

Analysis of the 300 and 600 MHz ^1H -NMR spectra of poly(3-vinyl thiophene)

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Summary

The 300 and 600 MHz ^1H -NMR spectra of poly-(3-vinyl thiophene) synthesized via free radical initiated polymerization are presented and analyzed. The spectra are similar to those of poly-(2-vinyl thiophene) and were interpreted in a like manner. The polymer was found to be atactic with a P_m value of $0.48 \pm .05$.

Introduction

Until quite recently, the ^1H - and ^{13}C -NMR spectra of polystyrene were difficult to interpret in terms of polymer stereochemistry(1-8). The approaches taken to solve this problem have included NMR studies on model polystyrene oligomers(1,2), NMR studies on epimerized polystyrenes derived from isotactic and syndiotactic polystyrene(3-7), theoretical calculations based on the RIS model(9), and NMR studies on analogs or derivatives of polystyrene(10-16). This latter approach was taken with the expectation that the analogs would have similar stereochemical structures to polystyrene but that their NMR spectra might be more easily interpreted and could provide a guide for understanding polystyrene spectra. In previous papers(10-14), we have shown that the NMR spectra of polymers derived from vinyl heterocycles are indeed more easily interpreted than those of polystyrene. In this communication, we report results obtained for poly-(3-vinyl thiophene).

Experimental

3-Vinyl thiophene was synthesized in 56 percent yield by the decarboxylation of 3-thienylacrylic acid (m.p. 153-154°C, lit. m.p. 152-154°C) (17,18) according to the procedure of Hachikara and Imoto (b.p. 52-54°C/26 mm, lit. b.p. 50-53°C/26 mm) (19).

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Poly-(3-vinyl thiophene) was prepared by bulk polymerization of twice-distilled monomer (from CaH_2) using 0.5 wt. percent AIBN as initiator. Prior to polymerization, monomer-initiator mixtures were submitted to three freeze-evacuation-thaw cycles to remove oxygen and the evacuated mixtures were sealed in glass tubes. Polymerizations were conducted for 48 hrs. at various temperatures (40-95°C). Polymers were obtained by pouring the mixtures into methanol and were purified by thrice reprecipitation from chloroform into methanol and dried in vacuo at 40°C for 72 hrs. Yields ranged from 27-35 percent.

The $^1\text{H-NMR}$ spectra of polymers prepared at various temperatures were not significantly different. Also, no significant differences were noted among spectra recorded for the polymers in CDCl_3 or C_6D_6 at 0-60°C. Consequently, only the ambient temperature spectra of CDCl_3 solutions (5-10 wt. percent) of the polymer prepared at 65° will be considered herein. 300 MHz $^1\text{H-NMR}$ were recorded using a Varian HR-300 spectrometer while 600 MHz spectra were recorded using the in-house instrument at Carnegie-Mellon University. Tetramethylsilane (tms) was used as an internal reference in all cases. Resonance areas were determined by cutting and weighing expanded spectra or by use of von Meerwall's program(20). Spectral simulations were done using a program written by Dr. B. L. Bruner of the University of Kentucky.

The polymer used for the NMR measurements was characterized by gel permeation chromatography using a calibration for polystyrene: $M_n = 58,000$; $M_w = 88,000$.

Results and Discussion

Figure 1A shows the 300 MHz ^1NMR spectrum of poly-(3-vinyl thiophene) in CDCl_3 solution. Assignments for the resonances of specific protons are provided on the figure. The resonances of many of the protons consist of multiple signals due to contributions from different stereo-sequences.

The resonance of the methine protons ($\delta = 6.15-6.60$ ppm) is very similar to that of polystyrene and related polymers. It has two components, the lower field one being attributed to CH protons centered in mm-triads (i.e. isotactic triads). Its relative intensity (~25% of total) suggests that the polymer is atactic.

