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# AN ANALYSIS OF THE $^{13}\text{C}$ -NMR AND $^1\text{H}$ -NMR SPECTRA OF POLY(*N*-METHYL-2-VINYL PYRROLE)

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## ABSTRACT

*N*-Methyl-2-vinyl pyrrole (NMVP) was synthesized and polymerized by free-radical initiation at 60 and 90°C. The 300-MHz  $^1\text{H}$ -NMR and 75.5-MHz  $^{13}\text{C}$ -NMR spectra were recorded at ambient temperature in  $\text{CDCl}_3$ . Analysis of both the  $^1\text{H}$  and  $^{13}\text{C}$  NMRs show that poly-NMVP is an atactic polymer when synthesized at polymerization temperatures of 60 and 90°C employing free-radical initiation.

## INTRODUCTION

For some time we have been investigating the stereochemistry of polyvinyl heterocycles synthesized via free-radical initiation [1–5]. In our investigations we have seen that the effect that a heteroatom has on a polymer's NMR spectra is considerable. We have reported on five-membered polyvinyl heterocycles where the heteroatom is O, S, or Se, and in this paper we report on a five-membered polyvinyl heterocycle where the heteroatom is N. Specifically, the subject of this paper is poly(1-methyl-2-vinyl pyrrole). Attempts were made to study poly(2-vinyl pyrrole) itself [6], but while the monomer and polymer could be made in good yields, the polymer proved unstable, rapidly crosslinking in the presence of air and light, making it nearly impossible to obtain good quality spectra. Finzi et al. [7] reported recently that 2-vinyl pyrrole could polymerize by two different modes. One mode involves standard polymerization through the vinyl group, the other involves the

oxidative coupling of the pyrrole rings. It is believed by some authors that the hydrogen bound to the nitrogen atom might facilitate such coupling [8]. Therefore, we decided to study the *N*-methyl derivative in the hope that it would be more stable. This was indeed the case, and this paper reports the results we obtained.

## EXPERIMENTAL

### General

All solvents were reagent grade and were used as received. The *N*-methyl-2-pyrrole carboxaldehyde, methyl triphenyl phosphonium bromide, and sodium hydride (60%) were purchased from the Aldrich Chemical Company and used without further purification. The  $^1\text{H}$  NMR were obtained at 300 MHz using a Varian HR-300 instrument operating in a CW mode and a Varian Gemini 300 operating in a FT mode.  $^{13}\text{C}$ -NMR spectra were obtained at 75.5 MHz using a Varian Gemini 300 FT spectrometer. The spectra were obtained at ambient temperature in  $\text{CDCl}_3$  using TMS as an internal standard. Resonance areas were measured by tracing peaks on high quality paper, cutting out the tracings, and weighing them on a five-place analytical balance. Molecular weight measurements were made with a Waters High Resolution 6000A GPC equipped with  $10^6$ ,  $10^5$ ,  $10^4$ ,  $10^3$ , 500, and 100A micro-styragel columns. Tetrahydrofuran was used as an eluent, and numerical values for the molecular weights were obtained by comparison to a polystyrene calibration curve.

### Monomer Synthesis

The monomer was synthesized via a Wittig reaction as previously described [6] and had the expected boiling point and  $^1\text{H}$ -NMR spectrum [6, 9].

### Polymer Synthesis

Polymers were synthesized by weighing 5.0 NMVP into clean, dry screw-cap vials. AIBN (0.7 wt%) was added and the monomer was sparged with dry  $\text{N}_2$  for 3 minutes. The vial was sealed with a Teflon-lined screw-cap and placed in a thermostated water bath at the desired temperature for the desired length of time. The polymerization conditions, conversions, and molecular weights are summarized in Table 1.

TABLE 1. Polymerization Conditions, Conversions, and Molecular Weights

Polymer	Polymerization temperature, °C	Polymerization time, h	% Conversion	$M_n$	$M_w$	$M_w/M_n$
NMVP 60 <sup>a</sup>	60	3.5	11.0	17,800	27,700	1.56
NMVP 90 <sup>b</sup>	90	3.5	38.8	10,700	14,000	1.31

<sup>a</sup>NMVP 60 = poly(*N*-methyl-2-vinyl pyrrole) synthesized at 60°C.

