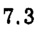
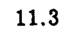
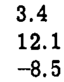
Table I
Kinetic Data in the Polymerization of Four Oxetanes by $BF_3 \cdot THF$ Catalyst at −20° in Methylcyclohexane

	 [a]	 [b]	 [b]	 [b]
k_p, l./(mol sec)	0.31	0.18	0.92	3.4
$\Delta H^‡$, kcal/mol	7.3	10.7	11.3	12.1
$\Delta S^‡$, eu	−28.0	−18.6	−14.6	−8.5

[a] This work. [b] Taken from ref 1.

Table II
Position of ν_{O-D} in Benzene

	ν_{O-D}, cm^{-1}	$\Delta\nu_{O-D}$, cm^{-1} [a]
CH_3OD	2664	0
CH_3OD + OSH	2562	102 [b]
CH_3OD + OX	2561	103 [c]
CH_3OD + MeOX	2558	106 [c]
CH_3OD + Me_2OX	2565	99 [c]

[a] $\Delta\nu_{O-D} = \nu_{O-D}$(benzene) − ν_{O-D}(monomer in benzene). [b] This work. [c] Taken from ref 1.

character of the activation parameters of the propagation of OSH is different from the characters of other oxetane monomers (Table I). The $\Delta H^‡$ value of OSH is extremely low (favorable for k_p) in the series of four oxetane monomers and the $\Delta S^‡$ value is also low (unfavorable). The reason probably relates to the particular structure of OSH monomer. Thus, the low $\Delta H^‡$ value may be ascribed to the increased ring-opening reactivity of the propagating oxonium ion having a higher strain. On the other hand, the explanation as to the more negative value of activation entropy (unfavorable) is not simple. The rigid structure of the S$_N$2 transition state due to the spiro ring may possibly be assumed, which gives rise to a decreased freedom of mobility, and hence the unfavorable entropy factor. The desolvation due to the charge dispersion at the transition state contributes to the favorable entropy gain. A lower contribution of desolvation may be explained either by the decreased solvation of the initial species of spiro oxonium ion **2** or by the decreased extent of desolvation at the transition state. At present a conclusive explanation is not given for the unfavorable entropy of activation.

The $\Delta\nu_{O-D}$ value obtained by the ir method has been taken as a measure of the monomer basicity.[7-9] Although the $\Delta\nu_{O-D}$ values are in a narrow range (Table II), the order of basicities is not the same as that of k_p values. Thus the monomer basicity is not the decisive factor in the polymerizability of these monomers.

References and Notes

(1) T. Saegusa, H. Fujii, S. Kobayashi, H. Ando, and R. Kawase, *Macromolecules*, **6**, 26 (1973).
(2) T. Saegusa and S. Matsumoto, *Macromolecules*, **1**, 442 (1968).
(3) T. Saegusa, *J. Macromol. Sci., Chem.*, **6**, 997 (1972).
(4) T. Saegusa and S. Kobayashi, *Prog. Polym. Sci. Jpn.* **6**, 107 (1973).
(5) S. Penczek and A. A. Vansheidt, *Vysokomol. Soed.*, **5**, 296 (1963).
(6) S. Searles, Jr., and E. F. Lutz, *J. Am. Chem. Soc.*, **81**, 3674 (1959).
(7) S. Iwatsuki, N. Takigawa, M. Okada, Y. Yamashita, and Y. Ishii, *Kogyo Kagaku Zasshi*, **67**, 1236 (1964).
(8) S. Aoki, Y. Harita, Y. Tanaka, H. Mandai, and T. Otsu, *J. Polym. Sci., Part A-1*, **6**, 2585 (1968).
(9) T. Kagiya, Y. Sumita, and T. Inoue, *Polym. J.*, **1**, 312 (1970).

Stereochemical Configuration of Polypropylene by Hydrogen Nuclear Magnetic Resonance

Ferdinand C. Stehling*[1a] **and Jack R. Knox**[1b]

Exxon Chemical Company, Plastics Technology Division, Baytown, Texas 77520, and
Amoco Chemicals Corporation, Research and Development Department,
Naperville, Illinois 60540.

