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

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Summary

The title polymer was synthesized by free radical initiation in bulk and its ^{1}H-NMR and ^{13}C-NMR spectra were recorded and analyzed in terms of polymer stereochemistry. The aliphatic region of the proton spectrum shows an unusual multiplicity due to stereochemical sensitivity and the resonances of several of the ring carbons displayed a sensitivity to higher order stereosequences. The analysis of these spectra showed that poly(5-vinyl-2,2'-thiophene) is an atactic polymer.

Introduction

Over the last few years our research has been concerned with the synthesis and characterization, in terms of polymer stereochemistry, of poly (vinyl heterocycles) (1-5 and references therein). In all cases we have found that when vinyl heterocyclic monomers are polymerized free radically the resulting polymer has an atactic stereochemistry. We have also found that ring substitution (in addition to the vinyl group) can have a significant effect on the nmr spectra of the resulting polymer. The type and magnitude of the effect depends on the nature and position of the substituent group. The nature of the group refers to the electronic characteristics of the substituent (electron withdrawing or releasing e.g.) as well as to the steric bulk of the substituent. Because electronic effects can alter the flow of electrons in the molecular orbitals of a monomer unit these effects can have a significant impact on the appearance of the nmr spectra of a given material (6,7). However, steric effects which force different conformations on the polymer chain and/or promote intrachain (or interchain group interactions can also have a profound effect on the appearance of the nmr spectra of a given species, in fact at times the steric effect of a substituent on the spectra can be more dramatic than any electronic effect(s) (8,9). In order to investigate the effect of a bulky substituent on the nmr spectra of vinyl thiophene polymers and to supplement our accumulated database on vinyl heterocyclic polymers, we synthesized and polymerized 5-vinyl-2,2'-bithiophene (5VBiT) free radically and analyzed its nmr spectra in terms of stereochemistry. This paper presents our preliminary results.

Experimental

General

All solvents and reagents used in this study were reagent grade and used without further purification. The nmr spectra were obtained on $CDCl_3$ solutions of polymer (10-15% w/v) at ambient temperature using a Varian Gemini 300 FT NMR; TMS was used as an internal standard. Polymer molecular weights were measured as previously described (1-5). The glass transition temperature was measured with a TA Instruments 2910 DSC at a heating rate of 10°C/min.

Monomer Synthesis

The monomer was synthesized as previously described (10).

Polymer Synthesis

The polymer synthesis was performed in bulk at 80°C (m.p. of 5VBiT = 59-60°). Four grams of monomer were weighed into a clean dry screw cap vial equipped with a magnetic stirring bar. The initiator (AIBN, 0.75 wt %) was then added and the vial was sealed with a teflon lined screw cap. The vial was placed in a thermostated water bath at 80°C and was kept at this temperature until the viscosity of the contents prevented any further stirring (2.0 h). The vial was removed from the bath and cooled to room temperature. The contents of the vial were dissolved in $CHCl_3$ and added to a 7-fold excess of CH_3OH. The polymer was purified by reprecipitating it 4 times from $CHCl_3$ solution into CH_3OH. Yield = 65.3%. M_n = 3100, M_w = 6600, M_w/M_n = 2.12, Tg = 68°C.

Results and Discussion

The ^1H-NMR spectrum and a linear expansion of the aliphatic and aromatic resonances are shown in Figure 1. While the aromatic proton resonance (1B) shows some multiplicity which may indicate sensitivity to stereochemistry, the pattern is insufficiently resolved for any reasonable estimates of tacticity to be made from it. On the other hand the aliphatic resonance (Figure 1C) shows considerable multiplicity and enough resolution for reasonable estimates of peak areas to be made. (Peak areas were measured by electronic integration and by cutting and weighing tracings of the peaks. This methodology was used for all area measurements made in this work). The aliphatic resonances are assigned as shown in the Figure; with the methine proton resonance occurring as a 7 peak pattern (A-G in the Figure). The relative intensity ratio of these peaks is 1:3:2:2:2:2:52, A:B:C:D:E:F:G. The sum of the relative intensities is 64 which is how many heptads would be expected for an atactic polymer (11). The resolution is not sufficient for a detailed assignment to be made in terms of heptads, but calculation of a P_m value from the fractional intensity of peak A (0.016 ± .002) yields 0.50 ± .07, this is the value of P_m expected for an atactic polymer.