<sup>b</sup>NMVP 90 = poly(*N*-methyl-2-vinyl pyrrole) synthesized at 90°C.

The polymerizations were terminated by cooling the vials and their contents to ambient temperature and then adding 3–5 mL hexane. The polymers were purified by reprecipitation from  $\text{CHCl}_3$  solution into hexane, a process that was repeated three times.

## RESULTS AND DISCUSSION

Figure 1 shows the 300-MHz FT-NMR spectra of NMVP 60 and NMVP 90, and Fig. 2 shows the horizontal expansion of the ring proton resonances of NMVP 60. The spectra obtained with the CW instrument look much the same, except that the S/N ratio is better with the FT instrument, and in the interest of space, only the FT spectra will be shown in this paper. The peaks are assigned as shown in Fig. 1 [10]. All of the protons in the spectra of NMVP 60 and NMVP 90 appear to be sensitive, in some fashion, to polymer stereochemistry. The  $H_c$  proton resonance occurs as an overlapped three-peak pattern for both NMVP 60 and NMVP 90. In both cases the relative intensity ratio of these three peaks is approximately 1:1:1 (A: B:C). We believe that this pattern does not reflect a triad sensitivity but a sensitivity to higher-order sequences. Analysis of the resonances due to other protons and the  $^{13}\text{C}$ -NMR spectra support this conclusion. Presently the resolution of the  $H_c$  proton resonance is not sufficient for any reasonable assignments to be made in terms of higher-order stereosequences. The same is true of the peaks in the  $H_b$  proton resonance; these peaks occur in a relative intensity ratio of 1:6:5 (D:E:F), the total of 12 indicates a sensitivity to higher-order stereosequences, possibly pentads, but again the resolution is not sufficient to allow any reasonable assignments to be made. The resonance assigned to the  $H_a$  proton for both NMVP 60 and NMVP 90 occurs as a seven-peak pattern (G, H, I, J, K, L, and M in Fig. 2). The chemical shifts and relative and fractional intensities of these peaks are summarized in Table 2. Since the values of the relative and fractional intensities of these seven peaks are virtually identical for NMVP 60 and NMVP 90, only the values for NMVP 60 are presented in Table 2.

For the peaks in the  $H_a$  proton resonance, the relative intensity ratios total 16. Because there are 16 pentads, all of equal concentration, in an atactic polymer, it is reasonable to assign this resonance in those terms. The tentative assignments for the peaks in the  $H_a$  resonance are given in Table 3. The assignments are for both NMVP 60 and NMVP 90.

The peaks are assigned as containing the pentads indicated. No specific order can be established at this time. While the assignments given above are not certain, the principles involved in developing them are believed to be correct [5]. Expansions of the aliphatic resonance are shown in Fig. 3. The peaks labeled A–H are due to the methine proton of the polymer chain and the methyl protons of the *N*-methyl group. Comparison of the areas of peaks A–C with the areas of peaks D–H revealed that all the methine resonance is not in peaks A–C. Only when peak D is added to the A–C resonance is the ratio of areas correct, i.e.,  $A\text{--}D/E\text{--}H = 1/3$ . The chemical shifts and relative and fractional intensities of the peaks in the methine resonance are given in Table 4. Again, the values of the relative and fractional intensities of the peaks in the methine resonances are the same for NMVP 60 and NMVP 90. Therefore, only the values for NMVP 60 are given in Table 4.