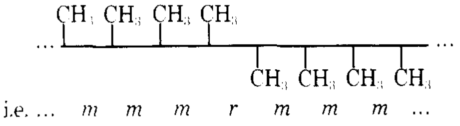
Received March 28, 1975

ABSTRACT: An investigation of the stereochemical structure of deuteriopolypropylene and polypropylene (PP) has been made using ^{1}H NMR. Our assignments of the tetrad methylene hydrogen bands in this polymer, determined from various deuteriopolypropylenes and epimerized PP, agree with previously published assignments for five of the possible six tetrads. Although we were not able to make a firm *mrm* assignment, our results favor the Flory-Fujiwara assignment of this tetrad. This tetrad absorbs in the *r* methylene region of the spectrum, and the uncertainty in its precise location does not limit the accuracy of stereoregularity determinations. Determinations made on the heptane insoluble fraction of several PP and deuteriopolypropylene samples gave a range of 1 to 5% for the *r* dyad content. We disagree with the interpretation of the ^{1}H NMR spectra of highly isotactic commercial PP published by other investigators. Such spectra are not inconsistent with the structures that we and others have found in highly isotactic deuteriopolypropylene fractions.

Numerous theoretical and experimental investigations of the stereoregularity of polypropylene (PP) have been made using ^{1}H NMR[2-15] and, more recently, ^{13}C NMR.[16-22] These investigations have been directed mainly to determining the degree of stereoregularity of PP and to obtaining more detailed information about the structure of the polymer chain. In ^{1}H NMR investigations the methylene portion of the spectrum has been most thoroughly studied. Numerous bands have been resolved in this region,[10,12,13,15] and much information about stereochemical structure can be deduced therefrom if the bands can be correctly assigned.

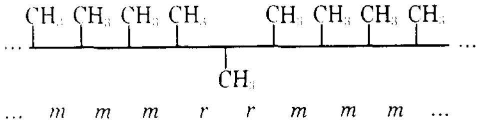
A complete ^{1}H NMR assignment of the six possible tetrads was first given by Flory and Fujiwara.[3a] Using conformation considerations, they calculated the expected chemical shifts of the various tetrad bands. Comparison of the calculated spectrum with experimental spectra showed sufficient similarity to allow them to assign the bands in the experimental spectrum. Subsequently, Heatley and Zambelli (HZ) made an assignment based on experimental approaches.[12] Their assignment, which is supported by other investigators,[14,15] agreed with that of Flory and Fujiwara except for the location of the *mrm* tetrad. The assignments of the *mrm* and *rrm* bands are particularly important in determining the mechanism for the generation of racemic (*r*) placements in isotactic PP.

The thrust of a number of investigations has been to determine the concentration of *r* placements in isotactic PP and to determine how these *r* dyads are distributed among the large number of meso (*m*) units in the chain.[8–15] Heatley, Salovey, and Bovey[13] and Ferguson[14] concluded that stereoregular fractions from commercial PP contained about 1% *r* dyads and that interruption of long *m* sequences occurred predominantly as depicted in structure I below:



I

An alternative structure,



II

was ruled out because the *rrm* tetrad was not detected. Recently, ^{13}C NMR spectra were reported to lead to the same conclusion.[21] However, both the accuracy of the ^{1}H NMR percent *r* dyad determination and the conclusion that structure I prevails in isotactic PP have been questioned by Flory.[3]

In the work reported here, we used ^{1}H NMR to further examine the stereochemical structure of PP. A complementary study using ^{13}C NMR will be reported later. The purposes of our investigation were (1) to make an independent assignment of the tetrad bands in PP, (2) to determine the *r* dyad concentration in the heptane insoluble fraction of PP, and (3) to see whether I or II, if either, correctly describes the structure of the heptane insoluble fraction of this polymer. To minimize the possibility of drawing incorrect conclusions, we examined PP, isomerized PP, and several deuteriopolypropylenes.

As we show below, our investigation confirms the Flory–Fujiwara and HZ assignments of the *mmm*, *mmr*, *rmr*, *rrr*, and *rrm* tetrads. We were unable to make a firm *mrm* assignment, but we believe our results favor the Flory–Fujiwara assignment of this band. This uncertainty in the *mrm* assignment does not affect the accuracy of the percent *r* determination. Finally, we contend that spectra which led others to conclude that isotactic PP has the structure I show definite signs of the presence of other structures.

