Polymer Bulletin 2, 37–42 (1980)

Polymer Bulletin

Methylene Carbon Resonance Spectra of Epimerized Isotactic Polystyrene

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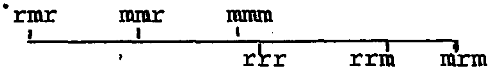
Summary

The methylene carbon resonance patterns of partially epimerized isotactic polystyrenes were measured and interpreted in terms of tetrad and hexad stereosequence distributions that were calculated by Monte Carlo simulation of the epimerization process. Empirical rules were developed for assigning hexad resonances. Calculated spectra based on these assignments and on the Monte Carlo results were in reasonably good agreement with experimental spectra. The resonances of mm-type methine carbons were noted to occur about 0.2 ppm downfield from other methine carbon resonances.

Introduction

A number of studies on the ^{13}C-magnetic resonance spectra of polystyrene have been reported (JOHNSON et al. 1970, INOUE et al. 1972, MATSUZAKI et al. 1972, MATSUZAKI et al. 1975, RANDALL 1975, EBDON and HUCKERBY 1976, URYU et al. 1979). The methylene carbon and aromatic C-1 carbon resonance patterns contain information about the stereo-chemical structure of polystyrene, but unequivocal assignments for these resonances have not been made.

Theoretical calculations (TONELLI, 1979) and studies on the cmr spectra of model tetramers (JASSI, et al. 1977) indicate that the methylene carbon tetrad resonances should be observed in the following order of increasing field.



INOUE et al. (1972) proposed a similar order, based on resonance area measurements and the use of necessary n-add relationships, except that the mmm and rrr resonances were interchanged, due to overlapping, viz.

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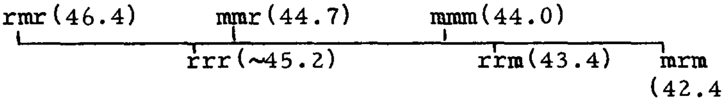
RANDALL (1972) proposed a completely different set of assignments, however, based on the relative intensities of the methylene carbon resonances and the belief that polystyrene is slightly isotactic (p(m)=0.57), with a Bernoullian distribution of stereosequences.

The purpose of the present paper is to present the results of preliminary studies on the methylene and methine carbon resonances of partially epimerized isotactic polystyrenes. It was hoped that such studies would enable reliable assignments to be made for these resonances.

Methylene Carbon Resonance Spectra of Partially Epimerized Isotactic Polystyrenes

Isotactic polystyrene was epimerized with KOt-Bu in HMPA using the procedure described previously (SHEPHERD et al. 1979). Cmr spectra of the epimerized products (~ 25% wt./vol.) in a 4:1 trichlorobenzene:perdeuterobenzene mixture at 120° were recorded using a Varian CFT-20 nmr spectrometer. The spectra were accumulated with pulse spacings of 0.4 sec. and a 90° flip angle. These were equivalent to spectra obtained with pulse spacings of 0.6 and 0.8 sec. The spectra were ^{1}H-noise decoupled. The transmitter offset was set 16 ppm (TO=54) downfield from TMS and the 16-66 ppm resonance region was measured. Studies on isotactic polystyrene indicated that these conditions did not result in rollover resonances in this region. The 300 MHz pmr spectra of the samples were also recorded to establish the extent of epimerization obtained for each sample studied. Thus, mm-contents of the polymers were evaluated from their methine proton resonance patterns and Monte Carlo simulations [SHEPHERD et al., 1979] that reached these mm contents were used to obtain tetrad and hexad distributions. These were used, in turn, to interpret the methylene carbon resonance spectra of the epimerized polystyrenes. Spectra simulations were made with the aid of a program developed by B. L. Bruner of the University of Kentucky, which plots the sums of Lorentzian curves from chemical shift, intensity and half-width information. Chemical shifts for hexad resonances were obtained from empirically developed shift rules (vide infra). Intensities were based on hexad distributions calculated by Monte Carlo simulation and a half-width of 0.35 ppm was used for all resonances. For reasons not understood at present, spectra simulations for polymers epimerized to low extents were in good agreement with experimental spectra only if they were based on Monte Carlo calculations that resulted in mm-contents about 0.06 less than those measured by ^1H-spectroscopy. Calculations show that the mmmmm hexad intensity is the only structural feature that is significantly influenced by small charges in extent of epimerization at the points where this effect is observed. For this reason, the assignments proposed in this paper are believed to be approximately correct, even though our present interpretations of the methine proton and methylene carbon resonance spectra are not completely consistent.

Figure 1 shows CH_2 and CH carbon resonances for several epimerized polystyrenes. The completely epimerized polymer has the same spectrum as that of free radical initiated polymer. Evident in the spectra of polymers epimerized to low extents are new signals at 43.4 and 44.7 ppm, in addition to the mmm tetrad at 43.7 ppm. The new signals are assignable to (mmr + rmm) and (mrr + rrm) tetrads, but it is not possible to decide which tetrad should be made to which peak since the calculated intensities of these tetrads are very similar in most of the samples. Following JASSE (1977) and TONELLI (1979), the higher field peak is assigned to (mrr + rrm) tetrads. The spectra of polymers epimerized to higher extents contain additional resonances near 46.4, 45.2 and 42.4 ppm. Again, it is difficult to make assignments from the relative intensities of rmr, rrr and mrm tetrads since they are all very similar. JASSE'S (1977) model compound studies and TONELLI'S (1979) calculations suggest that rmr should be observed at lowest field (46.4 ppm) and that mrm should be observed at highest field (42.4 ppm). According to these assignments the m- and r- centered tetrad resonances are more overlapped than previous assignments indicate, viz.



