Aromatic Quaternary Carbon Signals in the ^{13}C NMR Spectrum of Poly(2-vinylpyridine) in Methanol-d_4

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ABSTRACT: Modified ^{13}C NMR assignments of the aromatic C-2 carbon of poly(2-vinylpyridine) in methanol-d_4 are proposed on the basis of compliance with the necessary statistical relations between pentad sequence intensities. The spectral analysis shows that the C-2 resonance assignments are more complex than previously believed. The relative ordering of the mmrm and mmrr pentad resonances is opposite to previous assignments. Significant overlap between the rmmr and mmrr pentads is found, indicating that the separation of the isotactic and heterotactic triads is not clean. The three syndiotactic pentad resonances could be reliably identified.

Introduction

High-resolution NMR spectroscopy is a convenient and widely used method for determining the stereochemistry of vinyl polymers.[1–3] The assignment of the spectral fine structure is often aided by (a) X-ray diffraction studies[4–6] and (b) epimerization[7–9] of highly stereoregular polymer samples, (c) NMR studies of model oligomer compounds[10,11] and chemically related polymers,[12] (d) spectral analysis for conformity with certain statistical trials (Bernoullian, first-order Markoffian, etc.) or necessary relations between stereochemical sequence frequencies,[2,3,13] and (e) two-dimensional NMR techniques,[14,15] including ^{1}H–^{13}C heteronuclear correlated 2D NMR spectroscopy,[16–19] which allowed absolute configurational assignments for selected vinyl polymers. Chemical shift calculations based on the γ-gauche effect method[3,20] may be used to correlate experimental results. However, none of these methods is of universal applicability. Since the stereochemical NMR fine structure for each polymer is generally unique and has to be solved individually, the assignments are often tentative and incomplete.

The ^{13}C NMR spectrum of poly(2-vinylpyridine) (P2VP) was studied by several research groups.[21–27] The quaternary (C-2) aromatic carbon was studied in greatest detail[22–26] and has been claimed to be the most stereosensitive among the aromatic carbons.[22] The signals of the CH_2 and CH carbons show broader dispersity in chemical shifts,[27] but significantly overlap, thus complicating assignments. Although the C-2 carbon resonances in methanol-d_4 show at least pentad sensitivity,[24,25] the fine structure is poorly resolved and the pentad assignments proposed by different authors show certain discrepancies as seen in Table 1.

The original assignments were made on the basis of studies of highly isotactic P2VP first prepared by Natta et al.[28] with magnesium amides and Grignard reagents as initiators. The absolute configuration was determined by X-ray diffraction studies of crystallized polymer samples.[28,29] On this basis, the dominant signal in lowest field in the ^{13}C NMR spectrum of isotactic P2VP, marked as A1 in Figure 1, was assigned without any ambiguity to the mmmm pentad.[24,25]

The C-2 carbon region in the spectrum of atactic P2VP shows splitting into three main groups of signals (Figure 2). Fontanille et al.[24] assigned them to the three types of triads, i.e., mm, mr, and rr, in order of increasing field. However, from a comparison of the ^{1}H and the ^{13}C NMR spectra of the β,β-d_2 polymer, Matsuzaki et al. concluded[25] that the three C-2 resonances could not be directly attributed to triad tacticity. Thus, the relative intensity of the downfield C-2 carbon signal (signal B-I in Figure 2) was found to be considerably larger than the downfield signal in the methine proton spectrum assigned to the mm triad.[25] Harwood et al.[26] attributed the downfield C-2 absorption (signal B-I in Figure 2) to mm triads on the basis of ^{13}C NMR studies of partially epimerized isotactic P2VP and proposed heptad assignments for its fine structure (Table 1). However, deviations of the observed mr and rr contents from the simulated curves indicated that the other two resonance areas (signals B-II and B-III in Figure 2) may not be solely due to mr and rr triads.[26] Tonelli calculated[30] the relative chemical shifts of the 10 pentad signals in the C-2 carbon spectrum on the basis of the conformational characteristics of P2VP[31] using the γ-gauche effect method. His calculations suggest partial overlap of the hetero- and isotactic triads (see Table 1).

The stereochemistry of the anionic oligomerization and polymerization of 2-VP has been extensively studied in this laboratory.[32] Recently, we reported the first synthesis of syndiotactic P2VP by the *t*-BuLi-initiated polymerization of 2-VP in toluene at −78 °C in the presence of aluminum alkyls.[33] The corresponding P2VP samples provided the opportunity for new insight into the question of C-2 assignments, particularly in the heterotactic–syndiotactic C-2 region. Spectral analysis led us to the conclusion that some of the originally reported stereochemical assignments[24,25] need revision. In this paper we would like to present the rationale for these revised C-2 assignments.

