

An analysis of the ^1H - and ^{13}C -NMR spectra of poly(5-vinyl-1,3-benzodioxole)

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Summary

The title monomer was synthesized and subsequently polymerized via free radical initiation. The high field ^1H -NMR and ^{13}C -NMR spectra were recorded and analyzed in terms of polymer stereochemistry. The ^1H -NMR spectrum proved of limited value in this regard but the ^{13}C -NMR spectrum yielded a good deal of useful information. Analysis of the spectra strongly indicated that poly(5-vinyl-1,3-benzodioxole) is an atactic polymer.

Introduction

The initial aim of our work was to establish the tacticity of polystyrene synthesized by free radical initiation. Our approach was to synthesize and polymerize vinyl heterocyclic analogs of styrene and examine the nmr spectra of such polymers in the hope that the spectra would be more readily interpretable in terms of polymer stereochemistry. We reasoned that the ring current effect (1) would be less in these polymers than in polystyrene, resulting in more resolved spectra. Mostly, this was indeed the case (2-4). The vinyl heterocycles we investigated were primarily five membered ring systems, so in order to obtain more direct information on polystyrene, we decided to investigate ring substituted polystyrenes. It was hoped that the substitution would result in a diminished ring current effect yielding more resolved spectra. To date we have had some success (5-7) with this approach and now wish to report an extension of this work. Accordingly, we synthesized and polymerized 5-vinyl-1,3-benzodioxole (VBDO), in effect obtaining a de-ring substituted polystyrene. This paper is a preliminary account of our analysis of the nmr spectra of this polymer.

Experimental

General

All solvents and reagents employed in this study were reagent grade and were used without further purification. The nmr spectra were

recorded on CDCl_3 solutions of polymer (15% wt/v) at ambient temperature. The spectrometer used was a Varian Gemini 300 FT NMR. Individual resonance areas were determined by electronic integration and by tracing them on high quality paper, cutting out and weighing the tracings. All peak areas are the average of four measurements. Molecular weights were determined as previously described (2-4).

Monomer Synthesis

The monomer was synthesized via a Wittig reaction from the corresponding aldehyde as previously described (8). The monomer was purified by distillation from CaH_2 immediately before use.

Polymer Synthesis

The polymer was synthesized by weighing 3.5g of monomer into a clean, dry screw cap vial followed by 0.7 wt % AIBN. The monomer-initiator solution was sparged with dry N_2 and the vial was tightly sealed with a teflon lined screw cap. The vial was placed in a thermostated waterbath at 60°C for a period of 5 hours. The vial was removed from the bath and 8 ml of cold CH_3OH was added. The polymer was purified by reprecipitating it three times from CHCl_3 solution into excess CH_3OH . The polymer was dried at 30°C in vacuo for 90 hours, then weighed to determine conversion. Conversion = 16%, $M_n = 20000$, $M_w = 43000$.

Results and Discussion

The ^1H -NMR spectrum and an expansion of the aromatic proton resonance is shown in Figure 1. The peaks are assigned as shown in Figure 1A (9). The H_A proton resonance (Figure 1B) occurs as a three peak pattern with a relative intensity ratio of 28:2:1, A:B:C. The sum of this ratio is 31 which indicates a sensitivity to higher order stereosequences, possibly heptads. However, as the sum of the relative intensities is 31, not 32 as would be expected for a heptad sensitivity if the polymer is atactic ($32 \times 2 = 64$, the number of heptads expected for an atactic polymer); either the polymer is not atactic or the pattern represents a mixed response (heptads + pentads e.g.). Since analysis of the ^{13}C -NMR spectrum strongly indicates that the polymer is atactic the latter is most likely the reason for the pattern observed. Resolution however, is insufficient at this point for any meaningful analysis to be attempted. The resonance assigned to the H_B and H_C protons occurs as a three peak pattern in a relative intensity ratio of 1:1:1, D:E:F. No meaningful conclusions can be drawn from this resonance pattern at this time.

