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A preliminary analysis of the ^{1}H-NMR and ^{13}C-NMR spectra of poly(2-vinyl-5-methyl thiophene)

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Summary

Poly(2-vinyl-5-methyl thiophene) was synthesized via free radical initiation. The 300 MHz ^{1}H-NMR and 75.5 MHz ^{13}C-NMR spectra were recorded and analyzed in terms of polymer stereochemistry. The spectra were similar to those of other poly(2-vinyl thiophenes) and were interpreted in a like fashion. The poly(2-vinyl-2-methyl thiophene) was found to be an atactic polymer.

Introduction

Previously, we have examined and analyzed the NMR spectra of poly (2-vinyl thiophene) and several ring substituted poly(2-vinyl thiophenes (1-4). To date all the substituents were of the electron withdrawing type i.e. Cl, Br, F. The substituents had significant effect on the ^{1}H-NMR spectra of the respective poly(2-vinyl thiophenes) relative to the ^{1}H-NMR spectrum of unsubstituted poly(2-vinyl thiophene). The effect was most pronounced when the substituent was in the 5 position of the thiophene ring. We thought it would be of interest to explore the effect of an electron releasing group, in this case a methyl group, on the ^{1}H-NMR and ^{13}C-NMR spectra of a free radically initiated 2-vinyl thiophene. To this end we synthesized and polymerized 2-vinyl-5-methyl thiophene and examined the spectra of the polymer. This report summarizes our results.

Experimental

All the solvents employed in this study were reagent grade and were used as received. The initiators used were also employed as received. The 5-methyl-2-thiophene carboxaldehyde was obtained from Aldrich and was used as received. The NMR spectra were recorded with a Varian Gemini 300 FT-NMR. All spectra were recorded on 5% w/v solutions of polymer in $CDCl_3$. Tetramethylsilane was used as an internal reference. The resonance areas of individual signals were measured by electronic integration and by tracing peaks on high quality paper, then cutting and weighing the tracings. Molecular weight measurements were performed with a Waters 150 ALC/GPC equipped with 10^6, 10^5, 10^4, 10^3, 500 and 100A microstyragel columns. 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 (5). The monomer was purified by distillation from CaH_2 immediately before use b.p. = 73-75°/45 mm.

Polymer Synthesis

The monomer proved difficult to polymerize at a reasonable rate at temperatures below 100°C. Therefore, poly(2-vinyl-5-methyl thiophene) 2VMT, was synthesized at 120°C using benzoyl peroxide as the initiator. The polymerization was conducted as follows: a quantity of monomer (7.0g) was charged into a clean, dry 10 ml flask equipped with a magnetic stirrer and a thermometer. 1.0 wt% BPO was added and the solution was sparged with N_2. The flask was placed in a heating mantle and heated to the reaction temperature with stirring. Temperature was maintained by a Therm-o-Watch with a solid state temperature sensing head attached to the thermometer. The polymerization was allowed to proceed for 5.5h. The contents of the flask were allowed to cool to ambient temperature, diluted with $CHCl_3$ and added to excess CH_3OH. The polymer was purified by reprecipitating it twice from $CHCl_3$ solution into CH_3OH. The polymer was dried for 72h in vacuo at ambient temperature. Conversion = 17%, M_n = 19,000, M_w = 35,400, M_w/M_n = 1.86.

It should be noted that small amounts of polymer were obtained at lower temperatures (65-70°C) with AIBN as the initiator. The ^{1}H-NMR and ^{13}C-NMR spectra of these polymers were virtually identical to the spectra of the polymer obtained at 120°C. As a result, in the interest of brevity, only the spectra of the polymer obtained at 120°C will be discussed in this paper.

