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Preliminary analysis of the 300 MHz ^{1}H-NMR spectrum of poly(5-chloro-2-vinylthiophene)

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Summary

The 300 MHz ^{1}H-NMR spectrum of free radical initiated poly(5-chloro-2-vinylthiophene) was obtained and analyzed. The spectrum was found to be similar to that of poly(2-vinylthiophene) and was interpreted in a like fashion. The spectrum was found to be consistent with that of a polymer having atactic stereochemistry.

Introduction

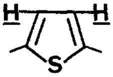
Previous work concerning the ^{1}H-NMR spectra of polyvinylheterocycles, synthesized via free radical initiation, has shown that such polymers have atactic stereochemistries (1-4). Additionally, work on ring substituted polystyrenes has shown that ring substitution can have a significant effect on the polymer's ^{1}H-NMR spectrum (5, 6) with features previously obscured by signal overlap becoming evident. In order to more fully assess the effect of ring substitution (substitution in addition to the vinyl group) on the ^{1}H-NMR spectrum and stereochemistry of vinylheterocyclic polymers, we synthesized polymers of some substituted vinylthiophenes (4) and examined their ^{1}H-NMR spectra. This paper summarizes our preliminary results for poly(5-chloro-2-vinylthiophene).

Experimental

General

All solvents were reagent grade and were used as received. The 300 MHz ^{1}H-NMR spectrum was recorded using a Bruker AC 300 spectrometer operating the FT mode. The spectrum was obtained at ambient temperature on a 7% w/v solution in $CDCl_3$. Tetramethylsilane was used as an internal standard. Individual resonance areas were determined by cutting and weighing tracings of the resonances made on high quality paper. Molecular weight measurements were made with a Waters 150 ALC/GPC equipped with 10^6, 10^5, 10^4, 10^3, 500 and 100 A ultrastyragel columns. Numerical values were obtained by comparison to a polystyrene calibration curve.

Monomer Synthesis

The monomer was synthesized by dehydration of the secondary alcohol formed by the $NaBH_4$ reduction of 5-chloro-2-thienyl ketone (Aldrich) via the dehydration procedure of Brooks (7). The yield of monomer was 75%. The monomer was purified by distilling three times from CaH_2 with the last distillation taking place immediately before use. B.p. = 55-56^{o}/6.0 mm (lit. b.p. = 78^{o}/10 mm) (8). ^{1}H-NMR, $CDCl_3$, δ 5.00-5.50 (2H, AB quartet, $-CH{=}\underline{CH_2}$); δ 6.45-6.55 (1H, multiplet, $-\underline{CH}{=}CH_2$); δ 6.60-6.85 (2H, multiplet, ).

Polymer Synthesis

The polymer used in this study was synthesized by charging 5.0g of monomer into a clean, dry screw cap vial. Recrystallized AIBN (CH_3OH) was then added in 0.8 wt % quantity. The monomer was sparged with dry nitrogen while cold (-40^{o}C) to minimize loss by evaporation (< 1%), and the vial was tightly capped with a teflon lined cap and placed in a thermostated water bath (65^{o}) for 7 hrs. The polymerization was terminated by removing the vial from the bath, cooling to ambient temperature with cool water, and adding 5 ml of cold CH_3OH. The polymer was purified by twice reprecipitating from $CHCl_3$ solution into excess CH_3OH. The polymer was dried in vacuo at 35^{o} for 72 hr and conversion was determined gravimetrically. The poly(5-chloro-2-vinylthiophene) used for the NMR measurements in this report had M_n = 6800, M_w = 13000 and M_w/M_n = 1.91. The conversion was 21%.

Results and Discussion

The 300 MHz ^{1}H-NMR spectrum of poly(5-chloro-2-vinylthiophene) (5ClVT), is shown in Figure 1. Resonance area assignments are as shown in the Figure (9). The resonance area assigned to the H_1 ring proton occurs as a three peak pattern (A, B, C in Figure 1). The fractional and relative intensities as well as chemical shifts of peaks A, B and C are summarized in Table 1.

The H_1 resonance pattern for 5ClVT is very similar to the H_1 resonance pattern for poly 2- and 3-vinylthiophene synthesized by free radical initiation (1, 2), with the exception that the pattern is somewhat less well resolved in the present case. For poly(2-vinylthiophene)

