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An analysis of the ^{1}H- and ^{13}C-NMR spectra of poly(3-bromostyrene)

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Summary

The 300 MHz ^{1}H-NMR spectrum of free radical initiated poly(3-bromostyrene) is similar to the ^{1}H-NMR spectra of certain poly(vinyl heterocycles) and can be interpreted in a like manner. The ^{13}C-NMR is typical of spectra for meta-substituted polystyrenes, with some of the carbon resonances showing a sensitivity to polymer stereochemistry. The spectra indicate that poly(3-bromostyrene) synthesized by free radical initiation is an atactic polymer.

Introduction

Previously, we have reported the effect of ring substitution on the ^{1}H-NMR spectra of polystyrenes synthesized via free radical initiation (1,2). Specifically, we have reported on poly(4-acetylstyrene) (1) and poly(4-bromostyrene) (2). In both cases para-substitution had a pronounced effect on the high field ^{1}H-NMR spectrum of the polymer. For example poly(4-acetyl-β-β dideuterostyrene) shows three readily discernable methine proton resonances that occur in a 1:2:1 relative intensity ratio, which would be the expected triad intensity ratio for an atactic polymer. A P_m value calculated from the fractional intensity of the peak assigned to the mm triad was 0.50 ± .02. For poly(4-bromostyrene) the Br in the para position had a pronounced effect on the aromatic proton resonances, particularly that of the protons ortho to the main chain carbon in the polymer. This resonance pattern was assigned in terms of pentad stereosequences for an atactic polymer with the aid of a computer simulation. A P_m value calculated from the fractional intensity of the mmmm pentad was 0.50 ± .04.

Because it seemed, based on the limited number of para-substituted polystyrenes that we investigated (3), that the ^{1}H-NMR is always changed relative to unsubstituted polystyrene, we thought it would be interesting to examine the effects of ring substitution in positions other than para on the NMR spectra (^{1}H- and ^{13}C-) of the resulting polystyrenes. This paper summarizes results obtained for

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poly(3-bromostyrene).

Experimental

3-Bromostyrene was obtained from the Aldrich Chemical Company and was distilled twice from CaH_2 before use. All solvents were reagent grade and were used as received. The ^1H-NMR spectra were recorded on both a Varian HR-300 CW instrument and a Varian Gemini 300 FT instrument. The ^{13}C-NMR spectra were recorded with a Varian Gemini 300 FT-NMR at 75.5 MHz. Resonance areas of signals were estimated by cutting and weighing and also by simulation, assuming a half-width of 0.05 ppm for each line of the ^{13}C-NMR and 0.08 ppm for each line of the ^1H-NMR. All spectra were recorded at ambient temperature of polymers in $CDCl_3$ solution with TMS added as an internal standard. Molecular weight measurements were made with a Waters High Resolution 6000A GPC equipped with 10^6, 10^5, 10^4, 10^3 and 500 A microstyragel columns. Tetrahydrofuran was used as an eluent.

Polymer Synthesis

3-Bromostyrene (4.0g) was charged into a thick walled screw cap bottle followed by 0.025g of AIBN. The polymer initiator solution was sparged with N_2 while cold (-10°C) and the vial was then sealed with a polyethylene-lined screw cap. The bottle was placed in a water bath at 65°C for 1h. The bottle was then removed from the bath, cooled with cold water and 5 ml of cold CH_3OH was added to precipitate the polymer. The crude polymer was purified by reprecipitating it twice from $CHCl_3$ solution into excess CH_3OH. It was dried in vacuo at 25°C for 72h. Conv. = 68%, M_n = 320,000, M_w = 645,000; PD = 2.02.

Results and Discussion

Figure 1 shows the 300 MHz ^1H-NMR spectrum of poly(3-bromostyrene). The resonances are assigned as shown in the Figure (4,5). Also shown in Figure 1 are linear horizontal expansions of the aromatic and aliphatic proton resonances. It appears that the resonances of all the aromatic protons are sensitive in some manner to polymer stereochemistry, but only the resonance of the H_6 protons has sufficiently well defined fine-structure to enable an interpretation to be made in terms of stereosequences.