Experimental Section

Reagents and Solvents. THF (Fisher) and toluene (EM Science) were stirred over Na/K alloy and were distilled through the vacuum line just prior to use. The monomer, 2-vinylpyridine (Aldrich), was purified by stirring over calcium hydride and potassium mirror followed by distillation. *tert*-Butyllithium (*t*-BuLi) from Aldrich was sublimed under high vacuum (10^{-6} Torr) and stored in the freezer as a toluene solution. Triethylaluminum ($AlEt_3$) and triisobutylaluminum (Al(*i*-Bu)$_3$) from Aldrich were used without further purification. (1*R*,2*S*,5*R*)-(−)-Menthol (Aldrich) was dried in vacuum and was dissolved in toluene to a 0.5 M solution. The *t*-BuLi/

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Table 1. Proposed Assignments for the C-2 Carbon Signal in the ^{13}C NMR Spectrum of P2VP in Methanol-d_4 and Calculated Relative Chemical Shifts on the Pentad Level

resonance region[a] Δδ, ppm[b]	Fontanille et al.[24]	Matsuzaki et al.[25]	Harwood et al.[26] heptad	Δδ, ppm[b]	Tonelli[30] pentad	Δδ, ppm[b]
B-1	mmmm	mmmm	mmmmmmm	0.0	mmmm	0.0
0.0−0.35			mmmmmmr	0.07		
			mmmmrm	0.09		
		mmmr	mmmmrr	0.12	mmmr	0.11
	mmmr		rmmmmr	0.14		
		rmmr	rmmmrm	0.16		
			mrmmrm	0.18	mmrm	0.22
			rmmmrr	0.19		
	rmmr	mmrm	mrmmrr	0.21	mmrr	0.27
			rrmmrr	0.24		
					rmmr	0.34
B-II	mmrm	mmrr				
0.35−0.75	mrmr	mrmr	mr		mrmr	0.42
	mmrr	mrrm				
	rrmr	rrmr			rrmr	0.44
B-III	rrrr				rrrm	0.80
0.75−1.1	rrrm	rrrm	rr		mrrm	0.93
	mrrm	rrrr			rrrr	0.96

[a] Refer to Figure 2 to identify resonance region. [b] Relative chemical shift upfield from the reference signal of the mmmm pentad.

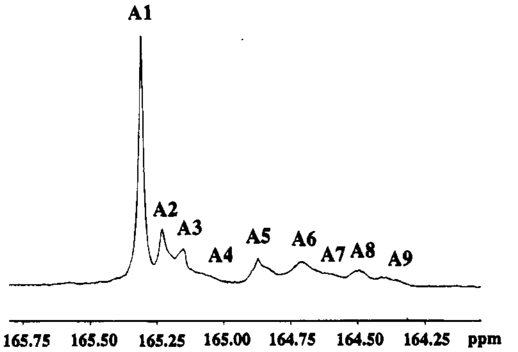

Figure 1. Aromatic quaternary ^{13}C NMR resonances of isotactic-like P2VP (sample A) in methanol-d_4 at 40 °C.

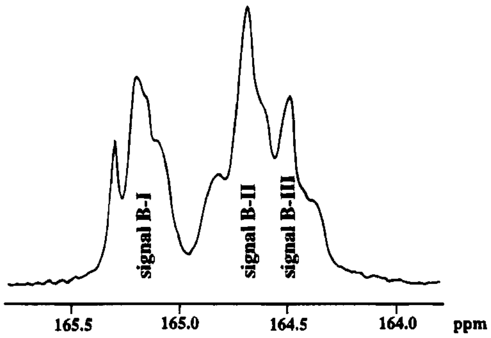

Figure 2. Aromatic quaternary ^{13}C NMR resonances of atactic P2VP (sample B) in methanol-d_4 at 40 °C.

alkoxide initiator was formed at 25 °C in situ by reacting *t*-BuLi and menthol in the desired ratio.

Polymerization Procedures. The polymerization runs were carried out under vacuum in an all-sealed glass apparatus equipped with break seals. $AlEt_3$ and $Al(i\text{-}Bu)_3$ were added to the toluene solution of *t*-BuLi at −78 °C. When THF was used as solvent, the *t*-BuLi solution in toluene (ca. 10^{-3} M) was cooled to −78 °C and only then THF was distilled into the flask. About 1 g of 2-VP was distilled onto the stirred initiator solution at −78 °C. Reactions were terminated with a small amount of methanol, and the polymer was recovered by partial solvent evaporation followed by precipitation in a large excess of hexane at room temperature. The P2VP samples prepared in the presence of additives were further purified by extraction in chloroform and subsequent reprecipitation in hexane.

Table 2. Poly(2-vinylpyridine) Samples Prepared at −78 °C with Initiator *t*-BuLi

sample	additive	[Add]/ [In]	solvent	polymer yield (%)	M_n calc	M_n SEC	M_w/M_n (SEC)
A	MenOLi[a]	10	toluene	30	5300	11400	1.6
B	no		toluene	70	4600	4600	4.9
D	$AlEt_3$	16	toluene	78	3660	15200	1.9
E	$Al(i\text{-}Bu)_3$	9	THF	20	2250	22000	1.4
F	$AlEt_3$[b]	15	toluene	60	3600		

[a] Li alkoxide of (1*R*,2*S*,5*R*)-(−)-menthol. [b] Stereoblock polymer; $[AlEt_3]/[t\text{-}BuLi]$ ratio refers to the preparation of the second stereoblock.