Results and Discussion

The ^{1}H-NMR spectrum of 2VMT and linear expansion of the aromatic proton resonances are shown in Figure 1. The resonances are assigned as shown in the Figure (6). The aromatic resonance pattern is very similar to that of poly(2-vinyl thiophene) but the resonances are not quite as well resolved in the present case. However, the resonance pattern is more well resolved than poly(2-vinyl thiophenes) with Br or Cl in the 5- position of the thiophene ring (3-5). As is shown in the Figure, peaks A and B are assigned to the H_2 ring proton and peaks C-F are assigned to the H_1 proton (6,7). Electronic integration and cutting and weighing analysis support these assignments in that the ratio of A+B/C-F is 1:1, if C is assigned to the H_2 resonances this ratio is no longer exactly 1:1.

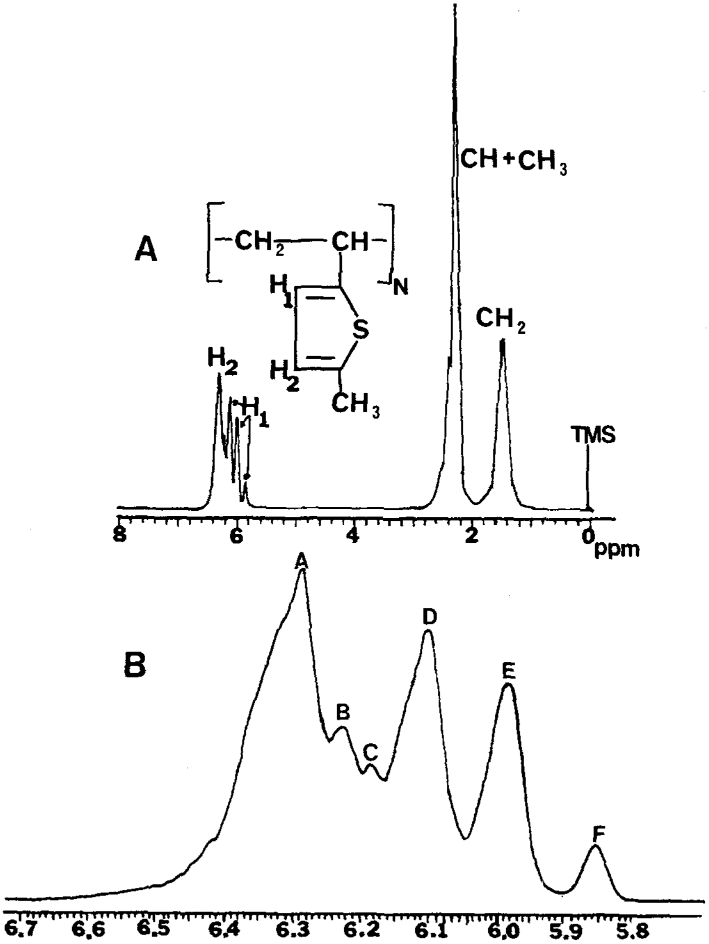

Figure 1

A) 300 MHz ^{1}H-NMR spectrum of poly(2-vinyl-5-methyl thiophene;
B) Linear expansion of the aromatic resonances

The relative and fractional intensities of peaks C-F are given in Table 1.

TABLE 1

Chemical Shifts, Relative and Fractional Intensities of the Peaks in the H_1 Resonance

Peak	Chemical Shift (ppm)	Fractional Intensity	Relative Intensity
C	6.19	0.090 ± .009	1
D	6.10	0.49 ± .05	8
E	5.99	0.36 ± .04	6
F	5.85	0.063 ± .003	1

In the poly(2-vinyl thiophene) case a 3-peak pattern virtually identical to D-F occurred, with the exception that their relative intensity ratio was 9:6:1, D:E:F. In the present case the ratio if 8:6:1, D:E:F. However, peak C is part of the H_1 ring proton resonance and if it's area is added to that of peak D then the relative intensity ratio becomes 9:6:1, C+D:E:F. Since there are 16 pentads all of equal concentration in an atactic polymer (1,2) it is logical to assign this pattern as being due to combinations of signals from the pentad stereosequences of an atactic polymer. This was done successfully for poly(2- and 3-vinyl thiophenes) and it is also done in the present case. Table 2 gives proposed assignments for the resonances in the present case. It should be noted that the pentads are assigned as being contained in the peak area given, no specific order is assignable at this time in the absence of any stereoregular polymer. However, the principles involved in making these assignments are believed to be correct (2,7).

