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A preliminary analysis of the 300 MHz ^{1}H-NMR spectra of poly(4-bromo-2-vinylthiopene) and poly(5-bromo-2-vinylthiopene)

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Summary

The 300 MHz ^{1}H-nmr spectra of poly(5-bromo-2-vinylthiophene) and poly(4-bromo-2-vinylthiophene) are presented and analyzed in terms of polymer stereochemistry. In both cases, the spectra could be explained in terms of the polymers having a Bernoullian, atactic stereochemistry.

Introduction

Previous work has shown that the homopolymers of 2- and 3-vinylthiophene, when synthesized via free radical initiation, have an atactic stereochemistry (1-3). Also, work on ring substituted polystyrenes has shown that ring substitution can have a significant impact on the ^{1}H-nmr spectrum of the polymer (4, 5) with features normally hidden becoming evident. in order then to assess the effect of ring substitution, i.e. substitution in addition to the vinyl group, on the stereochemistry of vinylthiophene polymers and on their ^{1}H-nmr spectra we synthesized homopolymers of bromo substituted 2-vinylthiophenes. This paper summarizes our preliminary analysis of the 300 MHz ^{1}H-nmr spectra of these polymers.

Experimental

General

All solvents were reagent grade and were used as received. The ^{1}H-nmr measurements were made with a Bruker AC 300 spectrometer operating in the FT mode. The spectra were obtained at ambient temperature on 5-7% w/v solutions in $CDCl_3$. Tetramethylsilane was used as an internal standard. 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 150 ALC/GPC equipped with 10^6, 10^5, 10^4, 10^3, 500 and 100 A ultrastyragel columns. Numerical values for the molecular weights were obtained by comparison to a polystyrene calibration curve.

Monomer Synthesis

The monomers were synthesized by purlished procedures (6, 7) and were purified by three distillations from CaH_2. The monomers had boiling points and ^{1}H-nmr spectra that matched those of authentic samples (6-9).

Polymer Synthesis

Polymerizations were performed by charging the desired quantity of freshly distilled monomer (3g) into a clean, dry screw cap vial. Recrystallized AIBN (CH_3OH) was added at the 0.7 wt % level. The monomer was sparged with dry N_2 while cold (-40°C) to minimize evaporation loss, and the vial was then sealed with a teflon lined screw cap. The vial was then placed in a thermostated water bath for the desired length of time. The polymerization was terminated by removing the vial from the bath and adding 4-5 ml of cold CH_3OH to the contents of the vial. The polymer was purified by reprecipitation from $CHCl_3$ solution into excess CH_3OH, a process that was repeated twice. The polymer was dried in a vacuum oven at 35°C for 72h and the conversion was determined gravimetrically. Table 1 summarizes the polymerization conditions used, conversions, and molecular weights obtained.

TABLE 1

Polymerization Conditions, Conversions and Molecular Weights

Polymer[a]	Pzn Temp. (0^o)	Pzn Time (h)	% Conv. (wt %)	M_n	M_w	M_w/M_n
5BrVT	65	6.0	26.0	7900	14700	1.86
4BrVT	65	6.0	41.5	8500	16800	1.98

a. 5BrVT = poly(5-bromo-2-vinylthiophene); 4BrVT = poly (4-bromo-2-vinylthiophene).

Results and Discussion

Figure 1A shows the full scale spectrum of poly(4-bromo-2-vinylthiophene). The resonances are assigned as shown in the Figure (8, 10). The upfield ring proton resonance, H_1 (shown expanded in Figure 1B), occurs in a pattern that is very similar to the upfield ring proton resonance patterns in poly 2- and 3-vinylthiophenes. In fact, it is virtually identical to the pattern observed for poly(2-vinylthiophene), with slightly more detail observable in the most upfield peak (peak C) in the present case (2, 3).

For both poly 2- and 3-vinylthiophenes the relative intensities of the 3 peaks in the H_1 resonance was 9:6:1 (A:B:C). Since there are 16 pentads of equal intensity for a Bernoullian, atactic polymer, any resonance pattern reflecting a pentad sensitivity in the nmr spectrum of such a polymer, will have relative signal intensities that sum to 16. Therefore, for poly 2- and 3-vinylthiophene, the H_1 resonance pattern was assigned as reflecting a sensitivity to pentad stereosequences for a Bernoullian, atactic polymer.

