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Preliminary analysis of the ^{1}H-NMR and ^{13}C-NMR spectra of poly(2-vinylpyrazine)

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Summary

The title polymer was synthesized by free radical initiation. The ^{1}H-NMR and ^{13}C-NMR spectra revealed several resonances that were sensitive to polymer stereosequence distribution. Analysis of these resonances showed that free radical initiated poly(2-vinyl pyrazine) is an atactic polymer, a result consistent with data accumulated for other poly vinylheterocycles initiated free radically.

Introduction

Our initial aim in assessing the stereochemistry of poly vinylheterocycles, synthesized via free radical means, was to ascertain if the ^{1}H-NMR and/or ^{13}C-NMR spectra of such polymers could be more readily interpreted in terms of stereochemistry than the corresponding spectra of polystyrene (1,2). If such was the case then, by analogy, we could extend our results to free radical initiated polystyrene. Most of the systems we have investigated to date have proven to have spectra that are more interpretable than those of polystyrene. Also, every poly vinylheterocycle we have investigated to date has proven to be atactic in terms of stereochemistry when synthesized by free radical initiation. By analogy then, given the similarity of the heterocyclic ring systems we investigated (thiophene, furan, pyrrole, selenophene) to benzene, free radical polystyrene should also be atactic. However, the heterocycles mentioned above are all 5-membered ring systems, and, it could be argued, are not then close enough in structure for such an analogy to be made. Therefore, we decided to study a polymer based on a 6-membered heterocycle ring system to ascertain if the nmr spectra obtained could be readily interpreted in terms of polymer stereochemistry. Since there has been a good deal of work done on poly vinylpyridines to date in this regard (3-6), all of which shows free radical initiated poly vinylpyridines to be atactic, we chose a vinyl monomer based on pyrazine for study. The pyrazine ring contains two nitrogen atoms, in the 1 and 4 positions of a six membered ring. It was hoped that this type of structure would yield a polymer with nmr spectra which would be readily interpretable. This paper reports the preliminary results we have obtained.

Experimental

General

The 2-vinylpyrazine used in the study was obtained from Lancaster Synthesis and was distilled from KOH before use. The AIBN was recrystallized from CH_3OH. All other solvents and reagents were used as received. The nmr spectra were recorded using a Varian Gemini 300 FT NMR on $CDCl_3$ solutions of polymer (7-12% w/v) at ambient temperature. Individual peak areas were determined by electronic integration and by tracing the peaks on high quality paper, cutting out and weighing the tracings on a five place analytical balance. Each measurement was repeated at least three times. Molecular weight measurements were made with a Waters 150 ALC/GPC equipped as previously described (7).

Polymer Synthesis

The 2-vinylpyrazine (2.0 g) was charged into a clean, dry screw cap vial followed by 0.6 wt % AIBN. The monomer-initiator solution was sparged with dry N_2 while cold to minimize evaporation loss and the vial was tightly sealed with a teflon lined screw cap. The vial was placed in a thermostated water bath at 70°C for a period of 2 hr. The vial was removed from the water bath, cooled to room temperature and diethyl ether was added to precipitate the polymer. The polymer was purified by two reprecipitations from $CHCl_3$ solution into diethyl ether. % Conv. = 7.0; M_n = 54000, M_w = 86000, M_w/M_n = 1.59.

Results and Discussion

The ^1H-NMR spectrum of poly(2-vinylpyrazine, PVPY), as well as a linear expansion of the ring proton resonances is shown in Figure 1. The resonances are assigned as shown in the Figure (8). The resonance assigned to the H_5 and H_6 protons occurs in a pattern of 11 discernable peaks (A-K). The relative intensity ratio of these 11 peaks is 1:1:2:5:4:3:6:3:3:3:1 (A:B:C:D:E:F:G:H:I:J:K), the sum of these relative intensities is 32 which is half that expected if this pattern was due to a heptad stereosequence sensitivity for an atactic polymer. However, the fractional intensities of peaks A, B and K are 0.031-0.032 which is twice the fractional intensity expected for a singlet heptad. Therefore, it is logical to multiply each relative intensity value by 2 to obtain a ratio of 2:2:4:10:8:6:12:6:6:6:2 (A - K). The sum of this relative intensity ratio is 64 which shows that this pattern is most probably due to heptad stereosequences. The resolution is not sufficient however, to permit any reasonably detailed assignments to be made in terms of heptads. Despite this lack of sufficient resolution for detailed assignments a P_m value can be calculated from the fractional intensity of peak A (or B, K); the value obtained is 0.50 ± 0.07, which is the value expected for an atactic polymer.

