
Precursor PVA[b]	0.207	0.497	0.296	0.702	0.225	0.073
PVAc						
Proton[c]	0.21	0.49	0.30	0.68	0.23	0.09
Carbon-13[d]	0.22	0.45	0.33	0.7	0.2	0.1

[a] mm, mr, and rr represent respectively isotactic, heterotactic, and syndiotactic triads. [b] From the hydroxyl proton spectra of the starting PVA in DMSO-d_6 solutions (ref 8). [c] From the nitromethane solution spectra of acetoxy methyl protons of the derived PVAc. [d] Calculated from the methylene carbon resonances of PVAc (see text).

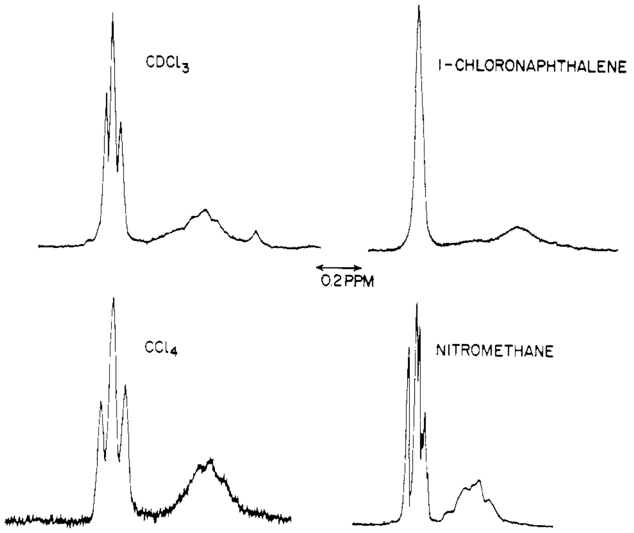

Figure 1. Solvent effects on 220-MHz proton spectra of poly(vinyl acetate).

spectrum of the atactic PVAc was compared with that of the isotactic PVAc. As a first step, we ignored the fine structures and assigned the three main features to mm, mr, and rr triads from low to high field. In so doing, the tacticity measurements of the PVAc polymers can be compared with the corresponding measurements on their precursor PVA. The good agreements of the data in Table II indicate that our spectral assignments are essentially correct. Moreover, the nitromethane solution spectra can be used for quantitative determination of triad tacticity in PVAc.

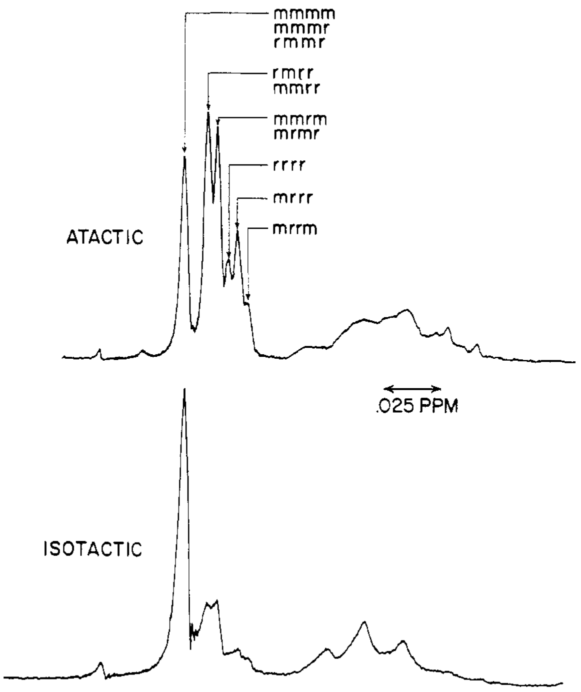

Figure 2. Proton spectra (220 MHz) of atactic and isotactic poly(vinyl acetate) in nitromethane solution.

Our pentad assignments of the fine structures shown in

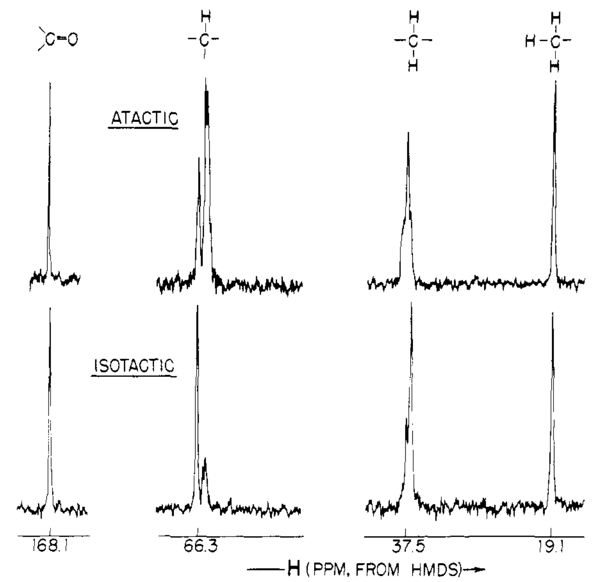

Figure 3. Noise-decoupled Fourier transform carbon-13 spectra (22.6 MHz) of atactic and isotactic poly(vinyl acetate) dissolved in $CDCl_3$.