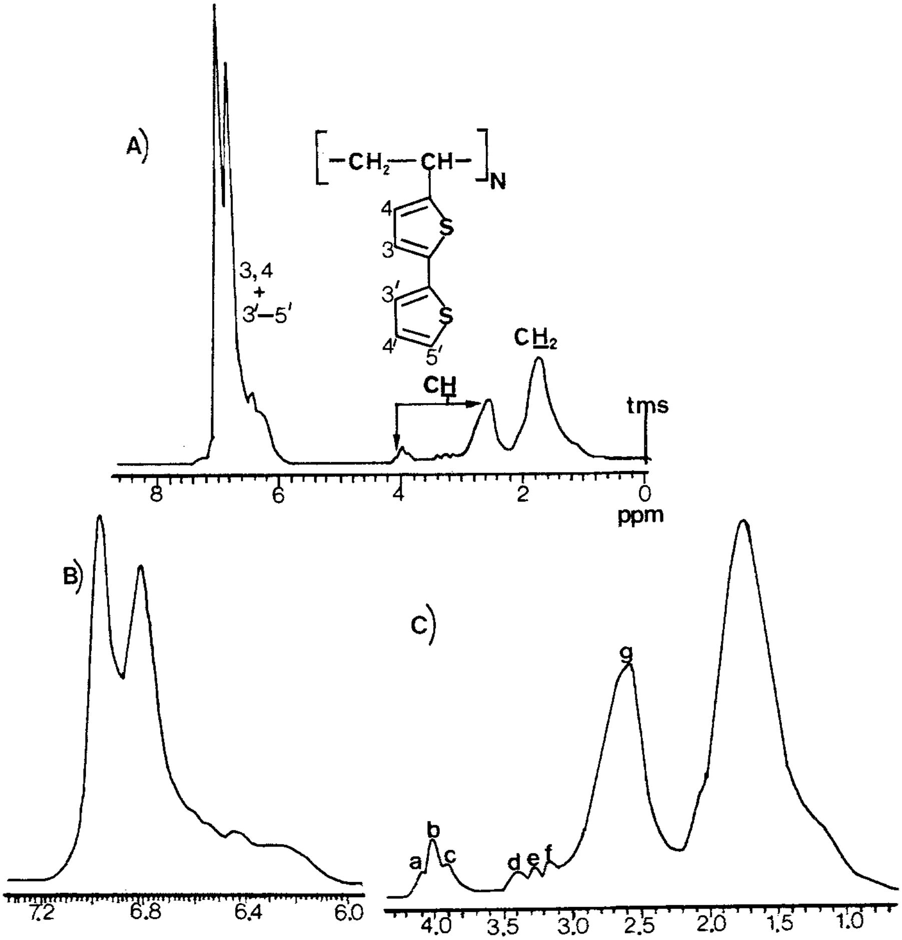

Figure 1

300 MHz ^{1}H-NMR Spectrum;
A) Full Scale Spectrum; B) Linear Expansion of the Ring Proton Resonance; C) Linear Expansion of the Aliphatic Proton Resonance

The ^{13}C-NMR spectrum of (5VBiT) and expansions of the carbon resonances of interest are shown in Figures 2 and 3. The resonances are assigned as shown in the Figure (12,13). The resonance assigned to the C_5 carbon is shown in Figure 2B.

