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Preliminary analysis of the ^{13}C-NMR spectrum of poly(3-vinyl furan)

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Summary

Poly(3-vinyl furan) was synthesized in bulk by free radical initiation. The polymerization was quite sluggish with long polymerization times resulting in relatively low yields of product. The 75.5 MHz ^{13}C-NMR spectrum could be analyzed in terms of stereochemistry even though signal/noise ratios were not optimum. The analysis indicates that poly(3-vinyl furan) (3VF), synthesized by free radical initiation, is an atactic polymer.

Introduction

We have previously published the results of our studies of the stereochemistry of several poly(vinyl heterocycles) synthesized via free radical initiation (1-5). Without exception all these polymers have spectra that strongly suggest that they are atactic. We have found that the position of the vinyl group relative to the heteroatom as well as the nature and position of any other ring substituents can have a significant effect on the ^{1}H-NMR and ^{13}C-NMR spectra of the poly(vinyl heterocycle). As we have previously reported analysis of the spectra of poly(2-vinyl furan) (6) and found that this polymer was atactic, we thought it would be of interest to investigate the tacticity of poly(3-vinyl furan). This paper summarizes our initial results.

Experimental

All solvents and reagents used in this study were reagent grade and were used as received. The ^{13}C-NMR spectra were recorded at 75.5 MHz at ambient temperature with a Varian Gemini 300 FT NMR. The polymer was dissolved in $CDCl_3$ (3% w/v) and TMS was used as an internal standard. The molecular weight was measured with a Waters 150 ALC/GPC equipped with 10^6, 10^5, 10^4, 10^3, 500 and 100 A microstyragel columns. Numerical values for the molecular weights were obtained by comparison to a polystyrene calibration curve.

Monomer Synthesis

The monomer was synthesized as previously reported (6,7) by decarboxylation of 3-furyl acrylic acid. The monomer was purified by distillation from CaH_2. B.p. 59-60°C/30 mm.

Polymer Synthesis

The polymer was synthesized by charging 3.0g of monomer into a clean, dry screw cap vial followed by 0.8 wt % AIBN. The monomer-initiator solution was sparged with dry N_2 and the vial was sealed with a teflon lined screw cap. The vial was placed in a thermostated water bath at 75°C for a period of 6.5 hr. The vial was removed from the water bath, cooled to ambient temperature and hexane was added to precipitate the polymer. The polymer was purified by reprecipitation from $CHCl_3$ solution into hexane. Conv. = 13.2%, M_n = 3600, M_w = 6800, M_w/M_n = 1.89.

Results and Discussion

Figures 1 and 2 show the 75.5 MHz ^{13}C-NMR spectrum and linear expansions of the carbon resonances of interest. The assignments are made as shown in the Figures (8,9). It appears as though all the carbon resonances show multiplicites that most probably reflect sensitivity to polymer stereochemistry. The most promising resonances, in terms of amenability to analysis, appear to be the C_5, C_4 and C_2 resonances.

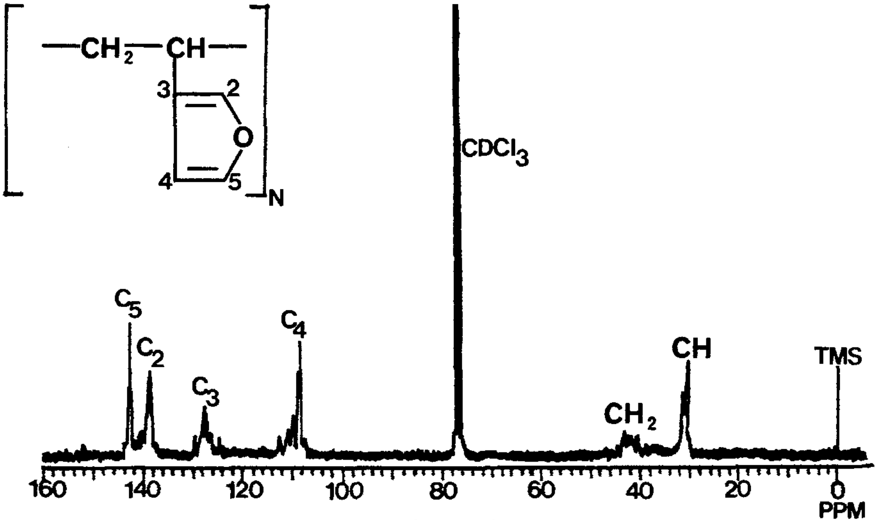

Figure 1

75.5 MHz ^{13}C-NMR Spectrum of Poly(3-Vinyl Furan)

The chemical shifts of the peaks in the resonance of the C_5 carbon (Figure 2A) and their fractional and relative intensities are listed in Table 1.

TABLE 1

Chemical Shifts, Relative and Fractional Intensities of the Peaks in the C_5 Resonance

Peak	Chemical Shift (ppm)	Fractional Intensity	Relative Intensity
A	143.35	0.061 ± .009	1
B	143.05	0.25 ± .04	4
C	142.59	0.69 ± .10	11

While the signal/noise ratio results in relatively large errors in the measurement of fractional intensities, the measurements are sufficiently accurate to ascertain a relative intensity ratio consistent with a pentad stereosequence sensitivity for an atactic polymer. As previously argued (1-5) an atactic polymer has 16 pentads of equal concentration and since the relative intensity ratio of the peaks in the C_5 resonance sums to 16 it is logical to ascribe this pattern to pentads. However, the resolution and signal/noise ratio is not sufficient for any detailed assignments to be made at this time. But, if one assigns peak A (resolution is sufficient to make a broad assignment) to a pentad of singlet intensity (rrrr, mmmm, mrrm or rmmr) then a P_m value of 0.50 ± .08 can be calculated. This is the value of P_m expected for an atactic polymer.