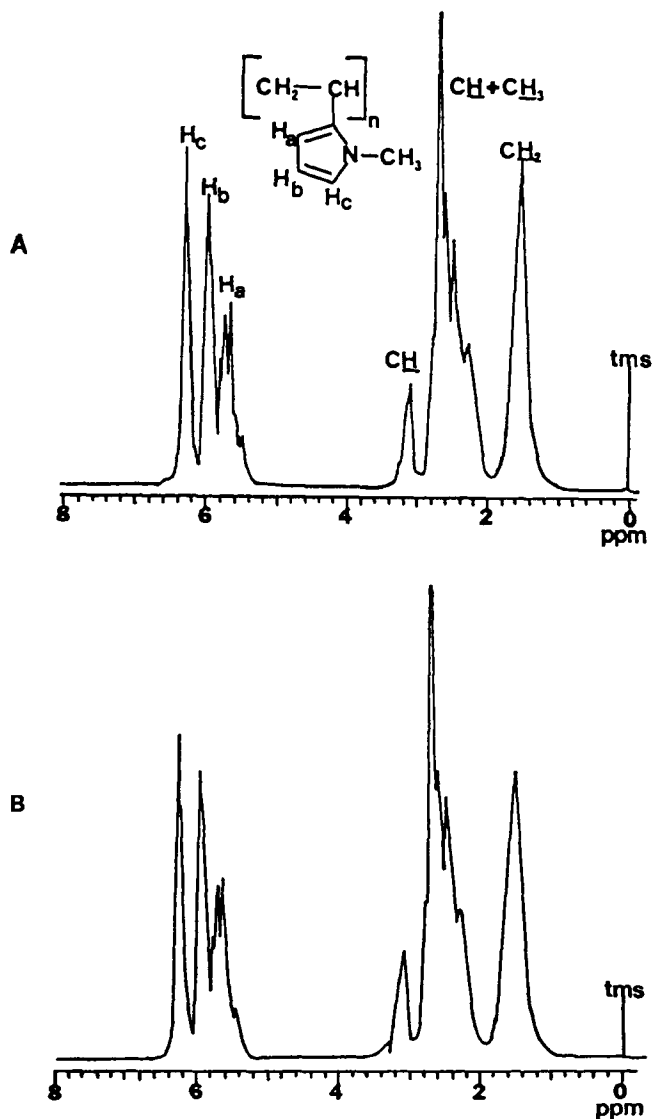


FIG. 1. 300 MHz FT-NMR spectra of (A) NMVP 60 and (B) NMVP 90.

As previously mentioned, there are 16 pentads of equal intensity for an atactic polymer, and the relative intensity ratio of the peaks in the methine resonance sum to 16. It therefore seems logical to assign the resonance in terms of pentads. The assignments are given in Table 5 and are based somewhat on the assignments made for the  $H_a$  proton resonance. Once again the assignments are not certain, but are believed to be reasonable.

An average  $P_m$  value calculated from the fractional intensities of the K, L, and M peaks in the  $H_a$  proton resonance is  $0.50 \pm 0.10$ , a  $P_m$  value calculated from

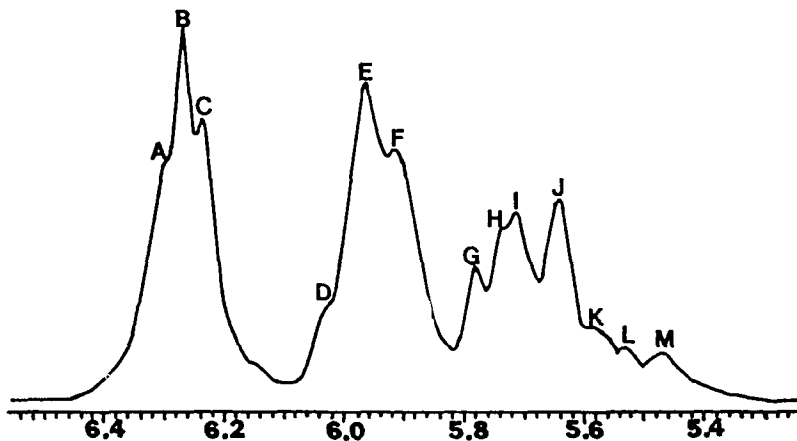


FIG. 2. Horizontal expansion of the ring proton resonance of NMVP 60.

TABLE 2. Chemical Shifts, Relative Intensities, and Fractional Intensities for the Peaks in the  $H_a$  Resonance

Peak	Chemical shift, ppm	Fractional intensity	Relative intensity
G	5.75	0.14 $\pm$ 0.03	2
H	5.70	0.14 $\pm$ 0.03	2
I	5.68	0.18 $\pm$ 0.04	3
J	5.61	0.33 $\pm$ 0.05	6
K	5.54	0.069 $\pm$ 0.01	1
L	5.50	0.063 $\pm$ 0.01	1
M	5.44	0.076 $\pm$ 0.01	1

