

An analysis of the ^1H - and ^{13}C -NMR spectra of poly(6-vinyl-1,4-benzodioxane)

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Summary

The title monomer was synthesized from the corresponding aldehyde via a Wittig reaction. The monomer was polymerized using free radical initiation and its high field ^1H - and ^{13}C -NMR spectra were recorded. When analyzed in terms of stereochemistry the spectra showed poly(6-vinyl-1,4-benzodioxane) is an atactic polymer when synthesized via free radical initiation.

Introduction

For some time we have been investigating the polymerization and copolymerization behavior of vinyl heterocycles and various ring substituted styrenes (1-6). We have found that the chemical nature, position and steric bulk of any substituent can have a significant effect on the copolymerization behavior and spectra of these vinyl monomers. For example, in many cases it seems that alkyl type substituents give better resolved spectra than those obtained for the parent unsubstituted vinyl monomers while halogen and other electron withdrawing groups sometimes yield spectra with less resolution than the spectra of the parent vinyl monomers. However, in all cases examined to date, substituents of any type have not exerted significant influence on the stereochemistry of polymers synthesized via free radical initiation; all such polymers have an atactic stereochemistry. But, because the work we are doing is proceeding by an inductive rather than deductive path, the results obtained so far do not mean that substituent influence on stereochemistry is nonexistent. Given such a possibility, we decided to investigate a disubstituted styrene monomer. We chose as a monomer one that had a bulky substituent yet, from previous work, we knew polymerizes with some facility, 6-vinyl-1,4-benzodioxane. This paper is a preliminary account of results obtained thus far.

Experimental

All solvents and other chemicals used in this study were reagent

grade and were used without further purification. The initiator was AIBN which was purified by recrystallization from methanol. Spectra were recorded with a Varian Gemini 300 FT NMR (^1H freq. = 300 MHz, ^{13}C freq. = 75.5 MHz) on CDCl_3 solutions of polymer (10% wt/v) at ambient temperature. Molecular weights were measured as previously described (1-5). Peak areas were determined by tracing the resonances on high quality paper, cutting out and weighing the tracings on a 5-place balance.

Monomer Synthesis

The monomer was synthesized as previously described (6) and purified by distillation from CaH_2 immediately before use (b.p. = 84-85° at 2 mm).

Polymer Synthesis

The polymer was synthesized by weighing 3.0g of monomer into a clean, dry screw cap vial followed by 0.7 wt % AIBN. The monomer-initiator solution was sparged with dry nitrogen and the vial was then sealed with a teflon lined screw cap. The vial was placed in a thermostated water bath at 70°C. The polymerization was allowed to proceed for 4 hours. The vial was removed from the water bath, cooled to room temperature and the contents of the vial were diluted with CHCl_3 . The CHCl_3 solution was added to excess CH_3OH to precipitate the polymer. The polymer was purified by three reprecipitations from CHCl_3 solution into excess CH_3OH . The polymer was dried for 72 hours in vacuo at 30°C. Yield = 69.8%, $M_n = 67000$, $M_w = 117000$.

Results and Discussion

The $^1\text{H-NMR}$ spectrum of poly(6-vinyl-1,4-benzodioxane) (VDIX) is shown in Figure 1 along with an expansion of the ring proton resonances (Figure 1B). The resonances are assigned as shown in the Figure (7). The H_A proton resonance occurs as an overlapped four peak pattern in a relative intensity ratio of 4:2:4:1, A:B:C:D. The sum of these relative intensities is 11, which indicates a sensitivity to higher order stereosequences, possibly pentads, but the resolution is insufficient for any reasonable assignment to a specific stereochemical sensitivity to be made. The resonance assigned to the H_B and H_C protons also occurs as a four peak pattern. The four peaks B have a relative intensity ratio of 10:14:7:1, E:F:G:H. The sum of this ratio is 32, which is what would be expected for a heptad sensitivity in an atactic polymer if peak H (fractional intensity = $0.032 \pm .004$) represented a heptad doublet or two heptad singlets; (the number of heptads expected for an atactic polymer = $32 \times 2 = 64$). However, since this resonance area is due to two protons, the fractional intensity of peak H is also that expected for a singlet pentad in an atactic polymer (intensity expected = 0.063, for peak H, $0.032 \times 2 = 0.064$).

