

Preliminary analysis of the ^1H -NMR and ^{13}C -NMR spectra of poly(2-iodostyrene)

David L. Trumbo

S. C. Johnson Polymer, S. C. Johnson & Son., Inc. 1525 Howe Street, Racine, WI 53403-2236, USA

Summary

The 300 MHz ^1H -NMR and 75.5 MHz ^{13}C -NMR spectra of poly(2-iodostyrene) were recorded and analyzed in terms of polymer stereochemistry. The aromatic protons were insufficiently resolved for any reasonable peak assignments to be made, but the methine proton resonance could be interpreted in terms of a pentad stereosequence sensitivity. The analysis suggested poly(2-iodostyrene) was an atactic polymer. The ^{13}C -NMR spectrum was somewhat better resolved and analysis supports the results from the ^1H -NMR i.e. poly(2-iodostyrene) is an atactic polymer.

Introduction

In previous studies concerning the tacticity of free radically initiated polymers, we found that substitution of the benzene ring moiety can simplify complex spectra by reducing signal overlap; particularly signal overlap that might be due, at least in part, to the ring current effect exerted by the benzene ring (1-3). We have found that the position occupied (o, m or p) and the type of substituent has a significant effect on the appearance of the ^1H -NMR spectrum. For example an acetyl group in the 4- (para) position effects the methine resonance in such a way that three peaks of 1:2:1 relative intensity ratio are readily discernable in a polystyrene where both methylene protons have been replaced by deuterium. This relative intensity ratio is that expected for the triads of an atactic polymer. A bromine in the meta or para position (2,3) makes possible the interpretation of aromatic proton resonances in terms of pentads. In order to further investigate the effects of ring substitution on the nmr spectra of free radically initiated polystyrenes, we decided to synthesize poly(2-iodostyrene), and examine the high field nmr spectra of this polymer.

Experimental

The 2-iodostyrene was obtained from Polysciences. The monomer was

purified by distilling it twice from CaH_2 . All solvents used were reagent grade and were used without further purification. AIBN was recrystallized from CH_3OH and stored at -5°C until needed. The ^1H - and ^{13}C -NMR spectra were obtained with a Varian Gemini 300 operating in the FT mode. The polymers were dissolved in CDCl_3 at 7-9% w/v and TMS was added as an internal standard. All spectra were recorded at ambient temperature. Relative peak areas were determined by electronic integration and by tracing the peaks on high quality paper, cutting out and weighing the tracings on a 5-place analytical balance. Polymer molecular weights were measured with a Waters 150 ALC/GPC equipped with 10^6 , 10^5 , 10^4 , 10^3 , 500 and 100A ultrastyrigel columns. Numerical values for the molecular weights were obtained by comparison to a polystyrene calibration curve.

Polymer Synthesis

Monomer (2.0 g) was weighed into a clean, dry screw cap vial. AIBN (0.8 wt %) was added and the resulting solution was sparged with dry N_2 while cold for 3 min. The vial was then placed in a water bath maintained at 65°C for the desired length of time. For the thermal polymerization a 3.0g sample of monomer was heated at 110°C for 4h.

In both cases the vials were removed from their respective baths and allowed to cool to ambient temperature. Approximately 5 ml of cold CH_3OH was then added to precipitate any polymer formed. The crude polymers were isolated by filtration and were purified by reprecipitating them twice from CHCl_3 solution into CH_3OH . The polymers were dried at 27°C in vacuo for 72h and conversions were determined gravimetrically. The conditions used and the results obtained are listed in Table 1.

TABLE 1

Molecular Weights and Conversions for Poly(2-Iodostyrene)

Polymer ^a	PZN Time (h)	% Conversion	M_n	M_w	M_w/M_n
2IS ^a	5.5	2.6	13000	22000	1.69
2IST	4	7.5	5800	10200	1.76

- a. 2IS = poly(2-iodostyrene) AIBN initiator; 2IST = poly 2-(iodostyrene) thermal initiator

Results and Discussion

The ^1H -NMR spectra are shown in Figure 1. The peaks are assigned as shown in the Figures (4,5). The aromatic proton resonances display a multiplicity that could indicate a sensitivity to polymer stereo-

chemistry. However, the patterns displayed by the aromatic protons of 2IS (AIBN and thermal) are complex and lack sufficient resolution for any reasonable assignments, in terms of stereochemistry, to be made.