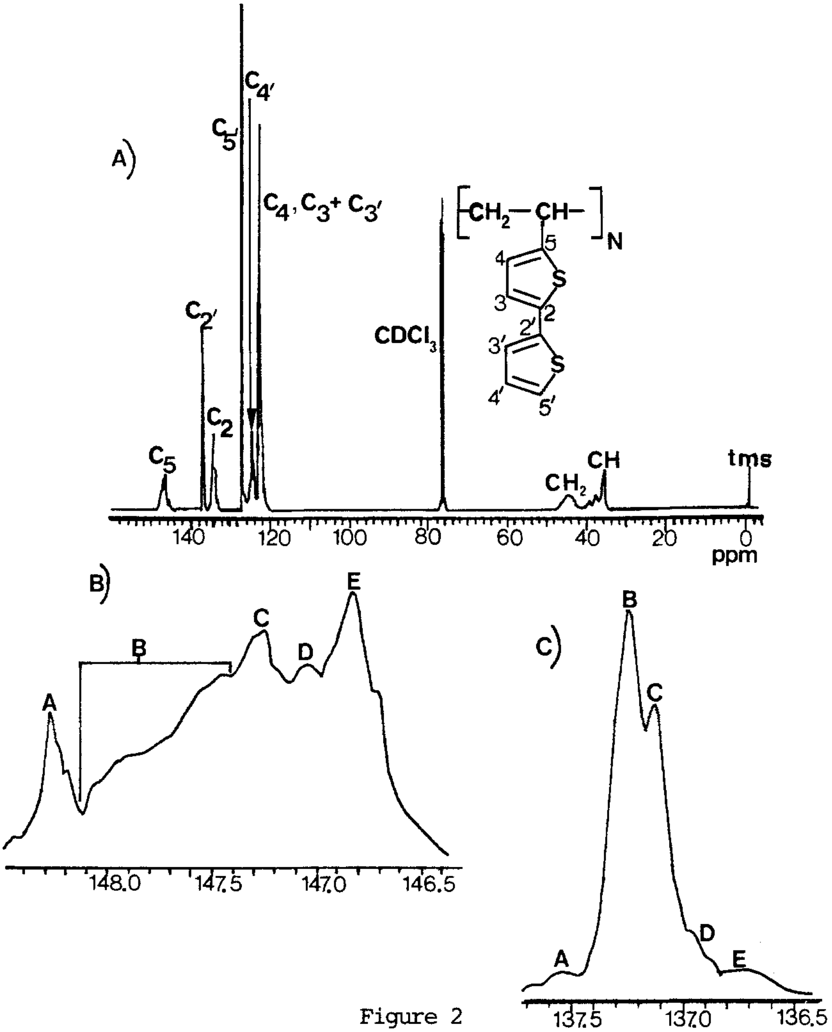

Figure 2

75.5 MHz ^{13}C-NMR Spectrum;
A) Full Scale Spectrum; B) Expansion of the C_5 Ring Carbon Resonance; C) Expansion of the $C_{2'}$ Ring Carbon Resonance

The resonance occurs as an overlapped 5 peak pattern, A-E. The relative intensity ratio of these peaks is 1:5:3:2:5, A:B:C:D:E. The sum of this ratio if 16, and since 16 pentads are expected for an atactic polymer (1-5) this pattern most probably reflects a sensitivity to pentad stereosequences. However, the resolution is not sufficient to permit detailed assignments in terms of pentads. Calculation of a P_m value from the fractional intensity of peak A (0.066 ± .007) yields 0.51 ± .05, approximately the value expected for an atactic polymer.

The resonance assigned to the C_2 carbon (Figure 2C) occurs as a 5 peak pattern also (A-E). The relative intensity ratio of these peaks is 1:18:10:2:1, A:B:C:D:E. The sum of this relative intensity ratio is 32. This total is to high to indicate a pentad sensitivity and to low for heptads. However, the fractional intensity of peak A is 0.031 ± .003, which is twice the value expected for a singlet heptad. Therefore if each relative intensity were multiplied by 2 the ratio would become 2:36:20:4:2 which sums to 64, which is the number of heptads expected for an atactic polymer. While the resolution is insufficient for any assignments in terms of heptads to be made, calculation of P_m from the fractional intensity of peak A yields $P_m = 0.50 ± .05$.

The resonance assigned to the C_2 carbon (Figure 3A) occurs as a 4 peak pattern with a relative intensity ratio of 3:2:3:1, A:B:C:D. The sum equals 9, which indicates a sensitivity to higher order stereosequences, most likely pentads with the influence of heptads (hence the total of 9). In any case, lack of resolution prevents any attempt at reasonable assignment.

TABLE 1

Assignment of the $C_{4'}$ Resonance in Terms of Pentads

Peak	Chemical Shift (ppm)	Fractional Intensity	Relative Intensity	Proposed Assignment
A	125.55	0.064 ± .006	1	rmmr
B	12.529	0.12 ± .02	2	mmmr + rmmm
C	125.03	0.12 ± .02	2	mmrm + mrmm
D	124.93	0.11 ± .02	2	mmrr + rrmm
E	124.80	0.12 ± .02	2	rmrm + mrmr
F	124.70	0.27 ± .04	4	mmmm, rmrr + rrmr, mrrm
G	124.44	0.13 ± .02	2	rrrm + mrrr
H	124.30	0.070 ± .008	1	rrrr