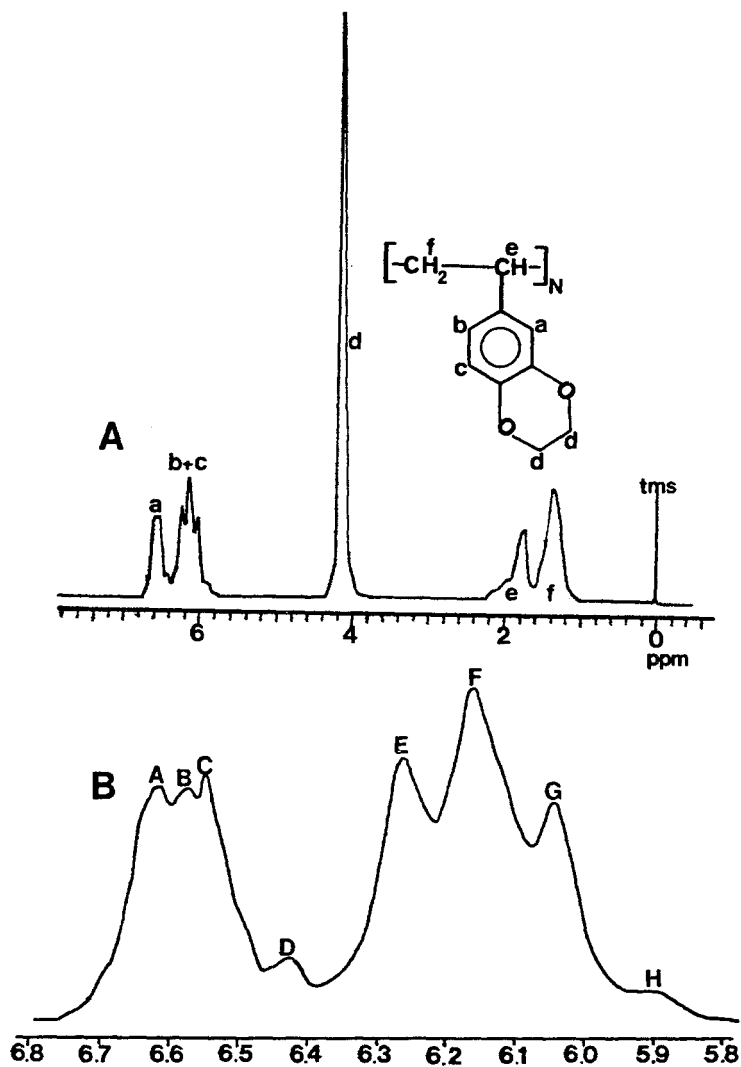


Figure 1

300 MHz $^1\text{H-NMR}$ Spectrum; A) Full Spectrum
 B) Expansion of the Ring Proton Resonances

It is more likely that the H_B-H_C proton pattern reflects a sensitivity to pentads, but the resolution is insufficient for any detailed assignments to be made. A P_m value (based on a pentad sensitivity) can be calculated from the fractional intensity of peak H and is equal to $0.50 \pm .06$. This is the value expected for an atactic polymer.

^{13}C -NMR Spectrum

The ^{13}C -NMR spectrum of VDI_X is shown in Figures 2 and 3. The spectrum is assigned as shown in Figure 2A (8,9). The resonance due to the C_5 carbon (Figure 2B) occurs as a three peak pattern in a relative intensity ratio of 10:5:1, A:B:C. The sum of these relative intensities is 16, the number of pentads expected for an atactic polymer (1-5). Therefore, it is reasonable to assign the C_5 resonance in terms of pentads. The tentative assignment of peaks A, B and C is presented in Table 1. The peaks are assigned as containing the pentads listed; no particular order can be assigned in the absence of data from a stereoregular polymer. However, based on previous results the assignments are believed to be reasonable (3-5,10).

TABLE 1

Assignments of the C_5 Carbon Peaks

Peak	Chemical Shift (ppm)	Relative Intensity	Fractional Intensity	Proposed Assignment
A	142.98	10	$0.64 \pm .07$	rrrrr + rrrrr, rrrrr, rrrrr + rrrrr, rrrrr, rrrr + rrrr rrrr + rrrr
B	142.88	5	$0.30 \pm .03$	rrrr + rrrr, rrrr + rrrr, rrrr
C	142.76	1	$0.062 \pm .007$	rrrr

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

The C_4 carbon resonance (Figure 2C) occurs as a five peak pattern in a relative intensity ratio of 3:4:6:2:1, A:B:C:D:E. The sum of this ratio is 16 which indicates a sensitivity to pentad stereosequences. As in the case of the C_5 carbon resonances a tentative

assignment of the C_4 resonance pattern was made and is summarized in Table 2. As previously, the peaks are assigned as containing the pentads listed in no particular order.