TABLE 2

Proposed Pentad Assignments

Peak	Chemical Shift (ppm)	Proposed Pentad Assignment
C+D	6.19 and 6.10	rmmr, mmmr + rmmm, mmmm, mmrm + mrmm, rmrr + rrmr, rrrr
E	5.99	rmrm + mrmr, rrrm + mrrr mmrr + rrmm
F	5.85	mrrm

A P_m value calculated from the fractional intensity of the mrrm pentad is 0.50 ± .03. It would seem that peak C is also a pentad of singlet intensity, possibly rmmr or mmmm, however, because of signal overlap, the fractional and relative intensity of peak C cannot be measured as accurately as that of peak F, so the P_m value was calculated from peak F.

^{13}C-NMR Spectrum

The 75.5 MHz ^{13}C-NMR spectrum of 2VMT is shown in Figure 2. Linear expansions of the resonances of certain carbons are shown in Figure 3. The resonances are assigned as shown in the Figure (8). The C_2 resonance occurs as 3 peaks, labeled A, B, C in Figure 3A. These peaks occur in a relative intensity ratio of approximately 1:2:1, A:B:C. The corresponding fractional intensities are A = 0.24 ± .02, B = 0.53 ± .05 and C = 0.23 ± .02. These are the relative and fractional intensities expected for the triads of an atactic polymer.

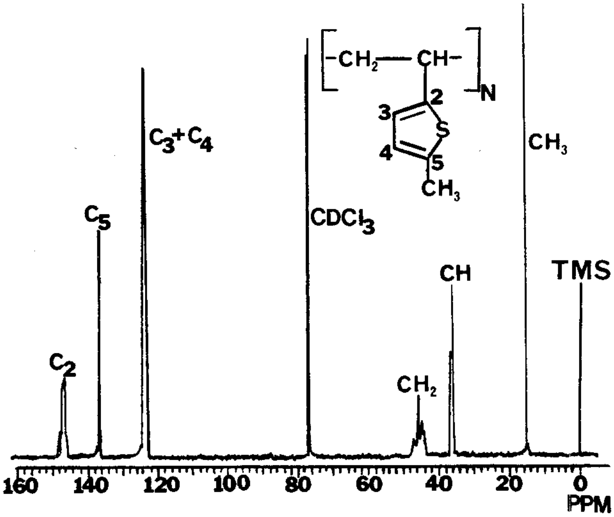

Figure 2

75.5 MHz ^{13}C-NMR spectrum of poly(2-vinyl-5-methyl thiophene)

Accordingly, the peaks were assigned as follows: A = mm, B = rm + mr and C = rr. There is more fine structure evident on peak B that most probably reflects a sensitivity to pentad stereosequences.

