

# Polymer Nuclear Magnetic Resonance Spectroscopy. XIII. Polystyrene at 220 MHz

F. Heatley and F. A. Bovey

Bell Telephone Laboratories, Inc., Murray Hill, New Jersey. Received May 10, 1968

**ABSTRACT:** The high-resolution nmr spectra of isotactic and atactic polystyrenes were reinvestigated at 220 MHz. In the moderately well-resolved spectrum of the former polymer, the appearance of a magnetically non-equivalent methylene group where none was distinguishable at lower field strengths confirms that it has indeed an isotactic structure. Spectra calculated on this basis are in good agreement with experiment. These calculations also show that as in other isotactic vinyl polymers, the coupling constants between each methylene proton and neighboring  $\alpha$  protons are unequal but no single explanation of this difference can at present be found.

Nuclear magnetic resonance spectroscopy has proved of exceptional value in the study of the stereochemical infrastructure of polymers.<sup>1,2</sup> With the aid of spectrum simplifying techniques, such as selective deuteration<sup>3–5</sup> and spin decoupling,<sup>5</sup> stereochemically different sequences of up to five monomer units ("pentads") have been distinguished in favorable instances. However, polystyrene has hitherto resisted most attempts to characterize the chain stereochemical structure.<sup>6,7</sup> A previous study<sup>6</sup> of isotactic polystyrene (prepared with a Ziegler–Natta catalyst) at 60 MHz showed moderately well-resolved spin-coupling fine structure, as expected from a regular structure, but within the experimental error, the two methylene protons (in principle nonequivalent) were indistinguishable in chemical shift. It was hoped that observations at 220 MHz would reveal this expected nonequivalence and perhaps enable a refinement of the vicinal coupling constants which are important in elucidating the chain conformation.

## Experimental Section

Isotactic polystyrene ( $\bar{M}_w = 494,000$ ;  $\bar{M}_v = 430,000$ ) was obtained from P. I. Roth (Minnesota Mining and Mfg. Co.).

Nmr spectra were obtained on a Varian Associates 220-MHz spectrometer using 2% solutions in *o*-dichlorobenzene. Hexamethyldisiloxane ( $\tau$  9.94) was used as internal reference.

Spectrum calculations were performed on a GE 635 computer using a FORTRAN program developed by L. C. Snyder and R. L. Kornegay of Bell Telephone Laboratories. The spectra were automatically plotted by a Stromberg–Carlson 4020 microfilm printer, both as "stick" spectra and also as the sum of Lorentzian line shapes of suitable width.

## Results and Discussion

Figures 1 and 2 show the backbone proton spectra of isotactic polystyrene at 80 and 130°, respectively. In both cases the nonequivalence of the  $\beta$  protons is

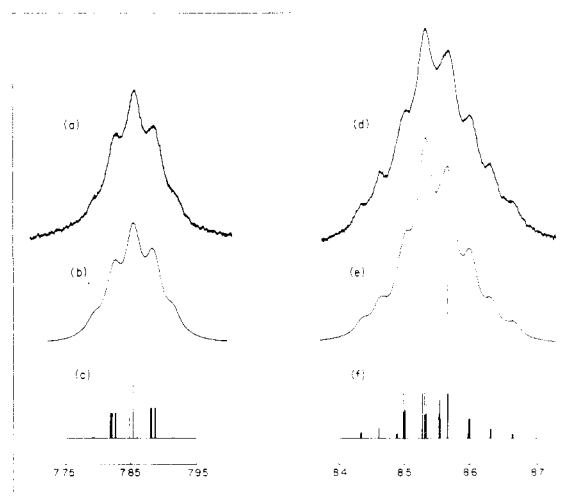


Figure 1. Backbone proton spectrum of isotactic polystyrene, 2% in *o*-dichlorobenzene at 80°: a and d,  $\alpha$  and  $\beta$  protons, respectively; b and e, spectrum calculated with parameters in Table I; c and f, "stick" spectrum corresponding to b and e.