The experimental details for the P2VP samples prepared in this study are summarized in Table 2. Precipitation of the polymer in the early reaction stages and incomplete initiator consumption were observed. As previously reported for 2-VP polymerizations in toluene, these two factors typically result in broad molecular polydispersities and molecular weights higher than calculated.[34] Sample E is a stereoblock polymer prepared by *t*-BuLi initiation of 2-VP in the presence of lithium alkoxides.[33] The "living" isotactic poly(2-VPLi) was then reacted with a 15-fold molar excess of $AlEt_3$ at −20 °C and after cooling to −78 °C, another portion of 2-VP was distilled into the flask to form the second stereoblock.

Polymer Characterization. SEC data were collected on a Waters chromatograph equipped with an M510 HPLC pump, an M410 differential refractometer, and an M484 tunable UV−vis absorbance detector. Two ultraStyragel columns with pore sizes of 10^3 and 500 Å were used in series. THF was eluent at 1.00 mL/min nominal flow rate. Calibration was based on P2VP standards (Polyscience).

The ^{13}C NMR spectra were recorded at 40 °C with 15−20% (w/v) P2VP solutions in methanol-d_4 on a Varian 200XL FT spectrometer at 50.3 MHz or a Bruker AM-360 FT spectrometer at 90.52 MHz. The deuterium signal of the solvent was used to lock the field. Twelve to sixteen thousand transients were taken at a pulse angle of 90° and a delay time of 3.5 s between the pulses. Chemical shifts were calibrated relative to TMS with the CD_3OD signal as a reference at 49.0 ppm downfield from TMS. The spectra of the aliphatic carbons were acquired under identical conditions on a Bruker AMX-500 FT spectrometer with a carbon frequency of 125.72 MHz in deuterated chloroform and referenced to the solvent signal at 77.0 ppm downfield from TMS. The areas under the NMR signals were determined by the method of cutting and weighing. Overlapping peaks were hand resolved.

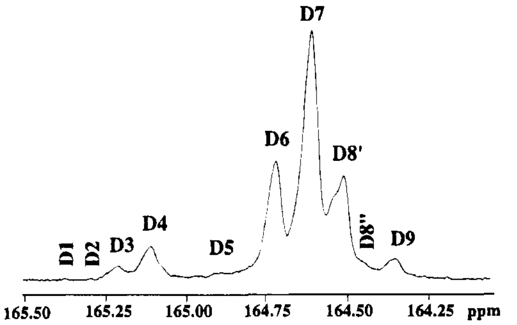

Figure 3. Aromatic quaternary ^{13}C NMR resonances of P2VP (sample D) in methanol-d_4 at 40 °C.

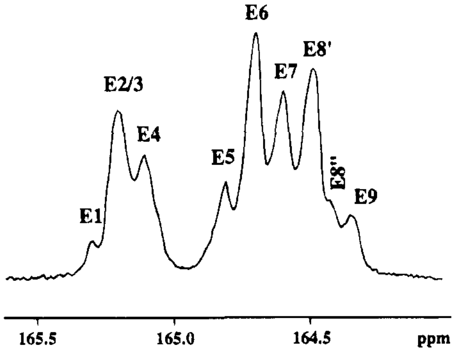

Figure 4. Aromatic quaternary ^{13}C NMR resonances of P2VP (sample E) in methanol-d_4 at 40 °C.

Results and Discussion

The ^{13}C NMR spectra of samples D and E recorded in $CDCl_3$ and in methanol-d_4 show different splitting patterns. Solvent sensitivity has been previously observed in cases of relatively narrow dispersity of the stereochemical fine structure in chemical shifts, e.g., poly(vinyl chloride)[3,35] and P2VP itself.[25] The C-2 resonance frequences are better resolved in methanol-d_4, and the following discussion is confined to the spectral assignments in this solvent only.

Figures 3 and 4 show the C-2 region of the ^{13}C NMR spectra of P2VP prepared at −78 °C by initiation with *t*-BuLi in the presence of $AlEt_3$ in toluene (sample D) and in the presence of Al(*i*-Bu)$_3$ in THF (sample E), respectively. The observed resonances are numbered in order of increasing field and are listed in Table 3 with the respective chemical shifts and molar fractions. Also included in Table 3 are the resonances observed in the spectrum of sample A (Figure 1). Note that the numbers refer to resonances occurring at roughly the same chemical shifts in all three samples although there are some deviations, e.g., A3−A5 compared to D3−D5 and E3−E5.

The spectra of the polymers prepared in the presence of aluminum alkyls are clearly very different from previously described P2VP spectra. Thus, for sample D three strong resonances, D6, D7, and D8, appear in the heterotactic−syndiotactic region of the spectrum,[24−26,30] at ca. 164.7, 164.6, and 164.5 ppm, respectively. The relative intensities of these resonances vary with the reaction conditions. Whereas resonance D7 is dominant in Figure 3, its relative intensity in sample E is substantially reduced (resonance E7 in Figure 4). The spectrum of sample E bears a certain resemblance with the spectra of both sample D (Figure 3) and atactic P2VP (Figure 2).

