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Preliminary analysis of the ^{1}H-NMR and ^{13}C-NMR spectra of poly(4-acetoxystyrene)

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Summary

The title polymer was synthesized via free radical initiation. The ^{1}H- and ^{13}C-NMR spectra of the polymer were recorded and analyzed in terms of polymer tacticity. Many resonances showed a multiplicity indicative of sensitivity to stereochemistry. Those resonances that could be analyzed with a reasonable degree of accuracy showed poly(4-acetoxystyrene) to be an atactic polymer.

Introduction

For some time we have been engaged in the study of the effect(s) of ring substitution (i.e. substitution in addition to the vinyl group) on the tacticity and nmr spectra of various vinyl polymers; mostly, we have studied polyvinyl heterocycles (1-3) and we have found that the type and position (relative to the vinyl group) of any substituents can have a significant effect on the spectra of the polymer. However, since the genesis of this work was the elucidation of the stereochemistry of free radical initiated polystyrene (4,5), it seemed germane to study the effect(s) of ring substitution on the nmr spectra of various polystyrenes. In this vien we have reported analysis of the nmr spectra of halogen substituted polystyrenes and polyacylstyrenes (6-9). In all cases ring substitution did indeed have an effect on the appearances of the nmr spectra of the polystyrenes studied.

In this work we present an analysis of the nmr spectra of poly(4-acetoxystyrene) synthesized by free radical initiation. Poly(4-acetoxystyrene) has been well studied (10-13) as it is a precursor to poly(4-hydroxystyrene), an important reactive polymer. However, a literature search revealed that there had been no study of the tacticity of this polymer.

Experimental

General

All solvents and other chemicals used in this study were reagent grade and were purified by distillation before use. The ^1H- and ^{13}C-NMR spectra were recorded at ambient temperature on $CDCl_3$ solutions of polymer (15% w/v) using a Varian Gemini 300 FT NMR. Tetramethylsilane was used as an internal standard. Individual resonance areas were determined by electronic integration and by tracing peaks on high quality paper then cutting out and weighing the tracings on a five-place analytical balance. Molecular weight was measured as previously described (6-9).

Polymer Synthesis

The polymer was synthesized by weighing 2.0g of 4-acetoxystyrene (Aldrich) into a clean, dry screw cap vial followed by 0.8 wt % AIBN. The monomer-initiator solution was sparged with dry nitrogen and the vial was then tightly sealed with a teflon-lined screw cap. The vial was placed in a thermostated waterbath at 65°C for 0.5 hours. The polymerization was terminated by removing the vial from that bath and adding 7.0 ml of cold CH_3OH. The poly(4-acetoxystyrene) was purified by two reprecipitations from $CHCl_3$ solution into excess CH_3OH. Conversion = 23.5%, M_n = 118300, M_w = 235000.

Results and Discussion

The 300 MHz ^1H-NMR spectrum is shown in Figure 1 along with an expansion of the ring proton resonance area (Figure 1B). The resonances are assigned as shown in the Figure (14,15). The ring proton resonance occurs as an eight peak pattern in which the peaks in the resonance pattern assigned to the H_B protons, A-D, have a relative intensity ratio of 6:3:6:1, A:B:C:D. The sum of this ratio is 16, which is the number of pentads expected for an atactic polymer (1-3). It is logical then to ascribe this pattern as being due to pentad stereosequences. The resolution is insufficient for any detailed assignments to be made but a P_m value can be calculated from the fractional intensity of peak D (0.063 ± .01) as 0.50 ± 0.08, the value expected for an atactic polymer.

The resonance pattern assigned to the H_A proton occurs as four peaks in a relative intensity ratio of 2:8:5:1, E:F:G:H. Again, the sum of this ratio is 16, indicating a sensitivity to pentad stereosequences. Additionally, this type of pattern has been previously observed for various polyvinyl heterocycles (1-3) and has been assigned to pentads. In the present case the resolution is sufficient for tentative assignments in terms of pentads to be made. These assignments are summarized in Table 1. The pentads are assigned as being contained in the designated resonance area, no specific ordering is possible at the present time, but the assignments listed are believed to be reasonably accurate (3,6).

