regular progression in chemical shift of the central *m* dyad as the flanking *m* dyads are replaced by *r* dyads. Such regularity is observed for the *mmm*, *mmr*, and *rmr* chemical shifts in poly(methyl methacrylate)[17] and poly(vinyl chloride).[18] The *mrr* tetrad is assigned by us on the basis of an examination of the spectrum of atactic poly(propylene-2-d_1) in which geminal coupling is introduced into the spectra of those tetrads with magnetically nonequivalent methylene groups. In this spectrum, no peaks were present at the chemical shift of either of the two peaks labeled *mrr* in Figure 1, indicating that both were split by geminal coupling and therefore belonged to the *mrr* tetrad. The *mrm* tetrad is assigned by us to the same chemical shift as the *rrr* tetrad since approximate measurements of the *mmr*, *rmr*, and *mrr* intensities, when substituted into the relationship[14]

$$(mmr) + 2(rmr) = (mrr) + 2(mrm)$$

gave a substantial proportion of the *mrm* tetrad which could be accommodated only within the central peak. Thus measurement of peak heights in Figure 1b gives the values 0.194, 0.113, and 0.250 for (*mmr*), (*rmr*), and (*mrr*), respectively, giving the value 0.085 for (*mrm*), which is comparable to the intensity of the (*rmr*) tetrad and can be placed reasonably only as suggested.

Several small peaks other than those assigned to tetrads are evident in Figure 1. These may be attributed variously to hexads, impurities in the monomers, or possibly head-to-head units.

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Polymer Nuclear Magnetic Resonance Spectroscopy. XVIII. The Nuclear Magnetic Resonance Spectrum, Dimensions, and Steric Interactions of Isotactic Polypropylene

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ABSTRACT: The 220-MHz proton nmr spectrum of a highly isotactic sample of polypropylene has been examined and interpreted in detail. The polymer was shown to contain 2% racemic dyads occurring randomly at junctions of isotactic sequences of opposite configurations. The mean-square end-to-end distance of this polymer was measured under Θ conditions, and comparison of the value obtained with theoretical predictions of Flory, Mark, and Abe[11] permitted an approximate measurement of the strength of steric interactions within the polypropylene chain. Additional information on the steric interactions was obtained from a comparison of the chemical shifts of racemic dyads in isotactic and syndiotactic chains.

Nuclear magnetic resonance has been well established as the most useful method of studying polymer configurational and conformational properties. The subject has been reviewed several times.[1–7] The advent of nmr instruments with superconducting magnets has greatly improved the sensitivity and resolution of this technique, as shown by recent studies of the 220-MHz proton spectra of poly(methyl methacrylate),[8] poly(vinyl chloride),[9] and isotactic polystyrene.[10] In this paper we wish to report a similar study of a highly isotactic polypropylene sample, having as its objective the accurate determination of its stereochemical structure. Calculations by Flory, Mark, and Abe[11] have shown that the end-to-end distance of an isotactic polymer chain and its temperature coefficient are sensitive to both intramolecular steric overlaps between large groups and to the incorporation of a small amount of syndiotactic dyad "impurity" within the chain. However, the latter has not been specified sufficiently accurately for the isotactic polymers whose dimensions have been reported in the literature,[12–15] thus making comparisons between theory and experiment of doubtful value. This paper reports the first measurement of the dimensions of an isotactic polymer of accurately known tacticity.

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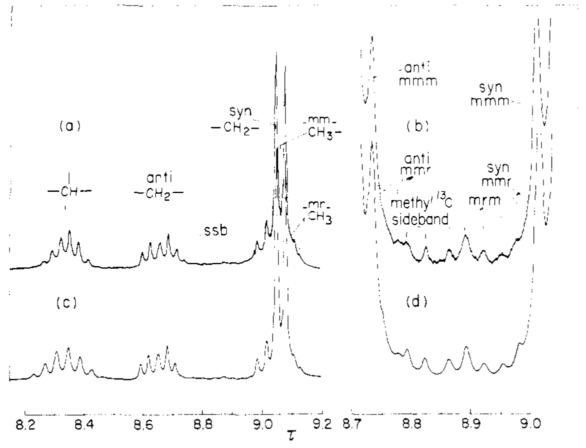

Figure 1. (a) Complete 220-MHz nmr spectrum of isotactic polypropylene; 10% (w/v) in *o*-dichlorobenzene at 140°. (b) Expanded portion of (a); (c) and (d) calculated spectra corresponding to (a) and (b).