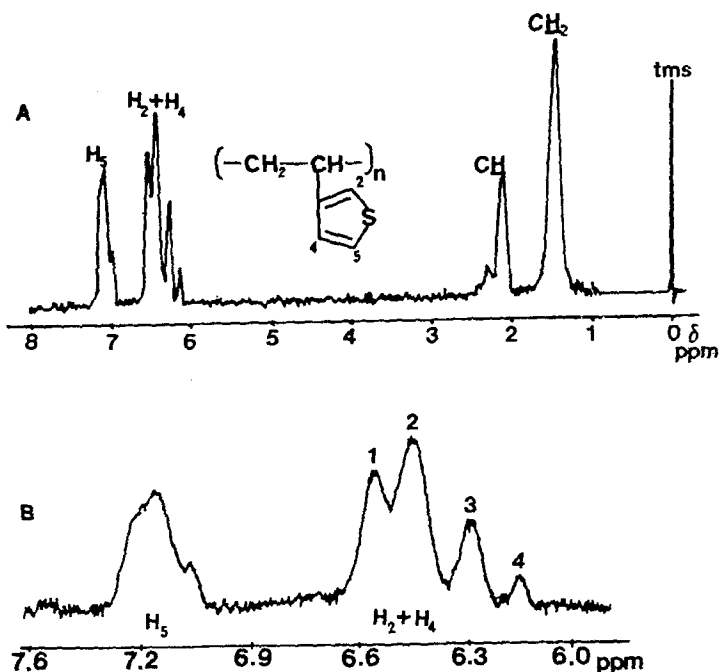


Figure 1

- A) 300 MHz ¹H-nmr spectrum of poly(2-vinyl thiophene); recorded at ambient temperature as a 7% w/v solution in CDCl₃
 B) 500 Hz horizontal expansion of the ring proton resonances

Figure 1B shows an expansion of the thiophene ring proton resonances. The resonance pattern assigned to H₅-ring protons seems to contain several components that may provide stereosequence distribution information, but it is poorly defined when recorded at 300 MHz. The resonances of the H₂- and H₄-ring protons ($\delta \approx 6.15\text{--}6.60$ ppm) are overlapped, but four distinct resonance areas are evident. These are designated 1-4 in order of increasing field and their relative (fractional) intensities are given in Table I.

Table I

Chemical Shifts and Fractional Intensities of the Signals in the H₂-H₄-Ring Proton Resonance of Poly-(3-Vinyl Thiophene)

Signal	Chemical Shift (ppm)	Fractional Intensity	Calculated Contribution From		
			H ₂	H ₄	H ₂ + H ₄
1	6.56	0.31 ± .03	-	0.28	0.28
2	6.47	0.46 ± .05	0.28	0.187	0.47
3	6.30	0.20 ± .03	0.187	0.031	0.22
4	6.18	0.036 ± .005	0.031	-	0.031

The H₂- and H₄-ring protons of poly-(3-vinyl thiophene) are analogous to the ortho protons of polystyrene and to the H₃-protons of poly-(2-vinyl thiophene). The resonances of such protons have been observed as 3-signal patterns having components whose relative intensities are in a 9:6:1 ratio. Since these polymers are believed to be atactic and since there are 16 pentad stereosequences, all having equal concentrations in an atactic polymer, the 9:6:1 patterns were attributed to combinations of signals from pentad stereosequences. Somewhat arbitrarily, the highest field signal (relative area = 1) was attributed to rrrr stereosequences, the central signal (relative area = 6) was attributed to rrmm + mmrr, rrrr + rrrr and rrrm + mrrr stereosequences, and all other stereosequences were attributed to the lowest field signal (relative area = 9). Based on recent work on the NMR spectra of epimerized syndiotactic polystyrenes(7), it now seems more reasonable to attribute the highest field signal to mrrm stereosequences and the central resonances to rrrm + mrrr, rrrm + mrrr and mrrm + mrrm stereosequences. Such assignments will be used in this paper.

Examination of the combined H₂- and H₄-proton resonance pattern depicted in Figure 1B suggests that it consists of two overlapped 9:6:1 patterns. In other words, the resonance of the "ortho" protons of poly-(3-vinyl thiophene) appears to be analogous that of the ortho protons of polystyrene and that of the "ortho" proton of poly-(2-vinyl thiophene). A four-peak pattern is observed in the case of poly-(3-vinyl thiophene) because the two "ortho" protons have different chemical shifts and the

9:6:1 patterns associated with them overlap. Table I shows that the relative fractional areas observed for signals 1-4 can be accommodated rather well by this interpretation.

Relying on the pentad assignments developed for polystyrene, resonance assignments for the H₂- and H₄-resonances of poly-(3-vinyl thiophene) are proposed. These are given in Table II. It should be emphasized that these assignments are not established with certainty but that the principles invoked in developing them are believed to be correct. Signal 4 is believed to be due solely to rrrr, mrrm, rmmr or mmmm because its relative intensity is 1/32 of the combined H₂- plus H₄-resonance area. We are assuming that it is due to mrrm and that the shielding responsible for its occurrence at highest field in the 9:6:1 pattern is

Table II

Pentad Assignments for H₂- and H₄-Ring Proton Resonances in the 300 MHz 1H-NMR Spectrum of Poly-(3-vinyl thiophene)