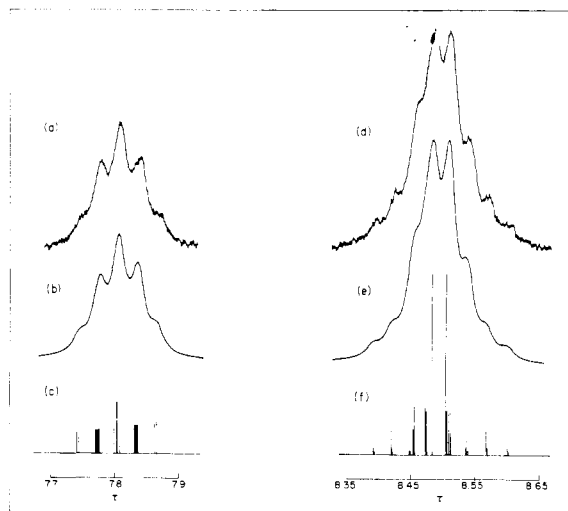


Figure 2. Backbone proton spectrum of isotactic polystyrene, 2% in *o*-dichlorobenzene at 130°: a and d,  $\alpha$  and  $\beta$  protons, respectively; b and e, spectrum calculated with parameters in Table I; c and f, "stick" spectrum corresponding to b and e.

- (1) F. A. Bovey, *Polym. Eng. Sci.*, **7**, 128 (1967).
- (2) K. C. Ramey and W. S. Brey, *J. Macromol. Sci., Part C*, **1**, 263 (1967).
- (3) A. Zambelli, A. L. Segre, M. Farina, and G. Natta, *Makromol. Chem.*, **110**, 1 (1967).
- (4) U. Johnsen and K. Kolbe, *Kolloid-Z.*, **221**, 64 (1967).
- (5) F. A. Bovey, E. W. Anderson, D. C. Douglass, and J. A. Manson, *J. Chem. Phys.*, **39**, 1199 (1963).
- (6) F. A. Bovey, F. P. Hood, E. W. Anderson, and L. C. Snyder, *J. Chem. Phys.*, **42**, 3900 (1965).
- (7) S. Brownstein, S. Bywater, and D. J. Worsfold, *J. Phys. Chem.*, **66**, 2067 (1962).

TABLE I  
CHEMICAL SHIFTS AND COUPLING CONSTANTS FOR ISOTACTIC POLYSTYRENE (2% IN *o*-DICHLOROBENZENE)<sup>a</sup>

Temp, °C	$\tau_A$	$\tau_B$	$\tau_C$	$J_{AB}$ , cps	$J_{AC}$ , cps	$J_{BC}$ , cps	Line width, cps
55	8.527	8.433	7.806	-14.5	7.5	6.0	8.0
80	8.518	8.436	7.795	-14.5	7.5	6.0	6.0
100	8.499	8.426	7.771	-14.5	7.25	6.25	6.0
130	8.462	8.403	7.746	-14.0	7.25	6.25	5.5
160	8.413	8.369	7.682	-14.5	7.25	6.25	4.0

<sup>a</sup> A, high-field  $\beta$  proton; B, low-field  $\beta$  proton; C,  $\alpha$  proton.

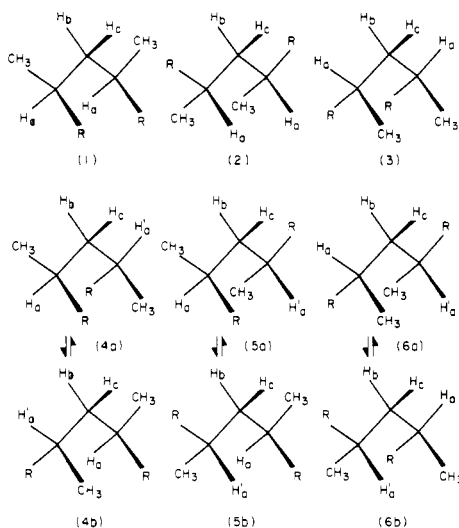


Figure 3. Staggered conformations of *meso*-2,4-disubstituted pentanes.

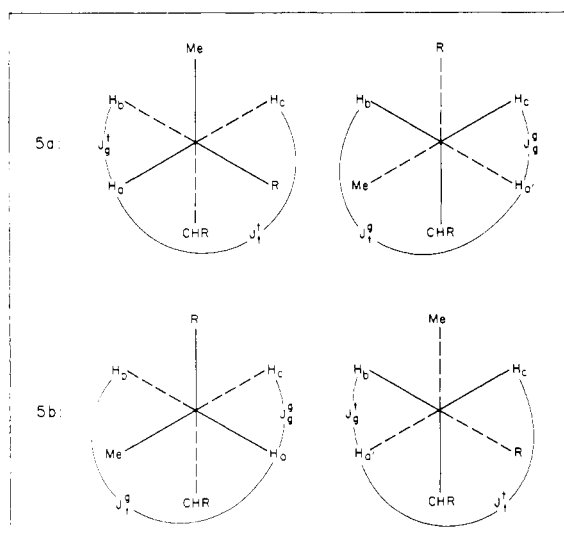


Figure 4. Coupling constants in conformations **5a** and **5b** of *meso*-2,4-disubstituted pentanes. In the designations of  $J$  couplings, the subscript denotes the relationship of the coupled protons and the superscript the conformation of this portion of the molecule.