The resonance due to the H_6 proton (A, B, C and D) occurs as four overlapped peaks, the fractional and relative intensities of which are listed in Table 1.

Each of the relative intensities is approximately a multiple of 1/16 (0.0625). In accord with our carbon interpretations this is regarded as an indication that the resonances are due to various combinations of pentad resonances and that the polymer is atactic. Based on arguments previously advanced (6,7,8), the pentad assignments summarized in Table 2 are proposed for the H_6 proton resonances. It should be noted that these assignments are tentative, however, previous work (2,7) has shown that they can be made with a reasonable

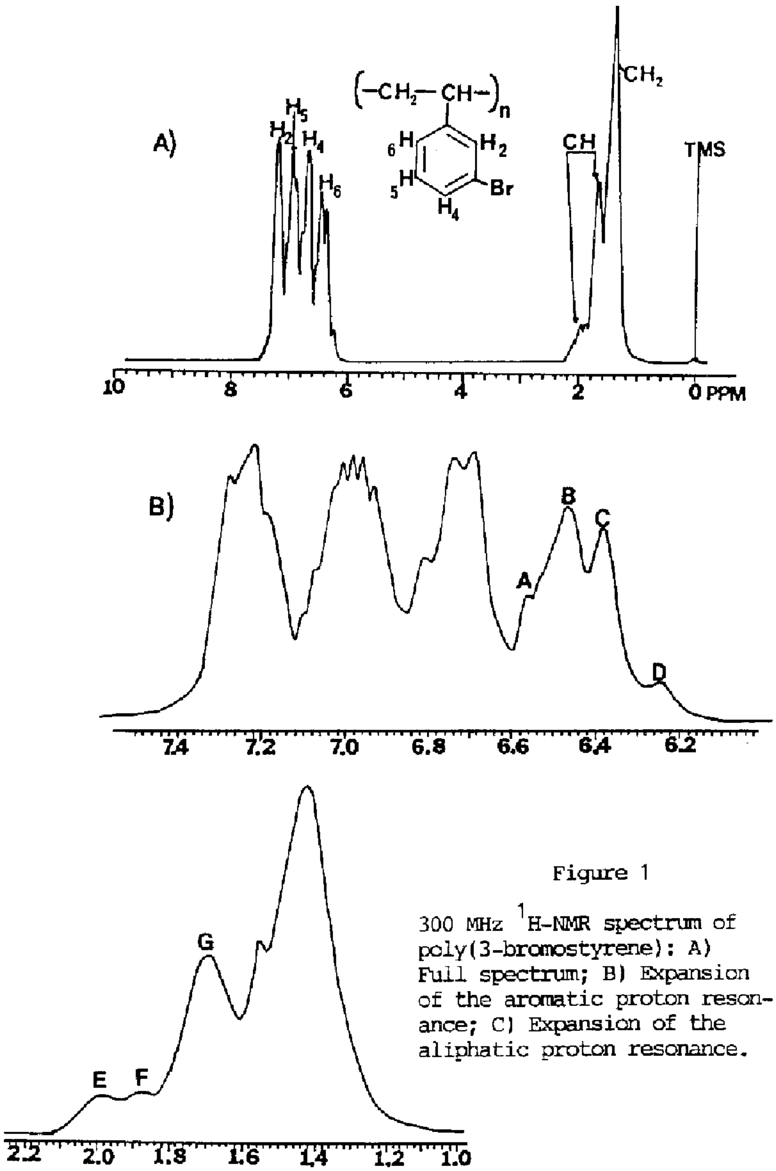

Figure 1

300 MHz ^{1}H-NMR spectrum of poly(3-bromostyrene): A) Full spectrum; B) Expansion of the aromatic proton resonance; C) Expansion of the aliphatic proton resonance.

degree of confidence. Studies of stereoregular poly(3-bromostyrene) samples and of epimerized samples derived from them need to be conducted before a specific order can be established with certainty.

