Nuclear Magnetic Resonance Data on Deuterated Polystyrenes

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ABSTRACT: The deuterium-decoupled 100 MHz nmr spectra of massively deuterated polystyrenes have been run. The degree of steric purity of isotactic Ziegler–Natta polystyrene appears to be at least 97%. The spectra of free radical initiated polystyrenes show that they are substantially atactic.

The purpose of this research is to establish the degree of steric purity of isotactic polystyrene, obtained using a Ziegler–Natta catalyst, and to achieve a steric characterization of styrene polymers obtained by free radical initiation, at different temperatures.

Such a study was previously attempted at 60 MHz by Bovey, *et al.*,[1] and by Brownstein, *et al.*;[2] nevertheless we thought it useful to run new spectra under very different experimental conditions.

In view of the good results of a previous study by one of us on massively deuterated vinyl polymers,[3] and of the high degree of resolution obtainable under conditions of deuterium decoupling, we applied the same technique to polystyrenes.

Experimental Section

Monomers A ($C_6D_5CD{=}CD_2$, isotopic purity 97.6%) and B ($C_6D_5CD{=}CD_2$, isotopic purity, 99%) were obtained by reduction of acetophenone-d_8 with $LiAlH_4$ or $LiAlD_4$, followed by dehydration. Acetophenone-d_8 was in turn obtained by a Friedel–Crafts synthesis from benzene-d_6 and acetyl-d_3 chloride, the latter being prepared from acetic acid-d_4 and benzoyl chloride.[4] The starting deuterated compounds (benzene-d_6, acetic acid-d_4, $LiAlD_4$) had isotopic purities greater than 99%. The over-all yield of the synthesis, calculated on acetic acid-d_4, was about 40%.

All the isotopic contents were obtained by mass spectrometry.

Polymers. 1. Isotactic polystyrene (MEK or acetone-insoluble fraction) was obtained by $AlEt_3$–$TiCl_3$ (Ara) catalysts under normal conditions and had $\bar{M}_v \backsim 2 \times 10^6$.

2.—Radical polystyrenes were obtained by bulk polymerization with bisazoisobutyronitrile at 100, 60, and 18° and had average molecular weights of 2–6 × 10^5.

The nmr spectra were obtained on a 5% solution in *o*-dichlorobenzene at 160°; the internal standard was HMDS. The spectrum running conditions are as previously described.[3]

Isotactic Polystyrene. We first examined the nmr spectrum of $[-C_6D_5CHCD_2-]_x$. The deuterium-decoupled spectrum of this polymer (Figure 1) shows a singlet having a width of 1.1 cps, centered at 218.8, and two small peaks at 216.4 and 223.0 cps, whose intensity is the same as that of another multiplet at 145 cps, the latter being clearly due to the residual β,β protons (as isotopic impurities).

We attribute the two small peaks at 216.4 and 223.0 cps to the normal vicinal coupling between β,β protons present as isotopic impurity in the isotactic polymer and the α protons; in fact, the distance between these two peaks represents the vicinal coupling constants.[1,5] This was also observed by us in the spectrum of a sample of isotactic polystyrene-*trans*-d_1.[6]

We do not see any other peak in the spectrum, and it can be deduced that the steric impurities content of this Ziegler–Natta isotactic polystyrene should be less than one-half of that of the isotopic impurities, therefore, the steric purity of this polymer should be better than 97.5%. Support for the high steric purity of the sample is the small line width.

Radical Polystyrenes. The deuterium-decoupled spectrum of a d_7 sample prepared at 18° is shown in Figure 2a.

This spectrum shows a larger number of peaks than previously described for a radical polystyrene-β,β-d_2.[1] At least six peaks are apparent in the spectrum, and these are broad and poorly resolved; a statistical interpretation of this spectrum in terms of triads does not appear possible.

In the attempt to improve the degree of resolution, by reducing the possible effect of the long-range coupling between different neighboring pentads, we prepared a *d* copolymer by the radical polymerization at 18° of a mixture of d_7 (20%) and d_8 (80%) monomers. Its spectrum is shown in Figure 2b.

We note only a slight improvement in the resolution. The number of resolved peaks is still six, at 193, 195, 199, 206, 216, and 226 cps from HMDS.