TABLE 3. Assignment of the  $H_a$  Proton in Terms of Pentads

Peak	Chemical shift, ppm	Assignment
G	5.75	<i>m m m r</i> + <i>r m m m</i>
H	5.70	<i>m m r m</i> + <i>m r m m</i>
I	5.68	<i>r m r m</i> + <i>m r m r</i> , <i>m m m m</i>
J	5.61	<i>m r r r</i> + <i>r r r m</i> , <i>m m r r</i> + <i>r r m m</i> , <i>r m r r</i> + <i>r r m r</i>
K	5.54	<i>r m m r</i>
L	5.50	<i>r r r r</i>
M	5.44	<i>m r r m</i>

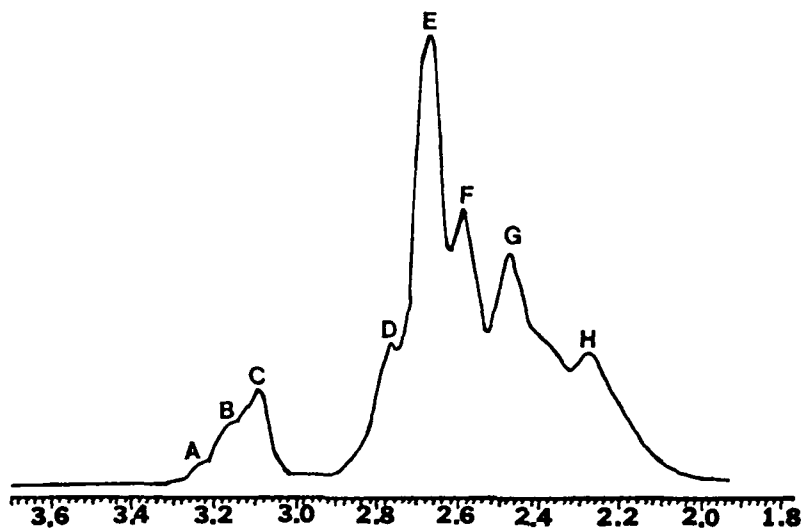


FIG. 3. Horizontal expansions of the methine and methyl proton resonances of NMVP 60.

TABLE 4. Chemical Shifts, Relative Intensities, and Fractional Intensities of the Peaks in the Methine Proton Resonance

Peak	Chemical shift, ppm	Fractional intensity	Relative intensity
A	3.20	$0.062 \pm 0.01$	1
B	3.14	$0.18 \pm 0.04$	3
C	3.06	$0.33 \pm 0.07$	5
D	2.77	$0.43 \pm 0.09$	7

TABLE 5. Peak Assignments for the Methine Proton Resonances

Peak	Chemical shift, ppm	Assignment
A	3.20	<i>rmmr</i>
B	3.14	<i>mmmr + rmmm, mmmm</i>
C	3.06	<i>mrmr + mrrm, mmrr + rrrm</i> <i>rrrr</i>
D	2.77	<i>rmrr + rrrr, rrrm + mrrr</i> <i>rrrr + mrrr, mrrm</i>

the fractional intensity of the *mmr* pentad peak in the methine proton resonance is also  $0.50 \pm 0.10$ . These  $P_m$  values are those expected for an atactic polymer.

### $^{13}\text{C}$ -NMR Spectra

The 75.5-MHz  $^{13}\text{C}$ -NMR spectra of NMVP 60 and NMVP 90 are shown in Fig. 4. Horizontal expansions of select carbon resonances from both NMVP 60 and NMVP 90 are shown in Fig. 5. The resonances are assigned as shown in Fig. 4 [11, 12]. It appears as though all the carbons are sensitive in some degree to polymer stereochemistry. However, the  $\text{C}_3$  ring carbon appears as a singlet with a small, ill-defined shoulder, and the methine and methyl carbon resonances are so over-