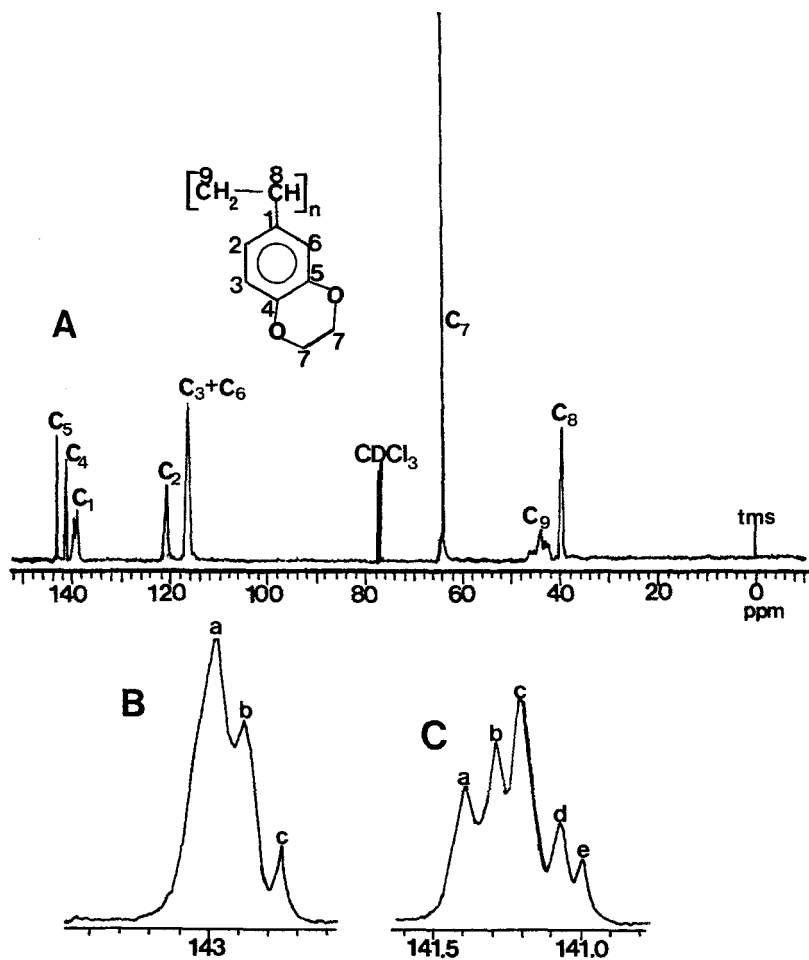


Figure 2

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

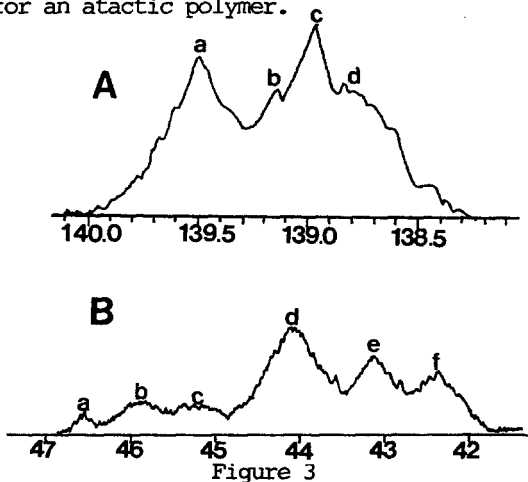
TABLE 2

 C_4 Carbon Resonance Assignments

Peak	Chemical Shift (ppm)	Relative Intensity	Fractional Intensity	Proposed Assignment
A	141.40	3	$0.20 \pm .02$	mmmm, rmmmm + mmrmm
B	141.29	4	$0.25 \pm .03$	mrrmm + mmrmm, mrrmr + rmmrr
C	141.19	6	$0.37 \pm .04$	rrmm + rmmr, rrrm + rrrr rrmr, rrrr
D	141.08	2	$0.12 \pm .01$	rrrm + mrrr
E	141.00	1	$0.063 \pm .006$	mrrm

A P value calculated from the fractional intensity of peak E is $0.50^m \pm .05$, again the value expected for an atactic polymer.

The resonance of the C_1 carbon (Figure 3A) occurs as a four peak pattern in a relative intensity ratio of 3:1:2:2, A:B:C:D. The sum of this ratio is 8, which is exactly half the number of pentads expected for an atactic polymer.



Expansion of: A) The C_1 Carbon Resonance
B) The Methylene Carbon Resonance

This fact and the fractional intensity of peak B (0.13 ± 0.02) being twice the value of a pentad singlet for an atactic polymer (i.e. $B =$ value for a pentad doublet), makes multiplication of the relative intensities of the peaks in this resonance by two a reasonable operation to perform. When this is done the relative intensity ratio becomes 6:2:4:4 which indeed sums to 16. The C_1 resonance pattern is most probably due to a pentad stereosequence sensitivity. Insufficient resolution prohibits any detailed assignments at this point, but a P_m value of $0.50 \pm .09$ can be calculated from the fractional intensity of peak B.

The methylene carbon resonance (Figure 3B) occurs as a six peak pattern in a relative intensity ratio of 1:3:3:13:7:5, A:B:C:D:E:F. The sum of this ratio is 32, which is the number of hexads expected for an atactic polymer. It is logical then to assign this pattern to hexad stereosequences but insufficient resolution prevents any reasonably detailed assignments from being made. However, a P_m value can be calculated from the fractional intensity of peak A ($0.031 \pm .005$); $P_m = 0.50 \pm .08$.

Conclusions

Analysis of the $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra of VDI_X revealed several resonances with multiplicities due to stereochemical sensitivity. While insufficient resolution and lack of a highly stereoregular polymer reference made exact assignment of individual resonances to specific stereosequences difficult or impossible; enough assignments could be made, and P_m values calculated, to show that VDI_X synthesized by free radical initiation is an atactic polymer.

References

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