The expanded aliphatic resonances of 2IS and 2IST (Figures 1B and 2B) show at least one resonance well downfield from the bulk of the aliphatic resonance (peak A in both cases). For both 2IS and 2IST this peak is part of the methine resonance as are peaks B + C for 2IS, and peaks C + D for 2IST.

However, the total area of peaks A-C for 2IS and A-D for 2IST is not 1/3 of the total aliphatic resonance. This means that some of the methine resonance is hidden under the methylene resonance. For 2IS the amount of resonance hidden is 22% of the total methine resonance, for 2IST the hidden amount resonance is 28% of the total methine resonance. The relative intensity ratio of the peaks in the methine resonance of 2IS is 1:1:1:1, A:B:C:overlapped resonance. The corresponding fractional intensities are $A = 0.24 \pm .01$, $B = 0.25 \pm .02$, $C = 0.28 \pm .03$ and overlapped resonance = $0.22 \pm .02$. These fractional intensities are each approximately four times the expected fractional intensity of a singlet pentad in an atactic polymer (0.0625). A reasonable approach might be to multiply each of the relative intensities by four, yielding a relative intensity ratio of 4:4:4:4. This ratio sums to 16 and, since there are 16 pentads of equal intensity in an atactic polymer, it is likely that the observed resonance pattern is reflecting a sensitivity to pentad stereosequences and that 2IS is an atactic polymer. While no specific assignments can be made at this time because no stereoregular polymer has been synthesized; previous results (6,7) have indicated that in general the pentad resonances progress from mm centered to rr centered in order of increasing field i.e. $xmxx \rightarrow xrrx$. For the 2IST material the downfield methine resonance occurs as two peaks, A+B in Figure 2. The total area of A+B is only 15% of the total methine resonance. Meanwhile peak C = 30%, peak D = 27% and hidden resonance = 28% of the total methine resonance. Calculation of a relative intensity ratio yields 1:2:2:2, A+B:C:D:hidden resonance. This relative intensity ratio and the corresponding fractional intensities indicate that this resonance pattern is not due to the pentad stereosequences of an atactic polymer. Or is it? $^{13}\text{C-NMR}$ spectroscopy strongly indicated that 2IST was an atactic polymer (see below); it therefore seems likely that the methine proton resonance pattern was that of an atactic polymer. If the resonance pattern observed was due to pentads then the sum of the relative intensity ratios must equal 16. In the present case this is apparently not so, however, note that the separation of A+B from the remainder of the aliphatic resonance is greater than for peak A in the 2IS case. This may be the reason that a small shoulder at $\delta = 2.69$ ppm is visible on peak C. If the area of this small shoulder is added to the area of A+B then A+B+ shoulder = 20% of

the methine resonance. Peak C now = 26% of the methine resonance (the other parts of the methine resonance remain the same). Within experimental error the relative intensity ratio becomes 1:1:1:1, A+B+shoulder:C:D:overlapped resonance. The same interpretation of this resonance pattern that was made for 2IS can now be made for 2IST. The fractional intensities of peak A and the shoulder on C indicate they may be due to heptads, but the resolution is insufficient for any assignments to be made. It should be noted that the explanation of the methine resonance pattern of 2IST given above is most probably not unique i.e. some others may be possible. In any case, while no detailed assignments of the methine proton resonances in terms of pentads can be made at this time for either 2IS or 2IST, the resonance patterns strongly indicate that both of these polymers are atactic.

