Polymer Bulletin 18, 27–32 (1987)

Polymer Bulletin

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

**D. L. Trumbo and H. J. Harwood**

Institute of Polymer Science, University of Akron, Akron, OH 44325, USA

## 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 $D_2SO_4$ (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 $P_m$ value of ~0.50 ± .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, $NH_2$, $NO_2$, $-OCH_3$ 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 ($9.0 \times 10^{-5}$ 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 $CHCl_3$ 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 $1 \times 10^6$, $5 \times 10^5$, $1 \times 10^5$, $1 \times 10^4$, $1 \times 10^3$, and 500Å microstyragel columns using THF as eluent. Numerical values for $M_n$ and $M_w$ 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 $CDCl_3$ 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 $CDCl_3$ solution of the polymer. Individual resonance areas were determined by cutting and weighing and by using a computer curve fitting program (6).

## Results and Discussion

Figure 1 shows the 300 MHz pmr spectrum of poly(p-bromostyrene) in $CDCl_3$ 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 $\delta$ = 1.13-1.49 ppm, is devoid of any fine structure. The methine proton resonance, $\delta$ = 1.50-2.08 ppm, is very similar to that of polystyrene, although somewhat more well defined in the present case.

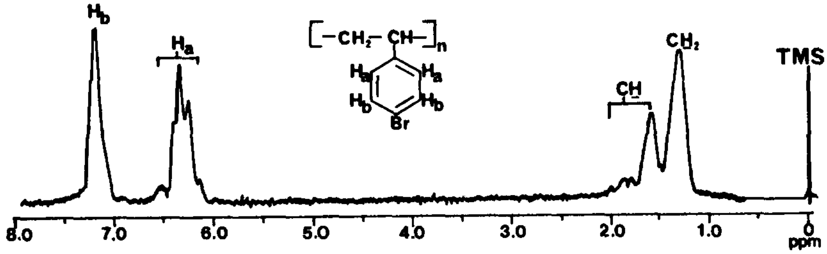

**Figure 1. 300 MHz pmr spectrum of poly(p-bromostyrene). Recorded on a 15% w/v solution in $CDCl_3$ at room temperature**

At least two major signals are evident, one centered at $\delta = 1.58$ ppm and one at $\delta = 1.85$ ppm, the lower field signal is approximately one-third the intensity of the higher field one. Previous studies on epimerized isotactic polystyrene (7) have shown that the lower field methine resonance for that polymer can be assigned to mm-triad stereosequences. Making the same assignment in the present case, it seems that poly(p-bromostyrene) has an atactic structure (the expected fraction of mm-triad in an atactic polymer is 0.25).

The aromatic proton resonances of poly(p-bromostyrene) occur in two general areas assigned as shown in Figure 1 (7). The resonance assigned to the $H_B$ protons, $\delta = 6.99$-$7.49$ ppm, is devoid of any fine structure. In the resonance assigned to the $H_A$ protons, $\delta = 6.06$-$6.67$ ppm, five separate signals are discernable, as is more clearly evident in Figure 2, which presents a horizontal expansion and computer simulation of the $H_A$ proton resonance. Based on results obtained previously for epimerized isotactic polystyrene (7) and poly 2- and 3-vinyl thiophenes (1,2), as well as the observed relative intensities of the five individual signals, 1:3:6:5:1 in order of increasing field strength, this resonance pattern was interpreted as reflecting a pentad stereosequence sensitivity. Additional support for such an interpretation was provided by a computer simulation (8) of this resonance pattern. Figure 2B.

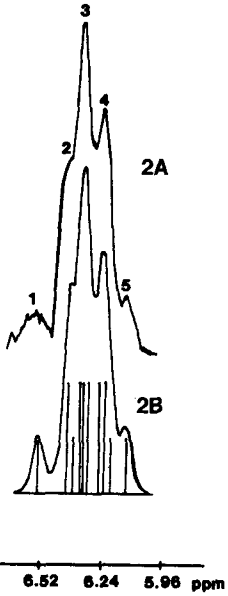

Figure 2. A) $H_a$ ring proton resonance of poly(p-bromostyrene). B) Simulation of the $H_a$ proton resonance by pentads using 0.05 ppm as the width at half-height.

A reasonably good fit was obtained using ten lines with an intensity distribution expected for the pentad stereosequences of an atactic polymer, i.e. 4 lines of single intensity and 6 lines of double intensity. Other parameters used in the simulation are given in the Figure. The experimental chemical shifts, fractional intensities and tenative assignments for each of the five signals in terms of pentads are given in Table 1. Chemical shifts and relative intensities for each of the ten lines used in the simulation are given in Table 2. It should be noted that the pentads are assigned as being contained in a given signal because at present no definate ordering is possible, even the fit obtained using the order shown in the computer simulation, while fairly good, is probably not unique. Definate assignments await the synthesis and analysis of a stereoregular poly(p-bromostyrene). However, based on arguments previously advanced (1,2,7), we believe the assignments in Table 1 to be reasonably correct. In any case, a $P_m$ value calculated on the basis of the fractional intensity of signals one or five is equal to 0.50 ± .04, which strongly indicates that poly(p-bromostyrene) when synthesized free-radically is an atactic polymer.