<u>Signal Number</u>	<u>Chemical Shift (ppm)</u>	<u>Pentad Assignments</u>	
		<u>H₂-proton</u>	<u>H₄-proton</u>
1	6.56		rmmr mmmm + rmmmm mmmm mmmm + mrrmm rmmr + rrrr rrrr
2	6.47	rmmr mmmm + rmmmm mmmm mmmm + mrrmm rmmr + rrrr rrrr	mrrm + mrrm rmmr + mrrm rrr + mrrr
3	6.30	mrrm + mrrm rmmr + mrrm rrr + mrrr	mrrm
4	6.18	mrrm	

one-half as effective for pentads with only one *rm* (or *mr*) terminal dyad (*mrmr* + *mrmm*, *mrmr* + *rmmr* and *mrrr* + *rrrm*) and is insignificant for the other pentads. To proceed further, it will be necessary to study stereoregular forms of poly-(3-vinyl thiophene), epimerized products derived from the stereoregular polymers, and model oligomers and to attempt RIS or similar modeling. It should be pointed out that several attempts were made in this study to prepare stereoregular poly-(3-vinyl thiophene) by ionic polymerization(15,18). These ended in failure because the polymers were either not stereoregular or else no polymer was obtained.

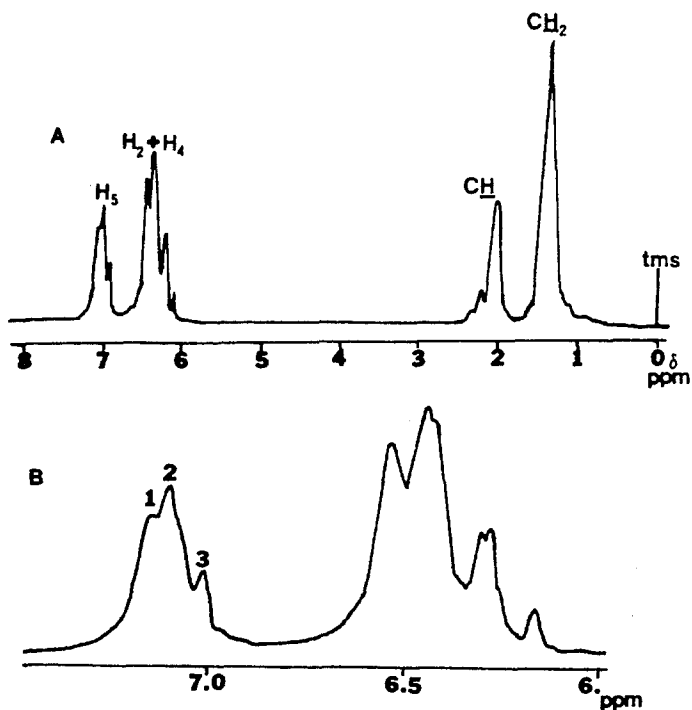
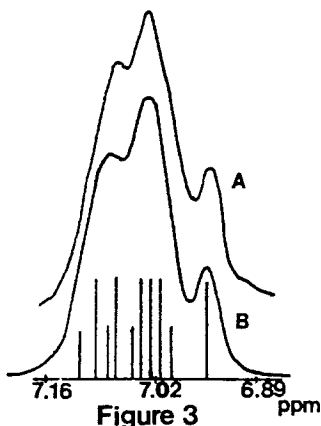


Figure 2

- A) 600 MHz ¹H-NMR spectrum of poly-(2-vinyl thiophene), 5% w/v solution in CDCl₃ recorded at ambient temperature
 B) 900 Hz horizontal expansion of the ring proton resonances

With the hope that improved definition of the various proton resonance patterns would be obtained, the 600 MHz ^1H -NMR spectrum of poly-(3-vinyl thiophene) was recorded. It is shown in Figures 2A and 2B. The ($\text{H}_2 + \text{H}_4$)-proton resonance region contains somewhat more fine structure than is present in the 300 MHz spectrum, but it is not sufficiently well developed to enable additional information to be obtained. The H_5 -proton resonance pattern is better defined than in the 300 MHz spectrum. It consists of three signals. A simulation of this pattern, which is not considered unique, is shown in Figure 3. The most useful feature of the simulation is the fact that the highest field signal (designated 3) has an area that is 1/16 of the total area. This suggests that it may be due to mrrm (or mrrm or rrrr or mrrm) stereosequences and that the three resonance areas that are evident in this pattern result from stereosequence effects.



Simulation of the H_5 ring proton resonance:
 A) Actual spectrum B) Computer simulation

Conclusion

While more definite signal assignments await the synthesis of a stereoregular poly-(3-vinyl thiophene), the evidence and arguments presented above indicate that poly-(3-vinyl thiophene), synthesized by free radical initiation, has an atactic stereochemistry.

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