The splitting of the main peak into two bands (193 and 195 cps, respectively) is not spurious, as it was checked by running the spectrum several times.

It is also possible to note that the multiplet pattern probably has unresolved components, as every peak is wide with respect to that observed for isotactic polymer and the spin couplings are here practically absent.

The only peak we can surely attribute is that centered at 216 cps, which corresponds exactly to the observed one in the isotactic polymer, and therefore is due to an *mmmm* pentad.[7] This peak is, however, rather weak.

We note at this point that in the atactic polypropene spectra[8] we succeeded in observing all the six possible tetrads and the bands are well separated even though they cover a small experimental range; the fact that the polystyrene spectrum is so broad, although it covers a larger frequency

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(1) F. A. Bovey, F. P. Hood III, E. W. Anderson, and L. C. Snyder, *J. Chem. Phys.*, **42**, 3900 (1965).

(2) S. Brownstein, S. Bywater, and D. J. Worsfold, *J. Phys. Chem.*, **66**, 2067 (1962).

(3) A. L. Segre, *Macromolecules*, **1**, 93 (1968).

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(5) F. Heatley and F. A. Bovey, private communication.

(6) A. L. Segre, unpublished results.

(7) D. Doskočilova, lecture presented at the Summer School in Polymer Spectroscopy, Prague, 1967.

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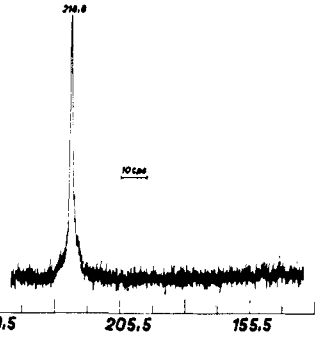

Figure 1. Nmr spectrum of isotactic polystyrene-d_7.

range, suggests the possibility that the presence of different heptads may affect the spectrum.

The apparent complexity of the spectrum of this radical polymer, which is characterized by a number of wide, poorly resolved peaks, leads to the conclusion that the polymer has to be considered as devoid of any appreciable degree of stereoregularity.

By increasing the polymerization temperature of radical d_7, d_8 copolymers, at 60 and 100°, we observed only a slight increase of the 216-cps peak and a loss of resolution in the 195- and 193-cps bands. The spectral differences are, however, very small.

Conclusion

The most important fact which can be drawn from these experimental data is the high steric purity of the isotactic polystyrene prepared by a typical Ziegler–Natta catalyst.

The problem of the degree of steric order of the partially crystalline polystyrenes invariably obtained by Ziegler–Natta catalysis arose since the discovery and the first studies of that polymer.[9] The initial hypothesis of its equally high degree of isotacticity soon became a generally accepted result of an extensive chemical investigation on kinetics and mechanism of the stereospecific polymerization of styrene[10] and of 30 other vinyl aromatic monomers.[11]

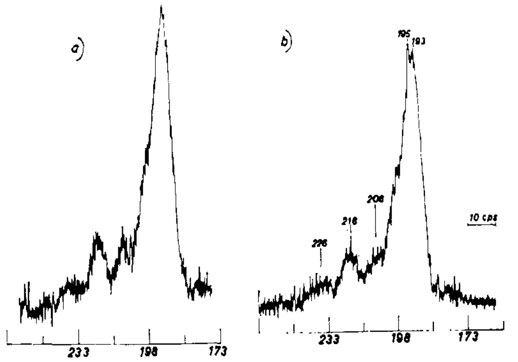

Figure 2. Nmr spectrum of free-radical polystyrene-d_7 (a) and of a d copolymer obtained by free-radical polymerization of a mixture (b) of styrene-d_7 (20%) and styrene-d_8 (80%). Polymerization temperature was 18°.

The present nmr data can, however, be considered as a direct experimental characterization of the steric structure of the isotactic polystyrene, leading to a significantly high degree of stereoregularity.

A further interesting conclusion is that a conventional radical polystyrene can be practically considered as an atactic polymer and this last conclusion is in agreement with the latest 220-MHz data by Heatley and Bovey.[5] Only slight differences can be observed in the distribution of the steric configurations along the polymer chain by varying the radical polymerization temperature in a fairly wide range.

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