The resonances D6, D7, and D8 are not seen so prominently in the ^{13}C NMR spectra of previously prepared P2VP samples. Their assignment is of obvious interest and is aided by the pentad−pentad statistical frequency relationships:[13]

$$(\mathrm{mmmr}) + 2(\mathrm{rmmr}) = (\mathrm{mmrm}) + (\mathrm{mmrr}) \qquad (1)$$

$$(\mathrm{rrrm}) + 2(\mathrm{mrrm}) = (\mathrm{rrmr}) + (\mathrm{mmrr}) \qquad (2)$$

These relationships hold regardless of the polymerization stereochemistry and can serve as a test of the validity of signal assignments.[3]

Since the mm-centered pentad resonances of P2VP are observed at low field[24−26] (cf. Figure 1), the downfield resonances D3 and D4 of sample D (Figure 3) can plausibly be attributed to the mmmr and the rmmr pentads, respectively. It is clear then from the data in Table 3 that the left-hand side of eq 1, i.e., the sum of the (mmmr) and 2(rmmr) intensities, is smaller than the intensity of D6, D7, or D8. Hence, none of these three resonances can be due to the mmrm or the mmrr pentad (see eq 1).

Since (D7) > (D6) + (D8), (D7) cannot appear on the left-hand side of eq 2. Moreover, since D7 cannot correspond to mmrr, from eq 2 we have

$$(\mathrm{D6}) + 2(\mathrm{D8}) = (\mathrm{D7}) + (\mathrm{mmrr}) \qquad (3)$$

or

$$(\mathrm{D8}) + 2(\mathrm{D6}) = (\mathrm{D7}) + (\mathrm{mmrr}) \qquad (4)$$

As seen from Table 3, eqs 3 and 4 yield (mmrr) = 0.175 and 0.148, respectively, while D4, which is the largest remaining resonance, is only 0.061. Thus, it would appear unlikely that any combination of D6, D7, and D8 could satisfy eq 2.

Consider now the spectrum of sample E shown in Figure 4, where signals E6 and E8, corresponding to D6 and D8, respectively, are of the highest intensity. Obviously, no set of resonances can satisfy eq 2 with the fractions of E6 and E8 on the left-hand side, confirming that eqs 3 and 4 cannot hold.

As seen from eqs 1 and 2, only 7 of the 10 pentads are interrelated. The fractions of the remaining three pentads, i.e., the isotactic (mmmm), the syndiotactic (rrrr), and the heterotactic (mrmr) pentads, can vary independently and are not subject to relationships with other pentads. Since the resonances 6, 7, and 8 in samples D and E fail to meet the statistical requirements, at least one of them is independent. Resonances 6 and 8 appear in a roughly 1:1 ratio in both spectra while the intensity of resonance 7 differs substantially. Such a pattern is typical of a stereoregular block and its terminal pentads as the average length of the stereoblock varies, suggesting that signal 7 belongs to one of the stereoregular pentads. The mmmm pentad was previously identified,[24,25] without any ambiguity, as the dominant lowest field resonance marked as A1 in Figure 1. Therefore, the D7 and E7 resonances belong to either the syndiotactic pentad, rrrr, or the heterotactic pentad, mrmr, neither of which has been reliably identified so far.[26]

In order to distinguish between the two possible assignments of resonance D7, we examined the other aromatic carbon signals of sample D. According to Harwood et al.,[26] the C-6 NMR signal shows a fine structure in order of increasing field as follows: (A) mrrm, (B) rrrm, (C) rrrr + mmrr + rmrr, and (D) mrmr + mrmm + mm. The strong absorption in resonance region C of the C-6 signal of sample D (Figure 5) is in

Table 3. Fractions and Relative Chemical Shifts of the C-2 Resonances in the Spectra of Samples A, D, and E

	sample A			sample D			sample E	
R[a]	Δδ, ppm[b]	F[c]	R[a]	Δδ, ppm[b]	F[c]	R[a]	Δδ, ppm[b]	F[c]
A1	0.0	0.37	D1	0.0	0.001	E1	0.02	0.17
A2	0.075	0.115	D2	0.08	0.002	E2/3	0.11	0.159
A3	0.16	0.10	D3	0.11	0.025			
A4	0.20–0.38	0.05	D4	0.21	0.061	E4	0.205	0.112
A5	0.45	0.12	D5	0.30–0.55	0.043	E5	0.505	0.070
A6	0.60	0.10	D6	0.60	0.185	E6	0.60	0.217
A7	0.65–0.75	0.03	D7	0.715	0.434	E7	0.705	0.130
A8	0.81	0.07	D8	0.78–0.92	0.212	E8	0.81	0.247
A9	0.88–1.00	0.045	D9	0.97	0.037	E9	0.96	0.048

[a] Resonance region. Refer to Figure 1 for sample A, Figure 3 for sample D, and Figure 4 for sample E to identify resonance region. [b] Chemical shift upfield from the reference signal of the mmmm pentad. [c] Resonance fraction.

