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Preliminary analysis of the ^{1}H- and ^{13}C-NMR spectra of poly(2-vinyl selenophene)

D. L. Trumbo

S. C. Johnson & Son, Inc., 1525 Howe St., Racine, WI 53403-5011, USA

Summary

The high field ^{1}H- and ^{13}C-NMR (300 MHz and 75.5 MHz respectively) spectra of poly(2-vinyl selenophene) synthesized by free radical initiation have been recorded and analyzed. Both the ^{1}H- and ^{13}C-NMR spectra of poly-(2-vinyl selenophene) have many similarities to the corresponding poly-2- and 3-vinyl thiophene spectra and could, therefore, be interpreted in a like manner.

Introduction

Previous work has shown that the homopolymers of ring substituted and unsubstituted 2- and 3-vinyl thiophenes, when synthesized by free radical initiation, have an atactic stereochemistry (1-4). Also, prior work on polyvinyl heterocycles such as poly(2-vinyl furan) and poly(2-vinyl pyridine (5,6) have shown that the identity of the heteroatom in the heterocycle has an effect on the NMR spectra (^{1}H- and ^{13}C) of the polymer. Therefore, in order to investigate the effect of the selenium atom not only on polymer stereochemistry, but also on the NMR spectra of the polymer, we undertook the investigation of the stereochemistry of poly(2-vinyl selenophene).

Experimental

General

All solvents used were reagent grade and were used as received. The ^{1}H- and ^{13}C-NMR spectra were recorded at 25° on $CDCl_3$ solutions of the polymer. Tetramethylsilane was used as an internal reference. The spectrometer used was a Varian Gemini 300 FT-NMR with a ^{1}H frequency of 300 MHz and a ^{13}C frequency of 75.5 MHz. Pertinent parameters were: ^{1}H-NMR: SW = 4500.5 Hz, PW = 33°, PD = 2 μs, NT = 200; ^{13}C-NMR: SW = 18761.7 Hz, PW = 87.5°, PD = 6 s, NT = 30000. Individual resonance areas were determined by tracing the resonances on high quality paper, cutting out and then weighing the tracings. Molecular weight measurements were made with a Waters High Resolution 600A chromatograph equipped with 10^6, 10^5, 10^4, 10^3 and 500A columns. Numerical values for the molecular weights were obtained by comparison to a polystyrene calibration curve.

Monomer Synthesis

The monomer was synthesized as previously described (7) and was purified by distillation from CaH_2.

Polymer Synthesis

Polymer was synthesized by charging 2.0 grams of freshly distilled monomer into a clean, dry, screw top vial, followed by 0.6 wt % AIBN. The contents of the vial were sparged with dry N_2 and the vial was sealed with a polyethylene lined screw cap. The vial was placed in a thermostated water bath at 65° for a period of 6 hrs. The polymerization was terminated by pouring the contents of the vial into a 7-fold excess of methanol. The polymer was purified by twice reprecipitating from $CHCl_3$ solution into methanol. % Conv. = 16%.

Results and Discussion

The molecular weight of the polymer was: $M_n = 6800$, $M_w = 13400$ and $M_w/M_n = 1.97$.

^{1}H-NMR spectrum of poly(2-vinyl selenophene), along with horizontal expansions of the ring proton resonances, is shown in Figure 1. The signal assignments are also given in Figure 1 (1,7,8). In the present case, as it also was for poly 2- and 3-vinyl thiophenes, the methylene proton resonance (1.62 ppm) occurs as a broad envelope with no evidence of stereochemical sensitivity. Likewise, the methine proton resonance (2.63 ppm) shows no readily analyzable sensitivity to polymer stereochemistry. There are two small shoulders visible on the downfield side of this resonance, but they are so poorly resolved that any reasonable analysis in terms of polymer stereochemistry is not possible.