TABLE 1

Fractional and Relative Intensities of the Peaks in the H_6 Proton Resonance Region

Peak	Chemical Shift (ppm)	Fractional Intensity	Relative Intensity
A	6.56	0.079 ± .009	1
B	6.48	0.50 ± .06	8
C	6.39	0.36 ± .04	6
D	6.24	0.065 ± .009	1

TABLE 2

Pentad Assignments for H_6 Proton Resonances

Peak	Chemical Shift (ppm)	Pentad Assignment
A	6.56	rmmr
B	6.48	mmmr + rmmm, mmmm, rrmm + mmrr rmrr + rrmr, rrrr
C	6.39	mrrr + rrrm, mmrm + mrmm rmrm + mrmr
D	6.24	mrrm

A P_m value calculated from the fractional intensity of peak D is 0.50 ± .07.

The methylene and methine proton resonances are overlapped, but the methine proton resonance (δ = 1.6 - 2.2 ppm) appears to have three components (E, F and G) which have relative intensities of 0.12 ± 0.02 (E), 0.11 ± 0.01 (F) and 0.77 ± 0.08 (G). According to interpretations we have provided for the methine proton resonance patterns of polystyrene and other similar polymers, area G can be attributed to mr + rm + rr triads. The relative area of the G peak (0.77) is very close to that expected for an atactic polymer (0.75). No rationalization for the occurrence of mm resonance in two peaks (E and F) can be provided at this time.

^{13}C-NMR Spectrum

The 75.5 MHz ^{13}C-NMR spectrum of poly(3-bromostyrene) is shown in Figure 2, along with horizontal expansions of some of the individual carbon resonances. The peak assignments are given in the Figure (9). The C_1 carbon resonance occurs as two broad signals of approximately equal area. This indicates a sensitivity to polymer stereochemistry, but resolution is too poor to permit any detailed analysis. The resonance assigned to the C_2, C_4 and C_5 carbons shows some multiplicity which may, in part, be due to a stereochemical sensitivity but is also due in part to the fact that this resonance area is composed of three somewhat different carbon resonances. The resonance pattern proved too complex for any reasonable interpretation to be made at the present time. Perhaps a more sophisticated analysis employing computer deconvolution of the resonances would be beneficial, or a spectrum obtained at a higher spectrometer power. The resonances due to the C_6 carbon (Figure 2C) occur in a four peak pattern (peaks A, B, C and D) that resembles the resonance pattern observed for the H_6 proton of the polymer (vide supra).

Thus, the relative intensities of the peaks are approximately multiples of 1/16 (i.e., 0.0625). Table 3 lists the chemical shifts of these peaks, their relative intensities and a set of pentad assignments that is consistent with these relative intensities assuming that the polymer is atactic. Peak D can be any of four possible pentads (mmmm, rmmr, mrrm or rrrr), and the other peaks can be due to various combinations of the remaining pentads. An extensive investigation involving stereoregular and epimerized polymers will be necessary to develop a reliable set of assignments. It does seem however that the resonance pattern observed for the C_6 carbon indicates the polymer is atactic.

The methylene carbon resonance, Figure 2D, occurs as a complex multipeak pattern. In the case of polystyrene, the methylene carbon resonance must be interpreted in terms of tetrad and hexad stereosequences (7-9). This is probably also true for poly(3-bromostyrene) but the spectrum is not defined sufficiently well to permit any reasonable assignments to be made at the present time. The methine carbon resonance occurs as two peaks (J and K) the relative intensities of which are 1:3 (J:K). In previous work on poly(2-vinylthiophene) (10) this pattern was assigned to the triads of an atactic polymer as follows: J = mm and K = mr + rm and rr. The fractional intensity of J = 0.24 ± .02 and a P_m value calculated from this fractional intensity is 0.49 ± .04.

