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Analysis of the ^{1}H-NMR and ^{13}C-NMR spectra of poly(5-ethyl-2-vinyl thiophene)

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Summary

The title polymer was synthesized by free radical initiation. The ^{1}H-NMR and ^{13}C-NMR spectra were recorded and analyzed in terms of polymer stereochemistry. By comparison of the results to those previously obtained, free radical initiated poly(5-ethyl-2-vinyl thiophene) was shown to be an atactic polymer.

Introduction

The results of our previous studies on free radical initiated poly vinyl heterocycles have shown that these polymers have atactic stereochemistries (1-5 and references therein). Our results have also shown that the nature and position of additional ring substituents has a significant affect on the appearance of the ^{1}H- and ^{13}C-NMR spectra. On occasion, the additional substituents have increased the resolution of the resonances due to the ring protons (and/or carbons) as well as providing additional resonances that might yield stereochemical information (1,2). Also, the additional ring substituents have proven capable of decreasing the resolution of the remaining ring protons and/or carbons (3,4), relative to the parent material i.e. unsubstituted poly(2- or 3-vinyl heterocycles). Results have indicated that electron withdrawing substituents (-Cl e.g.) decreased the resolution in the resonances of the other ring protons while electron releasing substituents ($-CH_3$ e.g.) increased the resolution. In order to further define such effects and also to explore the effect of substituent bulk on the NMR spectra of vinyl heterocycles, we synthesized and examined the NMR spectra of poly(5-ethyl-2-vinyl thiophene).

Experimental

General

All solvents and other reagents in this study were used as received. The nmr spectra were recorded on a Varian Gemini 300 FT NMR using

$CDCl_3$ solutions (10% w/v) of polymer at ambient temperature. Individual peak areas were determined by electronic integration and by tracing resonances on high quality paper then cutting out and weighing the tracings on a 5-place analytical balance. Each area measurement was repeated three times. The polymer molecular weight was measured as previously described (1-5).

Monomer Synthesis

The monomer was synthesized from 2-ethyl thiophene via a Vilsmeier formulation and a Wittig reaction (6,7). The monomer was obtained in 58% overall yield and was purified by distillation from CaH_2 (b.p. = 91-93°C/25 mm).

Polymer Synthesis

The polymer was synthesized by weighing 2.0 g of monomer into a clean, dry screw cap vial followed by 0.5 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 waterbath at 75°C for a period of 6.5 h. Agitation was by periodic vigorous shaking of the vial. The polymerization was terminated by removing the vial from the bath, cooling in cold water and adding 5 ml of cold CH_3OH to the vial. The polymer was purified by two reprecipitations from $CHCl_3$ solution into excess CH_3OH. Conv. = 21%, M_n = 6000, M_w = 10300.

Results and Discussion

The ^{1}H-NMR spectrum as well as linear expansions of the resonances of interest are shown in Figure 1.

The resonances are assigned as shown in the Figure (8,9). The aromatic proton resonances (Figure 1B) occur in two general areas. The peaks assigned to the H_3 proton resonance (E-I) occur in a relative intensity ratio of 2:2:5:6:1, E:F:G:H:I. The sum of this ratio of relative intensities is 16 and, as there are 16 pentads of equal intensity in an atactic polymer (4,10), it is logical to assign the H_3 resonance pattern in terms of pentads. The proposed assignments are given in Table 1. The peaks are assigned as containing the pentads specified because, in the absence of a stereoregular polymer spectrum and epimerization (5) studies, no specific order can be given. However, in the assignments previously made for poly(2- and 3-vinyl thiophenes) (4,5), the H_3 proton resonance appeared as a 3-peak pattern in a relative intensity ratio of 9:6:1. If the areas of peaks E, F and G are combined then the relative intensity ratio of the H_3 proton resonance becomes 9:6:1. Accordingly then, the assignments for these resonances could be and were based on those previously developed.