Experimental Section

Samples examined in this work and their identification are given in Table I. The monomers, *trans*-propylene-*1,2,3,3,3-d*$_5$ (Pd$_5$) and propylene-*2,3,3,3-d*$_4$ (Pd$_4$), with stated isotopic purities of 98.9 and ≥98.0 atom % D, respectively, were purchased from Merck Sharp and Dohme. NMR spectra (100 MHz) obtained on the Pd$_5$ monomer in the neat liquid state at −70° showed that 94.2, 4.0, and 1.8% of the hydrogen atoms in the molecule were attached to the number one, two, and three carbon atoms, respectively. Similar measurements on Pd$_4$ gave 95.5, 3.7, and 0.8% hydrogen atoms at the one, two, and three positions, respectively.

The deuteriopropylenes were polymerized with a titanium halide–metal alkyl catalyst. Propylene was polymerized under very similar although not identical conditions. The polymers were extracted successively with acetone, diethyl ether, and heptane at the boiling point of each solvent using a vapor jacketed Soxhlet-type extractor. Extraction with each solvent took ca. 24 hr. To illustrate the nomenclature of the fractions the term "acetone insoluble–ether soluble fraction" refers to the extract obtained by doing an ether extraction on a sample that was previously extracted with acetone. Several commercial polymers and fractions obtained therefrom were also examined. In an effort to obtain a sample in which the *rrm* tetrad was concentrated, a commercial PP was successively extracted with acetone, ether, pentane, hexane, and heptane. The hexane insoluble–heptane soluble fraction is designated as C-1. A predominantly syndiotactic PP was synthesized following Boor and Youngman.[23]

To generate sequences of known structure in polypropylene, a heptane insoluble PP fraction with low *r* content, C-2, was epimerized using procedures described by Listner.[24] The epimerization reaction was run at 200° in the polymer melt using 1% dicumyl peroxide and 4% tris(2,3-dibromopropyl) phosphate. The reaction product was extracted successively with acetone, ether, and heptane. C-2E is the ether insoluble–heptane soluble fraction from this preparation. Melting points of the parent polymer and the epimerized fraction were determined with a Perkin-Elmer Model 1B differential scanning calorimeter (DSC) at a heating rate of 10°C/min on samples that had been previously cooled from 200°C to ca. 60°C at a cooling rate of 10°C/min.

The NMR spectra were obtained at a concentration equal to 50 mg of polymer per cubic centimeter of solution using *o*-dichlorobenzene solvent and hexamethyldisiloxane (HMDS) internal standard. Chemical shifts are given in ppm with the chemical shift of HMDS equal to zero. Except where otherwise indicated, the spectra were obtained at 130°C. Spectra of deuteriopolypropylenes were obtained with Varian 100 and 220 MHz spectrometers. The deuteriopolymers were generally run with deuterium decoupling to improve band resolution.[9,29] Spectra of PP were obtained on Varian 220 and 300 MHz instruments. Quantitative measurements of *r* dyad concentrations in samples C-3 and C-4 were obtained from 220 MHz computer averaged multiple scans, about ten in number. Concentrations were calculated from the ratio of the intensity of the ^{13}C satellite of the *mm* methyl doublet to the intensity of the *r* methylene region.[29] The percent *r* of sample C-5 was calculated from methine and *r* methylene intensities.

Infrared spectra of sample PP-A were obtained with a Beckman IR-12 spectrophotometer using the procedure of Bucci and Simonazzi[25] to check for methylene sequence of length 1, 2, 3, and ≥4. Estimates of concentrations of such sequences were based on extinction coefficients provided by these authors. Films ca. 325 μ thick were used for the ir measurements.

Results and Discussion

I. Tetrad Assignments. The tetrad band assignments are based mainly on the spectra of the deuteriopolypropylenes and partly on the spectrum of epimerized polypropylene.