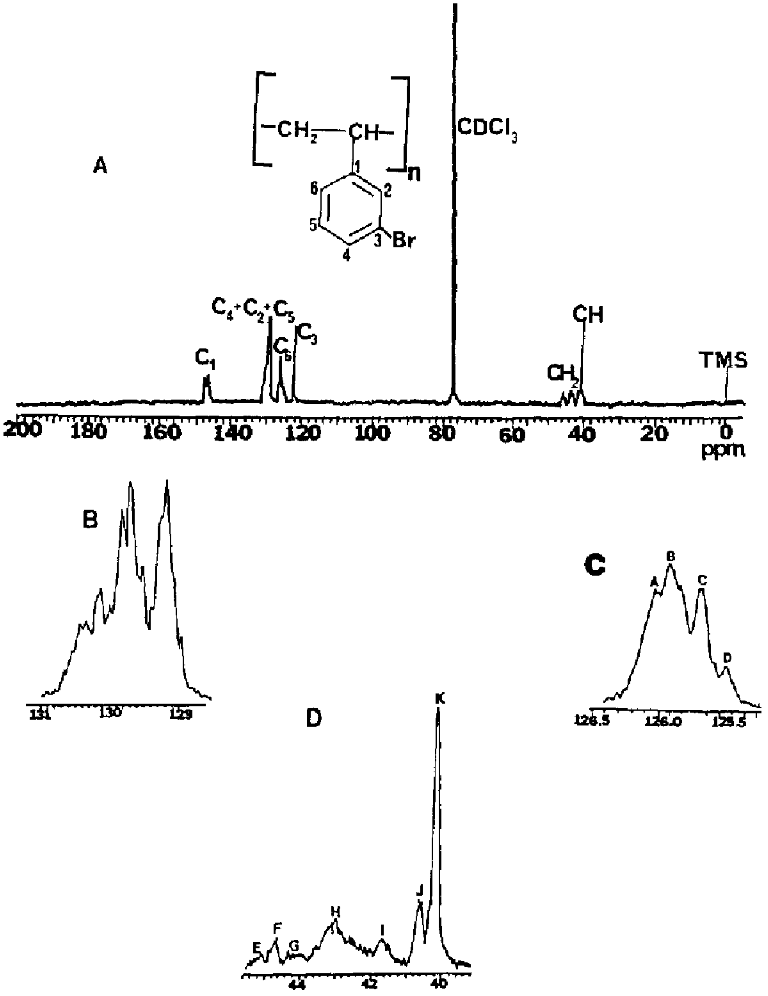

Figure 2

75.5 MHz ^{13}C-NMR spectrum of poly(3-bromostyrene): A) Full spectrum; B) C_2, C_4 and C_5 carbon resonances; C) C_6 carbon resonance; D) Aliphatic carbon resonances.

TABLE 3

Chemical Shifts, Intensities and Assignments of the Peaks in the C_6 Carbon Resonance

Peak	Chemical Shift (ppm)	Fractional Intensity	Relative Intensity	Assignment
A	126.02	0.30 ± .04	5	rmmr, mmmr + rmmm, rrmm + mmrr
B	125.91	0.37 ± .05	6	mmmm, rmrr + rrmr, mrrr + rrrm, rrrr
C	125.68	0.26 ± .03	4	rmrm + mrmr mmrm + mrmm
D	125.49	0.065 ± .007	1	mrrm

Conclusion

The 300 MHz ^{1}H-NMR and 75.5 MHz ^{13}C-NMR spectra of poly(3-bromostyrene) synthesized by free radical initiation have been recorded and analyzed. While the proton and carbon resonances that display sensitivity to stereochemistry are not as well resolved as those in the corresponding spectra of most of the poly(vinyl heterocycles) that we have studied previously (12-14, and references therein), all the data, from both ^{1}H-NMR and ^{13}C-NMR, when considered together support the conclusion that poly(3-bromostyrene) is an atactic polymer.

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