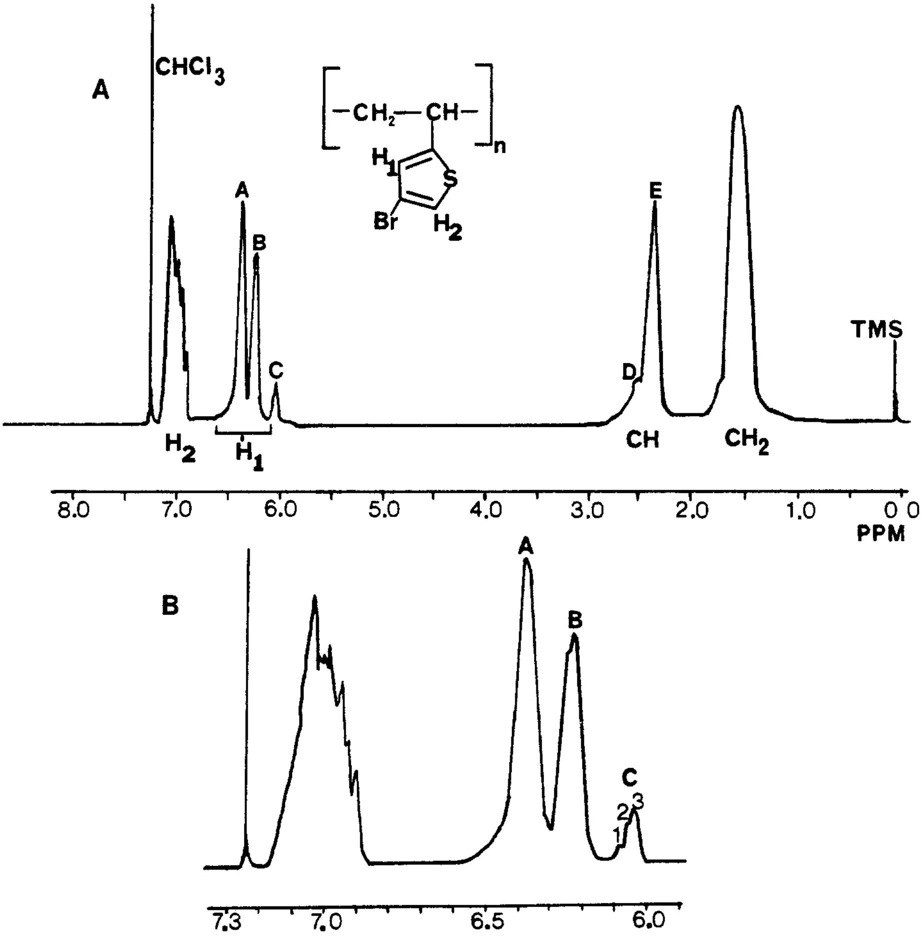

Figure 1

300 MHz ^{1}H-nmr spectrum of poly(4-bromo-2-vinylthiophene);
A) Full spectrum; B) Expansion of ring proton resonances.

The chemical shifts, fractional intensities and relative intensities for the peaks in the H_1 proton resonance of 4BrVT are given in Table 2. The relative intensities of the individual resonances are the same as those in the cases of poly 2- and 3-vinylthiophenes and can therefore be assigned in a like manner, i.e. as reflecting a sensitivity to pentad stereosequences.

TABLE 2

Chemical Shifts, Fractional Intensities and Relative Intensities for the H_1 Resonance Pattern of 4BrVT

Resonance	Chemical Shift (ppm)	Fractional[a] Intensity	Relative Intensity
A	6.38	0.570 ± .030	9
B	6.25	0.370 ± 0.20	6
C	6.05	0.063 ± .004	1

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

Examination of the ring proton resonance patterns of poly(5-bromo-2-vinylthiophene), Figures 2A and 2B, reveals a pattern of resonance for the H_1 protons, that while less well resolved, is very similar to the H_1 resonance pattern of 4BrVt. The chemical shifts, fractional intensities and relative intensities of the peaks in the H_1 resonance area of 5BrVT are summarized in Table 3.

