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An analysis of the 300 MHz spectrum of poly(3-vinyl pyridine)

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Summary

3-Vinyl pyridine was synthesized and the monomer was then polymerized employing free radical initiation. The 300 MHz ^{1}H-NMR spectrum was recorded and analyzed in terms of polymer stereochemistry. The results of the analysis strongly indicate that poly(3-vinyl pyridine) synthesized using free radical initiation is an atactic polymer.

Introduction

A great deal of work has previously been done concerning the stereochemistry of poly(2- and 4-vinyl pyridines) synthesized by various modes of initiation (1-7). Several investigators (3,6,7) have found that when these polymers are synthesized by free radical initiation, they have an atactic stereochemistry. A search of the literature revealed that no work of a comparable nature had been done on poly(3-vinyl pyridine). Additionally, some of our previous work (8,9) has shown how the position of the vinyl group relative to the heteroatom in vinyl heterocyclic polymers can effect the appearance of the NMR spectra (^{1}H and ^{13}C). Therefore, we thought it would be of interest to investigate the NMR spectra of poly(3-vinyl pyridine). This paper reports our ^{1}H-NMR results.

Experimental

All chemicals used in this study were reagent grade and were used as received. The AIBN was recrystallized from CH_3OH. The ^{1}H-NMR spectra were measured with a Varian HR-300 CW spectrometer and with a Varian Gemini 300 FT spectrometer. Spectra were obtained on 10% w/v solutions in either $CDCl_3$ or CH_3OD at ambient temperature. Individual peak areas were determined by electronic integration, planimeter and by tracing peaks on high quality paper, cutting out and weighing the tracings. All peak areas are the average of four measurements. The molecular weight was measured with a Waters 150

ALC/GPC equipped with 10^6, 10^5, 10^4, 10^3, 500 and 100A microstyragel columns. Numerical values for the molecular weights were obtained by comparison to a polystyrene calibration curve.

Monomer Synthesis

The monomer was synthesized from pyridine-3-carboxaldehyde via a Wittig reaction as previously described (10). The monomer was purified by distilling it twice from CaH_2, with the second distillation immediately before use. b.p. = 70-71/20 mm.

Polymer Synthesis

The polymer was synthesized by charging 2.0g of monomer into a clean, dry screw cap vial followed by 0.8 wt % AIBN. The monomer-initiator solution was sparged with dry N_2 while cold to minimize evaporation, and the vial was tightly capped with a teflon lined screw cap. The vial was placed in a thermostated water bath at 65°C for 3h. The polymerization was terminated by removing the vial from the bath and cooling with cold water. Cold diethyl ether was added to precipitate the polymer. The polymer was purified by reprecipitating it twice from $CHCl_3$ solution into excess diethyl ether. The polymer was dried in vacuo at 30°C for 72h. Conversion = 13.3% M_n = 54000, M_w = 86000, M_w/M_n = 1.59.

Results and Discussion

The 300 MHz ^{1}H-NMR spectrum of poly(3-vinyl pyridine), P3VP, is shown in Figure 1. The spectrum shown was obtained in $CDCl_3$ using the Varian Gemini 300 FT-NMR and the resonances are assigned as shown in the Figure (2,7,11). Figure 2 shows linear expansions of the ring proton resonances obtained from CH_3OD solutions of the polymer using a Varian HR-300 CW-NMR.

