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# Analysis of the $^1$H-NMR and $^{13}$C-NMR spectra of poly(3-methyl-1-vinylpyrazole)

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## Summary

The title monomer was polymerized in solution via free radical initiation. The polymer's 300 MHz $^1$H-NMR and 75.5 MHz $^{13}$C-NMR spectra were recorded and analyzed in terms of polymer stereochemistry. Most of the resonances in both the $^1$H-NMR and $^{13}$C-NMR spectra showed multiplicity consistent with sensitivity to polymer stereochemistry. However the $^{13}$C-NMR spectrum proved somewhat easier to interpret. The analysis of both the $^1$H-NMR and $^{13}$C-NMR spectra very strongly indicate that poly(3-methyl-1-vinylpyrazole) is an atactic polymer.

## Introduction

In previous communications we have reported analysis of the spectra ($^1$H-NMR and $^{13}$C-NMR) of several poly (vinyl heterocycles) (1-4). In all cases the polymers have proven to be atactic when synthesized by free radical initiation. We have also found that the nature of the heteroatom and the position and nature of any additional ring substituents has a significant effect on the nmr spectra observed. But, until recently (5), we have confined our work to heterocycles in which the vinyl group is attached to a carbon atom. A short time ago we investigated the stereochemistry. of poly(2-methyl-1- vinylimidazole). The monomer from which this polymer is synthesized has the vinyl group attached to a nitrogen atom and also has additional ring substitution viz. a methyl group in the 2-position. Previous work on poly(1-vinylimidazole) had shown that this polymer was atactic (6,7) and the addition of a methyl group to the ring did not alter this result.

From that work we learned that a vinyl group attached to an atom other than carbon does not alter the stereochemistry of the resultant polymer. However, the effect on the $^1$H-NMR and $^{13}$C-NMR spectra was significant in that the spectra were more well resolved and more individual resonances seemed to be displaying sensitivity to polymer stereochemistry. In order to further investigate this result we decided to examine the spectra of poly(3-methyl-1-vinylpyrazole) which can be regarded as an isomer of 2-methyl-1-vinylimidazole in that the N atoms in the rings have changed position. This paper discusses some of the results we obtained.

## Experimental

### General

All solvents used in this study were reagent grade and were used without further purification. The 3-methyl-1-vinylpyrazole (3MNVP) was purchased from Aldrich and was purified by distillation from $CaH_2$ immediately before use. The $^1$H-NMR and $^{13}$C-NMR spectra were recorded on $CDCl_3$ solutions (8% wt/v) of polymer at ambient temperature. Tetramethylsilane was used as an internal standard and the spectra were recorded at ambient temperature. The spectrometer employed was a Varian Gemini 300 FT NMR. The molecular weight was measured as previously described. (1-4)

### Polymer Synthesis

The 3MNVP (4.8 g) was charged into a 50 ml round bottom flask equipped with a magnetic stirrer, 20 ml of dry benzene was added followed by 0.8 wt % AIBN. The solution was sparged with dry $N_2$ and the flask was sealed with a rubber septum. The flask was then placed in a thermostated water bath at 65°C. The solution was stirred at bath temperature for 2 hr, after which time the flask was removed from the bath and the contents allowed to cool to ambient temperature. The polymer was isolated by pouring the benzene solution into a 7-fold excess of hexane. The polymer was purified by reprecipitation from $CHCl_3$ solution into hexane. Conversion = 28.4%, $M_n$ = 6300, $M_w$ = 13700, $M_w/M_n$ = 2.17.

## Result and Discussion

The polymer was synthesized in solution as previous work (8,9) has shown that polymerization in bulk can be explosively exothermic. The polymer produced proved to be 100% soluble in most common laboratory solvents, a behavior in contrast to that of poly(2-methyl-1-vinylimidazole) a substantial fraction of which was insoluble in any solvent tried.

The $^1$H-NMR spectrum of poly(3-methyl-1-vinylpyrazole) (P3MNVP) along with expansions of the resonances of interest is shown in Figures 1 and 2. The resonance area assigned to the $H_5$ ring proton resonance (1B) (10) occurs as a 6 peak pattern in a relative intensity ratio of 1:3:1:7:7:9 (A:B:C:D:E:F). The sum of these relative intensity ratios is 28, this indicates that a sensitivity to higher order stereosequences is being displayed, possibly heptad sensitivity or a combination of heptad and pentad sensitivities. However, the resolution is not sufficient for any reasonable assignments to be made at this point. The resonance assigned to the $H_4$ ring proton (1C) occurs as a four peak pattern, the fractional and relative intensities of which are summarized in Table 1.