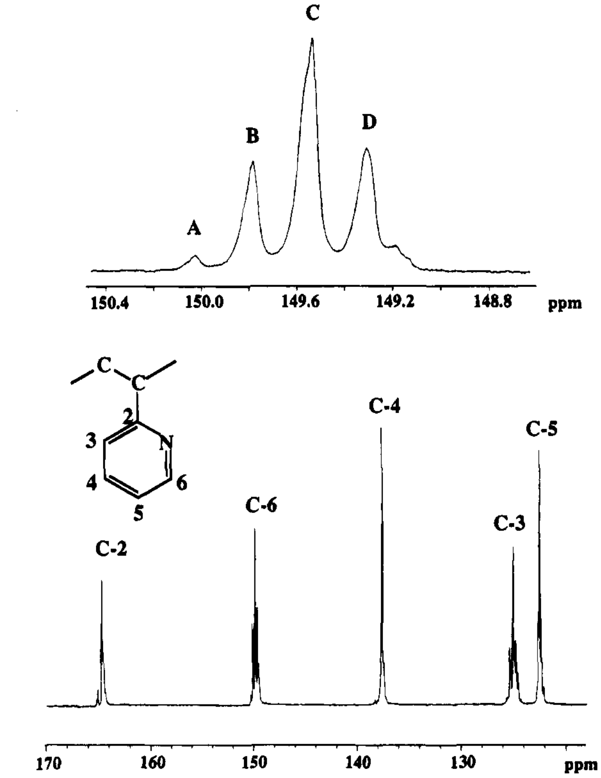

Figure 5. Aromatic ^{13}C NMR signals (below) and C-6 resonances (above) of P2VP (sample D) in methanol-d_4 at 40 °C.

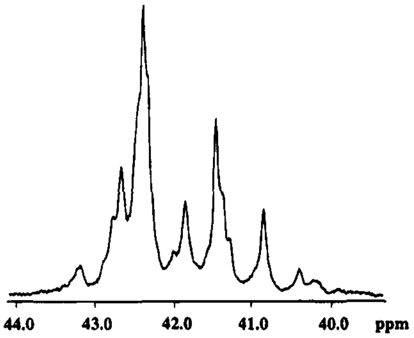

Figure 6. Methylene/methine ^{13}C NMR resonances of P2VP (sample D) in deuteriochloroform at 25 °C.

general agreement with the syndiotactic character of the polymer. Assignments for the fine structure of the C-3 carbon signal[26] similarly suggest increased syndiotactic rather than heterotactic content of sample D.

Scheme 1

Stereochemical sequence	**Pentads**	**Ratio**
A. **...rrrr - m - rrrr...**	**(rrrm) / (rrmr)**	**1 : 1**
...rrrr - mm - rrrr...	**(rrrm) / (mmrr) / (rmmr)**	**2 : 2 : 1**
...rrrr - mmm - rrrr...	**(rrrm) / (mmrr) / (mmmr)**	**1 : 1 : 1**
B. **...rrr - m - rrr - m - rrr...**	**(rrrm) / (rrmr)**	**1 : 1**
...rrr - m - rr - m - rrr...	**(rrrm) / (rrmr) / (mrrm)**	**2 : 4 : 1**
...rrr - m - r - m - rrr...	**(rrrm) / (rrmr) / (mrmr)**	**1 : 1 : 1**

Further evidence is provided by analyzing the ^{13}C NMR CH$_2$/CH region of sample D shown in Figure 6. The assignments based on epimerization studies of P2VP are as follows:[27] methylene carbon heterotactic tetrads, mrm at 39.7–40.7 ppm, rmr at 42.5–43.1 ppm; methine carbon mrmr pentad at ca. 43.0 ppm. Thus, strong resonances from heterotactic sequences are missing (see Figure 6). Syndiotactic P2VP fits better with the methylene mrr at 41.3–41.8 ppm and the rest of the strong resonances in close proximity, slightly upfield of the proposed assignments:[27] rrr at 42.0–42.4 ppm; the methine carbon rrrr, rrrm, and rrmr pentad resonances at ca. 42.6, 42.7, and 42.8 ppm, respectively.

X-ray diffraction studies of highly stereoregular polymers of the type of sample D could provide conclusive evidence of the true nature of resonance D7. The possibility of heterotactic P2VP would be of considerable interest since very few examples of heterotactic stereoregulation are known.[36] However, the ^{13}C NMR spectral fine structure strongly favors sample D being syndiotactic P2VP. For this reason, further discussion will be elaborated on the basis of the assignment of resonance D7 in Figure 3 to the rrrr pentad.

Pentads of strictly defined type and ratio occur at the termini of stereoregular sequences depending on the lengths of the two adjacent blocks. This is illustrated in Scheme 1 for (A) syndiotactic stereoblocks interrupted by one or more consecutive m diads and (B) syndiotactic stereoblocks of different length flanked by a single m diad on both sides.

In syndiotactic-like polymers such as sample D (see Figure 3), the probability of longer m sequences and shorter r sequences should decrease except for specific mechanisms of stereoregulation. On this basis, the strong resonances D6 and D8 appearing in a roughly 1:1 ratio are assigned to the rrrm/rrmr pair of pentads. The lower intensities of resonances D4 and D3 are consistent with the lower probability of pentads containing two m diads. They are observed in a roughly 2:1 ratio (see Figure 3 and Table 3), which identifies D3 as the resonance of the symmetric rmmr pentad and D4 as mmrr. The probabilities of pentads with three m diads, i.e., mmmr and mmrm, are even lower, which is reflected in their negligible fractions in sample D. The relatively strong resonance D9 is assigned to the mrrm pentad on the basis of higher probability than the mrmr pentad.