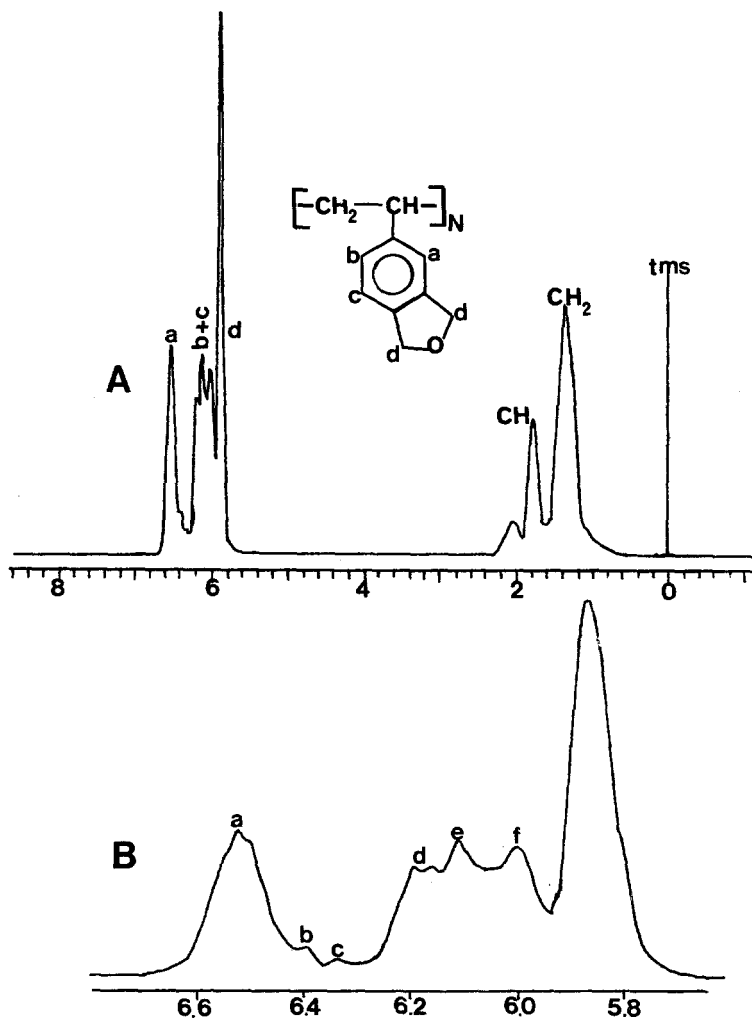


Figure 1

300 MHz $^1\text{H-NMR}$ Spectrum of p(VBDO):

A) Full Spectrum; B) Expansion of the Ring Proton Resonance

$^{13}\text{C-NMR}$

The 75.5 MHz $^{13}\text{C-NMR}$ spectrum of p(VBDO) is shown in Figure 2. The resonances are assigned as shown in the Figure (10,11). An expansion of the C₅ carbon resonance is shown in Figure 2B, this resonance

occurs in a five peak pattern with a relative intensity ratio of 1:3:9:2:1, A:B:C:D:E. The sum of this ratio is 16 and since there are 16 pentads of equal intensity in an atactic polymer it is logical to assign this pattern to pentads. The resolution is sufficient for tentative assignments to be made.

