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An analysis of the ^{1}H-NMR and ^{13}C-NMR spectra of poly(3-methyl-2-vinyl thiophene)

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Summary

The title polymer was synthesized by free radical initiation in bulk. The 300 MHz ^{1}H-NMR and 75 MHz ^{13}C-NMR spectra of the polymer were obtained at ambient temperature and analyzed in terms of stereochemistry. The ^{1}H-NMR spectrum provides limited information but suggests that the polymer is atactic. Analysis of the more detailed ^{13}C-NMR spectrum supports this result, i.e. poly(3-methyl-2-vinyl thiophene) is an atactic polymer.

Introduction

For quite some time we have been engaged in the study of the polymerization and copolymerization behavior of vinylheterocycles. Included in this work has been analyses of the stereochemistry of poly(vinylheterocycles) synthesized by free radical initiation (1-5). We have found that the type of heteroatom and the type and position of substituents other than the vinyl group, has a major impact on the nmr spectrum, both ^{1}H- and ^{13}C-, that is obtained. We have recently reported an analysis of the spectra of poly(5-methyl-2-vinyl thiophene) and found that this polymer was atactic (6). For comparison purposes, we thought it would be interesting to synthesize poly(3-methyl-2-vinyl thiophene) and examine its nmr spectra.

Experimental

All solvents used in this study were reagent grade and were used without further purification. All other chemicals used in the study were obtained from Aldrich and, unless otherwise noted, were used as received.

The ^{1}H-NMR and ^{13}C-NMR spectra were recorded with a Varian Gemini 300 operating in the FT mode. All spectra were obtained at ambient temperature on 7-10% w/v solutions of polymer in $CDCl_3$. Tetramethylsilane was used as an internal standard. Individual resonance areas were determined by electronic integration and by tracing them on high quality paper, cutting out and weighing the tracings. Each resonance area value is the average of three measurements. Molecular weights were measured with a Waters 150 ALC/GPC equipped with 10^6, 10^5, 10^4, 10^3, 500 and 100 Å microstyragel columns. Numerical values were obtained by comparison to a polystyrene calibration curve.

Monomer Synthesis

The monomer was synthesized from 3-methyl-2-thiophene carboxaldehyde (Aldrich) via a Wittig reaction as described in the literature (7). The monomer was purified by distillation from CaH_2 immediately before use. B.p. = 66-68°/40 mm.

Polymer Synthesis

Previous experience with the synthesis of poly(5-methyl-2-vinyl thiophene) showed that high temperatures were necessary to affect polymerization at a reasonable rate. Therefore, the polymerization of 3-methyl-2-vinyl thiophene was attempted at 120°C. Monomer (4.0 g) was charged into a 10 ml flask equipped with a magnetic stirrer and thermometer. Benzoyl peroxide (0.06 g of 70%) was added and the mixture was sparged with dry N_2 while cool for 5 min. The flask was sealed and the thermometer was attached to a Therm-O-Watch device (I^2R) connected to a heating mantle. The monomer-initiator solution was then heated, with stirring, to 120°C. After a period of ~30-40 min. the temperature increases to 140°C and remains at 140-145°C for 20 min. despite removal of the heating mantle. When the reaction mixture begins to cool there is a noticeable increase in viscosity, when the temperature reaches 80°C the mixture is no longer stirable by the magnetic stirrer. At this point 5 ml of CH_3OH was added and the reaction mixture was cooled to room temperature with cold water. The polymer was isolated by dissolving the reaction mixture in $CHCl_3$ and adding the solution to excess hexane. The polymer was purified by reprecipitating it three times from $CHCl_3$ solution into excess hexane. The polymer was dried in vacuo at 30°C for 72 h. % Conv. = 36.4, M_n = 30300, M_w = 46000, M_w/M_n = 1.52.

Results and Discussion

The 300 MHz ^{1}H-NMR spectrum of poly-3MVT (p3MVT) is shown in Figure 1 along with a horizontal expansion of the ring proton resonances. The ring proton resonances appear to be insensitive to polymer stereochemistry for the most part. However, the small peak centered at δ = 5.95 (part of the H_A resonance) may be due to a higher order stereosequence. In previous cases (1,2) concerning poly(2-vinyl thiophene) and poly(3-vinyl thiophene), the resonance pattern of at least one ring proton occurred as three peaks that had a 9:6:1 relative intensity ratio. This pattern was interpreted in terms of pentad stereosequences for atactic polymers. In the present case, no such three peak pattern exists.