Table 4. Stereochemical Assignments, Relative Chemical Shifts, and Fractions of the C-2 Resonances in the ^{13}C NMR Spectrum of Syndiotactic P2VP (Sample D, Figure 3)

resonance region[a]	assignment	chem shift Δδ, ppm[b]	exptl fraction	calc Bernoulli	fraction Markoff I
D1	mmmm	0.0	0.001	0.0016	0.002
D2	mmmr	0.05−0.08	0.002	0.013	0.016
D3	rmmr	0.11	0.025	0.0256	0.027
D4	mmrr	0.21	0.061	0.0512	0.056
D5	rmmr	0.30−0.55	0.017		
	mmrm		0.026	0.013	0.0135
D6	rrmr	0.60	0.185	0.205	0.194
D7	rrrr	0.715	0.434	0.410	0.419
c	mrmr	0.78	0.040	0.0512	0.047
D8′	mrrr	0.81	0.172	0.205	0.202
D8″	mrrr	0.85−0.92	*d*		
D9	mrrm	0.97	0.037	0.0256	0.0235
	mm		0.045	0.040	0.045
	mr		0.310	0.320	0.3105
	rr		0.645	0.640	0.6445

[a] Refer to Figure 3 to identify resonance region. [b] Upfield from the reference signal of the mmmm pentad. [c] Downfield shoulder of signal D8. [d] Total fraction of rrrm under D8′.

Resonances D6 and D8 were assigned on the basis of pentad−pentad statistical relations. The NMR spectra of samples D and E, and a number of other samples of different syndiotactic content,[33] were used in testing the compliance of resonance intensities with eq 2. The spectral analysis was in agreement with assignments of the D4, D6, D8, and D9 resonances to the mmrr, rrmr, rrrm, and mrrm pentads, respectively. The analysis also showed that the upfield shoulder of signal D8 in Figure 3, more clearly seen as shoulder E8″ in Figure 4, belongs to the rrrm pentad.

The stereochemical assignments of the C-2 region in the ^{13}C NMR spectrum of sample D (Figure 3) are listed in Table 4 with their chemical shifts, the pentad and triad fractions, and the calculated fractions for both Bernoullian and first-order Markoffian statistical trial. The persistence ratio $\rho = 1.03$ [$\rho = 2(\mathrm{m})(\mathrm{r})/(\mathrm{mr})$] and the triad contents are consistent with Bernoullian statistics, although the pentad fractions indicate a measurable deviation from Bernoullian trial, and the average length of the syndiotactic blocks is 5.2 r diads. All this supports the pentad assignments of resonances D3, D4, D6, D8, and D9 on the basis of statistical probabilities (see Scheme 1).

In another context, Figure 3 provides important insight into the quaternary carbon resonances in the downfield isotactic region. With the assignment of D6, D7, and D8 to eq 2 related pentads, the resonances D3 and D4 cannot both represent isotactic pentads, i.e., mmmr and rmmr. If so, the intensity of resonance region D5, which should then contain the signals of the mmrm and mmrr pentad,[24,25] is too low to conform with eq 1. It is clear that either D3 or D4 belongs to a heterotactic pentad, in support of the conclusion that at least one heterotactic resonance appears in the downfield spectral region.[25,30]

The spectrum of isotactic-like P2VP also provides evidence of the appearance of heterotactic resonances in the downfield C-2 region (Figure 1). Previous studies with highly isotactic samples[24,25] leave no doubt that the two most downfield resonances A1 and A2 belong to mmmm and mmmr, respectively. The problem arises when considering the origin of resonance region A4. It is impossible that both A3 and A4 are due to the symmetric rmmr pentad. If so, the combined intensities of resonances A5 and A6 (mmrm + mmrr) are too small to comply with eq 1. Moreover, resonance A6 appears at the same chemical shift as resonance D6, which would suggest that A6 actually belongs to rrmr (see above) and not to the mmrr pentad. All this confirms that either A3 or A4 belongs to a heterotactic pentad. Indeed, the spectral analysis of sample A (Figure 1) and other P2VP samples of various isotactic content[37] on the basis of eq 1 leads to assignments as follows: A3, mmrm or mmrr; A4, rmmr; A5, mmrm or mmrr; A6, rrmr.

Table 5. Stereochemical Assignments, Relative Chemical Shifts, and Fractions of the C-2 Resonances in the ^{13}C NMR Spectrum of Isotactic-like P2VP (Sample A, Figure 1)

resonance region[a]	assignment	chem shift Δδ, ppm[b]	exptl fraction	calc Bernoulli	fraction Markoff I
A1	mmmm	0	0.37	0.254	0.322
A2	mmmr	0.075	0.115	0.208	0.194
A3	mmrr	0.16	0.085	0.085	0.110
A4	rmmr	0.20−0.38	0.06	0.042	0.029
A5	mmrm	0.45	0.15	0.208	0.142
A6	rrmr	0.60	0.075	0.035	0.033
A7[c]	rrrr	0.65−0.75	0.01	0.007	0.024
	mrmr	0.65−0.75	0.02	0.085	0.043
A8	mrrr	0.81	0.07	0.035	0.063
A9	mrrm	0.88−1.0	0.045	0.042	0.040
	mm		0.545	0.504	0.545
	mr		0.33	0.413	0.33
	rr		0.125	0.084	0.125

[a] Refer to Figure 1 to identify resonance region. [b] Upfield from the reference signal of the mmmm pentad. [c] The fraction of resonance region A7 arbitrarily assigned to rrrr and mrmr.