Many studies of polypropylenes of widely varying tacticities have been made[16–28] at 60 and 100 MHz. Ferguson[29] has reported the 220-MHz spectra of isotactic and syndiotactic polypropylene but the spectra were not examined in detail. The spectra of predominantly isotactic and syndiotactic polymers are very different, indicating that the tacticity may be measured accurately. However, at the lower field strengths, the chemical shift differences are small with consequent difficulty in measuring the intensities of small peaks close to much larger ones. Thus Zambelli, *et al.*,[23] reported the 100-MHz spectrum of an isotactic polypropylene sample believed to have $\leq 2\%$ racemic dyads, but did not actually observe the racemic peaks because of low signal-to-noise ratio. The use of a 220-MHz nmr spectrometer has greatly facilitated the observation of low-intensity peaks. The interpretation of the isotactic polypropylene spectrum has also been aided by recent studies[26,28] of the proton spectra of atactic polypropylenes-d_5 in which tetrad[30] resonances have been clearly observed and tentatively assigned to the six possible tetrad structures.

Experimental Section

Nmr spectra were obtained using a Varian HR-220 spectrometer. Approximately 10% solutions in *o*-dichlorobenzene were employed with hexamethyldisiloxane (τ 9.94) as internal reference. The highly isotactic polypropylene sample used, supplied by Dr. D. Sianesi (Montecatini), is the residue from a boiling heptane extraction of the product from a conventional isotactic propylene polymerization.

Nmr spectrum calculations were performed using a program written by L. C. Snyder and R. L. Kornegay of the Bell Telephone Laboratories. Spectra were plotted on a Stromberg-Carlson 4020 microfilm printer as the sum of Lorentzian line shapes of suitable width.

Viscosity measurements were made on solutions of the isotactic polypropylene in diphenyl ether, containing Santonox R (Monsanto) antioxidant, in a Cannon–Ubbelohde semimicro dilution viscometer thermostated at 145°, *i.e.*, under Θ conditions.[12] The initial polymer concentration approximated 10^{-2} g cc^{-1}.

Light-scattering measurements were made on solutions of the isotactic polypropylene in middle-fraction α-chloronaphthalene containing Santonox R at 140° using a Sofica photometer at a wavelength of 546 mμ. Solutions were clarified by filtration in an oven at 140° using 0.45-μ metal membrane filters (Selas Flotronics).

Results

A. Nmr Spectra. Figure 1(a) shows the complete 220-MHz spectrum of the isotactic polypropylene sample. The multiplets from the methine, methyl, and *syn* and *anti meso*-methylene protons are readily distinguished. (The *syn* protons are defined as those on the same side of the backbone plane as the methyl groups when an isotactic sequence assumes the planar zigzag conformation; the *anti* protons are on the opposite side.) The chemical shift difference between the methylene protons corresponds closely to that for the *mmm*[31] tetrad in the spectra of atactic polymers.[26,28] Of special interest is the region between the *syn* and *anti* methylene multiplets, which is shown expanded in Figure 1(b). Several peaks of low intensity are apparent, and may be attributed to a very small proportion of racemic dyads. The triplet centered on τ 8.88 is assigned to the *mrm* tetrad since it lies at the same chemical shift from the *mmm* resonances as the line assigned[28] to the tetrad in atactic polymers.[26,28] Although the *rrr* chemical shift is the same as that of *mrm*, the *rrr* tetrad is excluded because there probably are very few syndiotactic sequences of three or more dyads in length in such a highly isotactic polymer. The alternative assignment of the prominent racemic resonance to the *mrr* tetrad is excluded on the evidence of trial calculations of its spectrum using the known chemical shift[28] and typical coupling constants. These calculations show that because of the magnetic nonequivalence of the methylene protons of this tetrad, the spectrum would be more complicated than a triplet.

