Polymer Bulletin 31, 687–692 (1993)

Polymer Bulletin

Preliminary analysis of the 300 MHz ^{1}H-NMR spectrum of poly(3-vinyl benzothiophene)

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Summary

Poly(3-vinyl benzothiophene) was synthesized by free radical initiation at 60° and 90°C. The 300 MHz ^{1}H-NMR spectra revealed that some of the aromatic protons were sensitive to polymer stereochemsistry. The resonance pattern fit a pentad stereosequence distribution for an atactic polymer and was interpreted in those terms. The polymer synthesized at 60°C was not significantly different in terms of stereochemistry than the polymer synthesized at 90°C.

Introduction

Previous work (1-5) has shown that vinyl heterocyclic polymers, when synthesized via free radical initiation, possess an atactic stereochemistry. Many times the spectra have proven much easier to interpret than corresponding polystyrene spectra. This was particularly true in the case of poly(2-vinyl benzofuran) (4). The proton in the 3-position of the furan ring of the benzofuran molecule had a resonance that was well separated from the remaining aromatic resonance and could therefore be more easily analyzed. In the hope of obtaining a similar result, we synthesized poly(3-vinyl benzothiophene) and examined it's high field ^{1}H-NMR spectrum. While the results obtained were not as dramatic as those for poly(2-vinyl benzofuran), a reasonable interpretation in terms of polymer stereochemistry was still possible.

Experimental

All solvents and other chemicals used in this study were reagent grade and were used as received. The ^{1}H-NMR spectra were recorded at 300 MHz using a Varian Gemini 300 operating in the FT mode. Resonance areas were determined by tracing the signals on high quality paper, cutting and then weighing the tracings on a five place analytical balance. Each area was the average of three tracings. The spectra were obtained on $CDCl_3$ solutions of the polymers (5% w/v) at ambient temperature. Tetramethylsilane was used as an internal reference. Molecular weight measurements were made with a Waters 150 ALC/GPC equipped with 10^6, 10^5, 10^4, 10^3, 500 and 100A ultrastyragel columns. Numerical values for the molecular weights were obtained by comparison to a polystyrene calibration curve.

Monomer Synthesis

The monomer was synthesized as previously described (6) and its boiling point and ^{1}H-NMR spectrum matched that of an authentic sample. The monomer was purified by twice distilling from CaH_2, the second time immediately before use.

Polymer Synthesis

The monomer (2.0g) was weighed into a clean, dry screw cap vial followed by 0.8 wt % Vazo 67. The monomer-initiator solution was cooled to -5°C and sparged with dry N_2. The vial and contents were allowed to warm to ambient temperature and were then placed in a thermostated water bath for the desired length of time. The conditions employed and results obtained are summarized in Table 1. The polymerizations were terminated by the addition of 4-5 ml of CH_3OH.

TABLE 1

Polymerization Times, Conversions and Molecular Weights

Polymer	PZN Temp. (°C)	PZN Time (hrs)	% Conv.	M_n	M_w	M_w/M_n
VBT 60[a]	60	2.5	30.0	10,000	19,900	1.99
VBT 90[b]	90	2.5	65.4	6,200	13,000	2.09

a. VBT 60 = poly(3-vinyl benzothiophene) synthesized at 60°;
b. VBT 90 = poly(3-vinyl benzothiophene) synthesized at 90°

The polymers were purified by reprecipitating them twice from $CHCl_3$ solution into excess CH_3OH. The polymers were dried in vacuo at 30°C for 88 hrs. The polymers were then weighed to determine conversion.

Results and Discussion

The 300 MHz ^{1}H-NMR spectra of VBT 60 and VBT 90 are shown in Figure 1. Linear expansions of the aromatic proton resonances are shown in Figure 2. The resonances are assigned as shown in Figure 1 (7). The resonances due to the H_5, H_3+H_2 and the aliphatic protons show no multiplicity indicative of stereochemical sensitivity. The H_1 proton resonance occurs as 3 peaks for both VBT 60 and VBT 90 (peaks A, B and C in Figure 2A and 2B). The chemical shifts and relative and fractional intensities of these resonances are summarized in Table 2.

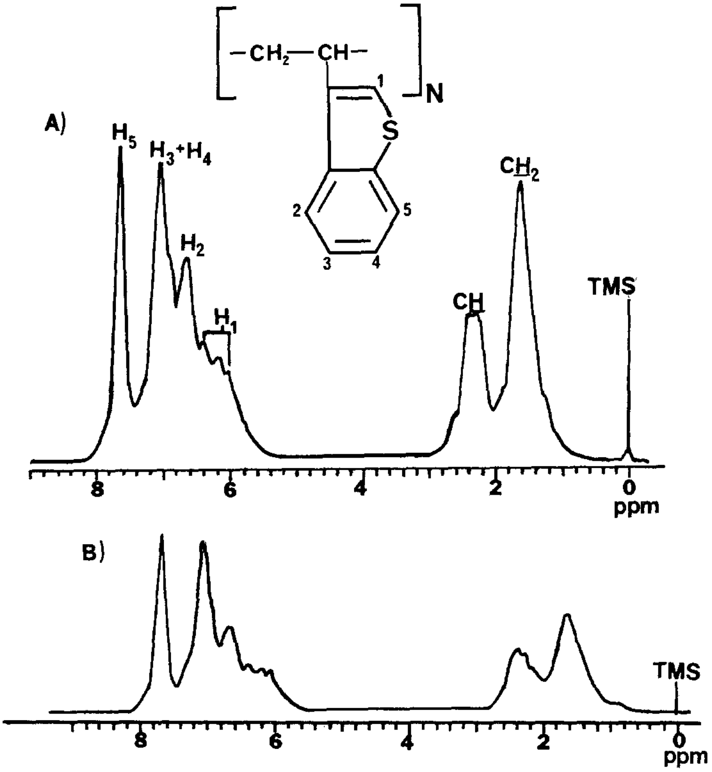

Figure 1

300 MHz ^{1}H-NMR Spectra of: A) Poly(3-vinyl benzothiophene) synthesized at 60°; B) Poly(3-vinyl benzothiophene synthesized at 90°

