Analysis of the 300 MHz PMR spectrum of poly(p-bromostyrene)

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Summary
The 300 MHz pmr spectrum of poly(p-bromostyrene) is presented and analyzed. The aliphatic proton resonance of this polymer is very similar to that of polystyrene, but the aromatic proton resonance is somewhat more well defined. The resonance of the ring protons ortho to the polymer backbone occurs in a 5 peak pattern that, in view of the previous results obtained for poly 2- and 3-vinyl thiophenes (1,2) and poly(p-acetylstyrene) (3), was interpreted in terms of pentad stereosequences. Based on the assignments made in this paper, poly (p-bromostyrene) synthesized by free-radical initiated polymerization seems to be atactic.

Introduction
In a previous paper (3) we detailed the changes wrought in the pmr spectrum of polystyrene by acetylation of the benzene ring in the para position. Specifically, the methine proton resonance of an acetylated poly(β,β-dideuteriostyrene) separates into three readily discernable signals, in the manner of the methine proton resonances of poly(β,β-dideuterio-2- and 4-vinyl pyridines) dissolved in D2SO4 (4,5), assignable to isotactic, heterotactic and syndiotactic triads in order of increasing field. The relative intensities of these three signals was 1:2:1, strongly indicating that poly(p-acetylstyrene) was an atactic polymer with a Pm value of ~0.50 ± 0.02. Additional experiments showed that the conditions of the acetylation did not alter the stereochemistry of the polystyrene. These results lead us to conclude that polystyrene synthesized free-radically was an atactic polymer.

In order to more fully understand the cause of the signal separation observed for poly(p-acetylstyrene) we investigated the pmr spectra of a series of para substituted polystyrenes (F, Br, Cl, NH2, NO2, -OCH3, and CN) prepared by free-radical polymerization. Some of the results obtained for poly(p-bromostyrene) are reported herein.

Experimental
The p-bromostyrene monomer was obtained from the Aldrich Chemical Company and was purified by distillation immediately before use (b.p. = 88°C at 15mm Hg). All solvents were reagent grade and were used without further purification. AIBN was purified by twice recrystallizing from methanol.
Polymerization was accomplished by charging 5.0 g (0.027 mole) of p-bromostyrene and 0.015 g (9.0 x 10^-5 mole) AIBN into a thick walled polymerization tube, degassing via three freeze-thaw cycles, sealing the tube under vacuum and placing it in a thermostated water bath at 65°C for a period of 8 hours. The contents of the tube were then poured while still warm (~40°C) into a 6-fold excess of methanol. The polymer was isolated by filtration and purified by reprecipitation (3X's) from CHCl₃ solution into methanol. The polymer was then dried in vacuo at 28°C for 72 hours and weighed to determine percent conversion, which was 40.0%.

Molecular weight analysis was performed on a Waters High Resolution 6000A GPC equipped with 1 x 10⁶, 5 x 10⁵, 1 x 10⁵, 1 x 10⁴, 1 x 10³, and 500A microstyrigel columns using THF as eluent. Numerical values for Mₙ and Mₚ were obtained by comparison to a polystyrene calibration curve, and where 98,000 and 181,000 (PD = 1.84) respectively.

The pmr spectrum of poly(p-bromostyrene) was obtained on a 15% w/v solution in CDCl₃ at ambient temperature (TMS added as an internal standard) using a Varian HR-300 NMR spectrometer operating in the CW mode. Other temperatures and other solvents were tried, but the results were not significantly different than those obtained on the CDCl₃ solution of the polymer. Individual resonance areas were determined by cutting and weighing and by using a computer curve fitting program.

Results and Discussion

Figure 1 shows the 300 MHz pmr spectrum of poly(p-bromostyrene) in CDCl₃ at room temperature. The aliphatic proton resonances of this polymer assigned as shown in the Figure, are nearly identical to those of polystyrene. The methylene proton resonance, occurring at δ = 1.13-1.49 ppm, is devoid of any fine structure. The methine proton resonance, δ = 1.50-2.08 ppm, is very similar to that of polystyrene, although somewhat more well defined in the present case.

Figure 1. 300 MHz pmr spectrum of poly(p-bromostyrene).
Recorded on a 15% w/v solution in CDCl₃ at room temperature