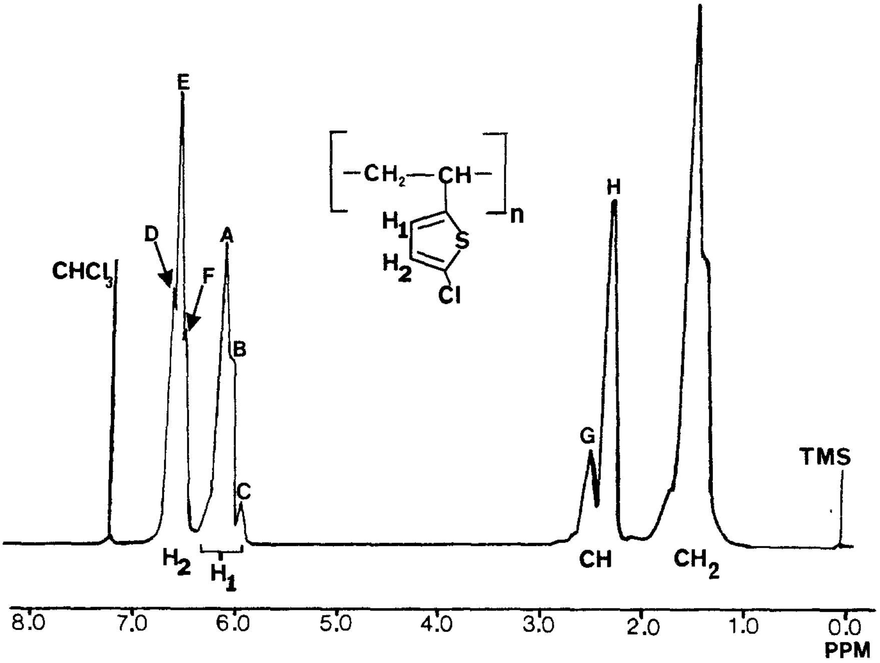


Figure 1

The 300 MHz ^{1}H-NMR Spectrum of Poly(5-Chloro-2-Vinylthiophene)

TABLE 1

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

Peak	Chemical Shift (ppm)	Fractional Intensity[a]	Relative Intensity
A	6.19	0.750 + .150	12
B	6.10	0.190 + .040	3
C	5.95	0.063 + .007	1

a. Fractional Intensity = intensity of a given signal/ total intensity of all signals in the resonance pattern.

peaks A, B and C occured in a 9:6:1 (A:B:C) relative intensity ratio. For an atactic polymer there are 16 pentads all having equal concentrations; so any resonance pattern in the NMR spectrum of an atactic polymer that reflects a sensitivity to pentad stereosequences will have signals that have relative intensities which sum to 16. For poly 2- and 3-vinylthiophenes then, the H_1 resonance pattern was attributed to a pentad stereosequence sensitivity and was assigned accordingly. In the present case the relative intensities of A, B and C are not in a 9:6:1 ratio, but the sum of the relative intensities is 16. Therefore, the H_1 resonance pattern of 5ClVT can be attributed to combinations of signals from pentad stereosequences. The most upfield peak, peak C (relative area = 1) is reasonably well resolved and its fractional intensity can be measured with a good degree of accurracy. The fractional intensity can then be used to calculate a P_m value which provides a measure of polymer tacticity. A P_m value of approximately 0.50 will be obtained if the polymer is atactic. In earlier work on polyvinylthiophenes signals corresponding to peak C were assigned to the rrrr pentad (1-3). Based on more recent work (10) however, it seems more reasonable to assign this peak to the mrrm pentad. In any case, P_m value calculated from the fractional intensity of peak C is 0.50 ± .06. This value strongly indicates that 5ClVT is a perfectly atactic polymer. Support for this assertion can be obtained by examining the resonance pattern of the other protons in the spectrum. The H_2 proton resonance occurs in a three peak pattern, D, E and F in the Figure. The relative intensity ratio of these three peaks is, within experimental error 1:2:1 (D:E:F). The corresponding fractional intensities are D = 0.25 ± .05, E = 0.53 ± .11 and F = 0.22 ± .05. This is the relative intensity ratio expected for triad stereosequences in an atactic polymer. Based on assignments made previously (1, 2, 10, 11) peaks D, E and F were assigned to the following triads; D = mm, E = (rm + mr) and F = rr. A P_m value calculated from the fractional intensity of peak D is equal to 0.50 ± .09. Again, a strong indication that 5ClVT is an atactic polymer. The methylene protons appear to be sensitive to polymer stereochemistry, but the peaks were too overlapped for any reasonable assignments to be made. The methine proton resonance occurs as a two peak pattern (G and H in Figure 1). The relative intensity ratio of these two peaks is 1:3, G:H. The corresponding fractional intensities are G = 0.24 ± .03 and H = 0.76 ± .08. In previous work (1-4) this pattern was interpreted in terms of triad stereosequences, with the downfield peak (G) being assigned to the mm triad and the upfield peak (H) being assigned to the rr and (mr + rm) triads. For an atactic polymer the relative intensities would be expected to be in a 1:3 ratio, which they are in this case. A P_m value of 0.49 ± .06 can be calculated from the fractional intensity of peak G. The relative and fractional intensities of the methine signals support the assertion that 5ClVT is an atactic polymer.

Based on pentad assignments previously developed for polystyrene (2, 10, 11) peak assignments for the H_1 proton resonance are proposed as shown in Table 2. These assignments are tentative but, based on previous arguments, are believed to be reasonable (2). The peaks are assigned as containing the pentads listed, no particular order has yet been established.

TABLE 2

Peak Assignments for the H_1 Proton Resonance

Peak	Chemical Shift	Pentad Assignments
A	6.19	rmmr mmmr + rmmm mmmm mmrm + mrmm rmrr + rrmr rrrr
B	6.10	mmrm + mrmm rmrm + mrmr rrrm + mrrr
C	5.95	mrrm

Conclusions

From the data presented in this paper, 5ClVT, when synthesized by free radical initiation is a perfectly atactic polymer in terms of stereochemistry. However, it must be pointed out that this polymer was synthesized under only one set of experimental conditions and the ^{1}H-NMR spectrum was obtained using only one set of conditions. If conditions were varied polymer tacticity might also vary, but, previous experience with other polyvinylheterocycles (1, 2, 12) has shown that polymer stereochemistry remains the same over a wide range of synthesis conditions. Additionally, a wide range of spectrometer conditions did not reveal significantly more detail in the ^{1}H-NMR spectra of the polyvinylheterocycles. Changes in initiator type (anionic, cationic) do significantly alter polymer stereochemistry, and initiation via these routes is currently being investigated in order to more firmly establish triad and pentad assignments.

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