Polymer Bulletin 36, 463–469 (1996)

Polymer Bulletin

Preliminary analysis of the ^{1}H-NMR and ^{13}C-NMR spectra of poly(5-methoxy-2-vinyl thiophene)

David L. Trumbo

S. C. Johnson Polymer, S. C. Johnson & Son, Inc., 1525 Howe Street,
Racine, WI 53403-2236, USA

Received: 31 October 1995/Accepted: 20 November 1995

Summary

5-Methoxy-2-vinylthiophene was synthesized from the corresponding aldehyde. The monomer was polymerized under free radical conditions using AIBN as the initiator. High field ^{1}H-NMR and ^{13}C-NMR spectra of the polymer displayed several resonances that were sensitive to polymer stereochemistry. Analysis of these resonances showed that the polymer had an atactic stereochemistry.

Introduction

For some time we have been investigating the stereochemistry of poly-vinyl heterocycles synthesized via free radical initiation and the effects of additional ring substituents on the spectra of such polymers (1-6). In all cases investigated to date the polymers were found to have atactic stereochemistries. We have also found that the type and position of ring substituents can have a significant effect on the nmr spectra. In some cases individual resonances were more resolved and in other cases less well resolved than the corresponding resonances of the non ring substituted vinyl heterocycle polymer. The largest affects seem to be related more to the steric bulk of the substituent, at least in terms of producing more well resolved spectra. However, electronic effects are not inconsequential and in order to more fully investigate such affects we decided to study the stereochemistry of poly(5-methoxy-2-vinylthiophene).

What follows is a preliminary account of our results.

Experimental

General

All solvents were reagent grade and were used as received. The polymer nmr spectra were recorded on a Varian Gemini 300 FT spectrometer (^{1}H freq. = 3000 MHz, ^{13}C freq. = 75.5 MHz). The spectra were recorded on 10% w/v solutions of polymer in CDCl$_3$ at ambient temperature. Relative resonance areas were determined by electronic integration and by tracing, cutting out and weighing the tracings on a 5-place analytical balance. The molecular weight of the polymer was determined as previously described (1-5).

Monomer Synthesis

The aldehyde, 5-methoxy-2-thiophenecarboxaldehyde was synthesized as described in the literature (7). The boiling point and ^{1}H-NMR spectrum matched those previously recorded.

The 5-methoxy-2-vinylthiophene monomer was synthesized from the aldehyde via a Wittig reaction as described in the literature (8). The monomer was purified by distillation from CaH_2 b.p. = 74-76°C/9 mm of Hg. The structure was confirmed by ^{1}H-NMR, $CDCl_3$; δ6.78-6.60 (m, 2H); δ 6.10 (d, 1H); δ 4.99, 5.35 (AB quartet, 2H); δ3.95 (s.s., 3H).

Polymer Synthesis

The polymer was synthesized by charging 2.0 g of monomer into a clean, dry screw cap vial, followed by 0.8 wt % AIBN as initiator. The monomer-initiator solution was sparged with dry N_2 and the vial was then tightly sealed with a teflon lined screw cap. The vial was placed in a thermostated bath at 65°C and the polymerization was allowed to proceed for 6 hr. The polymerization was terminated by removing the vial from the bath and adding 5 ml of cold CH_3OH. The polymer was purified by reprecipitating it three times from $CHCl_3$ solution into CH_3OH. The polymer was dried in vacuo at 30°C for 72h and weighed to determine conversion. Conversion = 11.0%, M_n = 10900, M_w = 22000, M_w/M_n = 2.01.