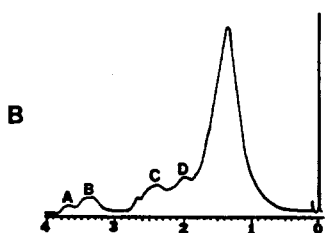
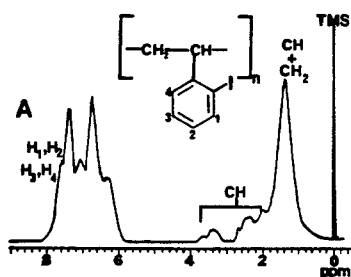


Figure 1

A) 300 MHz ^1H -NMR spectrum of 2IST; B) Linear expansion of the aliphatic proton resonances

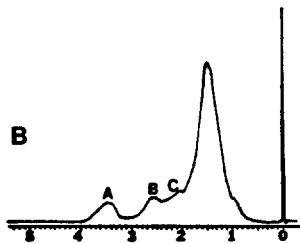
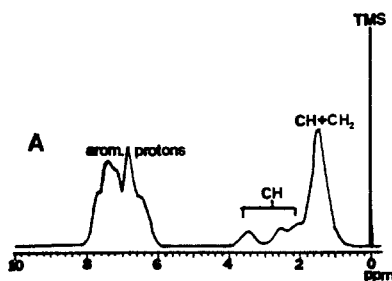


Figure 2

A) 300 MHz ^1H -NMR spectrum of 2IS; B) Linear expansion of the aliphatic proton resonances

$^{13}\text{C-NMR}$

The $^{13}\text{C-NMR}$ spectra of 2IS and 2IST are shown in Figures 3 and 4. The signals are assigned as shown in the Figures (9). The $^{13}\text{C-NMR}$ spectra of the other polymers used in this study showed resonances that displayed multiplicity that indicated a sensitivity to polymer stereochemistry. However, none of the resonances displayed sufficient resolution for any reasonable assignments to be made, with the exception of the C_5 resonance of 2IS and 2IST. The resonance occurs as a five peak pattern for 2IS (Figure 4A) and a four peak pattern for 2IST. For 2IS the small peak at 31.0 ppm is considered as part of peak A.

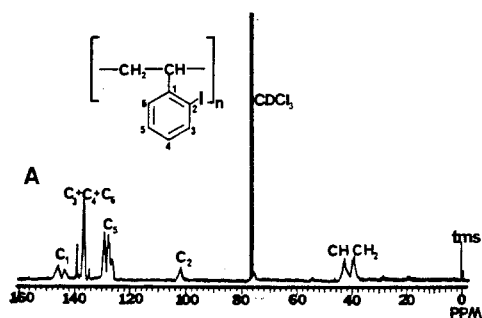


Figure 3

75.5 MHz $^{13}\text{C-NMR}$ spectra of
A) 2IS and B) 2IST

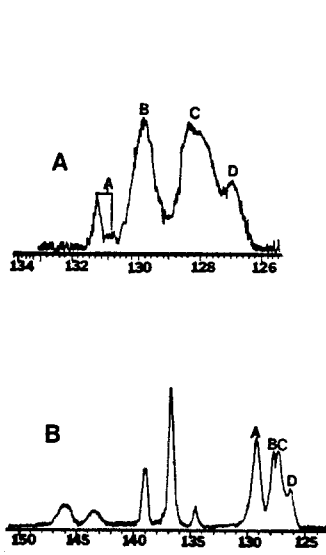


Figure 4

Linear expansions of the C_5
carbon resonance of A) 2IS
and B) 2IST

The relative intensity ratio for the peaks in the C_5 resonance of 2IS is 1:6:7:2 the sum of which is 16. This result strongly suggests that this pattern is reflecting a sensitivity to the pentad stereo-sequences of an atactic polymer. The small peak at 131.0 ppm most probably is due to a higher order stereosequence, possibly a heptad, which would be part of the further splitting of the pentad represented

by the area labeled A, hence this small peak was included as part of peak A's area. The fractional intensity of this area is $0.065 \pm .007$ (peak a) which means it should be assigned to a pentad of singlet intensity. Recent reports in the literature suggest the mmmr pentad (7,10). Tentative assignments for the other resonances in terms of pentads are given in Table 2. For the C_5 carbon resonance of 2IST (Figure 4B) the relative intensity ratio of A:B:C:D is 3:2:2:1 which sums to 8. However, the fractional intensities and the results from the C_5 resonance of 2IS strongly suggest that this pattern is displaying a pentad sensitivity.