TABLE 3

Chemical Shifts, Relative Intensities and Fractional Intensities for the Peaks in the H_1 Resonance of 5BrVT

Polymer	Peak	Chemical Shift (ppm)	Fractional Intensity	Relative Intensity
5BrVT	A	6.18	0.600 ± .080	10
5BrVT	B	6.09	0.330 ± .050	5
5BrVT	C	5.93	0.061 ± .008	1

The peaks in the H_1 resonance pattern for 5BrVT do not occur in the 9:6:1 relative intensity ratio of the H_1 resonance pattern of 4BrVT. However, the sum of their relative intensity ratios is 16. Therefore, the H_1 resonance pattern for 5BrVT most likely also reflects a sensitivity to pentad stereosequences. The most upfield peak (peak C) is reasonably well seperated from the remaining H_1 resonance. Consequently, peak C's area, hence fractional intensity, can be measured with relatively hich

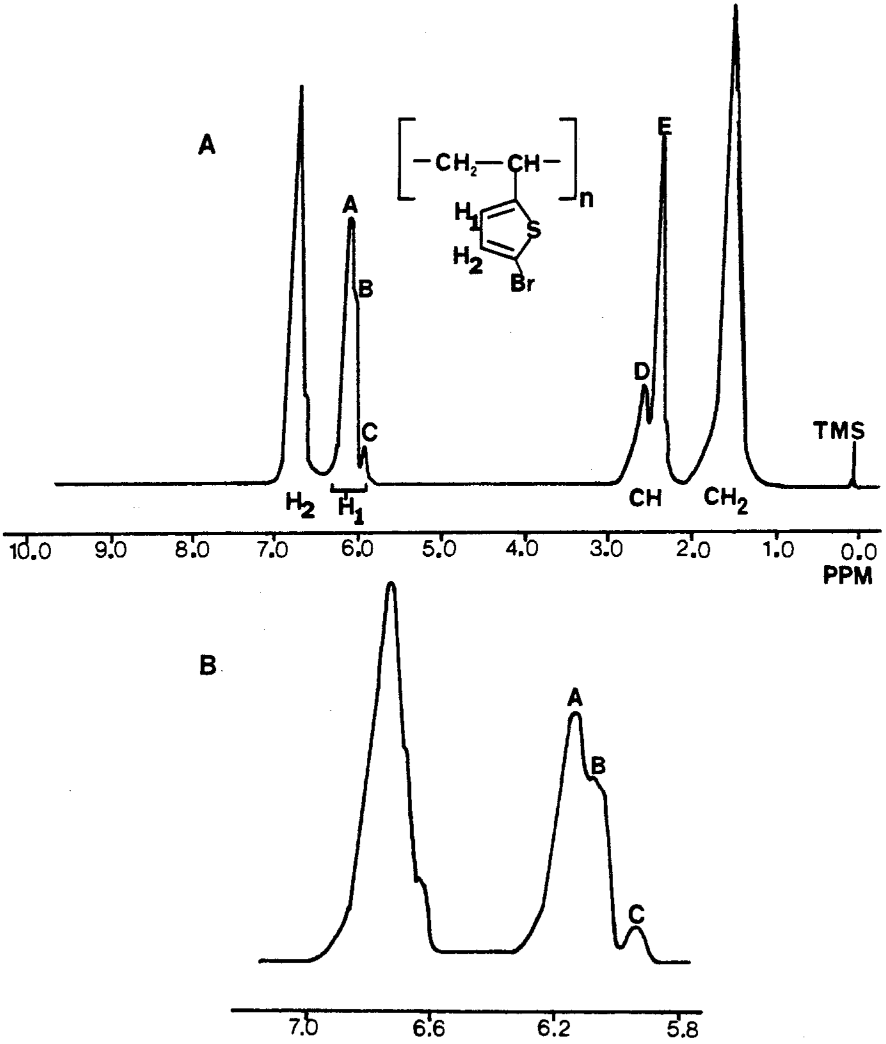

Figure 2

300 MHz ^{1}H-nmr spectrum of poly(5-bromo-2-vinylthiophene); A) Full spectrum; B) Expansion of the ring proton resonance.

accuracy. Also, since the H_1 resonance pattern for 4BrVT and 5BrVT has been interpreted as reflecting a pentad stereosequence sensitivity for Bernoullian, atactic polymers, then peak C in both cases, is due to a pentad of singlet intensity (11). Based on arguments previously advanced (2, 3, 12) peak C can be assigned to the rrrr pentad. The fractional intensity of peak C can now be used to calculate a P_m (11) value for 4BrVT and5BrVT. The P_m value reflects the probability of obtaining a meso placement of a monomer unit adding to a growing chain end for a Bernoullian process.

The nearer the value of P_m to 0.50 the more atactic a polymer is in terms of stereochemistry. The P_m values obtained from peak C of the H_1 resonances of the polymers examined in this study are summarized in Table 4.