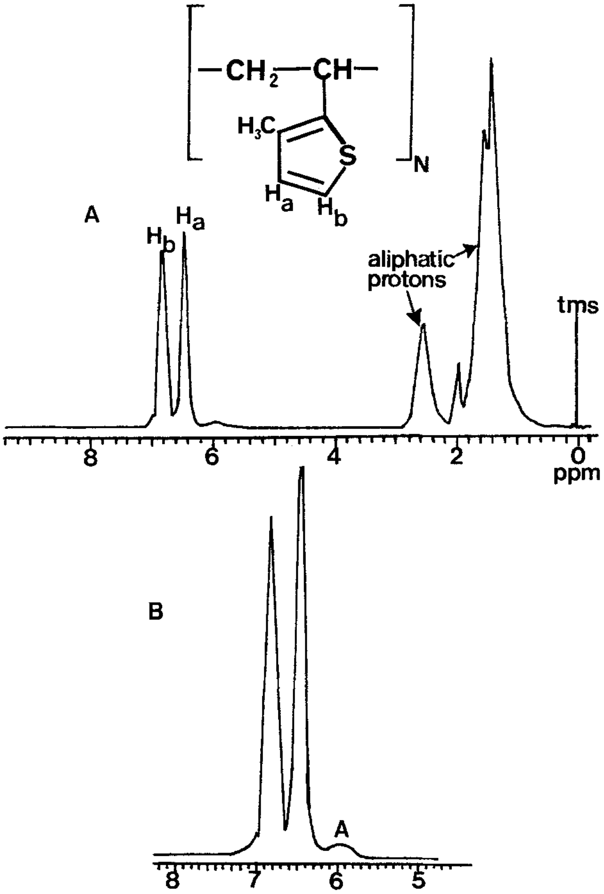

Figure 1

300 MHz ^{1}H-NMR of 3MVT; A) Full spectrum;
B) Linear expansion of ring proton resonance

However, if the resonance at $\delta = 5.95$ were due to a pentad stereosequence of singlet intensity in an atactic polymer, then its area should be 3.2% of the entire ring proton resonance area. The peak at $\delta = 5.95$ (peak A) is 3.4 ± .3% of the total ring proton resonance. This result suggests that 3MVT is a atactic polymer. However, due to lack of resolution none of the other resonances in the ^{1}H-NMR spectrum can be used to confirm this suggestion. Note that where the aliphatic proton resonances appear as a multiple peak pattern indicating stereochemical sensitivity, no reasonable interpretation could be made at this time due to peak overlapping. However, the ^{13}C-NMR spectrum provides much more detail, with several of the individual carbon resonances displaying a sensitivity to polymer stereochemistry. The ^{13}C-NMR spectrum is shown in Figure 2 and the relevant expansions are shown in Figure 3.

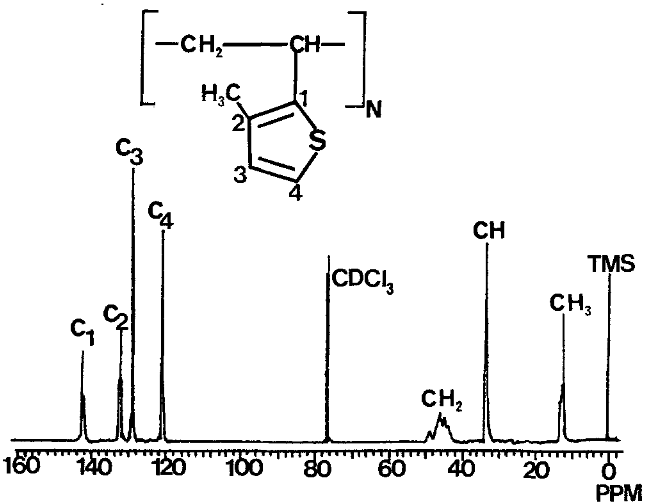

Figure 2

75.5 MHz ^{13}C-NMR of 3 MVT

The resonances are assigned as shown in Figure 2 (8,9). From the expansions shown in Figure 3 it is evident that the resonances of four carbons are showing sensitivity to polymer stereochemistry.