***mmm* and *rrr* Assignment.** From symmetry considerations the six possible tetrads yield ten different methylene hydrogen types. The two methylene hydrogens in *mmm*, *mmr*, *rmr*, and *rrm* tetrads are nonequivalent, giving rise to eight hydrogen types. The other two types of hydrogen derive from the equivalent methylene protons in the two tetrads, *rrr* and *mrm*. Nine of the possible ten hydrogens were detected by Zambelli and Segre.[10] In an incisive investigation, they showed that the methylene spectrum consists of three general regions: a downfield region, which we term the *m-a* region, where the anti-methylene protons in *m* centered tetrads absorb; an upfield region termed *m-s*, where the corresponding syn protons absorb; and a central region where some, if not all, of the *r* centered tetrads occur. The anti and syn *mmm* hydrogens and the *rrr* hydrogens are easily assigned because they correspond to the most intense bands in predominantly isotactic and predominantly syndiotactic PP.[10] A possible complication is that the chemical shift of a band can vary with the degree of stereoregularity of the polymer.[26] However, in the deuteriopolypropylenes and PP that we examined, chemical shifts of all methylene hydrogen types were independent of stereoregularity to ≤0.006 ppm over the stereoregularity

Table I
Designation and Description of Samples

Designation	Monomer	Source	Fraction
PPd4-A	$CD_3CD{=}CH_2$	Catalyzed with Ti	Acetone ins–ether sol
PPD4-B	$CD_3CD{=}CH_2$	Halide–metal	Ether sol–heptane ins
PPD4-C	$CD_3CD{=}CH_2$	Alkyl	Heptane ins
PPd5-A	*trans*-$CD_3CD{=}CDH$[a]	Catalyzed with Ti	Acetone ins–ether sol
PPd5-B	*trans*-$CD_3CD{=}CDH$[a]	Halide–metal	Ether sol–heptane ins
PP-A	$CH_3CH{=}CH_2$	Alkyl	Acetone ins–ether sol
C-1	$CH_3CH{=}CH_2$	Commercial polymer 1	Hexane ins–heptane sol
C-2	$CH_3CH{=}CH_2$	Commercial polymer 2	Heptane ins
C-2E	$CH_3CH{=}CH_2$		Epimerization product of C-2 with 13% *r*
C-3	$CH_3CH{=}CH_2$	Commercial polymer 3	Heptane ins
C-4	$CH_3CH{=}CH_2$	Commercial polymer 4	Heptane ins
C-5	$CH_3CH{=}CH_2$	Commercial polymer 5	Unfractionated
SPP	$CH_3CH{=}CH_2$	Syndiotactic polymer synthesized per ref 23	Unfractionated

[a] D on number one C atom is trans to methyl group.

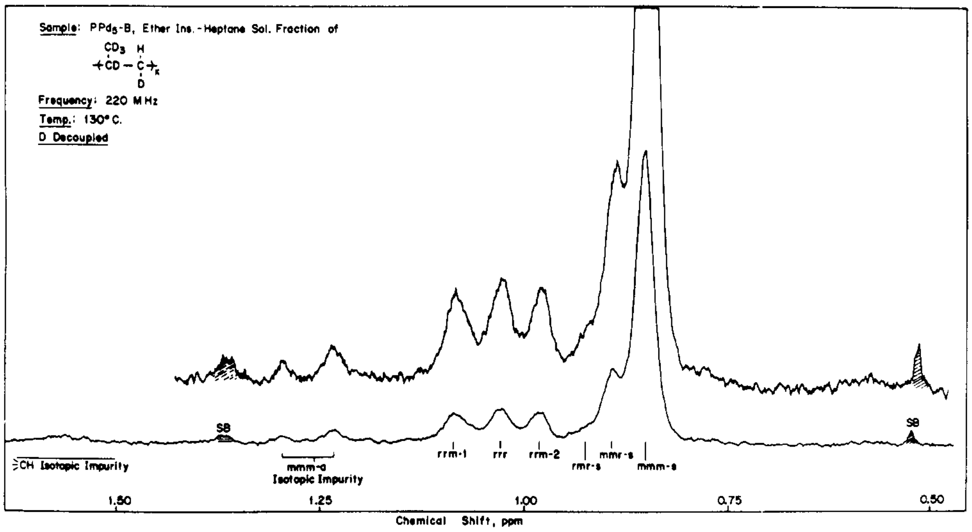


Figure 1. 220 MHz spectrum of PPd$_5$-B, ether insoluble–heptane soluble fraction of poly(*trans*-propylene-*1,2,3,3,3-d$_5$*).