Table 1

Chemical Shifts, Fractional Intensities and Proposed Assignments of the Signals in Figure 2A

| Signal | Chemical Shift (ppm) | Fractional Intensity | Proposed Assignment (Pentads) | Calculated Intensities (for $P_m$ = 0.50 |
|---|---|---|---|---|
| 1 | 6.52 | 0.065 ± 0.005 | mmmm | 0.0625 |
| 2 | 6.39 | 0.17 ± 0.02 | mmmr, rmmr | 0.1875 |
| 3 | 6.33 | 0.40 ± 0.04 | mrmm, mrmr<br>mmrr | 0.3750 |
| 4 | 6.25 | 0.30 ± 0.03 | mrrr, rmrr<br>mrrm | 0.3125 |
| 5 | 6.13 | 0.061 ± 0.005 | rrrr | 0.0625 |

Table 2

Chemical Shifts and Relative Intensities of the Lines in Figure 2B

| Line | Chemical Shift (ppm) | Relative Intensity |
|---|---|---|
| 1 | 6.52 | 1 |
| 2 | 6.40 | 2 |
| 3 | 6.38 | 1 |
| 4 | 6.34 | 2 |
| 5 | 6.32 | 2 |
| 6 | 6.30 | 2 |
| 7 | 6.26 | 2 |
| 8 | 6.24 | 2 |
| 9 | 6.22 | 1 |
| 10 | 6.13 | 1 |

In a previous publication concerning the analysis of the pmr spectrum of poly(p-acetylstyrene) (3), we stated that we believed the phenomenon responsible for the observed differences in the spectra of polystyrene and ring substituted (para) polystyrenes was not a decreased "ring current" effect due to the electronegativity of the ring substituent. We instead postulated an effect that was electronic in nature but which could or would have a considerable steric component, i.e. the substituent moiety would have to be of a certain size for such an effect to be operative. Of course, a substituent of sufficient size might be able to effect the observed changes by size alone, thus we investigated substituents of varying steric bulk as well as differing electronegativities. Briefly, we suggested that dipole-induced dipole interactions between carbonyl groups and neighboring aromatic rings were responsible for the shift effects observed as such interactions would influence the energies of the various conformations available to the polymer, thus changing the conformer population distribution and thereby effect the nmr shieldings.

Further work with the other para substituents has shown that the pmr spectrum is always changes relative to that of polystyrene even in cases where the para substituent is relatively small (e.g. F). However, the most dramatic effects are observed when substituents are both relatively bulky and somewhat electron withdrawing (inductive) as in the present case. These results indicate that the observed effects of para ring substitution on the pmr spectrum are most probably due to a combination of steric and electronic factors (including dipole-induced dipole phenomena). Obviously, as previously stated steric bulk and electronic factors such as dipole-induced dipole would more heavily favor some conformations while precluding others. Most likely, tttt sequences or sequences containing mostly t conformers would be favored and gggg sequences drastically reduced or eliminated altogether (9). More work of a theoretical nature will be necessary to confirm these predictions.

## Conclusions

The ortho ring protons of poly(p-bromostyrene) seem to be sensitive to pentad stereosequences. The reasons for the enhanced sensitivity of this resonance versus the same resonance in an unsubstituted polystyrene are most probably steric and electronic. A $P_m$ value calculated from the most downfield signal in this resonance pattern (assigned to the mmmm pentad) strongly indicates that free radical initiated poly(p-bromostyrene) is atactic.

## Acknowledgement

This study was supported by a grant from the National Science Foundation (DMR-80-10709).

## References

1. D. L. Trumbo, T. Suzuki and H. J. Harwood, Polymer Bull., 4, 677 (1981).
2. D. L. Trumbo, T. Suzuki and H. J. Harwood, Polym. Preps., Am. Chem. Soc., Div. of Polym. Chem., 24(2), 360(1983).
3. D. L. Trumbo, T. K. Chen and H. J. Harwood, Macromolecules, 14, 1138(1981).
4. K. Matsuzaki, T. Kanai, T. Matsubara and S. Matsumoto, J. Polym. Sci., Polym. Chem. Ed., 14, 1475(1976).
5. K. Matsuzaki, T. Matsubara and T. Kanai, J. Polym. Sci., Polym. Chem. Ed., 15, 1573(1977).
6. E. D. Von Meerwall, Comp. Phys. Comm., 11, 211(1976).
7. L. Shepherd, T. K. Chen and H. J. Harwood, Polymer Bull., 1, 445 (1979).
8. Computer Program Supplied by B. L. Bruner, The University of Kentucky.
9. P. C. Hagele and L. Beck, Macromolecules, 10, 213(1977).

Accepted May 8, 1987 K