The heterotactic resonances mmrm and mmrr (resonances A3 and A5) cannot be distinguished on the basis of eq 1 only. A similar ambiguity in identifying the mmmr and mmrr resonances arises in NMR studies of partially epimerized polymer samples and is solved by studies of both the isotactic and the syndiotactic polymer.[3] The fact that the mmrr pentad correlates with other pentads through both eqs 1 and 2 makes it possible to distinguish between mmmr and mmrr on the one hand and rrrm and mmrr on the other. Similarly, the synthesis of syndiotactic P2VP proves very useful for the stereochemical assignments of the C-2 NMR spectrum. A relatively strong resonance appears in the low-field region of both isotactic and syndiotactic P2VP, A3 in Figure 1 and D4 in Figure 3, respectively. As the probability of the mmrr pentad is relatively high in both isotactic and syndiotactic samples, resonances A3 and D4 belong to mmrr, downfield from the mmrm resonance A5 in Figure 1 and the rrmr resonance D6 in Figure 3.

The resulting assignments of the C-2 NMR pentad resonances for isotactic P2VP (sample A in Figure 1) are listed in Table 5 with their chemical shifts, the measured pentad and triad fractions, and the calculated fractions for both Bernoullian and first-order Markoffian statistical trial. Note that the assignments of the mmrm and the mmrr pentad resonances are in contrast to all previous studies, which give the opposite relative ordering of these resonances (cf. Table 1). The stereochemistry of sample A is clearly non-Bernoullian (the persistence ratio $\rho = 1.25$), and, as seen from the calculated pentad fractions, it also measurably deviates from a first-order Markoffian trial.

The assignments in the downfield C-2 region are supported by the spectrum of sample E in Figure 4. Signal E2/3 is broad, indicating that it may represent two peaks due to closely spaced mmmr and rmmr pentad resonances. Resonance E1 at lowest field obvi-

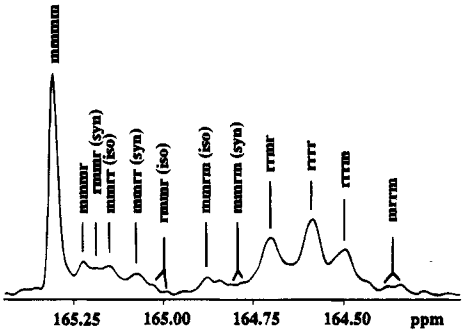

Figure 7. Aromatic quaternary ^{13}C NMR resonances of isotactic-syndiotactic stereoblock P2VP (sample F) in methanol-d_4 at 40 °C.

Table 6. Selected ^{13}C Chemical Shifts for the C-2 Carbons of P2VP and the Methyl Carbons of Polypropylene

pentad	P2VP chem shift,[a] ppm	heptad	polypropylene[38] chem shift,[b] ppm
rmmr (syn)[c]	0.105–0.115	r–rmmr–r	0.565
mmrr (iso)[d]	0.150–0.160	m–mmrr–m	0.682
mmrr (syn)[c]	0.205–0.215	m–rmmr–m	0.686
rmmr (iso)[d]	0.220–0.300	r–mmrr–r	0.823

[a] Relative chemical shift upfield from the mmmm pentad signal. [b] Relative chemical shift upfield from the mmmmmm signal, at 42 °C in 1,2,4-trichlorobenzene–p-dioxane-d_8; calculated.[38] [c] Signals of predominantly syndiotactic P2VP, presumably rrmmrr and rmmrrr, respectively. [d] Signals of predominantly isotactic P2VP, presumably mrmmrm and mmmrrm, respectively.

Table 7. Relative Chemical Shifts of the Quaternary Aromatic Carbon in ^{13}C NMR Spectra of P2VP in Methanol-d_4 at 40 °C

pentad	Δδ, ppm	isotactic P2VP Δδ, ppm	syndiotactic P2VP Δδ, ppm
mmmm	0	0	0
mmmr	0.050–0.100	0.075–0.080	
mmrr	0.100–0.350[a]	0.150–0.160	0.205–0.215
rmmr		0.180–0.300	0.105–0.115
mmrm	0.350–0.550	0.420–0.440	0.495–0.505
rrmr	0.550–0.650	0.595–0.605	0.595–0.605
rrrr	0.650–0.780[b]	c	0.705–0.715
rmrm		c	c
mrrr	0.800–0.920	0.800–0.810	0.805–0.815
mrrm	0.900–0.980	0.900–0.980	0.960–0.980

[a] Shared interval of overlapping heptad signals of the mmrr and the rmmr pentads. [b] Presumably shared interval of overlapping heptad signals of the rrrr and the mrmr pentads. [c] Not detected.

ously belongs to the mmmm pentad.[24,25] The fractions of mmmm and mmmr are larger than in sample D as the probability of longer isotactic sequences increases with the increased m content of sample E. Resonances E4 and E5 are readily identified with the aid of eq 1 as the absorptions of mmrr and mmrm, respectively.