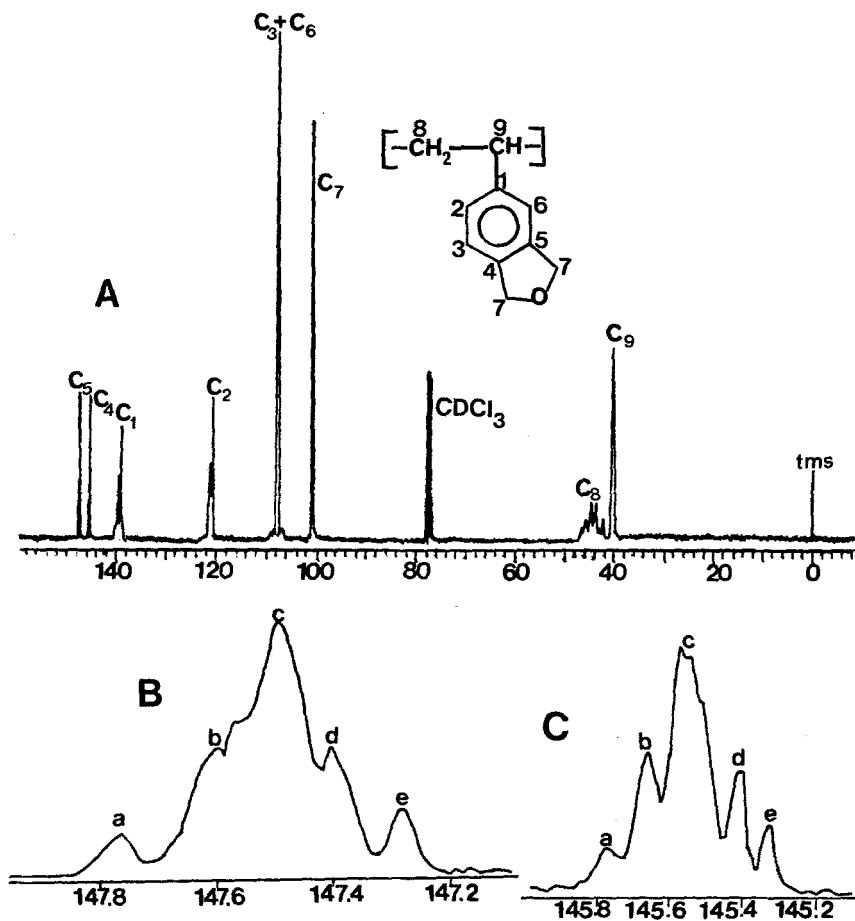


Figure 2

75.5 MHz ^{13}C -NMR Spectrum of p(VBDO): A) Full Spectrum
 B) Expansion of the C_5 Resonance; C) Expansion of the C_4 Resonance

The assignments are listed in Table 1. The peaks are assigned as containing the pentads listed. No particular order assignment is possible at this time with no highly stereoregular polymer having been synthesized or epimerization experiments conducted to determine exact assignments. However, based on previous results, the assignments are believed to be reasonable (4-7).

TABLE 1

PROPOSED ASSIGNMENTS FOR THE C₅ CARBON RESONANCE

Peak	Chemical Shift (ppm)	Relative Intensity	Fractional Intensity	Assignment
A	147.764	1	0.061 ± .005	mmmm
B	147.603	3	0.18 ± .03	mmmm + mmrm, rmmr
C	147.495	9	0.56 ± .07	mmmm + mmrm, mmrm + rmmr, rmmr + rmmr, rmmr + mmrm, rrrr
D	147.403	2	0.14 ± .02	rrrm + mrrr
E	147.282	1	0.064 ± .004	rrrm

Calculation of a P_m from the fractional intensity of peak E (or peak A) yields $P_m = 0.50^m \pm .03$ the value expected for an atactic polymer. It should be noted that while much of the resonance is overlapped peaks A and E are well separated from the other signals and their areas can be measured reasonably accurately (near baseline resolution). This yields a high degree of confidence in the P_m value obtained and in the assignment of this resonance pattern to pentads.

The C₄ carbon resonance pattern (Figure 2C) occurs as a five peak pattern also in a relative intensity ratio of 1:3:9:2:1, A:B:C:D:E. The sum of this ratio is 16, the same as for the C₅ carbon resonance; in fact the relative intensity ratio is exactly the same as for the C₅ carbon resonance. Because the pattern is exactly the same, the same pentad assignments that were made for the C₅ carbon resonance can be made for the C₄ carbon resonance (see Table 1). Calculation of a P_m value from the fractional intensity of peak E ($0.065 \pm .007$) yields $P_m = 0.50 \pm .05$.

The C₁ carbon resonance, Figure 3A, occurs as a six peak pattern in a relative intensity ratio of 1:5:4:3:2:1, A:B:C:D:E:F. The sum

of this ratio is 16, again most probably due to a pentad stereosequence sensitivity. While not as well resolved as either the C_4 or C_5 carbon resonances, assignments in terms of pentads were made⁴ for this resonance and are listed in Table 2. As before the pentads are only assigned as being contained in the specified signal, no order is implied.