The C_2 carbon resonance (Figure 2B) occurs as a five peak pattern, the chemical shifts, fractional and relative intensities of which are listed in Table 2.

TABLE 2

Chemical Shifts, Fractional and Relative Intensities of the Peaks in the C_2 Carbon Resonance

Peak	Chemical Shift (ppm)	Fractional Intensity	Relative Intensity
A	139.15	0.12 ± .02	1
B	138.90	0.22 ± .03	2
C	138.64	0.25 ± .04	2
D	138.42	0.27 ± .04	2
E	138.15	0.14 ± .02	1

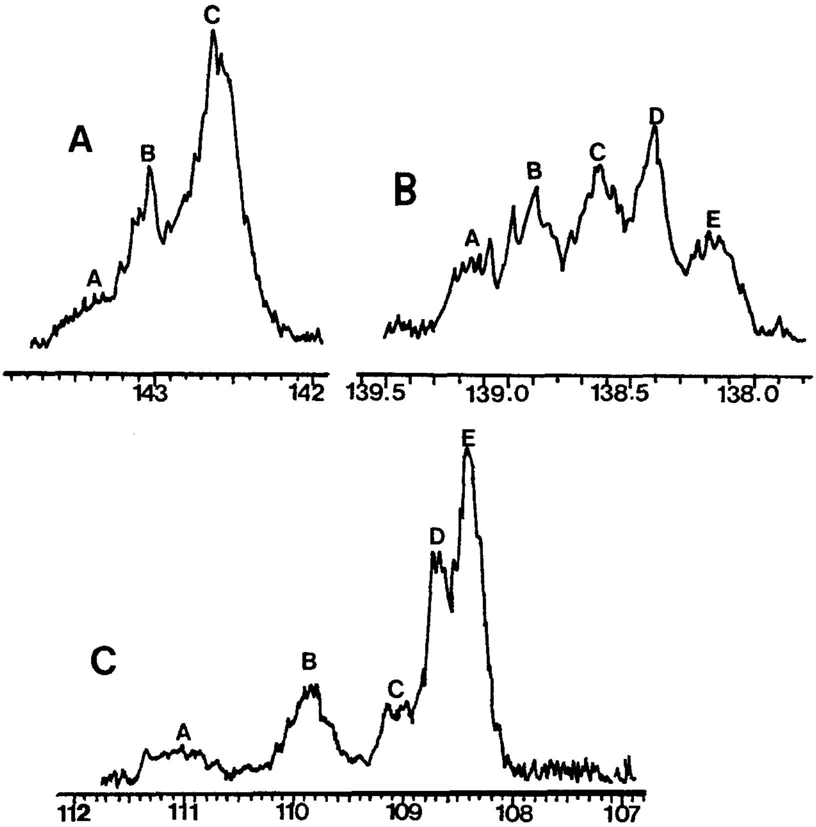

Figure 2

Expansions of A) The C_5 ring carbon resonance; B) C_2 ring carbon resonance; C) C_4 ring carbon resonance

The sum of the relative intensities = 8 which is not, on first inspection, consistent with a pentad sensitivity. However, the fractional intensities are multiples of the expected intensity of a pentad singlet in an atactic polymer, 0.0625 (10). Specifically, it seems that all the relative intensities should be multiplied by two. If this is done the ratio of the relative intensities becomes 2:4:4:4:2 which sums to 16, which is the number of pentads expected for an atactic polymer (4,5). While the resolution and signal/noise ratio prevents any reasonably detailed assignments at the present time, a P_m value of 0.45 ± .07 can be calculated from the fractional intensity of peak A.

The C_4 carbon resonance (Figure 2C) occurs as a five peak pattern. The chemical shifts, fractional and relative intensities of the individual signals are listed in Table 3.

TABLE 3

Chemical Shifts, Fractional and Relative Intensities of the Signals in the C_4 Carbon Resonance

Peak	Chemical Shift (ppm)	Fractional Intensity	Relative Intensity
A	111.00	0.11 ± .02	1
B	109.85	0.15 ± .02	1
C	109.10	0.13 ± .02	1
D	108.69	0.25 ± .04	2
E	108.41	0.36 ± .05	3

As it was for the C_2 carbon resonances the sum of the C_4 resonance's relative intensities = 8. Again, the fractional intensities indicate that the relative intensities should be multiplied by two. Then this is done the ratio of the relative intensities becomes 2:2:2:4:6, which sums to 16, which is the number of pentads of equal intensity expected for an atactic polymer. The peak resolution and signal/noise ratio is insufficient for any detailed assignments to be made at this point. However, a P_m value calculated from the fractional intensity of peak A is 0.48 ± .07.

Conclusions

Analysis of the ^{13}C-NMR spectrum of free radical initiated poly(3-vinyl furan) indicates that the polymer is atactic. While the signal/noise ratio and peak resolution made detailed assignments impossible, the P_m values calculated from the C_5, C_4 and C_2 resonances are the same within experimental error. This result supports a conclusion that poly(3-vinyl furan) is atactic.

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