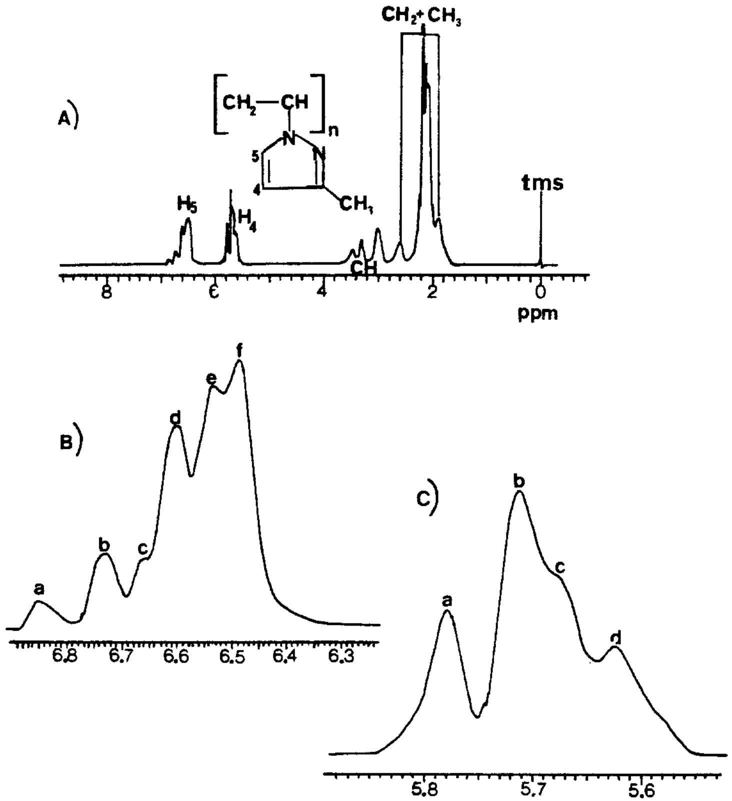

Figure 1

300 MHz $^1$H-NMR spectrum of poly(3-methyl-1-vinylpyrazole); A) Full spectrum; B) Expansion of the $H_5$ resonance; Expansion of the $H_4$ resonance

TABLE 1

Chemical Shifts, Relative and Fractional Intensities of the Peaks in the $H_4$ Proton Resonance

| Peak | Chemical Shift (ppm) | Fractional Intensity | Relative Intensity |
|---|---|---|---|
| A | 5.78 | 0.25 ± .03 | 1 |
| B | 5.71 | 0.33 ± .04 | 1 |
| C | 5.67 | 0.19 ± .02 | 1 |
| D | 5.62 | 0.23 ± .03 | 1 |

While the relative intensity ratio is 1:1:1:1 within experimental error and rounding off to the nearest whole number; it is obvious that peak B is significantly larger than peaks A, C and D, and that C is somewhat smaller than A and D. Since B and C are highly overlapped it is logical to combine them into one resonance area. When this is done the relative intensity ratio of A:B+C:D becomes 1:2:1. This is the relative intensity ratio expected for the triads of an atactic polymer. It is logical then to assign the $H_4$ resonance to triads as follows: A = mm, B+C = mr + rm and C = rr. A $P_m$ value calculated from the fractional intensity peak A is $P_m = 0.50 \pm .06$ which is the value expected for an atactic polymer.

An expansion of the aliphatic resonance is shown in Figure 2.