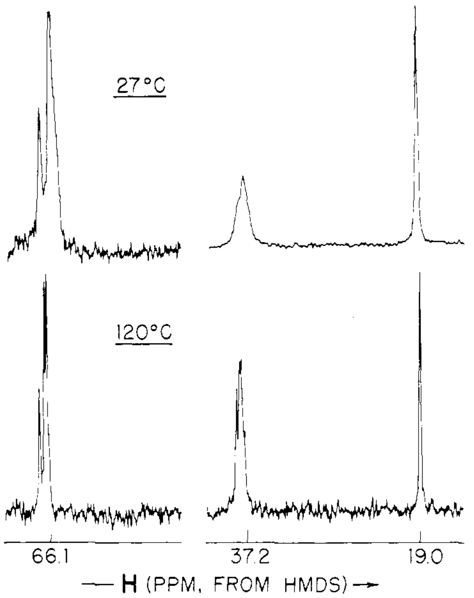

Figure 4. Temperature effects on carbon-13 spectra of poly(vinyl acetate) in $CDCl_2CDCl_2$ solution.

Figure 2 were confirmed by the following observations. In our previous studies of the proton and carbon-13 spectra of PVA, we concluded that radical polymerization of vinyl acetate is a Bernoullian process, *i.e.*, the stereochemical configuration of the derived polymer 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).[8] Then the various pentad placements in this polymer can be calculated from P_m, *e.g.* mmmm = P_m^4, etc.[10] In fact, we were able to make the calculated pentad distribution consistent with the observed acetoxy proton peak intensities. (See Table III.) It is also noteworthy that our assignments were qualitatively confirmed by the peak positions and intensities of the isotactic PVAc sample.

As having been reported by several authors, we observed that the 220-MHz spectra of methylene and methine protons of PVAc, usually consisting of broad and overlapping multiplets, are not appreciably changed from one solvent to another. Spin decoupling or selective deuteration has to be used to facilitate quantitative tacticity measurements.[1]

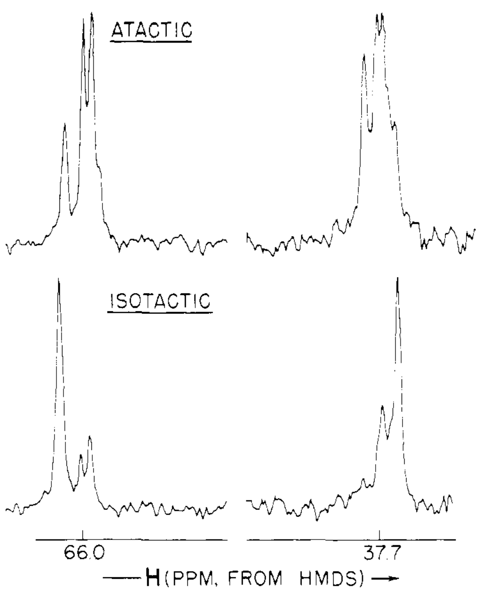

Figure 5. Methylene and methine carbon spectra of poly(vinyl acetate) in $CDCl_2CDCl_2$ solution at 120°.

Table III
Pentad Assignments of Acetoxy Methyl Proton Resonances of Poly(vinyl acetate) in Nitromethane Solution

Chemical shift, ppm, from HMDS	Pentad assign	Peak intensities			
		Atactic sample			Isotactic sample
		Calcd[a]		Obsd[b]	Obsd[b]
1.932	mmmm	0.043	0.208	0.21	0.68
	mmmr	0.103			
	rmmr	0.062			
1.914	mmrr	0.123	0.270	0.26	0.11
	rmrr	0.147			
1.905	mmrm	0.103	0.226	0.23	0.12
	mrmr	0.123			
1.900	rrrr	0.088		0.10	0.03
1.891	mrrr	0.147		0.14	0.04
1.886	mrrm	0.061		0.06	0.02

[a] The pentads were calculated by using the Bernoullian parameter, P_m = 0.456. [b] Observed relative peak intensities.

II. Carbon-13 Resonance Spectra. Proton-decoupled carbon-13 spectra of atactic PVAc dissolved in $CDCl_3$ have been reported by two groups of investigators.[6,7] In their spectra acetoxy carbonyl and methyl carbons appear as single peaks at low and high fields, respectively. Between these singlets methine and methylene carbons give rise to two multiplet resonance patterns which are too complex to permit complete analysis. The difficulties are illustrated in Figure 3, in which the $CDCl_3$ solution spectra of the atactic and the isotactic PVAc samples are shown. It is seen that the observed spectral features are not interpretable in terms of the simple dyad or triad statistics, *i.e.*, a doublet for the methylene and a triplet for the methine carbons. Moreover, the higher sequence placements of tetrads and pentads (*i.e.*, 6 and 10 lines for the methylene and methine carbons, respectively) cannot be readily applied to account for these spectra.