As a consequence of the apparent identification of the *mrm* resonance, we conclude that the interruptions in the long isotactic sequences occur predominantly by a reversal of the α-carbon configuration, thus

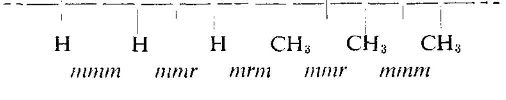

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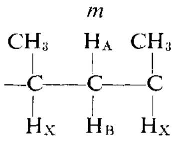
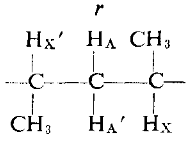
TABLE I

NMR PARAMETERS USED IN THE CALCULATION OF THE SPECTRUM OF ISOTACTIC POLYPROPYLENE

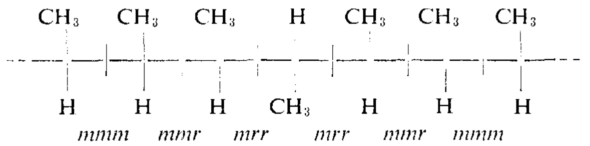
Spin system notation





Resonance	Chemical shift, τ	Coupling constants, Hz	Line width, Hz	Intensity
mmm	ν_A 9.05	$J_{AB} = -13.5$	3.0	0.94
	ν_B 8.67	$J_{AX} = 7.0$		
	ν_X 8.34	$J_{BX} = 6.0$		
mmr	ν_A 9.00	$J_{AB} = -13.5$	3.0	0.04
	ν_B 8.71	$J_{AX} = 6.0$		
	ν_X 8.34	$J_{BX} = 6.0$		
mrm	ν_A 8.88	$J_{AX} = 8.0$	3.0	0.02
	ν_X 8.34	$J_{AX'} = 5.0$		
		$J_{AA'} = -13.5$		
mm	ν_{CH_3} 9.07	$J_{\alpha\text{-}CH_3} = 6.5$	2.5	0.97
		$J_{^{13}C-H} = 124$		
mr	ν_{CH_3} 9.12	$J_{\alpha\text{-}CH_3} = 6.5$	2.5	0.03

The alternative structure



which also gives brief interruptions in the isotactic sequences, is not significant because of the relatively low proportion of the *mrr* tetrad.

As expected, if the first structure is correct, peaks from the *mmr* tetrad are observed with a total intensity approximately twice that of the *mrm* tetrad (Table I). There is no evidence for the presence of the *rmr* tetrad, in accordance with the low abundance of *r* dyads.

The ^{13}C side band of the intense isotactic methyl doublet was identified by its spacing, which is equal to that in the parent doublet, by the fact that an identical doublet occurred at the same distance to high field of the parent peaks, and by its intensity, which is equal to that expected from the 1.1% natural abundance of ^{13}C. This side band affords an excellent means of accurately measuring the racemic content of this polymer, as has been pointed out by Segre.[25]

In the methyl region, a small methyl resonance (labeled -*mr*- in Figure 1(a)) occurs slightly to high field of the main methyl doublet. This methyl group undoubtedly belongs to a heterotactic triad associated with the *r* dyads discussed above, and is most probably the *mmrm* pentad. Although pentad peaks were resolved in the spectrum of polypropylene-2-d_1, no assignment was attempted.

Figure 1(c) and (d) shows spectra calculated with the parameters in Table I according to the preceding interpretation of the spectrum. The central methylene resonances of the tretrads were calculated using an AA'BB'CC' dimer model,[32] the methyl groups as AB_3 systems (A is the methine proton), and the methine proton as an $AA'BB'CD_3$ system (A and B are the protons of each of the two adjacent methylene groups, C is the methine proton and D the methyl protons). The differences between tetrad chemical shifts are in agreement with those reported[28] for the tetrads in atactic deuterated polymers, but there is a small discrepancy (*ca.* 0.03) between the two measurements in their positions on the τ scale. This could conceivably be due to a combination of isotope, concentration, and solvent effects.