TABLE 2

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

Polymer	Peak	Chemical Shift (ppm)	Fractional Intensities	Relative Intensities
VBT 60	A	6.40	0.32 ± .05	1
VBT 60	B	6.19	0.30 ± .05	1
VBT 60	C	6.03	0.38 ± .06	1
VBT 90	A	6.64	0.31 ± .05	1
VBT 90	B	6.43	0.31 ± .05	1
VBT 90	C	6.30	0.38 ± .06	1

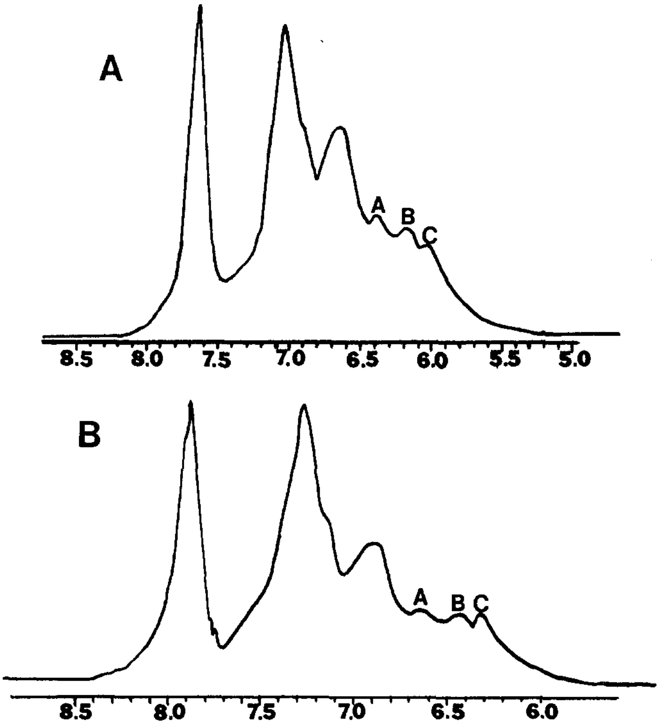

Figure 2

Linear expansions of the aromatic proton resonances of Poly(3-vinyl benzothiophene): A) synthesized at 60°; B) synthesized at 90°

Previous results (3-5) have shown that this type of pattern can be interpreted in terms of pentads for an atactic polymer. If such an interpretation is to be made for the A, B and C resonance of VBT 60 and VBT 90 then the fractional intensities of A, B and C based on the total aromatic resonances must be a multiple of 1/80 or 0.0125 (1/16 x 1/5) as there are 16 pentads of equal intensity in an atactic polymer and 5 aromatic protons. For VBT 60 the fractional intensity of A = 0.060, B = 0.060, C = 0.078, this corresponds to 5/80, 5/80 and 6/80. For VBT 90 A = 0.060, B = 0.060, C = 0.072 again 5/80, 5/80 and 6/80. This translates to relative intensity ratios of 5:5:6 which sum to 16. Since, as previously mentioned, there are 16 pentads of equal intensity for an atactic polymer, it seems quite likely that the H_1 proton resonance is indeed interpretable in terms of pentads. Table 3 summarizes the proposed assignments for these resonances.

These assignments must be regarded as quite tentative particularly in the absence of supporting evidence such as ^{13}C-NMR or a stereoregular poly(3-vinyl benzothiophene). However, given arguments previously advanced (3-5) the assignments are logical and fit the observed data. We believe that evidence such as ^{13}C-NMR or the synthesis of a stereoregular polymer would confirm the conclusion made here that poly(3-vinyl benzothiophene) synthesized by free radical initiation is an atactic polymer.

TABLE 3

Assignment for the H_1 Resonance in Terms of Pentads

Polymer	Peak	Assignment
VBT 60	A	mmmm, mmmr + rmmm, mrmm + mmrm
VBT 60	B	rmmr, rmrm + mrmr, rrmm + mmrr
VBT 60	C	rrrm + mrrr, rmrr + rrmr, mrrm, rrrr
VBT 90	A	mmmm, mmmr + rmmm, mrmm + mrrm
VBT 90	B	rmmr, rmrm + mrmr, rrmm + mmrr
VBT 90	C	rrrm + mrrr, rmrr + rrmr, mrrm, rrrr

Conclusions

Poly(3-vinyl benzothiophene) was synthesized by free radical initiation at two different temperatures. Analysis of the H_1 aromatic proton resonance in terms of a pentad sensitivity for an atactic polymer proved possible and the analysis showed that the resonance pattern is consistent with that expected for an atactic polymer. Further experiments, including ^{13}C-NMR spectroscopy are underway and will be reported at a later date.

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Accepted November 1, 1993 K