Figure 4 depicts the $CDCl_2CDCl_2$ solution spectra of the atactic PVAc at room temperature and 120°. As the solution temperature increases, all the resonance lines become sharpened and fine structures in the methylene and methine regions become resolved. Similar improvement in spec-

Table IV
Methylene Carbon Spectra of Poly(vinyl acetate)[a]

Chemical shift, ppm, from HMDS	Tetrad assign	Peak intensities: Atactic sample Calcd[b]	Obsd	Isotactic sample Calcd[b]	Obsd
38.2	rrr	0.17	0.20	0.04	0
37.8	rrm	0.25	0.25	0.06	0.1
37.7	rmr + mrm	0.28	0.25	0.08	0.1
37.6	mmr	0.19	0.17	0.25	0.2
37.3	mmm	0.11	0.13	0.57	0.6

[a] Methylene carbon spectra were obtained in $CDCl_2$-$CDCl_2$ at 120°. [b] The tetrads were obtained from the starting PVA (ref 8).

tral resolution was also achieved by examining PVAc dissolved in orthodichlorobenzene at about 140° in nitromethane at 100°, and in DMSO-d_6 at 100°. Therefore, the above-mentioned specific solvent shielding in the proton resonance spectra of PVAc does not significantly contribute to the corresponding carbon-13 spectra. The effect of raising solution temperature appears to impart increased mobilities to the polymer backbone carbons and the pendant groups, which, in turn, lead to improved spectral resolution.

In Figure 5 are shown the horizontal expansion of Figure 4 and the corresponding scan of the isotactic PVAc. The atactic samples give five methylene carbon lines centered at 37.7 ppm. Unlike the spectrum of its precursor PVA, neither the relative positions nor the intensities of these lines exhibit any regularities. They cannot, therefore, be unambiguously assigned to the two stereochemical dyads. However, by using the known tetrad distributions of the starting PVA samples, we have analyzed the methylene carbon resonances of the derived PVAc polymers as presented in Table IV. For such analyses, we have invoked the assumption, in accordance with the work of Schaefer and Natusch[11] and our previous studies on PVA,[8] that the integrated peak intensity of each methylene carbon line can be used to count the number of carbons contributing to that resonance. The nearly quantitative agreements between the observed intensities and the calculated values for both the atactic and isotactic samples indicate that our assignments are consistent. Thus, it follows that the methylene carbon spectra can be used for quantitative tacticity measurements of PVAc. In this work, we have also calculated the triad distributions by using the following relationships of tetrads and triads: mm = mmm + ½mmr, rr = rr + ½rrm, and mr = ½mmr + ½rrm + rmr + mrm.[10] The results are included in Table II to compare with the corresponding proton measurements.

The methine carbon region which ranged from 66.6 to 65.6 ppm consists of two main features. The lower field singlet was found to have relative intensities of 0.20 and 0.68 for the atactic and isotactic PVAc, respectively. Therefore, this peak must arise from the mm triads. On the other hand, the upfield feature with additional fine structures cannot be readily assigned to the mr and rr triads. For the atactic sample, it is conceivable that these lines could be attributed to the combinations of various pentads. However, fitting seven pentads into the three partially resolved peaks of the upfield feature is of rather questionable validity.

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Conformational Studies of Poly[(*S*)-β-aminobutyric acid]

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ABSTRACT: The conformation of high molecular weight and optically active poly[(*S*)-β-aminobutyric acid] in hexafluoroacetone sesquihydrate (HFA · $1.5(H_2O)$), hexafluoroisopropyl alcohol (HFIP), methanesulfonic acid, and their mixtures were examined by using circular dichroism, ultraviolet, and infrared spectroscopy. The results suggest that the polymer exhibits a β-associated conformation in HFIP. The addition of a trace amount of water to a solution of the polymer in HFIP enhances the association phenomenon. Circular dichroism spectra of the polymer films which were cast from HFA and HFIP solutions also show the same β structure. In methanesulfonic acid the poly[(*S*)-β-aminobutyric acid] assumes a disordered structure.

High molecular weight poly(β-amides) which have β-amino acids as the repeating units are similar to polypeptides and to silk fibroin. They have high melting points and also low solubility in typical organic solvents. The synthesis and fiber properties of various poly(β-amides) have been extensively studied in recent years.[2-4] Optically active poly(β-amides) have also been synthesized.[5]

The structure of poly[(*S*)-β-aminobutyric acid] (I) is similar to that of poly(L-alanine). The latter polymer exhibits an α-helical form both in solution and as a film.[6-10] With the additional α-methylene group, poly[(*S*)-β-aminobutyric acid] would be expected to have different conformational properties from poly(L-alanine).

Studies with X-ray and polarized infrared dichroism of