The spectra clearly indicate that they are affected by hexad stereosequences. This makes it difficult to

Table 1. Hexad Resonance Assignments (ppm from TMS) for Polystyrene in 1:4 Perdeuterobenzene-Trichlorobenzene Solution at 120^0.

*mmmmm	43.73	*mrmrm	46.06	*mmrrm	43.38
mmmmr	43.95	*rrmrm	46.32	rmrrm	43.12
rmmmr	44.16	*rrmrr	46.58	mmrrr	43.90
mrmmm	44.42	*rrrrr	45.72	**rmrrr	43.47
*rrmmm	44.68	rrrrm	45.20	*mmrmm	42.69
mrmmr	44.64	mrrrm	44.68	*rmrmm	42.43
rrmmr	44.90			*rmrmr	42.17

*Represents assignments made directly from observed spectra.

**The predicted value is 43.64 but 43.47 seems better.

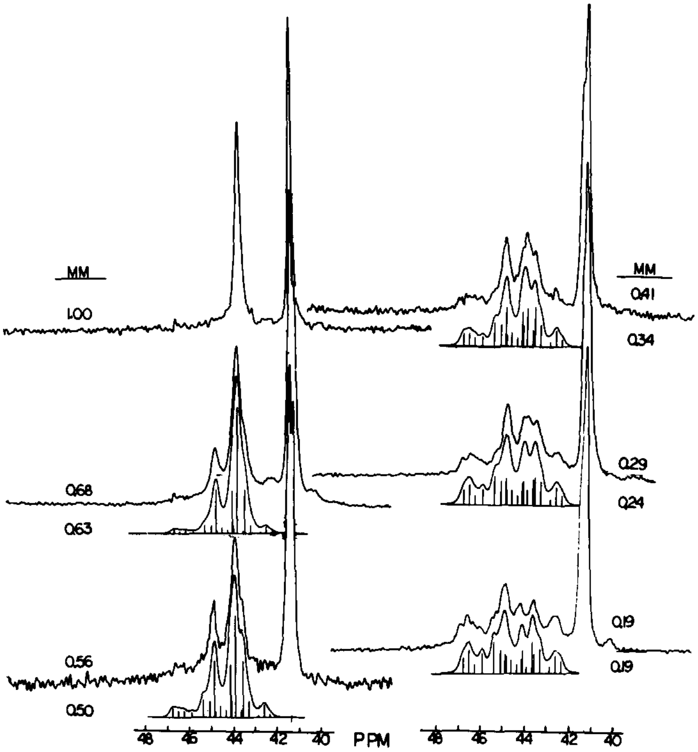


Figure 1. Observed and Simulated Methylene and Methine Carbon Resonance Spectra of Isotactic and Epimerized Polystyrene in 1:4 Perdeuterobenzene-Trichlorobenzene Solution at 120^0. The mm-contents indicated for the experimental spectra were measured by pmr spectroscopy; mm-contents associated with the simulated spectra are also indicated.

develop additivity rules for tetrad assignments, but the above assignments do obey the following rules.

Rule 1. Changing the central dyad of a tetrad from m to r causes an upfield shift of 1.2-1.6ppm

Rule 2. Changing an outer dyad of a tetrad from m to r causes a downfield shift of 0.7-1.0ppm if the other outer dyad is m and 1.7-1.8ppm if the other outer dyad is r.

In an effort to simulate spectra of the partially epimerized polymers, additional rules were developed for the chemical shifts of hexad stereosequences. The following rule led to assignments that enabled the observed spectra to be simulated reasonably well.

Rule 3. Changing the outer dyad of a <u>hexad</u> from m to r causes the following shifts, depending on the structure of the triad to which the dyad is connected.

a) -(mm)m-→-(mm)r- shift downfield 0.22 ppm
b) -(rm)m-→-(rm)r- shift upfield 0.26 ppm
c) -(mr)m-→-(mr)r- shift downfield 0.26 ppm
d) -(rr)m-→-(rr)r- shift downfield 0.52 ppm

These rules were developed empirically from measurable hexad shift differences, where observable, and by adjustment until they led to a series of hexad assignments that allowed the spectra to be simulated satisfactorily from Monte Carlo generated stereosequence distributions.

Rule 3b. was derived largely from assignments developed for the mrr centered hexads, which were difficult to make and are still not considered entirely satisfactory. It may require correction in the future.

Table 1 lists hexad assignments that were used to generate the simulated spectra depicted in Figure 1. Some of these may require adjustment as improved spectra become available. However, the fact that these assignments obey the simple rules presented above and yield simulated spectra that agree satisfactorily with observed spectra leads us to believe that they are reasonably correct.

Theoretical analyses similar to those reported by TONELLI (1979) may provide some rationale for the magnitudes and signs of the constants associated with the rules presented above. These, together with better resolved spectra that may become available in the future may provide a more complete understanding of the methylene carbon resonance of polystyrene. It should be noted that a single probability parameter (R=0.65, see SHEPHERD, et al. [1979]) was used for the Monte Carlo simulations employed in this study. The use of a more elaborate Monte Carlo simulation process might lead to spectra simulations that agree better with experimental spectra, but it does not seem reasonable to apply this easily programmed refinement to the presently available data.

Methine Carbon Resonances of Partially Epimerized Polystyrenes

As can be seen in Figure 1, splitting is observed in the methine carbon resonance region when the r-contents of the polymers are small. This has not been reported previously for a polystyrene sample. It appears that the mm-triad resonances occur about 0.2 ppm downfield from the (mr+rm)- and rr-resonances, which are probably separated by less than 0.05 ppm. This behavior is reminiscent of the behavior observed for the methine proton resonances in polystyrene [SHEPHERD, et al., 1979].

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Received November 8, 1979