Results and Discussion

Figure 1 shows the ^{1}H-NMR spectrum of poly(5-methoxy-2-vinyl thiophene) (PMT), along with a linear expansion of the ring proton resonances. The resonances are assigned as shown in the Figure (9,10). The H_4 resonance occurs as a four peak pattern in a relative intensity ratio of 1:4:6:5, A:B:C:D. The sum of this intensity ratio is 16, and since there are 16 pentads in an atactic polymer, it is logical to ascribe this pattern to pentads (1-6). While the resolution precludes a detailed assignment in terms of pentads at this time, calculation of a P_m value from the fractional intensity of peak A (0.062 ± .009), which is due to a pentad singlet, yields P_m = 0.50 ± .08. This is the value expected for an atactic polymer. The resonance pattern assigned to the H_3 proton occurs as a three peak pattern in a relative intensity ratio of 1:3:1, E:F:G. The sum of this ratio is 5, which most probably reflects sensitivity to higher order stereosequences, however resolution is insufficient for any reasonable kind of assignment to be made. The other proton resonances display little or no sensitivity to polymer stereochemistry.

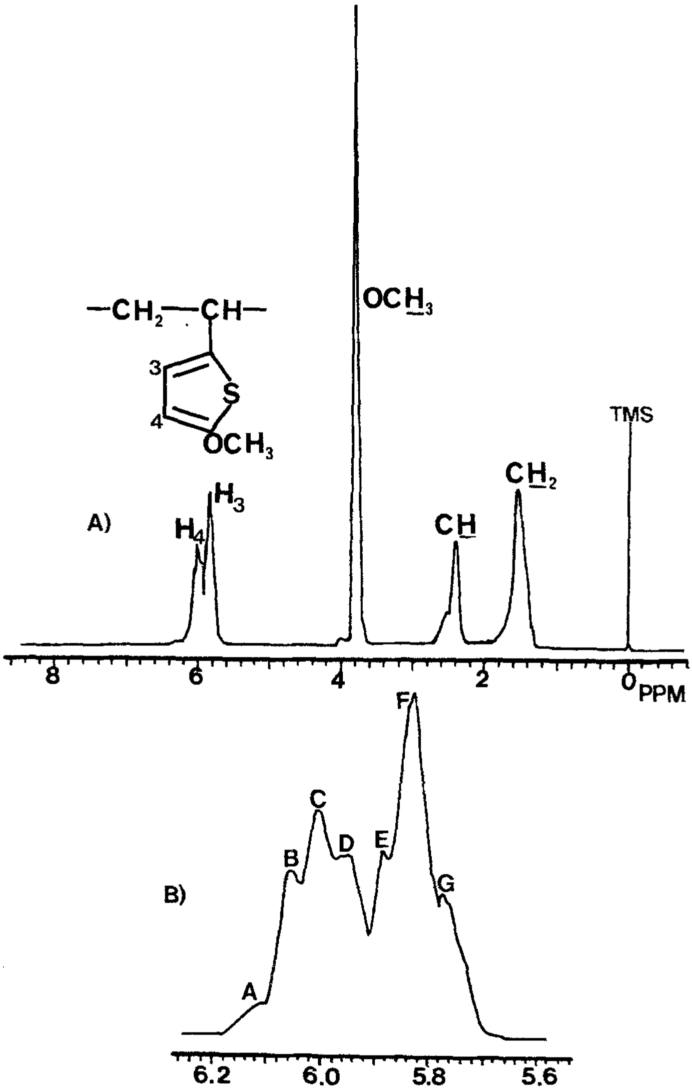

Figure 1

300 MHz ^{1}H-NMR spectrum of PMT; A) Full spectrum B) Linear expansion of the ring proton resonance

^{13}C-NMR Spectra

Figures 2 and 3 show the ^{13}C-NMR spectrum of PMT along with expansions of the resonances of interest. The resonances are assigned as shown in the Figure (11,12). The resonance due to the C_5 carbon (Figure 2B) occurs as a 5 peak pattern which is in a relative intensity ratio of 1:1:23:5:2; A:B:C:D:E. The sum of this intensity ratio is 32, which is exactly half of the value expected for the number of heptads in an atactic polymer.