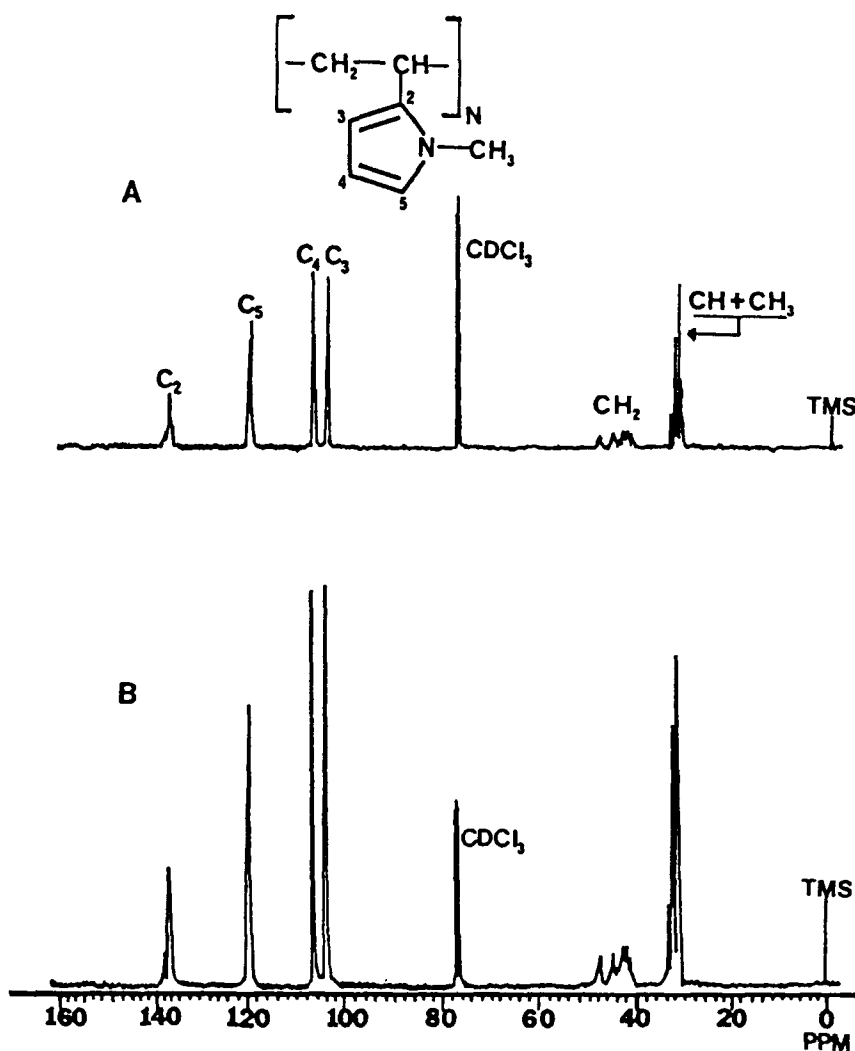


FIG. 4. 75.5 MHz  $^{13}\text{C}$ -NMR spectra of (A) NMVP 60 and (B) NMVP 90.