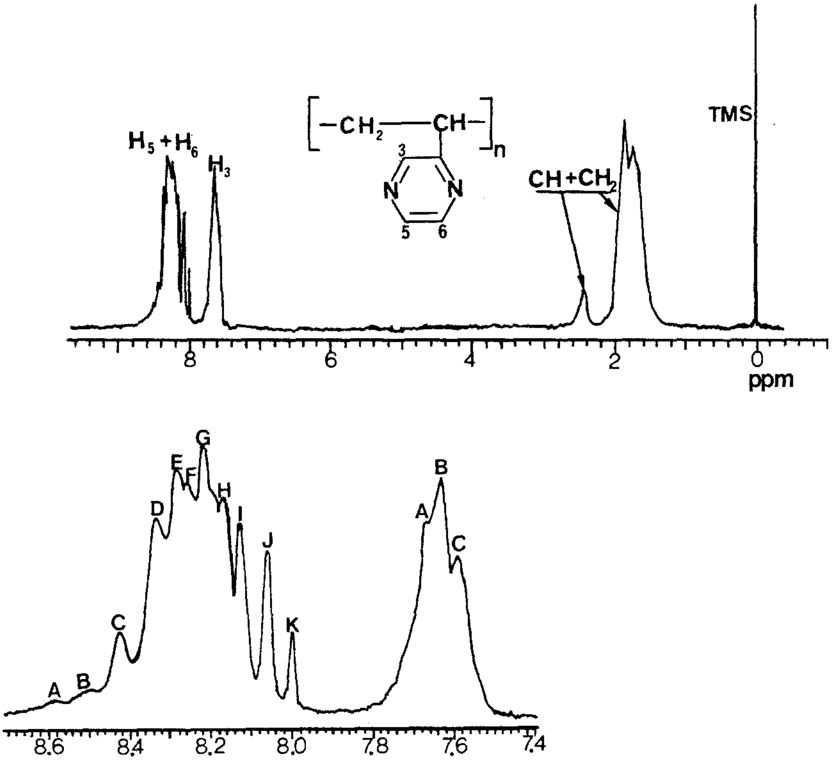

Figure 1

300 MHz ^{1}H-NMR of Poly(2-Vinyl Pyrazine); A) Full spectrum; B) Linear expansion of the ring proton resonances

The resonance assigned to the H_3 proton occurs as a three peak pattern which have fractional intensities of: A = 0.34 ± .04, B = 0.41 ± .05 and C = 0.25 ± .03. Rounding to the nearest whole number would yield a relative intensity ratio of 1:2:1, A:B:C. Even within experimental error (determined by repeat measurements and the S/N ratio of the spectrometer), the fractional intensities indicate that such a ratio would not present a truly accurate assessment of this resonance area. It is possible that the multiplicity represents a sensitivity to triad stereosequences (a 1:2:1 ratio would be expected for an atactic polymer) but it seems more likely that a combined sensitivity, perhaps to triads and pentads is being displayed. Given that is the case, the resonances are insufficiently resolved for any reasonable assignments to be made.

The ^{13}C-NMR spectrum and expansions of the resonances of interest are shown in Figures 2 and 3. The resonances are assigned as shown in Figure 2 (9,10). The resonance assigned to the C_2 ring carbon, Figure 2B, occurs as a 6 peak pattern with the individual peaks in a relative intensity ratio of 4:5:8:9:5:1, A:B:C:D:E:F. The sum of this ratio is 32, half what is expected for the total number of heptads in an atactic polymer. The fractional intensity of peak F is 0.031 ± .003, twice the value expected for a heptad singlet in an atactic polymer.

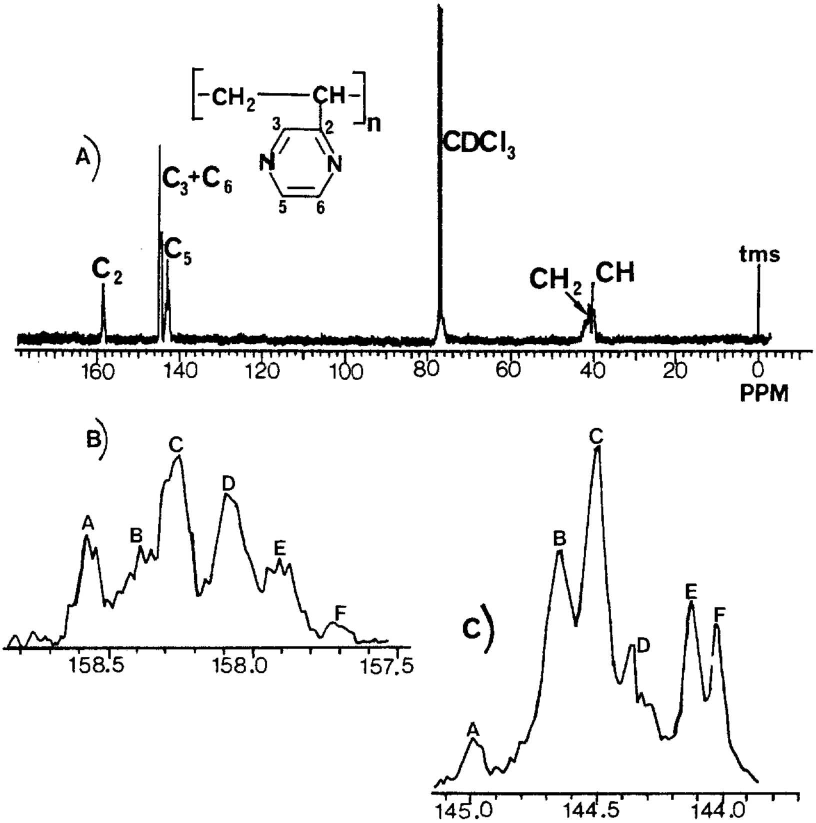

Figure 2

75.5 MHz ^{13}C-NMR Spectrum; A) Full spectrum;
B) Expansion of the C_2 ring carbon resonance;
C) Expansion of the C_3 + C_6 ring carbon resonances