clearly indicated by the weak outer lines of the methylene spectrum. In the  $ABX_2$  approximation ( $X = \alpha$  protons), the methylene spectrum consists of three AB subspectra which may readily be distinguished. However, a better representation of the actual spin system

is achieved using an  $AA'BB'CC'$  six-spin cyclic dimer model<sup>8,9</sup> in which  $AA'BB'$  represent  $\beta$  protons and  $CC'$   $\alpha$  protons. Good agreement with experiment was obtained at several temperatures using the chemical shifts, coupling constants, and line widths listed in Table I. The uncertainties are  $\pm 0.005$  ppm in the chemical shifts and  $\pm 0.5$  cps in the coupling constants.

As well as the methylene protons' chemical shift non-equivalence, which supports the isotactic structure of the chain, these calculations also reveal a small difference between the two  $\alpha, \beta$  vicinal coupling constants. This is also observed in isotactic polypropylene<sup>9</sup> and poly(isopropyl acrylate).<sup>10</sup> Within the experimental error the couplings are independent of temperature but the methylene protons' chemical shift difference decreases rapidly as the temperature increases.

In a previous study<sup>6</sup> of isotactic polystyrene and its model compound *meso*-2,4-diphenylpentane, it was concluded that the predominant conformations in the isotactic polymer are the helixlike mirror image conformers **5a** and **5b** in Figure 3. The revised results reported above give no grounds for any basic modification of this conclusion. The nmr parameters for the polymer and model compound differ in two respects but it must be remembered that *meso*-2,4-diphenylpentane is in no way an exact replica of a *meso* dyad in a polymer molecule, and that some differences are expected due to long-range effects of the chain.

First, in the diphenylpentane the chemical shift between the methylene protons increases from 0.20 ppm at 35° to 0.23 ppm at 180° whereas in the isotactic polymer this chemical shift decreases from 0.09 ppm at 55° to 0.03 ppm at 160° (all measurements were made in *o*-dichlorobenzene solution). This difference need not reflect conformational changes but could be due to the effects of the polymer chain mentioned above or to a change in the preferred orientation of the highly anisotropic phenyl ring.

Second, in the model compound each  $\beta$  proton is equally coupled to the  $\alpha$  protons whereas in the polymer the two vicinal coupling constants differ by about 1 cps. In this respect, the model compound is unusual since other *meso*-2,4-disubstituted pentanes<sup>11</sup> show two different vicinal coupling constants. Even if **5a** and **5b** of Figure 3 are the only populated conformers,  $J_{AC}$  and

(8) W. C. Tincher, *J. Polym. Sci.*, **62**, 5148 (1962).

(9) F. Heatley, unpublished results.

(10) T. Yoshino, Y. Kikuchi, and J. Komiyama, *J. Phys. Chem.*, **70**, 1059 (1966).

(11) P. E. McMahon and W. C. Tincher, *J. Mol. Spectrosc.*, **15**, 180 (1965).

$J_{BC}$  are not necessarily equal. Using the coupling constants defined in Figure 4, one obtains

$$J_{ab} = J_{a'b} = \frac{1}{2} (J_g^t + J_g^e)$$

$$J_{ac} = J_{a'c} = \frac{1}{2} (J_t^t + J_g^e)$$

(Lower case subscripts are used here since it is not known which of A or B is *threo* or *erythro*.)  $J_{ab}$  and  $J_{ac}$  are equal only in the fortuitous circumstances that the two sums of *trans* and *gauche* coupling constants are equal, but in cyclic compounds and halogenated ethanes<sup>12</sup> it has been found that *gauche* coupling constants are dependent on the substituents *trans* to the coupled protons to an extent sufficient to account for the observed difference of  $J_{AC}$  and  $J_{BC}$ . McMahon and Tincher<sup>11</sup> attributed the inequality of  $J_{AC}$  and  $J_{BC}$  to deviations from exact staggering presumably because of a repulsive interaction between bulky *gauche* substituents. However, in all the conformations shown in Figure 4, such an adjustment would still leave the dihedral angles of the two *trans* and two *gauche* coupling constants equal and hence if the vicinal coupling constant depended only on the dihedral angle,  $J_{AC}$  and  $J_{BC}$  would remain equal.