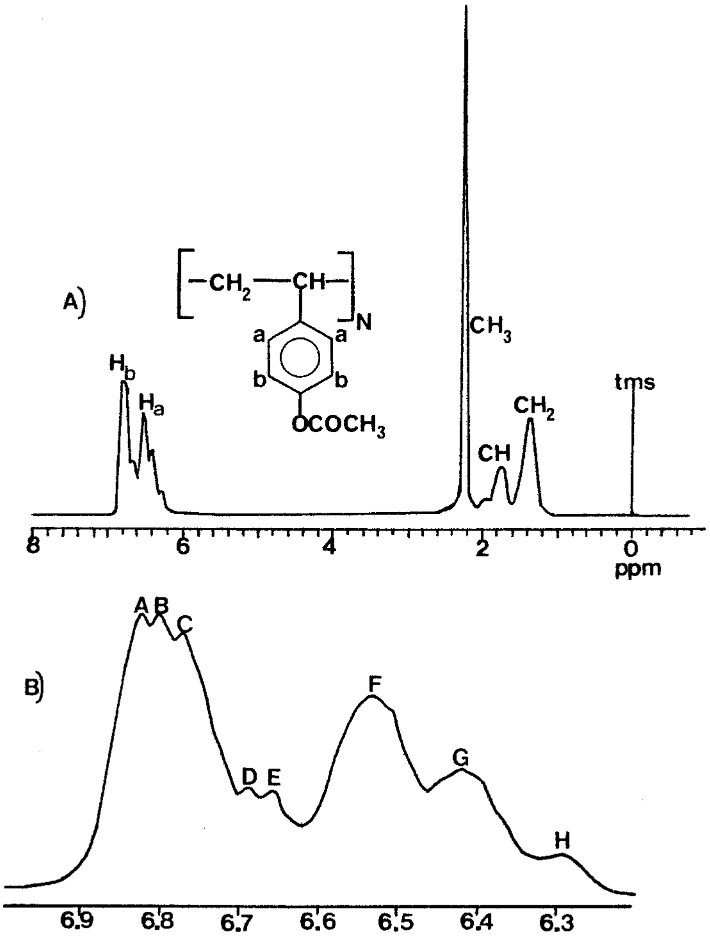

Figure 1

300 MHz ^{1}H-NMR Spectrum of Poly(p-acetoxystyrene):
A) Full spectrum; B) Expansion of the ring proton resonance

TABLE 1

Pentad Assignments for the H_A Ring Protons

Peak	Chemical Shift (ppm)	Fractional Intensity	Relative Intensity	Proposed Assignment
E	6.67	0.11 ± .02	2	rmmm + mmmr
F	6.54	0.52 ± .06	8	mrmm + mmrm, rmrm + mrmr, mmrr + rrmm, mmmm, rmmr
G	6.42	0.30 ± .04	5	rrmr + rmrr, rrrm + mrrr, rrrr
H	6.30	0.062 ± .007	1	mrrm

A P_m value calculated from the fractional intensity of peak H is 0.50 + .06, again, the value expected for an atactic polymer.

^{13}C-NMR Spectra

The 75.5 MHz ^{13}C-NMR spectrum of poly(4-acetoxystyrene) is given in Figure 2 along with expansions of certain individual carbon resonances of interest (Figures 2 and 3). The resonances are assigned as shown in Figure 2 (16). The C_4 carbon resonance (Figure 2B) occurs as a five peak pattern in a relative intensity ratio of 2:4:6:3:1, A:B:C:D:E. The sum of this ratio is 16, again the number of pentads expected for an atactic polymer. While the resolution is not sufficient for any detailed assignments to be made, the area of peak E can be measured with a relatively high degree of accuracy and a P_m value can be calculated from its fractional intensity (0.062 ± .004); P_m = 0.50 ± .04.

The resonance pattern assigned to the C_1 carbon (Figure 2C) occurs as a six peak pattern in a relative intensity ratio of 1:2:1:2:1:6, A:B:C:D:E:F. The sum of this relative intensity ratio is 13. While not directly assignable to pentads this pattern is certainly reflects sensitivity to higher order stereosequences. The resolution however, is insufficient at the present time for any reasonable assignments to be made.