The heterotactic pentad could not be reliably identified. A signal is observed in close proximity to the rrrm absorption as a downfield shoulder of resonance D8 in Figure 3. This resonance is tentatively assigned to the mrmr pentad. The correctness of this assignment cannot be tested by similar pentad–pentad relations since, as previously mentioned, the heterotactic pentad is not subject to statistical relations with other pentads. The mrmr resonance can possibly appear also in region D5 (Figure 3).

As seen from Tables 4 and 5, the relative ordering of the mmrr and the rmmr pentad resonances in the spectrum of syndiotactic P2VP (sample D) is inverted compared to the spectrum of the isotactic polymer (sample A). In order to calibrate the chemical shifts of all resonances in the C-2 NMR spectra of samples of different tacticity relative to a single reference, the resonance of the mmmm pentad in lowest field, we prepared samples of isotactic–syndiotactic stereoblock P2VP (Figure 7). Two separate resonances arising from different stereochemical environment are clearly evident in this spectrum for at least three pentads: rmmr, mmrr, and mmrm. Their chemical shifts relative to the mmmm resonance and the rrrr resonance are in excellent agreement with the values found from the spectra of samples A and D, respectively. Plausibly, the splitting of the rrrm resonance (Figure 3) into D8′ (main absorption) and D8″ (shoulder) also reflects different stereochemical environment. Also, including weak absorptions and shoulders, about 20 resonances are usually visible in the C-2 NMR spectrum of P2VP samples. All this seems to indicate stereochemical sensitivity of the C-2 carbon at the heptad level.

Spectral fine structure to heptad stereosequences has been previously observed in the ^{13}C NMR spectra of vinyl polymers, e.g., for polypropylene[38] and polystyrene.[39] The chemical shifts of the mmrr and the rmmr C-2 pentad resonances of isotactic and syndiotactic P2VP and the corresponding methyl carbon heptad resonances calculated for polypropylene are listed in Table 6. The spectrum of polypropylene is completely resolved at the pentad level and shows some small overlapping at the heptad level,[38] as seen from Table 6 for the heptad signals of the mmrr and rmmr pentads. The C-2 carbon resonances of P2VP show a smaller dispersity in chemical shifts than the methyl carbon signal of polypropylene, ca. 1.0 vs 2.33 ppm, respectively. Hence, a more pronounced overlapping of the C-2 heptad signals is not surprising. In isotactic P2VP the mmrr (presumably the mmmrrm) resonance appears downfield from the mrrm (presumably the mrmmrm) resonance. In syndiotactic samples both resonances are shifted but in opposite field directions and appear in inversed order, rrmmrr downfield from rmmrrr.

Assignments for the C-2 carbon resonances of P2VP at the heptad level would provide access to valuable information of the polymerization stereochemistry. However, they would require extensive computer simulations of the NMR spectra. The revised pentad assignments as discussed in the paper are summarized in Table 7. The first column gives the range of observed pentad chemical shifts. The chemical shifts of pentad resonances as they appear in the C-2 spectrum of isotactic and syndiotactic P2VP are listed separately in the second and third columns.

The downfield spectral region, between 0 and 0.35 ppm upfield from the mmmm pentad resonance, i.e., signal B-I in Figure 2, is mainly due to isotactic absorptions but also contains heterotactic resonances as correctly assumed by Matsuzaki et al.[25] and Tonelli.[30] Hence, this region cannot be directly assigned to the mm triad as suggested by others.[24,26] These are resonances of the mmrr pentad, which appear downfield from the mmrm resonances, contrary to what has been anticipated.[24,25,30] The rmmr and the mmrr pentad resonances appear in a common absorption interval and substantially overlap at the heptad level as clearly observed in the spectra of P2VP samples of different tacticity.

The intermediate spectral region (signal B-II in Figure 2), from 0.35 to 0.75 ppm upfield from the mmm pentad, in addition to heterotactic absorptions, also contains syndiotactic resonances as clearly shown by the spectrum of syndiotactic P2VP. These are the rrrr pentad resonances, unlike assignments by Matsuzaki et al., who assumed that the mrrm resonance will appear in this range.[25] Presumably, the rrrr and the mrmr resonances share a common absorption interval and overlap at the heptad level.

The upfield spectral region, from 0.75 ppm upfield from the mmmm pentad (signal B-III in Figure 2), contains only two syndiotactic pentad absorptions, the rrrm and the mrrm in order of increasing field. Fontanille et al. correctly predicted the relative ordering of the three syndiotactic pentads[24] but ascribed them all to signal B-III (see Table 1) so that the rrrr pentad was assigned to a resonance too far upfield which we showed to belong to the rrrm pentad. It is possible that mrmr resonances also appear in this spectral region.

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