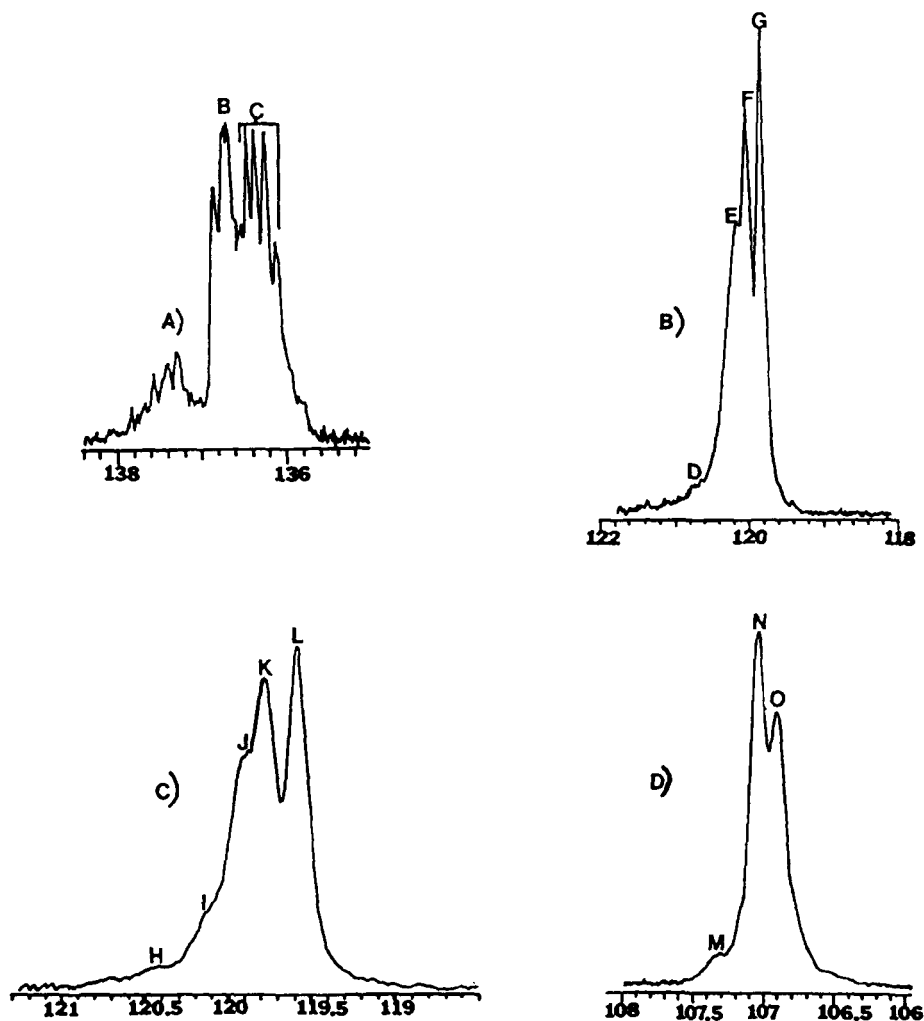


FIG. 5. Horizontal expansions of select carbon resonances: (A)  $C_2$  ring carbon of NMVP 60; (B)  $C_3$  ring carbon of NMVP 60; (C)  $C_5$  ring carbon of NMVP 90; (D)  $C_4$  ring carbon of NMVP 60.

lapped that interpretation in terms of stereosequence sensitivity is not possible at the present time. Accordingly, these resonances will not be further discussed in this paper. The quaternary ring carbon resonance appears as three peaks, with some fine structure evident, Figure 5(A). The three peaks (A, B, and C) occur in a relative intensity ratio of 1:2:3, A:B:C. This relative intensity ratio is not readily assignable in terms of any specific stereosequences (triad, pentads, etc.) but probably does reflect a sensitivity to higher-order sequences, particularly in view of the fine structure evident. Analysis of this fine structure was attempted, but the results obtained were inconclusive at best, due mostly to incomplete resolution. A spectrum obtained at higher spectrometer power might prove useful in analysis of this resonance. The

TABLE 6. Relative and Fractional Intensities of the Peaks in the C<sub>5</sub> Resonance of NMVP 60 and NMVP 90

Polymer	Peak	Chemical shift, ppm	Fractional intensity	Relative intensity
NMVP 60	D	120.69	0.063 ± 0.007	1
NMVP 60	E	120.15	0.29 ± 0.03	5
NMVP 60	F	120.05	0.27 ± 0.03	4
NMVP 60	G	119.85	0.37 ± 0.04	6
NMVP 90	H	120.90	0.064 ± 0.006	1
NMVP 90	I	120.63	0.068 ± 0.007	1
NMVP 90	J	120.43	0.23 ± 0.02	4
NMVP 90	K	120.31	0.28 ± 0.03	4
NMVP 90	L	120.09	0.36 ± 0.04	6

TABLE 7. Relative and Fractional Intensities of the Peaks in the C<sub>4</sub> Carbon Resonance

Peak	Chemical shift, ppm	Fractional intensity	Relative intensity
M	107.31	0.062 ± 0.006	1
N	107.03	0.51 ± 0.05	8
O	106.90	0.43 ± 0.04	7

TABLE 8. Assignments for the C<sub>4</sub> and C<sub>5</sub> Carbon Resonances

Peak	Chemical shift, ppm	Assignment
D	120.69	<i>rmmr</i>
E	120.15	<i>mmmr + rmmm, mrrm + mrrm</i> <i>mmmm</i>
F	120.05	<i>rmmr + mrrr, mmrr + rrrm</i>
G	119.85	<i>rrrm + mrrr, rrrr + rrrr</i> <i>rrrr, mrrm</i>
H	120.90	<i>rmmr</i>
I	120.63	<i>mmmm</i>
J	120.43	<i>mmmr + rmmm, mrrm + mrrm</i>
K	120.31	<i>rmmr + mrrr, mmrr + rrrm</i>
L	120.09	<i>rrrm + mrrr, rrrr + rrrr</i> <i>rrrr, mrrm</i>
M	107.31	<i>rmmr</i>
N	107.03	<i>mmmr + rmmm, mmrr + rrrm, mrrm + mrrm,</i> <i>rmmr + mrrr</i>
O	106.90	<i>mmmm, mrrr + rrrm, rrrr + rrrr, rrrr, mrrm</i>