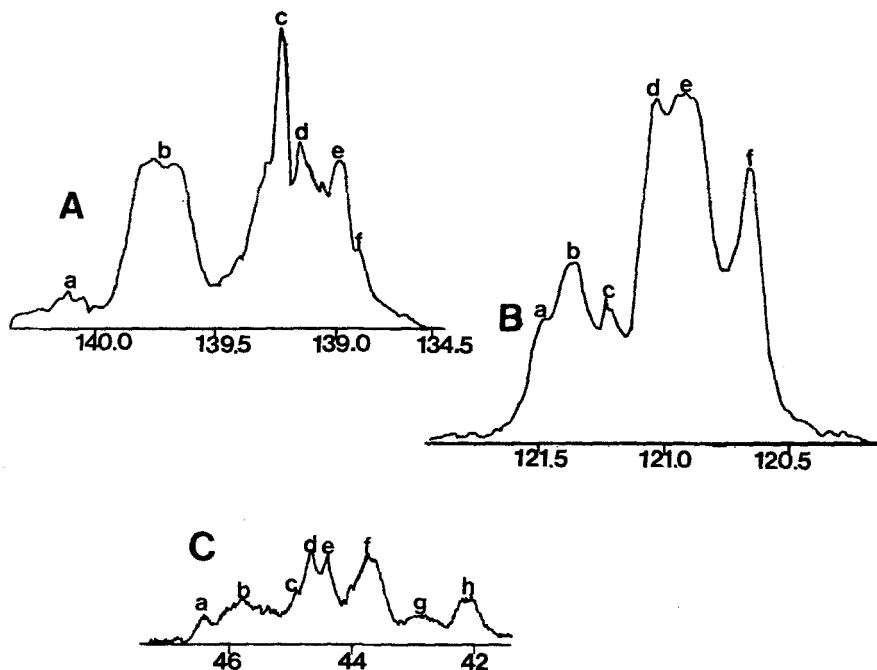


Figure 3

Expansions of the A) C_1 Carbon Resonance
 B) C_2 Carbon Resonance; C) Methylene Carbon Resonance

A P value calculated from the fractional intensity of peak A is $0.50^m \pm .06$.

The C_2 carbon resonance (Figure 3B) occurs as a six peak pattern in a relative intensity ratio of 1:2:1:3:6:3, A:B:C:D:E:F.

TABLE 2
 PENTAD ASSIGNMENTS FOR THE C¹ CARBON RESONANCES

Peak	Chemical Shift (ppm)	Relative Intensity	Fractional Intensity	Assignment
A	140.12	1	0.061 ± .007	mmmm
B	139.73	5	0.32 ± .05	mmmm + mmmr, mmrm + mmrm, rmmr
C	139.25	4	0.26 ± .05	mmmr + rmmr, mmrm + mmrm
D	139.16	3	0.17 ± .03	rrmr + rrrr, rrrr
E	138.99	2	0.11 ± .02	rrrm + mrrr
F	138.91	1	0.064 ± .009	rrrm

The sum of the relative intensity ratio is 16 once again a pattern assignable to the pentad stereosequences of an atactic polymer. In this case the resolution is significantly less than that obtained for the C₄ and C₅ carbon resonances, however, based on assignments made for those resonances and the C₁ carbon resonance, tentative assignments for the peaks in the C₂ resonance can be made and are listed in Table 3. The same caveats apply as in the previous cases. A P value calculated from the fractional intensity of peak A is $0.50^m \pm .07$.

The methylene carbon resonance (Figure 3C) occurs as an eight peak pattern in a relative intensity ratio of 1:6:2:4:4:8:3:4, A:B:C:D:E:F:G:H. The sum of this ratio is 32 which is the number of hexads expected for an atactic polymer. The resolution is insufficient for a detailed assignment of this resonance in terms of hexads but a P value can be calculated from the fractional intensity of peak A ($0.032 \pm .007$) as $0.50 \pm .1$.

Conclusions

The ¹H-NMR spectrum of VBDO proved to be less readily interpreted than that of polystyrene. However, most of the carbons showed sensitivity to polymer stereochemistry. In many cases the resonances were sufficiently resolved for at least reasonable assignments to be made. All assignments were made in terms of the pentad stereosequences of an atactic polymer as this assignment best fit the observed data. While more definitive assignments await the synthesis

of a stereoregular polymer, we believe the assignments are sufficiently accurate to conclude that VBDO is an atactic polymer.

TABLE 3
ASSIGNMENTS FOR THE C₂ CARBON RESONANCE

Peak	Chemical Shift (ppm)	Relative Intensity	Fractional Intensity	Assignment
A	121.50	1	0.061 ± .008	mmmm
B	121.39	2	0.14 ± .03	mmmm + mmmr
C	121.23	1	0.064 ± .009	mmmr
D	121.05	3	0.19 ± .04	mmmm + mmmr, rrrr
E	120.91	6	0.35 ± .07	mmmr + mmmr, rrmm + mmmr, rrmr + mmmr
F	120.67	3	0.20 ± .04	rrmm + mmmr, mmrm

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