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

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Summary

The title polymer was synthesized via thermal and AIBN initiation. The 300 MHz ^{1}H-NMR and 75.5 MHz ^{13}C-NMR spectra were recorded and analyzed in terms of polymer stereochemistry. The ^{1}H-NMR was very similar to the ^{1}H-NMR spectra of poly(2- and 3-vinyl thiophene) and could be interpreted in a like manner. The analysis of the ^{1}H-NMR led to the conclusion that poly(2-vinyl-5-methyl furan) is an atactic polymer when synthesized under free radical conditions. Analysis of the ^{13}C-NMR spectrum supported this conclusion.

Introduction

For some time we have been engaged in the study of the polymerization and copolymerization behavior of vinyl heterocycles (1-5). We have been particularly interested the effect additional (in addition to the vinyl group) ring substitution has on the ^{1}H-NMR and ^{13}C-NMR spectra of the resulting poly vinyl heterocycle (4-7). We have found that the nature and position of the additional ring substituent can have a significant effect on the ^{1}H-NMR spectrum and a somewhat less effect on the ^{13}C-NMR spectrum as compared to the unsubstituted poly vinyl heterocycle. We recently published a paper on the analysis of the ^{1}H-NMR and ^{13}C-NMR spectra of poly(2-vinyl-5-methyl thiophene) in order to examine the effect of the methyl group on the nmr spectra of that polymer (8). Since the effect was significant we thought it would be of interest to examine the nmr spectra of poly(2-vinyl-5-methyl furan) synthesized under conditions similar to those employed for 2-vinyl- 5-methyl thiophene.

Experimental

All solvents used in this study were reagent grade and were used as received. The AIBN was purified by recrystallization (CH_3OH). The nmr spectra were recorded with Varian Gemini 300 FT NMR. All spectra were recorded on 10% w/v solutions of polymer in $CDCl_3$. Tetramethylsilane was added as an internal standard. The areas of individual signals were measured by electronic integration and by tracing the signals on high quality paper, cutting out and weighing the tracings. Each fractional intensity given in this work is the average of four measurements. 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 microstyragel columns. Numerical values for the molecular weights were obtained by comparison to a polystyrene calibration curve.

Monomer Synthesis

The monomer was synthesized from 5-methyl-2-furan carboxaldehyde (Aldrich) as previously described (9). Yield 56%, b.p. = 125-126°C/ 40 mm. The monomer was purified before use by distillation from CaH_2.

Polymer Synthesis

The thermal polymer was synthesized by charging 2.0g of monomer into a clean, dry screw cap vial. The monomer was sparged with dry N_2 for 5 min. and the vial was then sealed with a teflon lined screw cap. The vial was placed in a thermostated bath at 135°C for a period of 4h. The vial was removed from the bath, cooled to ambient temperature and 5 ml of CH_3OH was added to precipitate the polymer. The polymer was purified by reprecipitating it twice from $CHCl_3$ solution into CH_3OH. Conversion = 13.1%. M_n = 9900, M_w = 20500, M_w/M_n = 2.07.

The polymerization using AIBN as the initiator was conducted at 75°C. The monomer (3.0g) was charged into a clean, dry screw cap vial (followed by AIBN, 0.8 wt %) and sparged with dry N_2 and sealed as above. The vial was then placed in a thermostated water bath for a period of 6h. The polymer was isolated and purified as described previously. Conversion = 6.2%. M_n = 18600, M_w = 34500, M_w/M_n = 1.85.

Results and Discussion

The 300 MHz ^{1}H-NMR spectra of the thermally initiated polymer and the AIBN initiated polymer are shown in Figure 1A and 1B respectively. As is obvious the spectra are virtually identical, so, in the interest of space only the spectrum of the thermally initiated polymer will be discussed in detail. However, all results and conclusions apply equally to the AIBN initiated polymer. The resonances are assigned as shown in the Figure. Figure 2 shows a linear horizontal expansion of the ring proton resonances of the thermally initiated polymer. The resonances labeled A-D are assigned to the H_2 proton (10) and occur in a relative intensity ratio of 1:8:4:3, A:B:C:D.