The C_1 carbon resonance (Figure 3A) occurs in a four peak pattern the relative intensities of which are 1:3:2:2, A:B:C:D. The sum of the relative intensities = 8, however, if these relative intensities are multiplied by two the sum of the relative intensities is 16, which is what would be expected for a pentad sensitivity in an atactic polymer (2,10). Historically, (10,11) the C_1 carbon resonance has been shown to be sensitive to odd numbered stereosequences (triads, pentads, etc.) in most cases. Therefore, it is logical to assign the C_1 resonance pattern as being due to a pentad stereosequence sensitivity, particularly showing an atactic pentad stereosequence distribution. However, the resolution is not quite good enough for a detailed assignment to be made at this time.

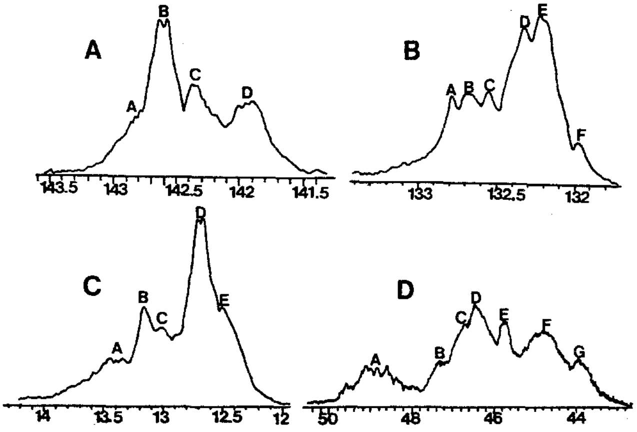

Figure 3

Expansions of select carbon resonances:
A) C_1 ring carbon; B) C_2 ring carbon;
C) CH_3 carbon; D) CH_2 carbon

But, if peak A could be said to contain two singlet pentads (mmmm and rmmr e.g.) then a P_m value of 0.51 ± .06 can be calculated. The C_2 carbon resonance (Figure 3B) occurs as a 6 peak pattern (A-F) with relative intensity ratios of 2:2:2:4:5:1, A:B:C:D:E:F. Again, the sum of the relative intensities is equal to 16, strongly indicating a sensitivity to pentad stereosequences for an atactic polymer.

However, as for the C_1 resonance pattern, the C_2 resonances are not well enough resolved for detailed assignments to be made, except that peak F has a fractional intensity of 0.062 ± .007 which is the fractional intensity expected of a singlet pentad in an atactic polymer. In this case, this pentad is due to either the rrrr or mrrm pentad, most probably the mrrm pentad (2). In any case a P_m = 0.50 ± .06 can be calculated.

The resonances due to the methyl and methylene carbons (Figures 3C and 3D) have multiplicities that reflect stereochemical sensitivity. The relative intensities of the peaks in the methyl resonance are: 2:2:1:5:2, A:B:C:D:E. The sum of the relative intensities = 12 which means that sensitivity to higher order stereosequences, possibly pentads, is being displayed. However, the resolution is insufficient for any reasonable assignments to be made. The relative intensities of the peaks in the methylene carbon resonance are: 2:1:1:3:2:3:1, A:B:C:D:E:F:G. The sum of the relative intensities = 13, indicating that a sensitivity to tetrads and hexads is probably being shown but once again, the resolution is not sufficient for any reasonable assignments to be made.

Conclusions

3-Methyl-2-vinyl thiophene has been synthesized and polymerized by free radical initiation. Relatively high polymerization temperatures were used to affect polymerization to high conversion at a reasonable rate. The ^{1}H-NMR and ^{13}C-NMR spectra of the polymer were recorded at ambient temperature in $CDCl_3$ and the relative and fractional intensities of the H_A ring proton resonances suggested an atactic stereochemistry of the polymer. However, none of the other proton resonances had sufficient resolution/sensitivity to confirm this analysis. The two quaternary ring carbon resonances displayed sufficient sensitivity and resolution for analysis in general terms i.e. the peaks in each of these resonances were sufficiently resolved for a P_m values of 0.50-.51 ± .06 to be calculated, strongly indicating that poly(3-methyl-2-vinyl thiophene) is an atactic polymer. Absolute peak assignments cannot be made at this time but await the synthesis of stereoregular polymer and the results of epimerization studies.

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