As explained elsewhere,[32] because of symmetry considerations the methylene protons of *m* dyads approximate the AB part of an ABX_2 system, the X nuclei being the adjacent α protons, whereas the methylene protons of *r* dyads resemble the AA' part of an AA'XX' system. The nmr parameters in Table I are identified according to these descriptions of the spin systems. Since an ABX_2 system can be analyzed simply and explicitly,[33] the errors in the calculated coupling constants for *m* dyads are relatively small, about ±0.5 Hz. However, it has been shown[34] that under certain conditions, which unfortunately occur here, an AA'XX' system may give a spectrum sensitive only to the sum of the two vicinal coupling constants J_{AX} and $J_{AX'}$ and not to their difference. The quantity $(J_{AX} - J_{AX'})$ can be determined accurately only by a close comparison of the relative widths and heights of the central and outer peaks of the *mrm* triplet; this is difficult because of the low signal-to-noise ratio. Hence the errors in J_{AX} and J_{AX}' are fairly large, being ±1.5 Hz in J_{AX} and ∓1.5 Hz in $J_{AX'}$. Zambelli, Giongo, and Natta[27] have reported accurate values of 8.3 and 4.8 Hz for J_{AX} and $J_{AX'}$ in predominantly syndiotactic polymers (*i.e.*, *rrr* tetrads) using selective deuteration to remove the indeterminacy in AA'XX' spectra mentioned above. These values are close to those reported here for the *mrm* tetrad. Further in-

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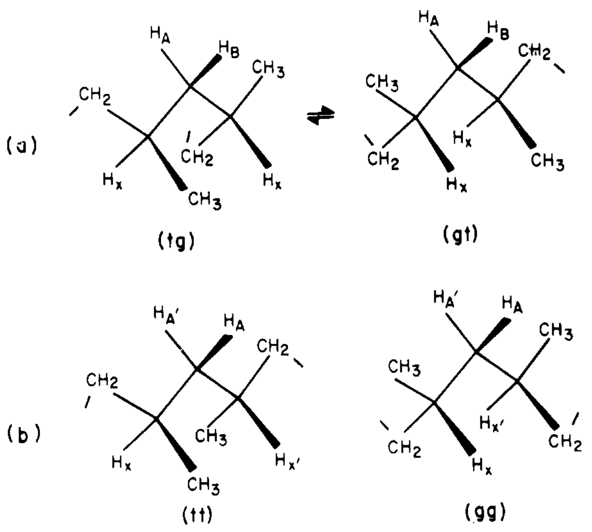

Figure 2. Principal dyad conformations of (a) *meso* and (b) racemic dyads.

terpretation of the significance of this similarity is postponed until the Discussion.

Satisfactory agreement between calculated and experimental spectra was obtained without including the *mrr* tetrad, but because of the low signal-to-noise ratio it is not possible to exclude it completely. However, trial calculations indicate that its probability of occurrence must be considerably lower than that of the *mrm* tetrad. An estimated upper limit is 0.005. The relationship[28] (*mmr*) = 2(*mrm*) is obeyed within experimental error, as expected if both (*rmr*) and (*mrr*) are small. The tetrad intensities indicate that the *r* dyad content of this polymer is 2%.

B. The Dimensions of Isotactic Polypropylene. The mean square end-to-end distance of a polymer chain, $\langle r^2 \rangle$, is obtainable from measurements of molecular weight and intrinsic viscosity using the Flory-Fox equation[35]

$$[\eta] = \Phi[\langle r^2 \rangle / M]^{3/2} M^{1/2}$$

where Φ is a constant which for polypropylene takes the value[36] 2.5×10^{21}. The unperturbed end-to-end distance, $\langle r^2 \rangle_0$, is obtained by measuring the intrinsic viscosity under Θ conditions. Usually the chain dimensions are expressed in terms of the characteristic ratio $\langle r^2 \rangle_0 / nl^2$, where n is the number of bonds of length l in the chain. For polypropylene, $n = M/21$ and therefore

$$\frac{\langle r^2 \rangle_0}{nl^2} = \frac{21}{Ml^2}\left(\frac{[\eta]M}{\Phi}\right)^{2/3} \qquad (1)$$