Therefore, it is reasonable to multiply each relative intensity by two and obtain 6:4:4:2 as a revised ratio of A:B:C:D. This ratio sums to 16 reflecting the pentad sensitivity of this resonance pattern. The proposed assignments for these resonances are given in Table 2.

TABLE 2

Chemical Shifts, Intensities and Tentative Assignments
for the C_5 Resonance of 2IS and 2IST

Polymer	Peak	Chemical Shift (ppm)	F.I. ^a	R.I. ^a	Proposed Assignment
2IS	B	129.88	$0.38 \pm .04$	6	rrmmn + mmrmr, mrrmm + mmrmm, rmmrn + mrrmr
2IS	C	128.19	$0.44 \pm .05$	7	rrmmn + mmrmr, rrrmr + rmmrn, rrrm + mmrmm
2IS	D	126.95	$0.13 \pm .02$	2	rrrr, mrrm
2IST	A	129.20	$0.39 \pm .04$	6	mmrmr + rmmrn, mrrmm + mmrmm, mmrmm
2IST	B	127.80	$0.22 \pm .03$	4	rrmmn + mmrmr mrrmr + rmmrn
2IST	C	127.38	$0.27 \pm .04$	4	mrrrr + rrrm rmmrn + rmmrn
2IST	D	126.35	$0.12 \pm .02$	2	mrrm, rrrr

a. F.I. = fractional intensity; R.I. = relative intensity

It should be emphasized that the assignments provided in Table 2 are tentative and the peaks are assigned as containing the pentad(s)

listed. No specific order can be assigned in the absence of a stereoregular polymer and epimerization studies, or model compounds. Precisely why the resonance patterns are not exactly the same for 2IS and 2IST is not known at the present time. Perhaps the differences in the molecular weights and the corresponding effect on solution viscosity may be partly responsible for the observed differences in the spectra but more detailed experiments are necessary before any reasonably accurate explanations can be advanced. In any case P_m values can be calculated from the fractional intensities of some of the signals. The values are $P_m = 0.51 \pm .06$ for 2IS and $P_m = 0.49 \pm .06$ for 2IST.

Conclusions

The ^1H -NMR and ^{13}C -NMR spectra of free radical and thermally initiated poly(2-iodostyrene) have been recorded. A preliminary analysis of the methine proton resonances of these polymers and the C_5 carbon resonances of revealed patterns that could be interpreted in terms of pentad stereosequence sensitivity. While the resolution of the ^1H -NMR spectra is not that good, the analysis strongly indicates that these polymers are atactic. This contention is supported by the analysis of the ^{13}C -NMR spectra of 2IS and 2IST.

References

1. D. L. Trumbo, T. K. Chen and H. J. Harwood, *Macromolecules*, **14**, 1138 (1981).
2. D. L. Trumbo and H. J. Harwood, *Polym. Bull.*, **18**, 27 (1987).
3. D. L. Trumbo and H. J. Harwood, *Polym. Bull.*, **32**, 207 (1994).
4. L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry", Pergamon Press, NY (1972).
5. J. L. Koenig, "Chemical Microstructure of Polymer Chains", J. Wiley and Sons, NY (1980).
6. H. J. Harwood, T. K. Chen and F. T. Lin, *ACS Symposium Series*, **247**, 197 (1984).
7. S. J. Tsau, E. R. Santee and H. J. Harwood, *ACS Polym. Prep.*, **31**(2), 472 (1990).
8. T. K. Chen, T. A. Gerkin and H. J. Harwood, *Polym. Bull.*, **2**, 34 (1980).
9. F. W. Wehrli and T. Wirthlin, "Interpretation of Carbon-13 Spectra", Heyden, NY (1976).
10. D. L. Trumbo, F. T. Lin, F. M. Lin and H. J. Harwood, *Polym. Bull.*, **28**, 87 (1992).

Received: 22 August 1994/Revised version: 6 September 1994/
Accepted: 6 September 1994