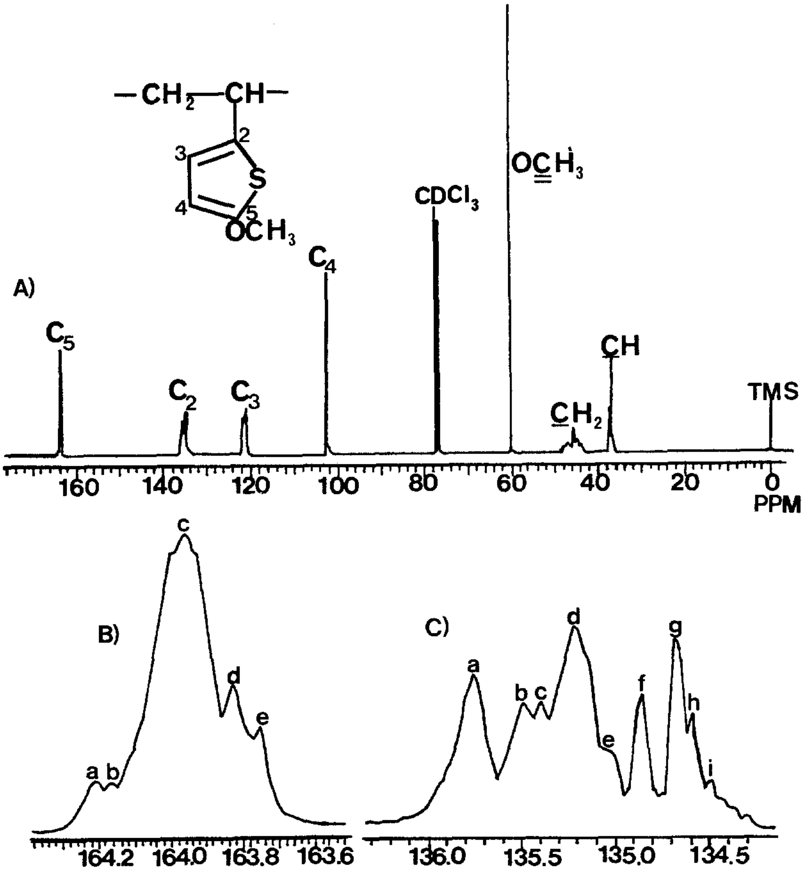

Figure 2

75.5 MHz ^{13}C-NMR spectrum of PMT; A) Full spectrum; B) Expansion of the C_5 resonance; C) Expansion of the C_2 resonance

It makes sense then to multiply all the relative intensities by two, which yields 2:2:46:10:4 as the true relative intensity ratio. While the resolution is not good enough for any assignments in terms of heptads to be made, calculation of a P_m value for the fractional intensity of peak B (0.034 ± .007) yields $P_m = 0.51 \pm 0.10$.

The C_2 carbon resonance (Figure 2C) occurs as a nine peak pattern in a relative intensity ratio of 7:4:2:9:1:3:4:1:1, A:B:C:D:E:F:G:H:I. The sum of this ratio is 32, which, as above is half the value expected for the number in heptads of an atactic polymer. Again multiplying by two gives a true relative intensity ratio of 14:8:4:18:2:6:8:2:2. While the resolution is not sufficient for detailed assignments to be made, a P_m value can be calculated from the fractional intensity of peak I (0.035 ± .005) which is due to a heptad doublet or two heptad singlets; $P_m = 0.51 \pm .08$.

The C_3 resonance (Figure 3A) occurs as a overlapped eleven peak pattern in a relative intensity ratio of 1:8:5:2:2:11:4:6:7:7:11, A:B:C:D:E:F:G:H:I:J:K. The sum of this ratio is 64, which is the number of heptads expected for an atactic polymer. The peak overlap of this resonance pattern makes a detailed assignment in terms of heptads impossible, a P_m value can be calculated from the fractional intensity of peak A (0.015 ± .001) which is certainty due to a heptad singlet and is resolved sufficiently to permit a relatively accurate area measurement; $P_m = 0.50 \pm .04$.