Viscometer flow times for the isotactic polypropylene solutions were treated as usual[37] and gave an average intrinsic viscosity in diphenyl ether at 145° of 0.55 dl g^{-1}. Light-scattering data were analyzed according to the method of Zimm,[38,39] assuming a refractive index increment for isotactic polypropylene in α-chloronaphthalene of -0.188 cc g^{-1}, and gave a weight average molecular weight of 316,000. Analysis of the light-scattering data by the dissymmetry technique[38,40] gave a molecular weight of 302,000. Substitution of these results in (1) gave a characteristic ratio of 4.73. This value is lower than the value 7.48 reported by Kinsinger and Hughes,[12] who, however, used a value of 2.1×10^{21} for Φ, or the value 5.78 reported by Nakajima and Saijyo.[15] Our relatively low value is probably a consequence of using M_w instead of M_n in (1), but since the characteristic ratio is proportional to $M^{-1/3}$, the difference between the results is probably not very significant.

Discussion

Because of the interdependence of the internal rotation energy about bonds in a polymer chain,[11,32] it is helpful to consider polymer conformation in terms of two consecutive monomer units. First, let us consider the conformational equilibrium within a dyad, *i.e.*, the conformations assumed by the two bonds on either side of a methylene group. The predominant conformations of both *m* and *r* dyads in vinyl polymers have been well established by infrared and nmr studies[32,41-43] of small molecule model compounds, by potential energy calculations,[44] and by nmr studies[9] of the polymers themselves. Figure 2 shows the conformations in question; others are of little importance because of strong steric interactions.

For isotactic dyads, the vicinal coupling constants given here are comparable to those reported previously for isotactic polystyrene[10] and poly(isopropyl acrylate)[45] and for isotactic dyads in poly(vinyl chloride),[9] and approximate the expected value[32] of $\frac{1}{2}(J_t + J_g)$ if each dyad interconverts rapidly between the equivalent (*tg*) and (*gt*) conformations shown in Figure 2(a). (J_t is the vicinal coupling constant between protons *trans* to each other and J_g that *between gauche* protons.) When repeated, each conformation generates the 3_1 helices found in crystalline isotactic polypropylene.[46]

Syndiotactic dyads may occupy either of the nonequivalent (*tt*) and (*gg*) conformations shown in Figure 2(b). The conformational distribution may be determined experimentally from J_{AX} and J_{AX}', the averaged values of which are given by

$$J_{AX} = J_{A'X'} = X_{tt}J_t + (1 - X_{tt})J_g$$

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$$J_{AX'} = J_{A'X} = X_{tt}J_g + (1 - X_{tt})J_t$$

where X_{tt} is the mole fraction of the *(tt)* conformation. Since $J_t > J_g$, it has been implicitly assumed in writing $J_{AX} > J_{AX'}$ in Table I that $X_{tt} > 0.5$. This assumption is very probably correct since in a syndiotactic polymer the *(tt)* conformation may be adjacent to either *(tt)* or *(gg)* conformations without steric hindrance whereas a *(gg)* conformation may succeed or precede only the *(tt)* conformation if steric overlaps are to be avoided. Using typical values of 11 ± 1 and 2 ± 1 Hz for J_t and J_g, we obtain the value 0.7 ± 0.1 for X_{tt}. The proportion of the *(gg)* conformation is much larger than in poly(vinyl chloride)[9] where it was found that essentially only the *(tt)* conformation is allowed. Since methyl groups and chlorine atoms have approximately the same van der Waals radii, the difference is probably due to a large electrostatic repulsion between chlorine atoms in the *(gg)* form.[47]

Equally as important as dyad conformations, but less susceptible to direct measurement, are the allowed conformations about the two bonds flanking an α carbon, *i.e.*, the conformations of the $-CH_2CHRCH_2-$ unit. It is useful to regard this situation in terms of the allowed distribution of adjacent dyad conformations described above. This conformational equilibrium may be studied using either polymer molecular properties, such as end-to-end distance, or by determining the effect on the dyad conformational equilibrium of changing the configuration of adjacent dyads, in particular by determining the conformational difference between *r* dyads isolated in syndiotactic and isotactic chains.