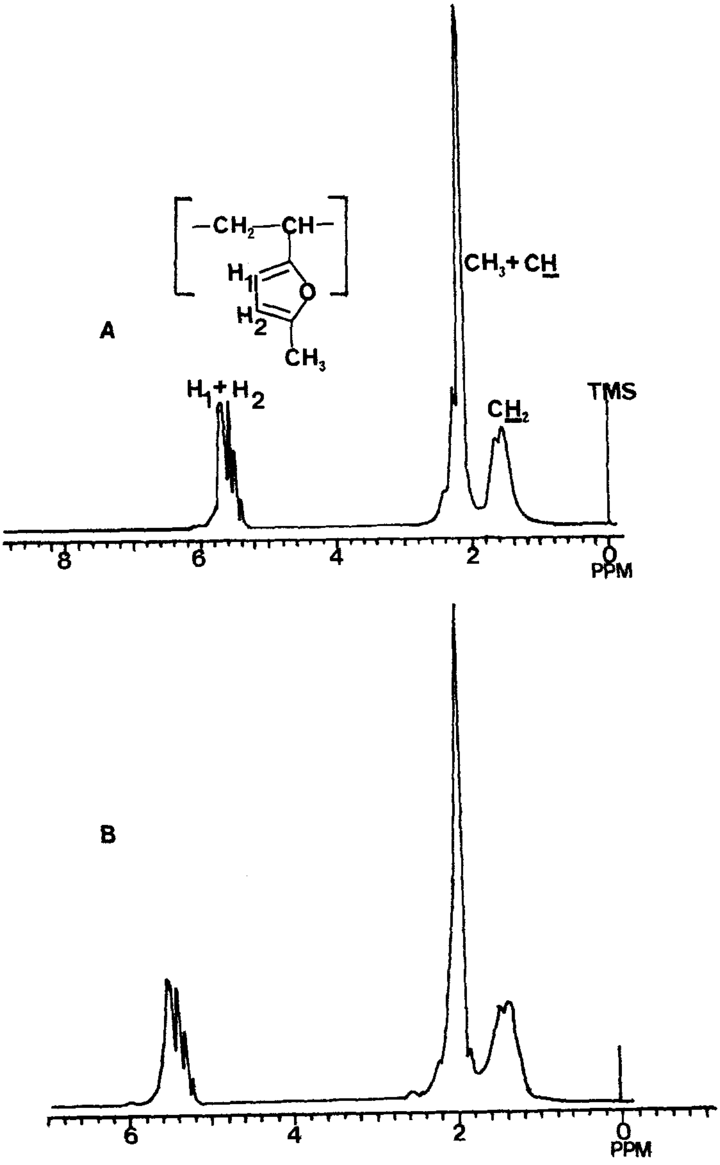

Figure 1

300 MHz ^{1}H-NMR spectra of A) Thermally initiated poly(2-vinyl-5-methyl furan) and B) AIBN initiated poly(2-vinyl-5-methyl furan)

The total of the relative intensities = 16 and since, as previously argued (1-8), there are 16 pentads of equal intensity in an atactic polymer, it is reasonable to ascribe the H_2 resonance pattern to the pentads of an atactic polymer. Signal overlap prevents a detailed assignment from being made at this time, however, the fractional intensity of peak A (0.065 ± .008) allows the calculation of a P_m value of 0.50 ± .06. This is the value expected for an atactic polymer.

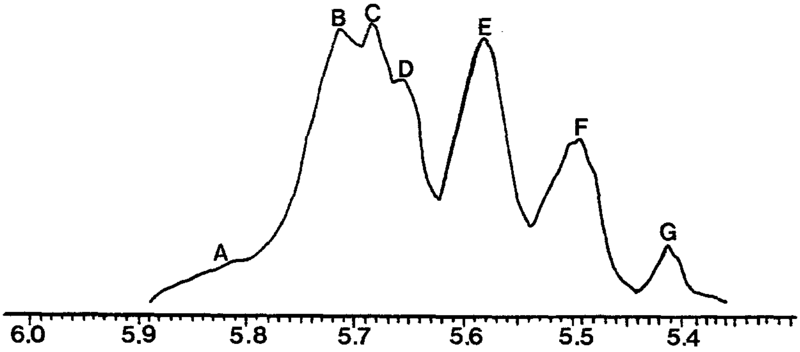

Figure 2

Horizontal expansion of the ring proton resonance of thermally initiated poly(2-vinyl-5-methyl furan)

The resonance pattern assigned to the H_1 proton (10), peaks E-G, occur in a 9:6:1, E:F:G relative intensity ratio. This is exactly the same ratio this proton's resonance occurred in for the cases of poly(2- and 3-vinyl thiophene), poly(2-vinylselenophene) and poly(2-vinyl-5-methyl thiophene) (1-8). In all of these cases this resonance pattern was assigned in terms of a pentad stereosequence sensitivity for an atactic polymer. A calculation of P_m from the fractional intensity of peak G (0.064 ± .006) yields a value of 0.50 ± .05. Tentative pentad assignments for peaks E-G are given in Table 1. The peaks are assigned as containing the pentads listed, no specific order assignment is possible at this time, but awaits the synthesis of a stereoregular polymer. However, the assignments are believed to be reasonable based on previous results (11).