The methylene carbon resonance (Figure 3B) occurs in an eight peak pattern in a relative intensity ratio of 1:2:3:3:11:3:5:4, A:B:C:D:E:F:G:H. The sum of this ratio is 32 which is exactly the number of hexads expected for an atactic polymer. Again, resolution is insufficient to make detailed assignments possible, but a P_m value calculated from the fractional intensity of peak A (0.033 ± .004) is = 0.51 ± .06.

The methine carbon resonance (Figure 3C) occurs as a six peak pattern in a relative intensity ratio of 1:4:4:2:8:13, A:B:C:D:E:F. The sum of this ratio is 32. As above, the pattern was assigned to heptads multiplying each relative intensity by two yields 2:8:8:4:16:26 as the true relative intensity ratio. Calculation of a P_m value from the fractional intensity of Peak A (0.031 ± .005) yields $P_m = 0.50 \pm .08$.

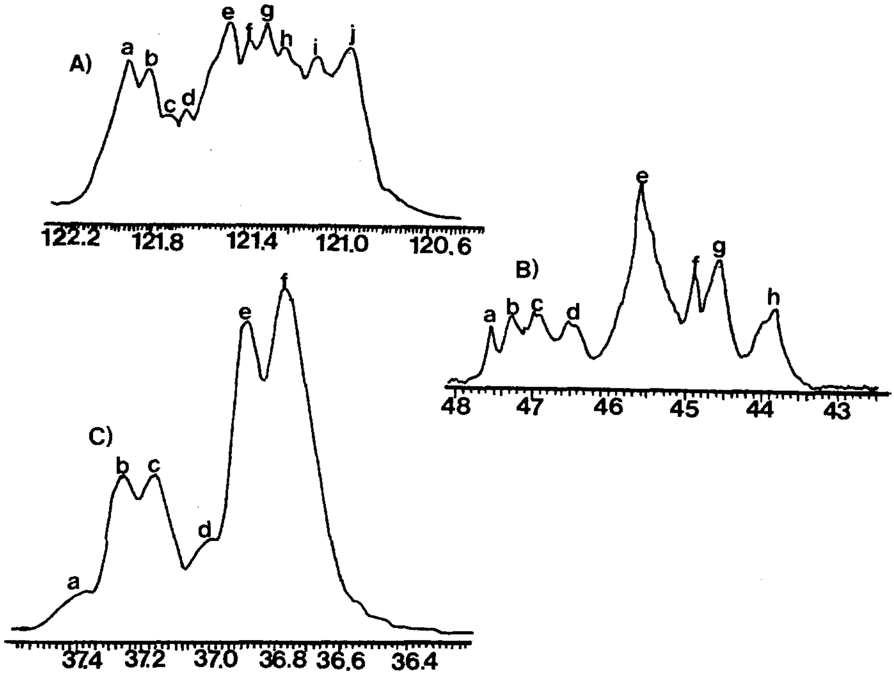

Figure 3

Expansions of: A) C_3 resonance
B) Methylene resonance; C) Methine resonance

Conclusions

5-Methoxy-2-vinyl thiophene was synthesized and polymerized via free radical initiation. The ^{1}H-NMR and ^{13}C-NMR spectra revealed several resonances that displayed sensitivity to polymer stereochemistry. No individual resonance pattern had sufficient resolution for detailed peak assignments, in terms of specific stereosequences to be made. However, P_m values could be calculated from certain fractional intensities in each resonance pattern. The P_m values were all approximately 0.50 which is the value expected for an atactic polymer. Collectively then the data shows that PMT is an atactic polymer. Because most of the resonances display sensitivity to relatively long stereosequences, the certainty regarding polymer stereochemistry is increased.

Regarding the effect of methoxy substitution on the nmr spectra; it seems that while many of the carbons and protons display sensitivity to polymer stereochemistry, this is more the result of the field strength of the spectrometer. Actually, the PMT spectra are less well resolved than the corresponding spectra of the unsubstituted polymer. This supports our contention that while inductive effects exert influence on the spectra, steric effects tend to produce more well resolved spectra (when compared to the unsubstituted polymers).

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