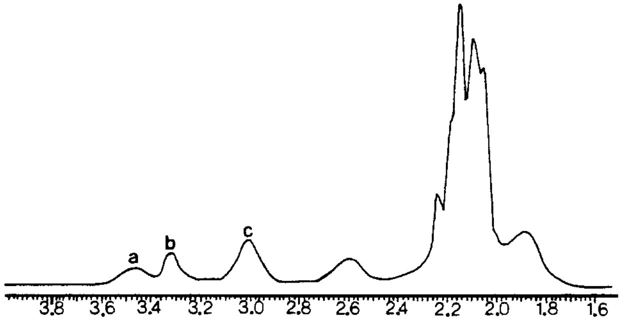

Figure 2

Expansion of the aliphatic proton resonances

The resonances are assigned as shown in the Figure (6,10). The methylene and methyl proton resonances occur as an overlapped multiplet with insufficient resolution for any assignments, in terms of stereochemistry, to be made. The methine proton resonance occurs as a 3 peak pattern with a relative intensity ratio of 1:1:2 (A:B:C). The fractional intensities are A = 0.24 ± .02, B = 0.23 ± .02 and C = 0.53 ± .05. In previous poly(vinyl heterocycle) cases the methine proton resonance has appeared as two peaks with varying degrees of overlap (1-4), but always in a 1:3 ratio (downfield/upfield) within experimental error. This pattern was assigned in terms of triads for an atactic polymer, with the downfield resonance assigned to the mm triad and the upfield resonance assigned to the rr and mr + rm triads. In the present case, the 1:3 ratio could be obtained if the fractional intensities of B+C were combined (B+C = 0.76). It is logical then to assign the methine resonance in the present case as being due to the triads of an atactic polymer. However, in the present case the resolution is such that the mm and rr triads are both resolved. So, the proposed assignments in terms of triads for A, B and C are mm, rr and rm + mr respectively. A $P_m$ value calculated from the fractional intensity of the mm triad is 0.49 ± .05, which is in good agreement with the value obtained from the $H_4$ ring proton resonance.

### $^{13}$C-NMR Spectrum

The 75.5 MHz $^{13}$C-NMR spectrum and linear expansions of the resonances of interest are shown in Figures 3 and 4.

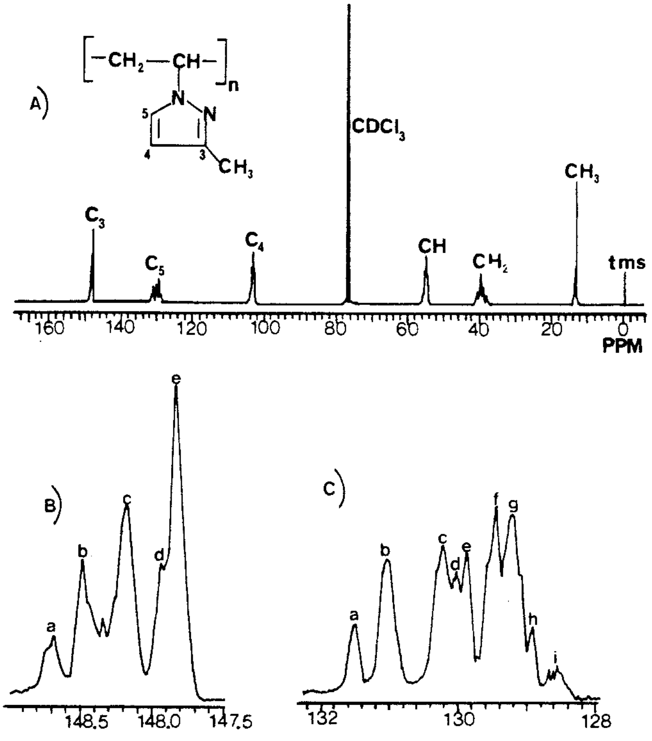

Figure 3

75.5 MHz $^{13}$C-NMR spectrum; A) Full spectrum;
B) Expansion of the $C_3$ resonance;
C) Expansion of the $C_5$ resonance

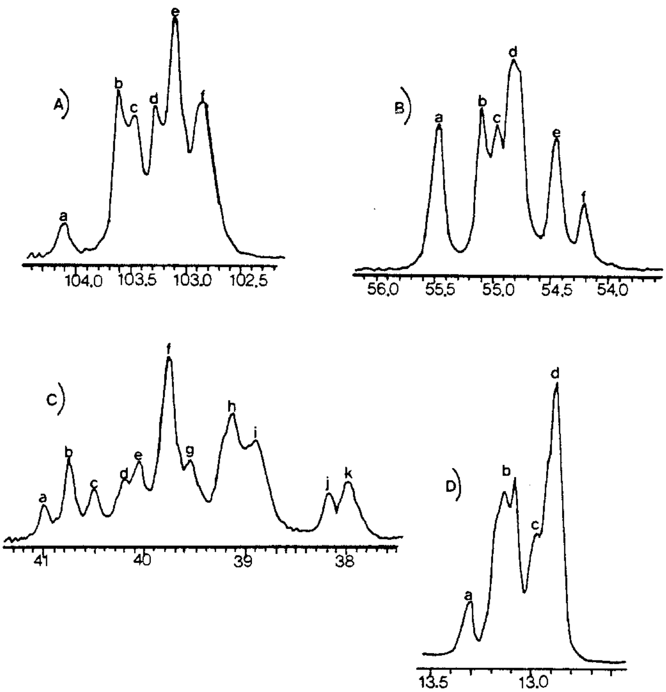

Figure 4

Expansions of: A) $C_4$ resonance; B) Methine carbon resonance; C) Methylene carbon resonance; D) Methyl carbon resonance