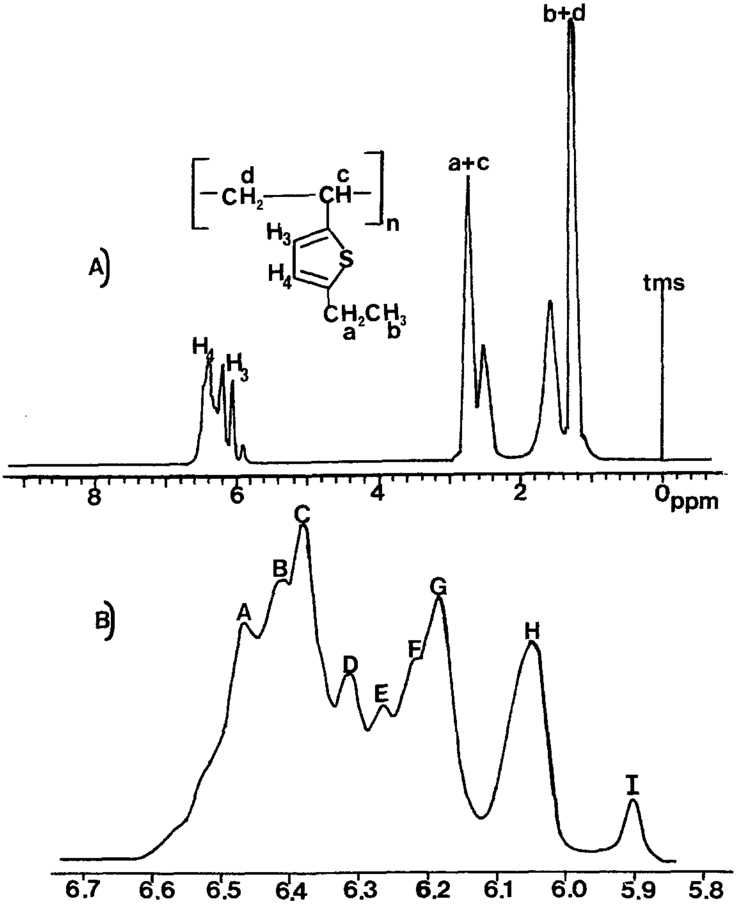

Figure 1

300 MHz ^{1}H-NMR spectrum of poly(2-vinyl-5-ethyl thiophene): A) Full spectrum; B) Expansion of the ring proton resonance

TABLE 1

Peak Assignments for the H_3 Proton Resonance

Peak	Chemical Shift (ppm)	Fractional Intensity	Relative Intensity	Proposed Assignment
E	6.27	0.12 ± .02	2	rmmr, mmmr + rmmm
F	6.22	0.15 ± .03	2	mrmm + mmrm, mmmm
G	6.18	0.30 ± .05	5	rmrr + rrmr, rrrr
H	6.05	0.36 ± .04	6	rmrm + mrmr, rrrm + mrrr mmrr + rrmm
I	5.90	0.062 ± .004	1	mrrm

A P_m value calculated from the fractional intensity of peak I is 0.50 ± .03, the value expected for an atactic polymer.

The relative intensity ratio of the peaks in the H_4 proton resonance (A-D) is 2:2:2:1, A:B:C:D. The sum of this ratio is 7, which indicates a sensitivity to higher order stereosequences, possibly pentads. However, the resolution is insufficient for any reasonable assignments to be made at this time.

The aliphatic proton resonances occur in two general areas in a ratio of 3:5. Because these resonances consist of contributions from more than one type of proton (as shown in the Figure) lack of resolution makes assignment in terms of stereochemistry is not possible at this time.

^{13}C-NMR Spectroscopy

The ^{13}C-NMR spectrum of poly(5-ethyl-2-vinyl thiophene) and expansions of the resonances of interest are shown in Figures 2 and 3. The resonances were assigned as shown in the Figure (3, 11). The resonance assigned to the C_2 ring carbon (Figure 2B) occurs as a seven peak pattern with a relative intensity ratio of 10:6:20:4:8:2:1, A:B:C:D:E:F:G. The sum of this relative intensity ratio is 51, which indicates a sensitivity to higher order stereosequences, possibly heptads. However, the resolution is not sufficient for any reasonable assignment in terms of heptads to be made at this time. The resonance assigned to the C_5 ring carbon occurs as a 6 peak pattern (Figure 2C) in a relative intensity ratio of 2:1:4:4:2:3, A:B:C:D:E:F. The sum of this ratio is 16, which is the number of pentads expected for an atactic polymer.