The ring protons all appear to be sensitive to polymer stereochemistry to some degree. The H_3 proton resonance, Figure 1C is approximately a 1:2:1 (A:B:C) relative intensity pattern (the chemical shifts, relative and fractional intensities are given in Table 1). In the case of poly (2-vinyl thiophene) the H_3 proton resonance occurred in almost exactly the same pattern (1). For poly(2-vinyl thiophene) the pattern was interpreted in terms of a triad stereosequence sensitivity with the relative intensity ratio of 1:2:1 which strongly indicated this particular triad pattern was that of a Bernoullian atactic polymer. It seems most likely that a similar interpretation can be made in the present case, i.e. that the H_3 proton resonance pattern is due to a triad stereosequence sensitivity and the relative intensity ratio of 1:2:1 for peaks A:B:C indicates

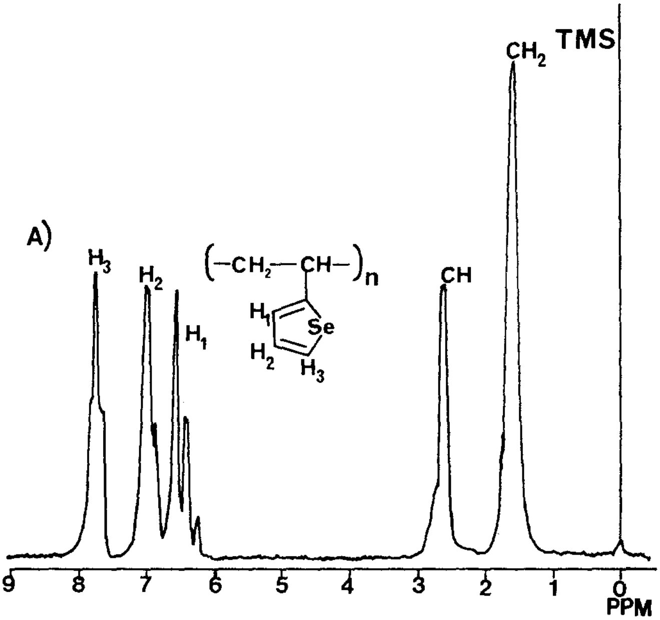
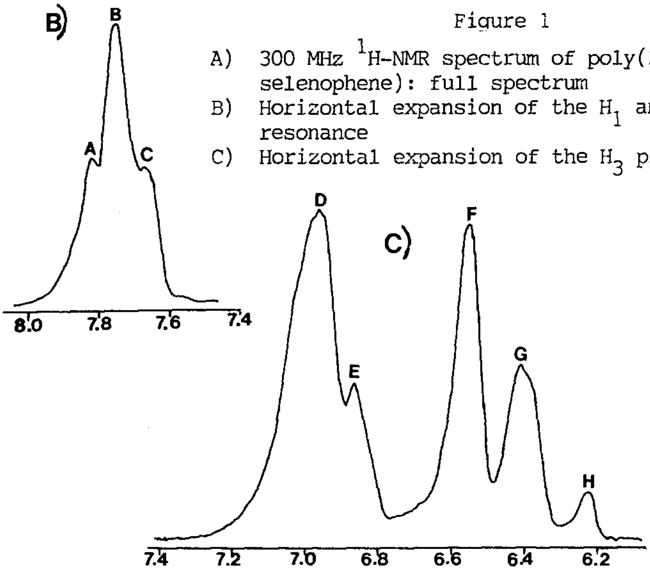


Figure 1

A) 300 MHz ^{1}H-NMR spectrum of poly(2-vinyl selenophene): full spectrum

B) Horizontal expansion of the H_1 and H_2 proton resonance

C) Horizontal expansion of the H_3 proton resonance



that poly(2-vinyl selenophene) is an atactic polymer.

Support for this contention can be found in examination of the resonance pattern of the H_1 proton. The resonance occurs as a three peak pattern with a relative intensity ratio of 9:6:1 (F:G:H). This same pattern occurred in the resonance of the H_1 proton of poly(2-vinyl thiophene) and poly(3-vinyl thiophene). In fact this pattern occurs, although less well resolved, in the resonance of the ortho proton in polystyrene (2,9). Since these polymers are believed to be atactic and since there are 16 pentad stereosequences, all expected to have equal concentrations in an atactic polymer, an interpretation of the H_1 proton resonances of poly(2-vinyl selenophene) in terms combinations of signals from pentad stereosequences is most probably correct. The chemical shifts, relative and fractional intensities of the signals are given in Table 1.

TABLE 1

Chemical Shifts, Relative and Fractional Intensities of the Ring Proton Resonances of Poly(2-Vinyl Selenophene)

Peak	Proton	Chemical Shift (ppm)	Relative Intensity	Fractional Intensity
A	H_3	7.78	1	0.270 ± .020
B	H_3	7.74	2	0.500 ± .040
C	H_3	7.66	1	0.240 ± .020
F	H_1	6.56	9	0.570 ± .040
G	H_1	6.40	6	0.360 ± .030
H	H_1	6.22	1	0.610 ± .004

The H_2 proton resonance resonance occurs as a two peak pattern (D,E) which indicates a sensitivity to polymer stereochemistry. The relative intensity ratio of 4:1 (D;E) is not readily assignable to any particular stereosequence sensitivity. Perhaps, as in the case of poly(3-vinyl thiophene), a spectrometer operating at a higher field could reveal a hidden pattern that could be assignable in terms of triads of pentads or higher order sequences. However, under the present conditions a reasonable analysis of the resonance in terms of polymer stereochemistry is not possible.