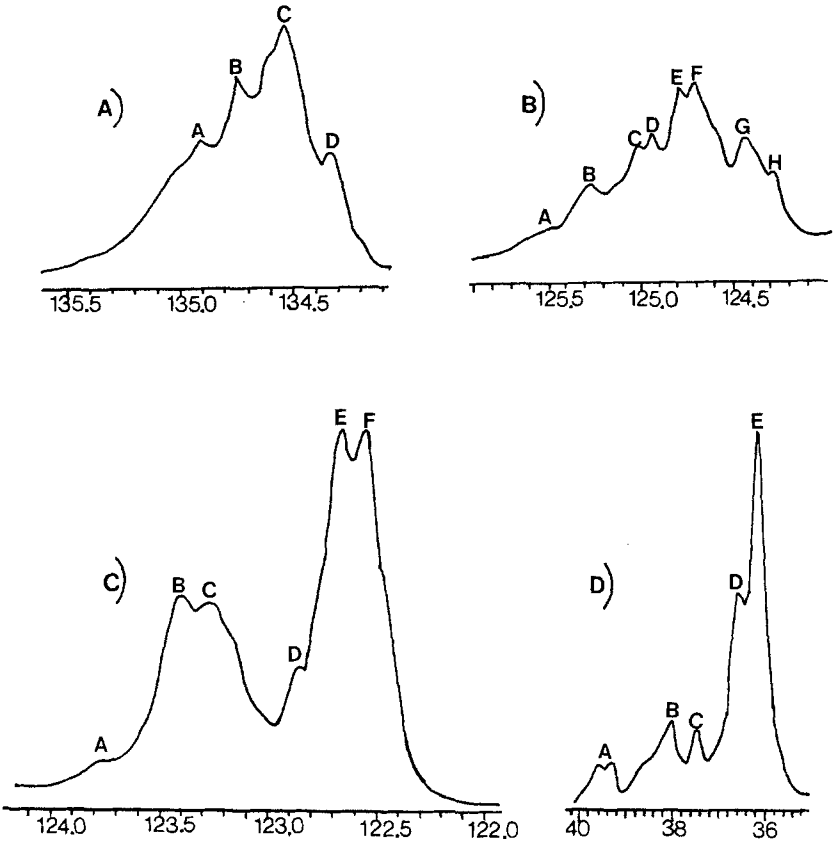

Figure 3

A) Expansion of the C_2 Ring Carbon Resonance; B) Expansion of the $C_{4'}$ Ring Carbon Resonance; C) Expension of the $C_{3'}$ + C_3 + C_4 Ring Carbon Resonance; D) Expansion of the Methine Carbon Resonance

The resonance pattern due to the $C_{4'}$ carbon (Figure 3B) occurs as an 8 peak pattern with the following relative intensity ratio: 1:2:2:2:2:4:2:1, A:B:C:D:E:F:G:H. The total of this ratio is 16 and, as previously stated, since there are 16 pentads expected for an atactic polymer, it is reasonable to assign this resonance in terms of pentads.

Tentative peak assignments for the $C_{4'}$ carbon resonance are given in Table 1. The peaks are assigned as containing the resonances given, no ordering or absolute assignments can be done or made in the absence of a stereoregular poly(5VBiT). However, the assignments are believed to be reasonable based on previous results (1-5).

An average P_m value calculated from the fractional intensities of peak A and peak H is 0.49 ± .06, within experimental error the value expected for an atactic polymer.

The resonances assigned to C_3, $C_{3'}$, and C_4 are shown in Figure 3C. The peaks in the $C_3 + C_{3'}$ resonance occur in a relative intensity ratio of 1:6:7, A:B:C. The sum of these relative intensities is 14. This is insufficient for a pentad sensitivity and in light of the results obtained from analysis of other resonances, a triad assignment is not reasonable. The resonance pattern probably is exhibiting sensitivity to higher order stereosequences (most likely pentads) but insufficient resolution prevents any type of reasonable pattern from being discerned. The C_4 carbon resonance occurs as three overlapped peaks in the relative intensity ratio of 1:3:4, D:E:F. The sum of this ratio if 8. Since the fractional intensity of peak D is ~ 0.12 ± .02 and this is the fractional intensity expected for a pentad doublet in an atactic polymer then it is reasonable to multiply the relative intensities by 2. The ratio then becomes 2:6:8 which totals 16. The overlap of these resonances makes any reasonable assignment in terms of pentads impossible, however, the pattern observed is consistent with the results obtained from other resonances i.e. poly(5VBiT) is an atactic polymer.

The methine carbon resonance, Figure 3D, is a 5 peak pattern with a relative intensity ratio of 1:3:1:4:7, A:B:C:D:E again the sum of these relative intensities is 16, which strongly indicates that the resonance pattern is displaying a sensitivity to pentad stereosequences. While signal overlap prevents any reasonably detailed assignments, peak A can, with some confidence (1-5) be assigned to the mrrm pentad. A P_m value calculated from the fractional intensity of this resonance (0.061 ± .006) = 0.49 ± .05.

Conclusions

The addition of a bulky group in the 5(2) position of vinyl thiophene has a significant effect on the ^1H- and ^{13}C-NMR spectra of the resulting polymer. The aliphatic region of the ^1H-NMR shows a multiplicity that is due to a heptad stereosequence sensitivity something unsaturated poly(vinyl thiophenes) do not show. Several of the resonances in the ^{13}C-NMR spectrum show multiplicities that are readily assignable to pentad stereosequence (also heptads, $C_{2'}$) sensitivities. While the resolution is insufficient in most cases for detailed assignments to be made, there was enough resolution for P_m values to be calculated. The P_m values were all 0.50 ± .05 which shows that poly(5VBiT) is an atactic polymer i.e. the presence of a bulky group did not cause the polymer to become stereoregular. In fact, because heptads were visible for some resonances, more confidence in the P_m value generated is warranted (11).

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