TABLE 4

P_m Values

Polymer	P_m
4BrVT	0.50 ± .04
5BrVT	0.50 ± .07

The values of P_m obtained strongly indicate that both the polymers are perfectly atactic, Bernoullian polymers in terms of stereochemistry. Support for this assertion can be obtained by examining the resonances due to other protons in the spectra of these polymers. The H_2 proton resonance for 4BrVT appears to be sensitive to stereochemistry, but is too highly overlapped for any reasonable analysis to be made. However, peak C in the H_1 proton resonance appears to be an overlapped 3 peak pattern (Peaks 1, 2 and 3 in Figure 1B). This pattern might be due to the influence of heptad stereosequences 913). The fractional intensities of the three peaks in this pattern, based on comparison to the total H_1 resonance are 1 = .0063 ± .0006, 2 = 0.013 ± .002 and 3 = 0.037 ± .005, these values correspond to a relative intensity ratio of 1:2:6 (peak 1 : peak 2 : peak 3). If peak C is due to the rrrr pentad of an atactic polymer, then a splitting of peak C into pure heptad pattern would yield peaks in a relative intensity ratio of 1:2:1 (rrrr centered heptads). Obviously, this is not so for peaks 1, 2 and 3 in the present case. The observed pattern is most probably due to an incomplete resolution being obtained with the spectrometer power and conditions employed in this work or possibly due to the influence of higher order sequences which also cannot be resolved under the conditions employed. In any case, if it is assumed that peak 1 is due to an rrrr centered heptad of singlet intensity, a P_m value calculated from peak 1's fractional intensity is equal to 0.47 ± .04 which again supports the contention that 4BrVT is a Bernoullian, atactic polymer. The H_2 resonance of 5BrVt appears to be insensitive to polymer stereochemistry.

The aliphatic proton resonances for each polymer are assigned as shown in the Figures. The methylene proton resonances for 5BrVT and 4BrVT occur as broad envelopes that appear to have no sensitivity to polymer stereochemistry. The methine proton resonance occurs as a two peak pattern, with a small shoulder evident on the downfield peak in the 4BrVT case, for both of the polymers. The fractional intensities, chemical shifts and relative intensities of these signals are summarized in Table 5.

TABLE 5

Chemical Shifts, Fractional Intensities and Relative Intensities of the Peaks in the Methine Proton Resonances of 4BrVT and 5BrVT

Polymer	Peak	Chemical Shift (ppm)	Fractional Intensity	Relative Intensity
4BrVT	D	2.54	0.19 ± .04	1
4BrVT	E	2.35	0.81 ± .10	4
5BrVT	D	2.62	0.27 ± .04	1
5BrVT	E	2.42	0.73 ± .08	3

For poly 2- and 3-vinylthiophenes this pattern was interpreted in terms of a triad sensitivity for an atactic polymer (2, 3, 9).

The downfield peak was assigned to the mm-triad and the upfield peak to the rr and (mr + rm) triads. For an atactic polymer, then the relative intensity ratios of the two signals should be 1:3, and a P_m value can be calculated from the fractional intensity of the mm peak. In the present case the peaks from the methine region of 5BrVT are in the relative intensity ratio of 1:3 and P_m value calculated from the fractional intensity of the downfield peak is 0.52 ± .08, consistent with the results obtained from analysis of the aromatic proton resonances of this polymer, i.e. that the polymer has an atactic stereochemistry. The relative intensity ratio for peaks D and E in the spectrum of 4BrVT is 1:4. This most probably represents resolution that is not as complete as that for these same peaks in the spectrum of 5BrVT. The relative intensity ratio is not so radically different from 1:3 so that a completely different assignment of the peaks is necessary. The downfield peak is assigned to the mm-triad and the upfield peak to the rr and (mr + rm) triads. A P_m value calculated from the fractional intensity of peak D is 0.44 ± .09, within experimental error this result is consistent with the results obtained from the analysis of the aromatic proton resonances of this polymer, i.e. 4BrVT is an atactic polymer.

Conclusion

preliminary analysis of the ^{1}H-nmr spectra of radical initiated halogen ring substituted polyvinylthiophenes shows that the polymers have spectra consistent with a Bernoullian, atactic polymer stereochemistry. It must be stressed that this is a preliminary analysis, all the polymers were synthesized under only one set of experimental conditions and all the spectra were obtained under only one set of experimental conditions. However, previous experience with similar systems has shown that variation of synthesis and spectrometer conditions within a certain broad range does not significantly alter the stereochemistry of the resulting polyvinylheterocycle. However, a change in initiator type (anionic, cationic) can significantly alter polymer stereochemistry. Investigation of different initiation modes, in the hope of producing more stereoregular polymers so definate peak assignments can be made, is currently underway as well as ^{13}C-nmr experiments to more accurately define polymer stereochemistry.

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