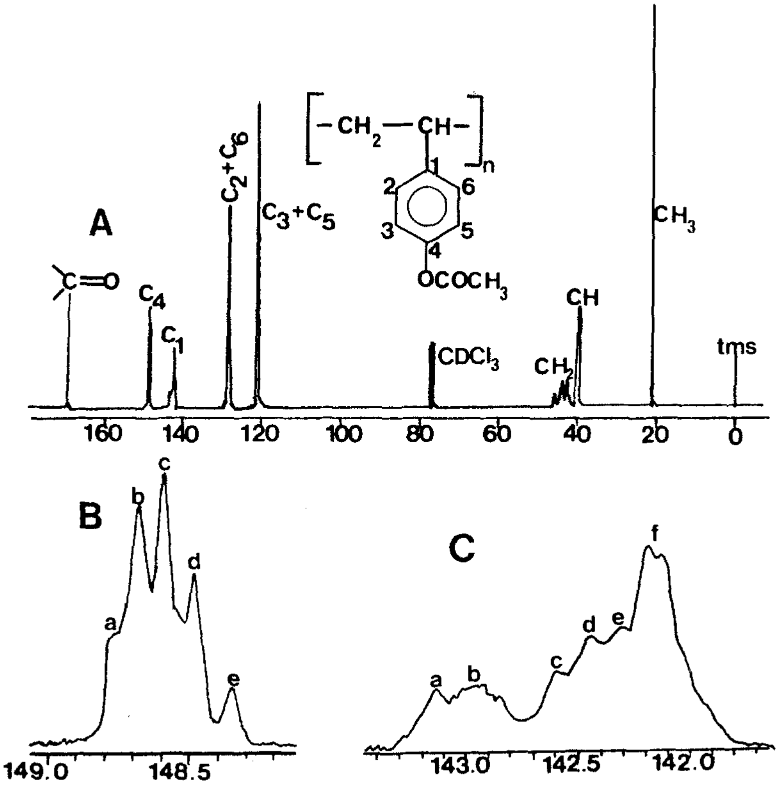

Figure 2

75.5 MHz ^{13}C-NMR Spectrum of Poly(p-acetoxystyrene):
A) Full spectrum; B) C_4 Carbon resonance
C) C_1 Carbon Resonance

The resonance pattern assigned to the C_2 and C_6 carbons (Figure 3A) occurs as a five peak pattern in a relative intensity ratio of 1:4:7:3:1, A:B:C:D:E. The sum of this ratio is 16 so this pattern is most probably due to pentads. As above, the resolution is insufficient for any detailed assignments to be made, but a P_m value calculated from the fractional intensity of peak A (0.065 ± .007) is 0.50 ± .06.

The resonance pattern assigned to the C_3 and C_5 carbons (Figure 3B) occurs as a three peak pattern in a 1:12:3 relative intensity ratio which sums to 16.

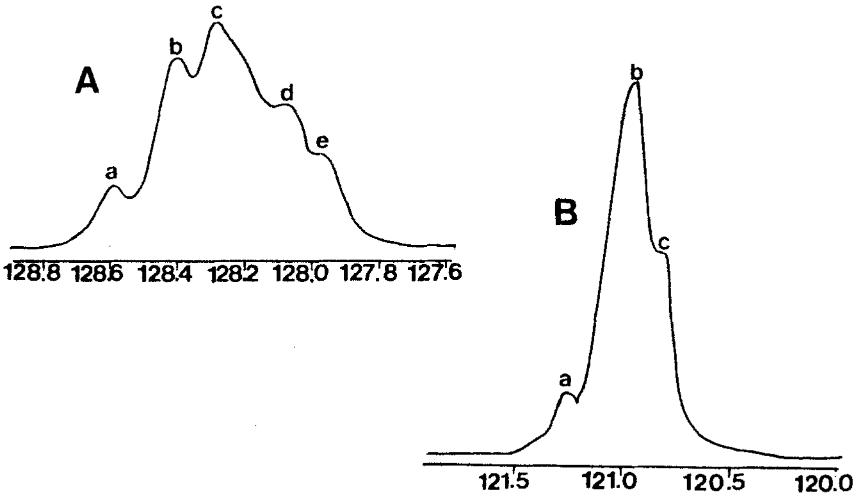

Figure 3

A) Expansion of the C_2 and C_6 carbon resonances
B) Expansion of the C_3 and C_5 carbon resonances

Again, this pattern is most probably due to pentads but insufficient resolution prevents any detailed assignments from being made. A P_m value calculated from the fractional intensity of peak A (0.061 ±.009) is equal to 0.50 ± .07.

The methylene and methine carbon resonances show multiplicipes indicative of sensitivity to polymer stereochemistry. However, both resonances display patterns which are not reasonably assignable to any single stereochemical sensitivity e.g. pentads, hexads, heptads, etc. Experiments at higher fields may be necessary to increase the resolution of these signals.

Conclusions

While the ^{1}H- and ^{13}C-NMR spectra of poly(4-acetoxystyrene) are not extremely well resolved, the resolution is significantly better than that obtained under similar conditions for polystyrene itself. This is particularly true for the ^{1}H-NMR spectrum in which the aromatic protons display resolution approaching that obtained for poly(2-vinylthiophene) (1). While definitive peak assignments await the synthesis of a stereoregular polymer, we believe our conclusion that poly(4-acetoxystyrene) is atactic is justified by the total weight of evidence presented here.

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