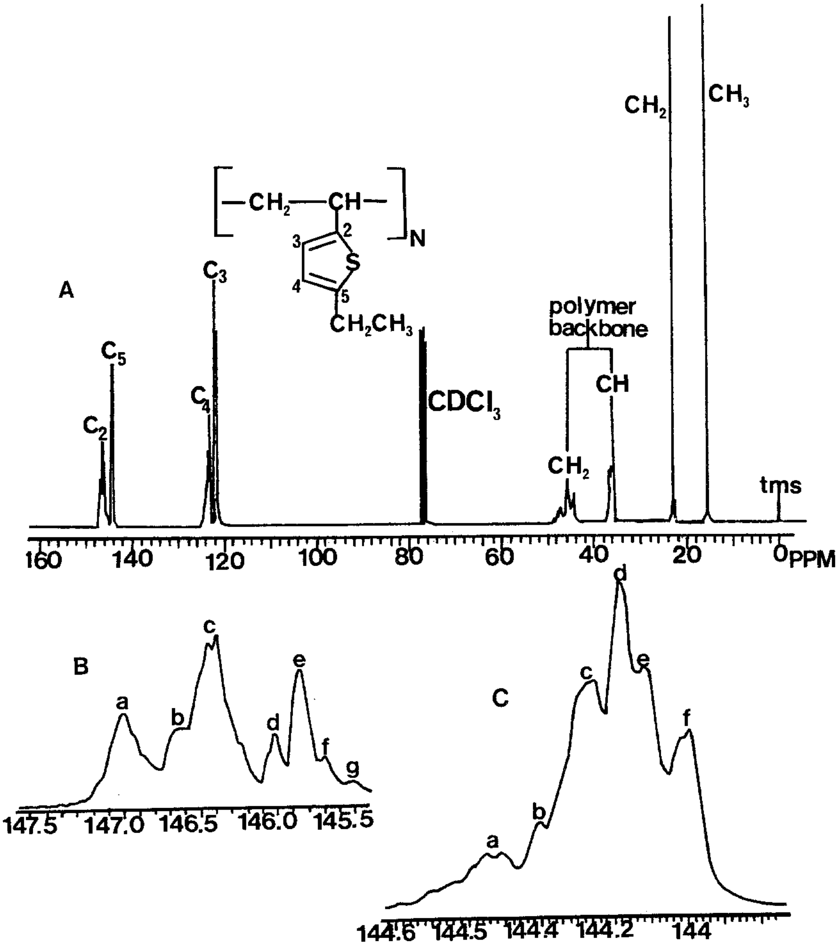

Figure 2

75.5 MHz ^{13}C-NMR spectrum of poly(2-vinyl-5-ethyl thiophene):
A) Full spectrum; B) Expansion of the C_2 carbon resonance
C) Expansion of the C_5 carbon resonance

Therefore, this pattern is most probably due to pentad stereosequences and, while the resolution is not sufficient for any detailed assignments to be made, a P_m value can be calculated from the fractional intensity (0.061 ± .006) of peak B which is assignable to a pentad of singlet intensity. The value obtained is 0.50 ± .05, which is the value expected for an atactic polymer.

The resonance assigned to the C_4 ring carbon (Figure 3A), occurs as a 7 peak pattern with a relative intensity ratio of 1:2:5:9:11:17:19, A:B:C:D:E:F:G. The sum of this ratio is 64 which is the number of heptads expected for an atactic polymer. While the resolution is insufficient for any detailed assignments to be made, a P_m value can be calculated from the fractional intensity of peak A (0.016 ± .002), which is due to a heptad singlet. The value obtained is 0.50 ± .06, again the value expected for an atactic polymer.