The resonances are assigned as shown in the Figures (11,12). All the resonances show multiplicities indicative of a sensitivity to polymer stereochemistry. The resonance assigned to the $C_3$ carbon occurs in a 5 peak pattern (A, B, C, D and E in Figure 3B). These peaks occur in a relative intensity ratio of 1:3:5:1:6 (A:B:C:D:E). The sum of this relative intensity ratio is 16, since there are 16 pentads of equal concentration in an atactic polymer it is logical to assign the $C_3$ carbon resonance as being due to a pentad stereosequence sensitivity. At this time, without the synthesis of a stereoregular polymer and epimerization studies, definate peak assignments are not possible. A $P_m$ value can be calculated however from the fractional intensity of peak A (0.64 ± .007); $P_m = 0.50 \pm .06$, which is the value expected for an atactic polymer and in good agreement with the results obtained from the analysis of the $^1$H-NMR spectrum.

The $C_5$ carbon resonance (Figure 3C) occurs as a nine peak pattern in the relative intensity ratio of 2:4:5:2:2:5:5:1:1 (A:B:C:D:E:F:G:H:I). The sum of this relative ratio is 27. This is too large for a totally pentad sensitivity and too small to be totally due to heptads. The pattern is most likely due to a combination of pentad and heptad stereosequence sensitivities, but the resolution is insufficient for a detailed assignment in terms of either.

The resonance assigned to the $C_4$ carbon, Figure 4A, occurs as a 6 peak pattern in the relative intensity ratio of 1:3:2:2:4:4 (A:B:C:D:E:F). The sum of the relative intensity ratio is 16 which indicates that the multiplicity being displayed is due to pentad stereosequences. Again, in the absence of stereoregular polymer spectra, definate assignments are not possible at this time. However, as above, a $P_m$ value can be calculated from the fractional intensity of peak A (0.060 ± .005). The value is $P_m$ = 0.49 ± .03. Again, a value consistent with the others obtained in this work and the value expected for an atactic polymer.

The methine carbon resonance (Figure 4B) contains 6 peaks in the relative intensity ratio of 3:3:2:5:2:1 (A:B:C:D:E:F). The sum of this ratio is 16 which indicates a sensitivity to pentad stereosequences. For the reasons previously stated no definate assignments are possible at this time. A $P_m$ value calculated from the fractional intensity of peak F (0.066 ± .006) is 0.51 ± .05, again the value expected for an atactic polymer.

The methylene carbon resonance, Figure 4C, occurs as an 11 peak pattern. The relative intensity ratio of 1:2:1:2:2:7:3:6:5:1:2 (A:B:C:D:E:F:G:H:I:J:K), the sum of which is 32, which is the number of hexads expected for an atactic polymer. Again no definite assignments are possible at this time. However, a $P_m$ value calculated from the fractional intensity of peak A (0.031 ± .003) is 0.50 ± .05 again strongly indicating an atactic polymer.

The resonance due to the methyl carbon (4D) occurs as four peaks in a relative intensity ratio of 1:6:2:7 (A:B:C:D). The sum of these relative intensities is 16, which shows a pentad stereosequence sensitivity. The resolution is not sufficient for any reasonable assignments to be made, but a $P_m$ value can be calculated from the fractional intensity of peak A (0.069 ± .007); $P_m$ = 0.51 ± .05. This value is that expected for an atactic polymer and is consistent with the other $P_m$ values obtained in this work.

## Conclusions

3-Methyl-4-vinylpyrazole was polymerized in solution via free radical initiation. The $^1$H- and $^{13}$C-NMR spectra were recorded and analyzed with regard to polymer stereochemistry. The weight of the evidence strongly indicates that poly(3-methyl-1-vinylpyrazole) is an atactic polymer. Conclusive proof awaits the synthesis of a stereoregular polymer and possible epimerization studies, but we expect the results of such experiments to support the conclusion that the polymer is atactic.

The salient feature of the spectra is the fact that almost all the individual proton and carbon have resonances show sensitivity to polymer stereochemistry. In particular the resonance pattern of each individual proton or carbon displays several peaks that are readily discernible, and hence fairly accurately measured in terms of area. These results are somewhat atypical for poly(vinyl-heterocycles). Usually, only a few of the individual protons and/or carbons display sufficient multiplicity/resolution for any reasonable conclusions to be made concerning polymer stereochemistry. In the present case we feel the resolution observed is due to the relative position of the two ring N-atoms. To date no quantitative theory on any specific interactions of the two N-atoms relating to nmr spectra can be offered, however, the poly(3-methyl-1-vinylpyrazole) is the object of further studies in this regard and the results obtained will be reported at a later date.

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