(12) R. J. Abraham, L. Cavalli, and K. G. R. Pachler, *Mol. Phys.*, **11**, 471 (1966).

If the equality of  $J_{AC}$  and  $J_{BC}$  in *meso*-2,4,-diphenylpentane indicates no substituent effect on the *gauche* coupling constants and if this lack of effect also occurs in the polymer, then the observed difference of  $J_{AC}$  and  $J_{BC}$  in the polymer must arise from the presence of some other conformation. Assuming all-*trans* and all-*gauche* couplings to be equal, which is valid as a first approximation, then  $J_{ab}$  and  $J_{ac}$  are given

$$J_{ab} = X_1 J_g + X_2 J_t + X_3 J_g + X_4 J_g + [X_5 (J_t + J_g)/2] + [X_6 (J_g + J_t)/2]$$

$$J_{ac} = X_1 J_t + X_2 J_g + X_3 J_g + [X_4 (J_t + J_g)/2] + [X_5 (J_g + J_t)/2] + X_6 J_g$$

where  $X_i$  is the population of conformation  $i$  in Figure 3. Since the experimental value of  $J_{AC}$  is of the order of magnitude expected for the quantity  $\frac{1}{2}(J_t + J_g)$ , then the most probable additional contributor to the conformer equilibrium is either 4 or 6 depending on whether A or B is *threo* or *erythro*. Any one of these forms would leave one coupling constant essentially unchanged while the other would be reduced. However, the lack of sufficiently accurate data on the temperature variation of the vicinal coupling constants prevents a test of this argument.

## Polymer Nuclear Magnetic Resonance Spectroscopy. XIV. The Nuclear Magnetic Resonance Spectrum of Poly(isopropyl acrylate)

F. Heatley and F. A. Bovey

Bell Telephone Laboratories, Inc., Murray Hill, New Jersey 07974. Received May 10, 1968

**ABSTRACT:** The 100-MHz nmr spectrum of isotactic poly(isopropyl acrylate) shows that this polymer actually contains 5% racemic dyads. This degree of stereoirregularity is evidently sufficient to lower the characteristic ratio  $\langle r_0^2 \rangle / nl^2$  from a high theoretical value to the experimental value of 9.7, which is comparable to the characteristic ratios for atactic and syndiotactic polymers. It is also found that the chemical shift of an *r* dyad is almost the same in both isotactic and atactic chains. This suggests that the conformational equilibria of *r* dyads in isotactic and syndiotactic chains are not very different, in contrast to a recent proposal.

Mark, Wessling, and Hughes<sup>1</sup> have recently measured the chain dimensions of predominantly syndiotactic, atactic, and isotactic poly(isopropyl acrylate). They found that for these three polymer samples, the values of the characteristic ratio  $\langle r^2 \rangle_0 / nl^2$  were  $7.2 \pm 1.0$ ,  $7.1 \pm 0.6$ , and  $9.7 \pm 0.8$ , respectively. According to calculations performed by Flory, Mark, and Abe,<sup>2</sup> as  $P_m$  (the probability of two consecutive monomer units having the same configuration) increases from 0 to 1, the characteristic ratio should remain constant at about 10 until  $P_m$  reaches a value of approximately 0.95 whereupon it increases very rapidly to a value much higher

than that reported above for an isotactic chain. In considering this discrepancy, Flory, *et al.*,<sup>2</sup> suggested that "isotactic" polymers are not in fact as stereoregular as generally believed.

We wish to report here a reexamination of the nmr spectrum of isotactic and atactic poly(isopropyl acrylate) at 100 MHz (Figure 1a and d). In both spectra the  $\alpha$  protons give a pentuplet at  $\tau$  7.42, with no fine structure due to triads, but the  $\beta$  protons of *m* and *r* dyads are well separated in chemical shift as indicated in Figure 1. The identification of *threo* and *erythro* protons in the *m* dyad was reported by Yoshino, Shinomiya, and Komiyama.<sup>3</sup> Calculations of the isotactic

(1) J. E. Mark, R. A. Wessling, and R. E. Hughes, *J. Phys. Chem.*, **70**, 1895 (1966).

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(3) T. Yoshino, M. Shinomiya, and J. Komiyama, *J. Amer. Chem. Soc.*, **87**, 387 (1965).