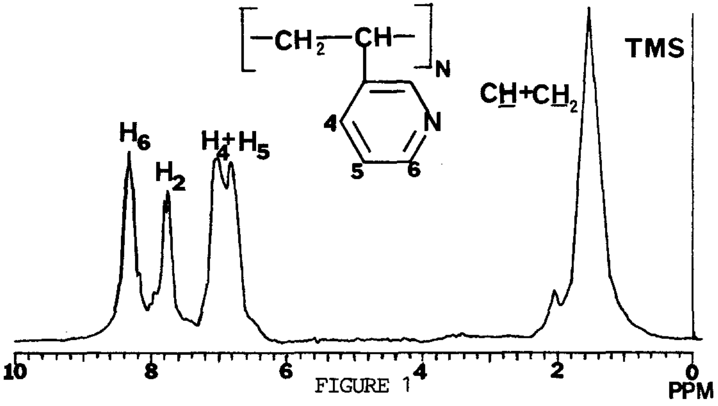

FIGURE 1

300 MHz FT ^{1}H-NMR spectrum of poly(3-vinyl pyridine)

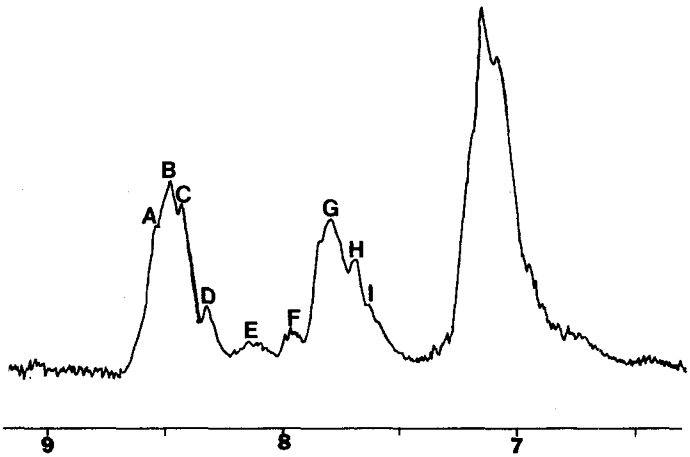

FIGURE 2

Linear expansion of the aromatic proton resonances of poly(3-vinyl pyridine) CW 300 MHz ^{1}H-NMR

The CH_3OD experiments show more signal definition in the aromatic resonances, an observation also made by Matsuzaki et al (2) who obtained their best results in d_4- methanol in a study of poly(2-vinyl pyridine).

The aliphatic resonance of P3VP shows two peaks. In previous studies of poly 2- and 4-vinyl pyridine the small downfield resonance, $\delta = 2.12$ in the present case, has been assigned to the mm triad. If the polymer is atactic then this resonance should have an area that is 1/12 of the total aliphatic resonance (1/4 of the methine resonance which is 1/3 of the total aliphatic resonance, 1/4 x 1/3 = 1/12). In the present case the area of this resonance is 8.1% of the total area (1/12 = 8.33%). Within experimental error this value is equivalent of 1/12 of the area of the aliphatic resonance. A P_m value calculated from the fractional intensity of this peak is 0.49 ± .07. This value suggests that P3VP is an atactic polymer. Support for such a conclusion is obtained by analyzing the ring proton resonances. The H_6 proton resonance occurs as five discernible peaks, A-E in Figure 2. The relative intensity ratio of these peaks is 4:5:4:2:1, A:B:C:D:E. The sum of the relative intensity ratio is 16 and since there are 16 pentads all of equal concentration in an atactic polymer, it is logical to assign this resonances those terms. The proposed assignments are listed in Table 1. The resonance assigned to the H_2 proton occurs as four peaks labeled F-I in Figure

2. The relative intensities occur in a 1:9:3:3 ratio, F:G:H:I. Once again this ratio sums to 16 and again it is logical to assign this resonance pattern in terms of pentads. The proposed assignments are listed in Table 1.

TABLE 1

Proposed Pentad Assignments for the H_6 and H_2 Proton Resonances

Proton	Peak	Chemical Shift	Proposed Assignment
H_6	A	8.36	mrmm + mmrm, rrrm + mrrr
H_6	B	8.30	rrmm + mmrr, mrmr + rmrm rmmr
H_6	C	8.26	rrmr + rmrr, mmmm, rrrr
H_6	D	8.18	mmmr + rmmm
H_6	E	8.10	rmmr
H_2	F	7.95	mrrm
H_2	G	7.80	mrmm + mmrm, rrrm + mrrr rrmm + mmrr, mrmr + rmrm mmmm
H_2	H	7.74	rrmr + rmrr, rrrr
H_2	I	7.60	mmmr + rmmm, mrrm

It should be noted that the peaks are assigned as containing the pentads listed. No specific order can be assigned without a spectrum of a stereoregular P3VP and epimerization studies. However, the assignments are based on assignments made for poly 2- and 4-vinyl pyridines (2,6,7) and are believed to be reasonably accurate. P_m values calculated from the fractional intensities of peaks E and F are 0.51 ± .07 and 0.50 ± .07 respectively. These are the values expected for an atactic polymer.

Conclusions

3-Vinyl pyridine has been synthesized and polymerized by free radical initiation. An analysis of the ^{1}H-NMR spectrum of the resulting polymer showed resonances with the intensity distributions expected for atactic polymers. The P_m values calculated from the fractional intensities of peaks assigned to pentad singlets and triad singlets are all 0.50. The strongly suggests that P3VP, synthesized by free radical initiation, is an atactic polymer.

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