Based on assignments developed for polystyrene (10) and poly 2- and 3-vinyl thiophenes, the resonance assignments for the H_1 and H_3 protons of poly(2-vinyl selenophene) can be proposed. These assignments are summarized in Table 2. As in previous cases it must be emphasized that these assignments are not established with certainty, but are believed to be correct based on the arguments and principles previously advanced (2,10).

TABLE 2

Triad and Pentad Assignments for the H_1 and H_3 Proton Resonances of Poly(2-Vinyl Selenophene)

Peak	Chemical Shift	Assignment
A	7.78	mm
B	7.74	rm + mr
C	7.66	rr
F	6.56	rmmr, rmmm + mmmr mmmm, mrmm + mmrm, rmmr + rrmr
G	6.40	rrrm + mrrr, rmrm + mrmr mmrr + rrmm
H	6.22	mrrm

P_m values calculated from the fractional intensities of the mm triad and the mrrm pentad are 0.52 ± .04 and 0.55 ± .04 respectively. The P_m values indicate that the polymers are atactic within experimental error, with possibly a slight preference for isotactic placement of repeat units.

The 75.5 MHz ^{13}C-NMR spectrum of poly(2-vinyl selenophene) along with horizontal expansions of select resonances, is shown in Figure 2. The resonances are assigned as shown in the Figure (7). The pattern due to the C_1 or quaternary ring carbon (Figure 2A) is very similar to the resonance pattern of the quaternary ring carbon of poly(2-vinyl thiophene) in o-dichlorobenzene-d_4 at room temperature.