Consider first the relationship between the dimensions of an isotactic polymer and the allowed sequences of *m* dyad conformations. Flory, Mark, and Abe[11] have pointed out that no steric conflicts occur in the sequences . . .*(gt)(gt)*. . ., . . .*(tg)(tg)*. . ., or . . .*(gt)(tg)*. . . whereas in the sequence . . .*(tg)(gt)*. . ., there is a destabilizing steric overlap between CHR moieties. Their calculations using a three-state rotational isomeric matrix treatment showed that $\langle r^2 \rangle_0$ is very sensitive to the statistical weight, ω, which they assigned to this interaction. As $\omega \rightarrow 0$, the characteristic ratio increases rapidly to a value much higher than the value 5-10 usually found for isotactic polymers. Flory, *et al.*, also considered the effect on $\langle r^2 \rangle_0$ of the presence of a small proportion of *r* dyads in a highly isotactic polymer and found that even if $\omega = 0$, only 5% *r* dyads are sufficient to bring $\langle r^2 \rangle_0$ within the range of experimental results. Hence it is not possible to determine ω from measurements of $\langle r^2 \rangle_0$ without knowing the syndiotactic content of the polymer. In fact a small amount of *r* dyads in the most carefully prepared isotactic polymer is not unreasonable since it is unlikely that a polymerization process could be completely stereospecific for the addition of 1000 or more consecutive units nor is it easy to obtain pure isotactic polymer by separating molecules differing by only 1 or 2% in their stereochemistry.

For the isotactic polymer used in this study, containing 2% of randomly distributed *r* dyads, the results of the calculations of Flory, *et al.*,[11] indicate that if $\omega = 0$, then the characteristic ratio should be ≥ 30, which is at least sixfold greater than the experimental value. Hence the characteristic ratio is determined primarily by the parameter ω. Using the data presented by Flory, *et al.*,[11] on the dependence of the characteristic ratio on ω for a purely isotactic chain, we may estimate that for isotactic polypropylene at 145°, ω is in the range 0.05–0.2, depending on the deviation from exact staggering of the *g* and *t* conformations. The deviation was taken to lie in the range 0–20°. This statistical weight corresponds to an interaction energy E_ω of 1200–2400 cal/mol. No greater precision is possible since no calculations were performed giving the effect on $\langle r^2 \rangle_0$ of varying ω and the proportion of *r* dyads simultaneously. The upper limit of E_ω is close to values calculated by Borisova and Birshtein[48] using interatomic potential functions. Estimates of the temperature coefficient of $\langle r^2 \rangle_0$, expressed in the form $d \ln \langle r^2 \rangle_0 / dT$ lie in the range -2.5×10^{-3} to -3.5×10^{-3} deg^{-1}, slightly lower than the experimental value[15] of -4.09×10^{-3} deg^{-1}.

Further information on the interdependence of dyad conformations may be obtained from a comparison of the nmr parameters for syndiotactic polypropylene[28] and for the *mrm* tetrad in isotactic polypropylene. Flory and Baldeschwieler[49] have suggested that the conformational equilibrium of an *r* dyad in these two situations may differ considerably. Thus, assuming little intrinsic preference for either *(tt)* or *(gg)*, which applies to polypropylene, then in a syndiotactic chain, as explained earlier, an *r* dyad will show a slight predominance of the *(tt)* conformation. However, in an *mrm* tetrad in an otherwise isotactic chain, the *(gg)* conformation of the *r* dyad is sterically unhindered only in the . . .*(gt)(gg)(tg)*. . . sequence whereas in the three other possibilities, . . .*(tg)(gg)(tg)*. . ., . . .*(gt)(gg)(gt)*. . ., and . . .*(tg)(gg)(gt)*. . ., there are varying degrees of steric overlap. In the sequences where *(gg)* is replaced by *(tt)* there is no hindrance. As before, the steric interaction is measured by the parameter ω. Hence if ω is small enough, then the population of the *(gg)* form would be very small for the *mrm* tetrad compared to the syndiotactic polymer. However, both the chemical shift and coupling constants for *r* dyads in the two cases are equal within the experimental error, showing that the conformational equilibrium between the *(tt)* and *(gg)* conformers is the same. Semiquantitative calculations put the required value of ω at 0.2 or greater.

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