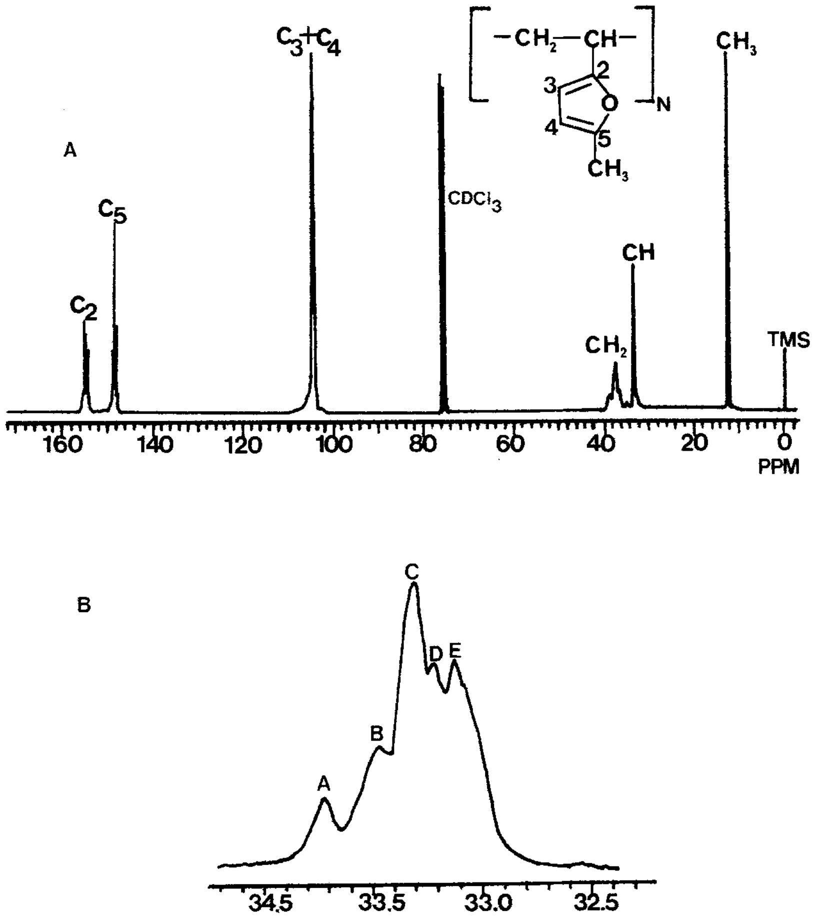

Figure 3

75.5 MHz ^{13}C-NMR of poly(2-vinyl-5-methyl furan)
A) Full spectrum; B) Expansion of the methine carbon resonance

^{13}C-NMR Spectrum

The ^{13}C-NMR spectrum of the thermal polymer (virtually identical to the AIBN polymer) is shown in Figure 3 along with an expansion of the methine carbon resonance (peaks are assigned as shown in the Figure (12)).

TABLE 1

Pentad Assignments for Peaks E-G

Peak	Chemical Shift (ppm)	Proposed Pentad Assignment
E	5.58	rmmr, mmmr + rmmm, mmmm mmrm + mrmm, rmrr + rrmr rrrr
F	5.50	rmrm + mrmr, rrrm + mrrr mmrr + rrmm
G	5.42	mrrm

The peaks in the methine carbon resonance, A-E occur in a 1:3:5:2:5 ratio, A:B:C:D:E. The sum of this ratio is 16 so it again seems reasonable to assign this resonance pattern as being due to pentads in an atactic polymer. While signal overlap prevents detailed assignment of these signals at this point, calculation of a P_m value from the fractional intensity of peak A (0.065 ± .007) yields $P_m = 0.50 \pm .05$.

Conclusions

The ^{1}H-NMR and ^{13}C-NMR spectra of thermal and AIBN initiated poly(2-vinyl-5-methyl furan) have been recorded and analyzed. The ^{1}H-NMR spectrum proved very similar to that of substituted and unsubstituted poly vinylthiophenes and was analyzed and assigned in the same fashion. The analysis shows that poly(2-vinyl-5-methyl furan) is an atactic polymer. This conclusion was supported by analysis of the methine resonance in the ^{13}C-NMR spectrum.

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