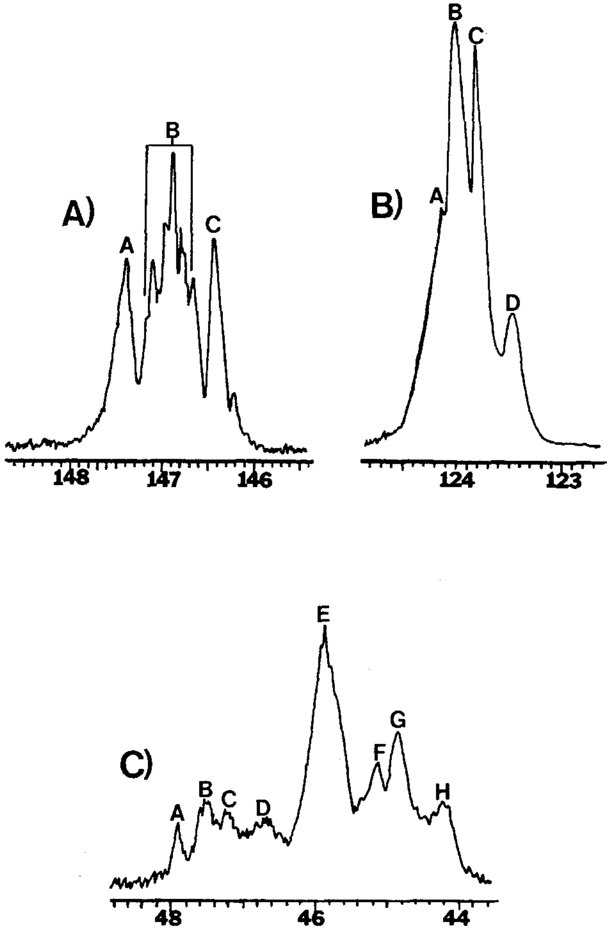

Figure 3

LInear expansions of A) C_2 carbon resonance; B) C_5 carbon resonance; C) methylene carbon resonance[5]

However, resolution is insufficient at the present time for any reasonable assignments to be made. In any case a P_m value calculated from the fractional intensity of peak A is 0.49 ± .05. The C_5 resonance is shown in expanded form in Figure 3B. The four peak pattern has a relative intensity ratio of 2:3:2:1, A:B:C:D. The corresponding fractional intensities are A = 0.24 ± .02, B = 0.36 ± .04, C = 0.26 ± .03 and D = 0.13 ± .01. The relative intensity ratio sums to 8 which could indicate a tetrad sensitivity, but this is unlikely based on previous results (2,7,9). If the relative intensities are multiplied by 2, a relative intensity ratio of 4:6:4:2 is obtained which sums to 16. As previously stated there are 16 pentads of equal concentration in an atactic polymer, it therefore seems most likely that the resonance pattern observed is reflecting a sensitivity to pentad stereosequences. Unfortunately the resolution is insufficient at the present time for any detailed assignments to be made. However, the observed pattern strengthens the argument that 2VMT is an atactic polymer.

The methylene carbon resonance pattern (Figure 3C) occurs as an 8 peak pattern. A similar pattern is observed in the 90 MHz ^{13}C-NMR spectrum of poly(2-vinyl thiophene) (9). In the case of poly(2-vinyl thiophene) this pattern was interpreted in terms of hexads for an atactic polymer with the aid of a computer simulation (10). However, in the present case the resolution is not as good as in the 90 MHz ^{13}C-NMR spectrum of poly(2-vinyl thiophene), therefore no detailed assignments can be made at the present time. But, the resolution is sufficient to obtain approximate relative intensities of peaks A-H. These relative intensities are 1:3:2:3:12:3:5:3, A:B:C:D:E:F:G:H. The sum of these relative intensities is 32 which would be expected for the hexads of an atactic polymer. In addition the fractional intensity of peak A can be measured with reasonable accuracy. The fractional intensity = 0.031 ± .003. A P_m value calculated from this fractional intensity (assuming peak A represents a hexad singlet, which is a very reasonable assumption), is equal to 0.50 ± .05.

Conclusions

The 300 MHz ^{1}H-NMR and 75.5 MHz ^{13}C-NMR spectra of poly(2-vinyl-5-methyl thiophene) have been recorded and analyzed in terms of polymer tacticity. The spectra proved very similar to those of unsubstituted poly(2-vinyl thiophene) and were interpreted in a like manner. Calculation of P_m values from measured fractional intensities are 0.50 ± .05 which strongly suggests poly(2-vinyl-5-methyl thiophene) is an atactic polymer. Absolute assignment of polymer stereochemistry awaits the synthesis of stereoregular polymers and the results of subsequent epimerization experiments.

The effect of the methyl group is that a ^{1}H-NMR spectrum with less resolution than that of poly(2-vinyl thiophene) is produced, particularly as concerns the ring proton resonances. However, the ring protons are more well resolved in poly(2-vinyl-5-methyl thiophene) than the corresponding protons in the 5-Cl or 5-Br substituted poly vinylthiophenes. The possible reason(s) why this is so in a quantitative sense remain the object of MO calculations and is the subject of a future publication.

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