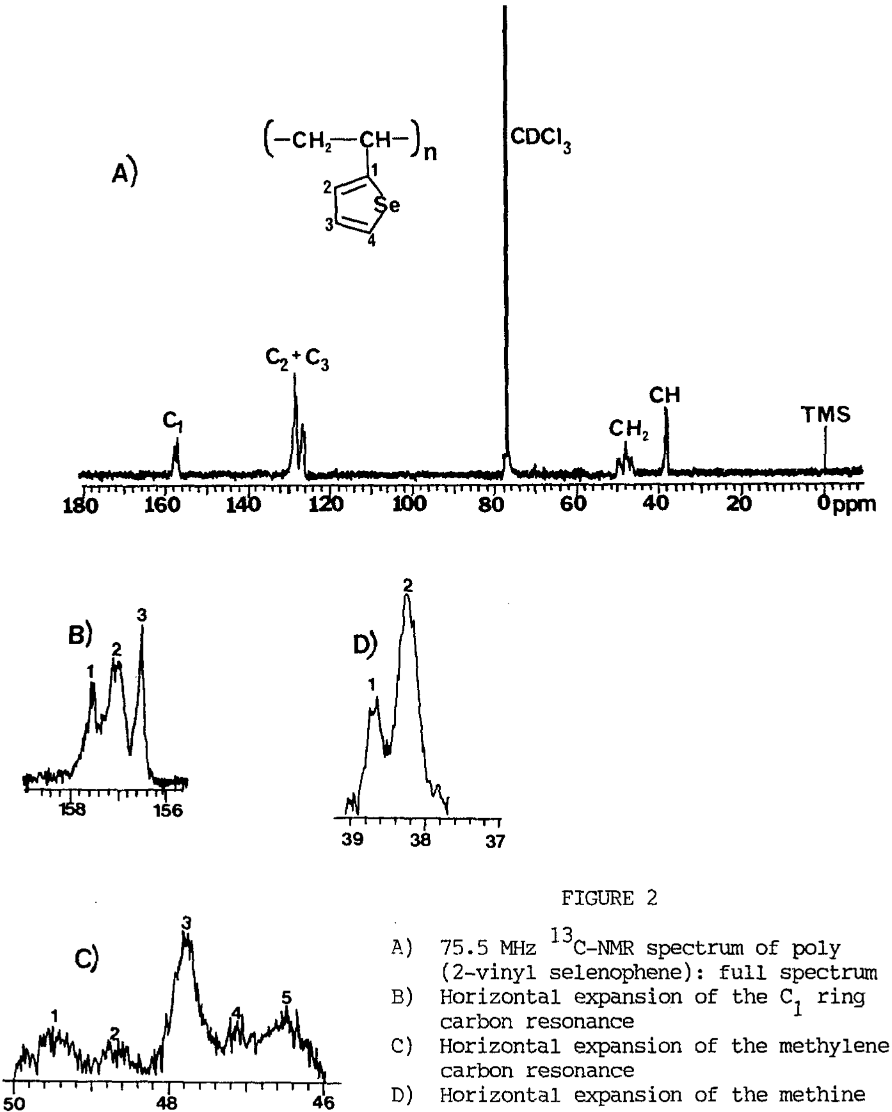


FIGURE 2

A) 75.5 MHz ^{13}C-NMR spectrum of poly (2-vinyl selenophene): full spectrum

B) Horizontal expansion of the C_1 ring carbon resonance

C) Horizontal expansion of the methylene carbon resonance

D) Horizontal expansion of the methine carbon resonance

As in the case of poly(2-vinyl thiophene), the relative intensity ratio of peaks 1, 2 and 3 in the present case is 1:2:1 respectively. This is the triad intensity pattern one would expect for an atactic polymer and in the case of poly(2-vinyl thiophene) this pattern was assigned to triads (5, 11). The fractional intensities, chemical shifts and peak assignments are given in Table 3.

TABLE 3

Chemical Shifts, Relative and Fractional Intensities and Peak Assignments for the C_1 Carbon

Peak	Chemical Shift (ppm)	Relative Intensity	Fractional Intensity	Assignment
1	157.62	1	0.27 ± .02	mm
2	157.08	2	0.48 ± .05	rm + mr
3	156.58	1	0.25 ± .03	rr

The methylene carbon resonance (Figure 2B) shows a multiplicity that indicates a sensitivity to polymer stereochemistry. The relative intensities of peaks 1-5 are 2:1:5:1:3 respectively, for a total of 12. Since there are 8 tetrads and 32 hexads for an atactic polymer, the methylene carbon resonance pattern is due to a combination of tetrad and hexad sensitivities. However, the resonance pattern is to complex for a straightforward interpretation in terms of tetrads and the resolution is insufficient for an interpretation in terms of hexads. Possibly, a spectrum obtained at a higher field would yield more resolution of this resonance and an interpretation in terms of hexads would be possible.

The methine resonance (Figure 2C) shows two peaks $\sigma = 38.75$ for peak 1 and $\sigma = 38.30$ for peak 2. The relative intensity of the two peaks (1/2) is 1:3. In the 90 MHz ^{13}C-NMR spectrum of poly(2-vinyl thiophene) the methine resonance appeared as a three peak pattern that was 1:2:1 relative intensity ratio (11). The resonance was assigned in terms of triads for an atactic polymer. In the present case the relative intensity ratio of 1:3 indicates a probable triad sensitivity with the two upfield peaks occurring together i.e. a relative intensity of 1 added to a relative intensity of 2 equals a relative intensity of 3. The fractional intensities of peaks 1 and 2 are 0.26 ± .02 and 0.74 ± .05 respectively. Based on assignments developed for poly(2-vinyl thiophene) peaks 1 and 2 are assigned in terms of triads as: 1 = mm and 2 = (rm + mr) and rr.

P_m values calculated from the fractional intensities of the triads of the C_1 quaternary carbon resonance and the triads of the methine carbon resonance are 0.52 ± .06 and 0.51 ± .03. The values of P_m support the conclusion drawn from the ^{1}H-NMR data, i.e. that poly(2-vinyl selenophene) is basically an atactic polymer with a slight preference for isotactic placements.

Conclusions

The ^{1}H- and ^{13}C-NMR spectra of a free radical initiated poly(2-vinyl selenophene) have been recorded and analyzed. In most respects the spectra were very similar to those of poly 2- and 3-vinyl thiophene and were analyzed accordingly. P_m values calculated from the resonance assignments made strongly indicate that poly(2-vinyl selenophene) is predominately an atactic polymer with a slight preference for isotactic monomer unit placements. The resonance area assignments given in this paper, while not yet established with certainty, are based on principles believed to be correct. More definitive assignments await the synthesis of a stereoregular poly(2-vinyl selenophene).

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