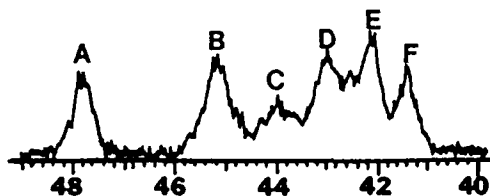


FIG. 6. Horizontal expansion of the methylene carbon resonance of NMVP 90.

$C_3$  carbon resonance occurs as a four-peak pattern for NMVP 60 and a five-peak pattern for NMVP 90 (Figs. 5B and 5C). The relative and fractional intensities for these peaks are summarized in Table 6.

The resonance for the  $C_4$  ring carbon (Fig. 5D) appears as a three-peak pattern for both NMVP 60 and NMVP 90. The relative and fractional intensities are summarized in Table 7 for NMVP 60; the results were the same for NMVP 90, so only the NMVP 60 results are shown in Table 7.

As previously stated, relative intensity ratios that sum to 16 strongly indicate a pentad sensitivity for an atactic polymer. For each of the carbon resonances above, the relative intensity ratios sum to 16, so it is logical to assign these resonances in terms of pentads. Tentative assignments for the peaks in the  $C_4$  and  $C_3$  carbon resonances are summarized in Table 8.

Once again the peaks are assigned as containing the pentads indicated. No specific order assignments are possible given the lack of a stereoregular NMVP polymer. As before, the assignments are believed to be reasonable [5]. Calculation of an average  $P_m$  value from the fractional intensities of the singlet peaks gives  $P_m = 0.50 \pm 0.06$ . This is the same  $P_m$  value obtained from the analysis of the  $^1H$ -NMR spectra. The methylene carbon resonance (Fig. 6) is a six-peak pattern occurring in the relative intensity ratio of 1:2:1:2:2:1, A:B:C:D:E:F. The sum of the relative intensity ratio is 9; this indicates a sensitivity to at least tetrad stereosequences overlapped by a sensitivity to higher-order stereosequences. Unfortunately, the resolution is insufficient to make any reasonable assignments of peaks in terms of higher-order stereosequences, and the resonance is too complex to permit assignment solely in terms of tetrads. Again, a spectrum at a higher magnetic field strength might provide sufficient resolution for higher-order structures to be assigned.

## CONCLUSIONS

*N*-Methyl-2-vinyl pyrrole was synthesized via a Wittig reaction and was polymerized by free-radical initiation at two different temperatures. The polymerization temperature did not have any effect on the polymer stereochemistry as determined by NMR spectroscopy. Both  $^1H$ -NMR and  $^{13}C$ -NMR spectra were virtually identical for NMVP 60 and NMVP 90. The analyses of the  $^{13}C$  NMR and  $^1H$  NMR for both polymers show that they are atactic polymers with  $P_m$  values of  $0.50 \pm 0.1$ . More definite assignments of resonances to specific triads, pentads, and other stereosequences will require the synthesis of a stereoregular poly(*N*-methyl-2-vinyl pyr-

role) and possibly a higher magnetic field NMR instrument. But we believe that such experiments will only serve to confirm the conclusion advanced here, that poly(*N*-methyl-2-vinyl pyrrole) synthesized by free-radical initiation is an atactic polymer.

### Effects of Heteroatoms on Polymer NMR Spectra

As previously stated, we have observed that the effect that the type of heteroatom has on the  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectra of a polyvinyl heterocycle can be considerable [1-5, 13-16]. The presence of an O atom [poly(2-vinyl furan)] separates the ring proton chemical shifts by 1-1.5 ppm; however, no useful stereochemical information could be obtained from this portion of the spectrum at either 300 or 360 MHz. In contrast, the ring proton resonances of poly(2- and 3-vinyl thiophene) are less well separated, with all of them occurring with a 0.6-0.8-ppm range. In the present case, poly(*N*-methyl-2-vinyl pyrrole), the ring proton resonances also occur within a small chemical shift range of 1.0 ppm. In both of these cases however, a good deal of multiplicity is evident, indicating high sensitivity to polymer stereochemistry. For poly(2-vinyl selenophene) the ring proton resonances are well separated, all occurring within an  $\sim 1.8$ -ppm range; however, the resonance pattern was very similar to that of poly(2-vinyl thiophene) and could be interpreted in a like manner. The aliphatic regions for all the polyvinyl heterocycles are quite similar, with the exception of the present case. The methine and methylene protons are more well resolved for poly(*N*-methyl-2-vinyl pyrrole) than for any polyvinyl heterocycle examined to date. This may be due to spin interaction with the methyl group or to a particular conformation that is forced on the chain by the presence of the methyl group.