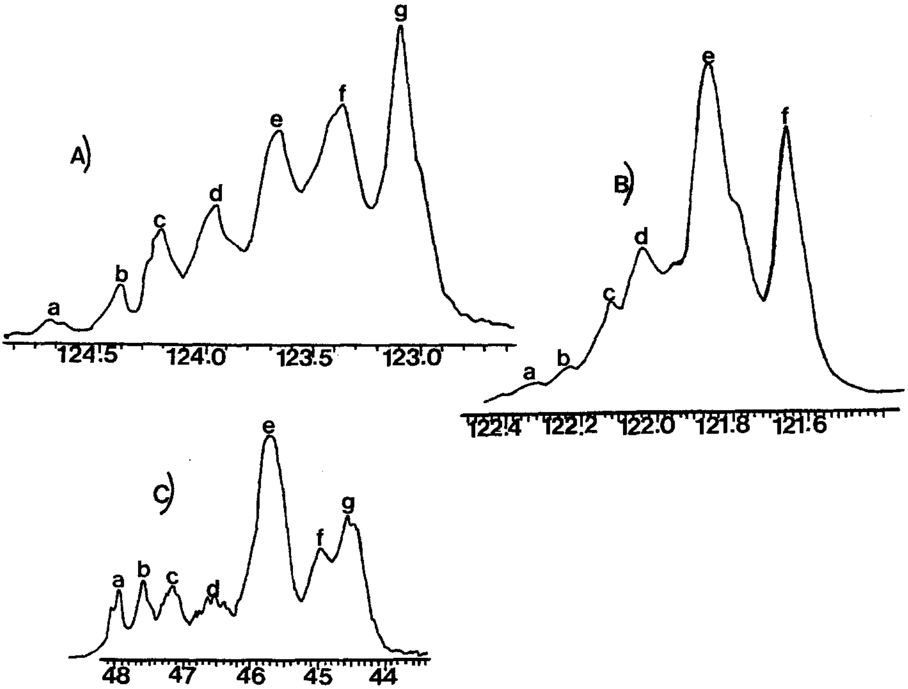

Figure 3

Expansions of select carbon resonances:
A) C_4 carbon resonance; B) C_3 carbon resonance
C) Methylene carbon resonance

The C_3 carbon resonance (Figure 3B) occurs in a 6 peak pattern in a relative intensity ratio of 1:1:5:8:33:16, A:B:C:D:E:F. The sum of this relative intensity ratio is 64 which, as above, is the number of heptads expected for an atactic polymer. Once again the resolution is not sufficient for any detailed assignments to be made. However, a P_m value can be calculated from the fractional intensity of peak A (0.016 ± .003); the value obtained is 0.50 ± .09, the value expected for an atactic polymer.

The methylene carbon resonance (Figure 3C) occurs as a 7 peak pattern in a relative intensity ratio of 1:1:1:2:6:2:3, A:B:C:D:E:F:G. The sum of this ratio is 16, which could be interpreted as being due to a pentad sensitivity, but this is unlikely given the fractional intensities of the individual resonances and that methylene resonances are sensitive to even numbered stereosequences (10) such as tetrads and hexads, etc. If all the relative intensities are multiplied by 2 then the relative intensity ratio becomes 2:2:2:4:2:4:6 which sums to 32, which is the number of hexads expected for an atactic polymer. Lack of resolution precludes a detailed assignment of resonances, but a P_m value calculated from the fractional intensity of peak A is 0.49 ± .05, a value expected for an atactic polymer.

The remaining carbon resonances either show no sensitivity to polymer stereochemistry or have insufficient resolution for any reasonable conclusions to be drawn from them i.e. even a P_m value cannot be calculated.

Conclusions

5-Ethyl-2-vinyl thiophene has been synthesized and polymerized via free radical initiation. Examination of the ^{1}H-NMR spectrum revealed the similarity to the spectra of poly(2- and 3-vinyl thiophenes) at least in the ring proton resonances. The resonance pattern of the H_3 proton could be interpreted in terms of pentads in the same manner as the resonances of like protons were interpreted in the poly(2- and 3-vinyl thiophene) cases. When this was done the polymer was found to be atactic. The carbon spectrum, while not as well resolved as the ^{1}H-NMR spectrum, nonetheless showed several resonances that were sensitive to polymer stereochemistry. Some of the sensitivities were shown to be to heptads, and while no detailed assignments would be made, P_m values could be calculated,and the values obtained were those expected for an atactic polymer. The fact that longer sequences could be measured and yielded P_m values of 0.50 strengthens the conclusion the free radical initiated poly(5-ethyl- 2-vinyl thiophene) is an atactic polymer.

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