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

$$J_{ab} = J_{a'b} = {}^1/_2\,(J_g{}^t + J_t{}^g)$$

$$J_{ac} = J_{a'c} = {}^1/_2\,(J_t{}^t + J_g{}^g)$$

(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[12] 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[11] 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.

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

$$J_{ab} = X_1J_g + X_2J_t + X_3J_g + X_4J_g + [X_5(J_t + J_g)/2] + [X_6(J_g + J_t)/2]$$

$$J_{ac} = X_1J_t + X_2J_g + X_3J_g + [X_4(J_t + J_g)/2] + [X_5(J_g + J_t)/2] + X_6J_g$$

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 ${}^1/_2(J_t + J_g)$, 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.

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

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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[1] 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 ± 1.0, 7.1 ± 0.6, and 9.7 ± 0.8, respectively. According to calculations performed by Flory, Mark, and Abe,[2] 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.*,[2] 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 α protons give a pentuplet at τ 7.42, with no fine structure due to triads, but the β 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.[3] Calculations of the isotactic

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

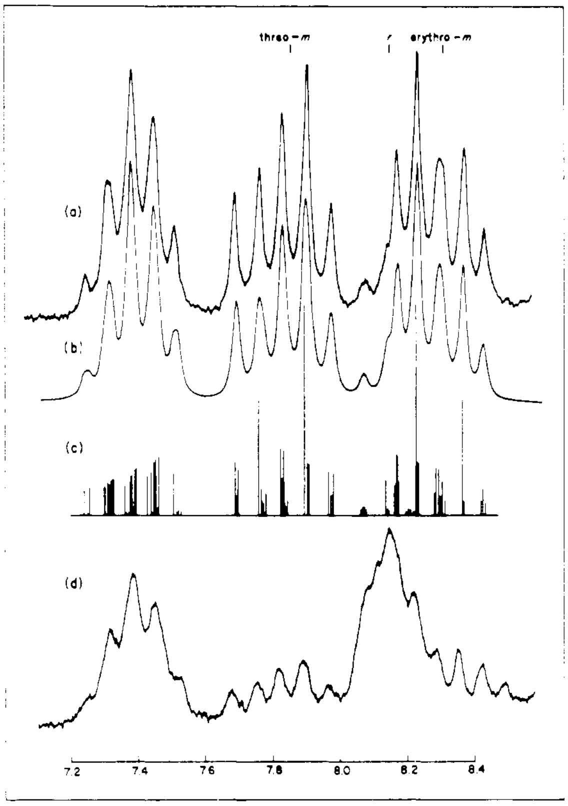


Figure 1. Backbone proton spectrum of poly(isopropyl acrylate): a, isotactic polymer, 10% in chlorobenzene at 140°; b, spectrum calculated with parameters given in text; c, "stick" spectrum corresponding to b; d, atactic polymer, 10% in chlorobenzene at 140°.

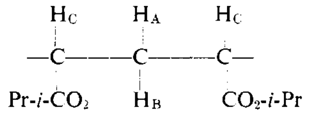
polymer spectrum were performed using a six-spin dimer model,[4] with the parameters in Chart I giving the best agreement with experiment (Figure 1b and c). Errors are ±0.01 ppm in the chemical shifts and ±0.2 cps in the coupling constants.

The isotactic polymer thus contains 5% *r* dyads, which is evidently sufficient to reduce the characteristic ratio to its observed value. Earlier investigations[1,5] of this spectrum at 60 MHz failed to reveal the presence of the *r* dyad resonance.

A further point of interest is the fact that the chemical shift of *r* dyads is almost the same in both isotactic and atactic polymers (τ 8.16 and 8.18, respectively). Flory and Baldeschwieler[6] have suggested that the resonance of an *r* dyad in an isotactic chain could be shifted appreciably from that in a syndiotactic chain because of a difference in the predominant conformations. Thus in an isotactic chain with strong "four-bond" interactions,[2] the most common conformation of an isolated *r* dyad would be the *tt* form whereas in a syndiotactic chain both *tt* and g^-g^- forms would be of almost equal occurrence. However, investigations[7,8] of the conformational equilibrium in *rac*-2,4-disubstituted pentanes (model compounds for vinyl polymers) have shown that the g^+g^+ conformation is in general less stable than the *tt* form by 1 kcal or more. If this situation applies also in syndiotactic polymers, which is probable, then the environments of an *r* dyad in isotactic and syndiotactic chains would not be very different. Unfortunately, accurate nmr coupling constant data, which would permit some conclusion as to the local chain conformation, are not at present available for syndiotactic polymers.

In terms of the statistical weights defined by Flory, Mark, and Abe,[2] the appreciable energy difference between *tt* and g^+g^+ conformations requires that the parameter η take a value greater than unity. This would not seriously affect the conformation of an isotactic chain.

CHART I

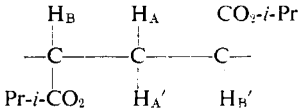


$$\begin{array}{ccccc} H_C & & H_A & & H_C \\ | & & | & & | \\ -C & - & C & - & C- \\ | & & | & & | \\ \text{Pr-}i\text{-CO}_2 & & H_B & & \text{CO}_2\text{-}i\text{-Pr} \end{array}$$

m dyad

τ_A 8.31 τ_B 7.86 τ_C 7.42

$J_{AB} = -14.0$ cps $J_{AC} = 6.0$ cps $J_{BC} = 7.5$ cps



$$\begin{array}{ccccc} H_B & & H_A & & \text{CO}_2\text{-}i\text{-Pr} \\ | & & | & & | \\ -C & - & C & - & C- \\ | & & | & & | \\ \text{Pr-}i\text{-CO}_2 & & H_A' & & H_B' \end{array}$$

r dyad

τ_A 8.16 τ_B 7.42

$^1/_2(J_{AB} + J_{AB'}) = 7.0$ cps

Line width at half-height 2.4 cps

$$\frac{(m)}{(m) + (r)} = 0.95$$

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