The nature of the heteroatom also has an effect on the  $^{13}\text{C}$ -NMR spectrum of the polyvinyl heterocycle. The ring carbon resonances of poly(2-vinyl furan) are well separated from each other (occurring over a 65-ppm range), and the  $\text{C}_2$ ,  $\text{C}_3$ , and  $\text{C}_4$  carbon resonances show multiplicities indicating stereochemical sensitivity. For poly(2- and 3-vinyl thiophene) the  $\text{C}_2$  (quaternary) carbon is well separated ( $\sim 30$  ppm) from the remaining resonances, which occur within a 6-ppm range (120-126 ppm). The  $\text{C}_3$  and  $\text{C}_4$  carbon resonances showed a multiplicity indicative of stereochemical sensitivity and were interpreted in terms of pentads as was the  $\text{C}_2$  carbon resonance. The  $^{13}\text{C}$ -NMR spectrum of poly(2-vinyl selenophene) is similar to poly(2-vinyl thiophenes), i.e., the quaternary carbon resonance is well separated from the other carbon resonances ( $\sim 26$  ppm). The other carbon resonances occur within a 4-ppm range (126-130 ppm); however, of the ring carbons, only the  $\text{C}_2$  or quaternary ring carbon has any discernible sensitivity to polymer stereochemistry. In the present case the ring carbon resonance pattern resembles that of poly(2-vinyl furan) with all the resonances being reasonably well separated and occurring over an  $\sim 36$ -38-ppm range, with the  $\text{C}_2$ ,  $\text{C}_4$ , and  $\text{C}_6$  carbon resonances showing stereochemical sensitivity. The aliphatic carbons for all the polyvinyl heterocycles show multiplicity that can be interpreted in terms of polymer stereochemistry. The nature of the heteroatom does not seem to have much effect on the multiplicity or chemical shift of the methylene carbon resonance. In fact, given equal field strengths, all methylene carbons occur in the 40-48-ppm range and have quite similar multiplicities. The methine carbon resonances also appear in approximately the same location,

31–38 ppm, in all cases. The multiplicity of the methine resonance is very nearly the same for poly(2- and 3-vinyl thiophene), poly(2-vinyl selenophene), and poly(2-vinyl furan). In the present case the methine resonance is complicated by the methyl carbon resonances; the similarity between it and the methine resonances of the other polyvinyl heterocycles is hard to judge.

The effect of different heteroatoms on polymer tacticity is negligible. All the polymers we have synthesized and examined to date have proven to be atactic. Our original aim in this work was to obtain polymers that had NMR spectra that would be easier to interpret than the corresponding spectra of polystyrenes, yet be enough like polystyrene chemically and physically so that the results obtained could be extrapolated to polystyrenes synthesized under like conditions. For the most part the  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectra of these polyvinyl heterocycle materials have proven easier to interpret than those of polystyrene. The reasons why this is so and why the spectra of the various polyvinyl heterocycles are different obviously lie in the chemical and physical nature of the heterocycle, with factors such as heteroatom electronegativity and atomic size being crucial. While a quantitative discussion of these factors is beyond the scope of this report, it is interesting to note that the largest atoms, S and Se, yield polyvinyl heterocycles with  $^{13}\text{C}$ -NMR spectra most like that of polystyrene, while the smaller more electronegative atoms, O and N, yield polymers with spectra least like polystyrene. However, the  $^{13}\text{C}$ -NMR spectra of polyvinyl thiophenes and poly(2-vinyl selenophene) yield stereochemical information that is less ambiguous than the corresponding spectra of polystyrene, as do poly(2-vinyl furan) and poly(*N*-methyl-2-vinyl pyrrole).

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