Therefore, as above, it is logical to multiply each relative intensity by 2 to obtain a relative intensity ratio of 8:10:16:18:10:2 (A - F) the sum of which is 64. While the lack of sufficient resolution prohibits any detailed assignment in terms of heptads at this point, a P_m value calculated from the fractional intensity of peak F is equal to 0.50 ± .05, the value expected for an atactic polymer.

The resonance assigned to the C_3 and C_6 carbons occurs as a 6 peak pattern in a relative intensity ratio of 1:9:9:5:4:4, A:B:C:D:E:F. The sum of this ratio is 32, again half the value expected if the observed pattern was due to the heptads of an atactic polymer. If, as above, the relative intensities are multiplied by 2 than the relative intensity ratio becomes 2:18:18:10:8:8 which totals 64. It seems very likely than that the pattern observed is due to heptad stereosequences of an atactic polymer. It should be noted that this resonance area is assigned to two ring carbons. In so far as we can ascertain from the literature and from calculation using a computer simulation (9,10) the chemical shifts of the C_3 and C_6 ring carbons are identical.

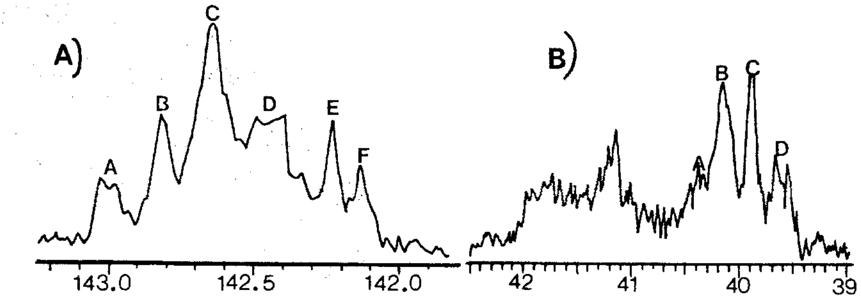

Figure 3

A) Expansion of the C_5 ring carbon resonance;
B) Expansion of the aliphatic carbon resonance

But, it is possible that slight differences may exist and that the results obtained concerning relative intensity ratios are simply fortuitous. We believe that our calculations of chemical shift are reasonably accurate and that the pattern observed is indeed due to a heptad stereosequence sensitivity. A P_m value calculated from the fractional intensity of peak A (0.033 ± .002) is 0.50 ± .03, the value expected for an atactic polymer. The pattern is not sufficiently resolved for any reasonable assignments, in terms of heptads, to be made.

The resonance assigned to the C_5 carbon occurs as a 6 peak pattern, the individual peaks of which are in a relative intensity ratio of 1:2:6:4:2:1, A:B:C:D:E:F which sums to 16. Since there are 16 pentads of equal intensity in an atactic polymer, it is logical to assign this pattern as being due to pentads. While the resolution and signal-to-noise ratio preclude any detailed assignments at this point, peaks A and F can be assigned to pentads of singlet intensity. Recent work indicates (11) that most probably A = rmmr and E = mrrm. A P_m value calculated from the fractional intensity of either peak is 0.51 ± .06.

The methine carbon resonance shows four peaks in a ratio of 1:2:2:1, A:B:C:D. This pattern indicates a sensitivity to higher order stereosequences, but the resolution is not sufficient to determine which stereosequences the methine resonance is displaying a sensitivity to.

Conclusions

The ^{1}H-NMR and ^{13}C-NMR spectra of poly(2-vinylpyrazine) synthesized via free radical initiation, display many signals which show multiplicities due to stereochemical sensitivity. Several of these signals showed multiplicities indicating sensitivity to stereochemical sequences as long as heptads. While resolution was not sufficient for detailed assignments in terms of heptads or pentads to be made, the resolution was sufficient for P_m values to be calculated. All the P_m values obtained strongly indicate that poly(2-vinylpyrazine) is an atactic polymer. This statement can be made with more confidence if one can calculate P_m values from increasingly large stereosequences i.e. triads give more confidence than dyads, pentads more than triads, heptads more than pentads, etc. In this context the 6-member ring heterocycle did yield spectra that were more readily interpretable than the corresponding spectra of polystyrene. More detailed assignment of the resonances awaits synthesis of stereoregular poly(2-vinylpyrazine) and possibly epimerization studies. We believe that such studies will confirm that poly(2-vinylpyrazine) is an atactic polymer.

It should be noted that recent work on epimerization of stereoregular polystyrenes (11) has confirmed that free radical initiated polystyrene is indeed an atactic polymer. Work such as that detailed above serves the purpose of providing additional corroborating evidence of the tacticity of free radical initiated vinyl ring containing polymers.

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