range from $r \sim 2\%$ to $>60\%$. Consequently, the assignments of the *rrr* and the anti and syn *mmm* protons, which are designated *mmm-a* and *mmm-s,* respectively, are secure.

rrm **Assignment.** The two nonequivalent methylene hydrogens in the *rrm* tetrad, designated as *rrm*-1 and *rrm*-2, must occur in equal abundance in a long chain polymer.[3a] This fact, together with the multiplicity of the bands observed in the deuteriopolypropylenes, is the key to the assignment of these bands. The deuterium decoupled 220 MHz spectrum of sample PPd$_5$-B, a sample of intermediate stereoregularity, is shown in Figure 1. All bands are singlets and the anti protons in *m*-centered tetrads are absent, except for small bands that are present because the monomer was not isotopically pure. The *rrm*-1 and *rrm*-2 bands have nearly equal intensity, as required, and the chemical shift difference, Δ, between the bands is 0.102 ppm. If this assignment is correct, then the *rrm* spectrum of PPd$_4$ samples should be an accurately predictable AB quadruplet. The predicted spectra at 220 and 100 MHz obtained using $\Delta = 0.102$ ppm and $J = 13.5$ Hz, the value found for *m* dyads,[8] are given in Table II.

Experimental spectra of PPd$_4$-B at 220 and 100 MHz were obtained, and the 220 MHz spectrum is shown in Figure 2. In both the 220 and 100 MHz spectra, the two outer members of the *rrm* AB quadruplet are partly overlapped. However, the two central bands are clearly seen in both spectra. Also Table II shows that the separation between the central bands agrees well with the predicted value. This agreement is indisputable evidence for the validity of the *rrm*-1 and *rrm*-2 assignments.

mrm **Assignment.** Our *mrm* assignment is based largely on the 100 MHz spectrum of PPd$_5$-A shown in Figure 3. Six relatively intense bands are seen, together with some small bands that are caused by isotopic impurities. Additionally, there are indications of fine structure within the six major bands. No attempt was made to interpret the fine structure

Table II
Comparison of Predicted and Experimental Spectra of *rrm* Tetrad in PPd_4

Bands in AB quadruplet	220 MHz Predicted	220 MHz Exptl	100 MHz Predicted	100 MHz Exptl
Separation between low field pair of bands	13.5 Hz	~14 Hz	13.5 Hz	
Separation between central pair of bands	11.6	13	3.7	3.5 Hz
Separation between high field pair of bands	13.5	~14	13.5	
Relative intensities	0.33:1.0:1.0:0.33		0.12:1.0:1.0:0.12	

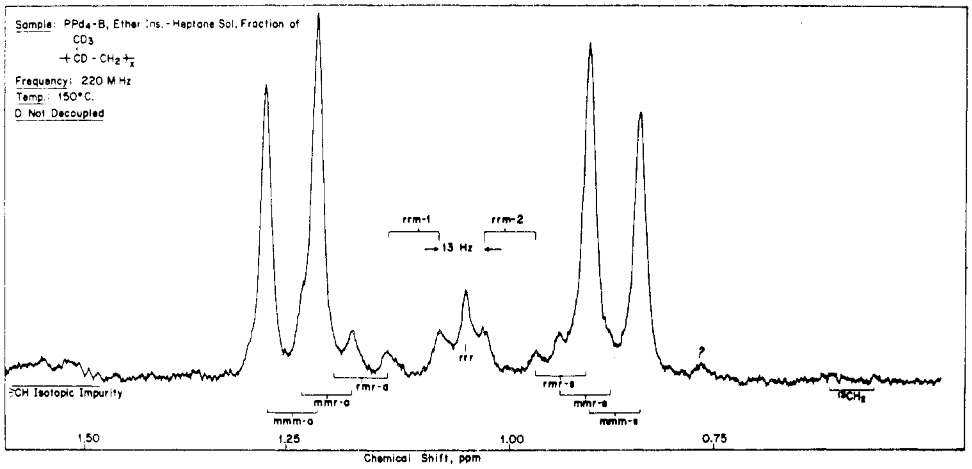


Figure 2. 220 MHz spectrum of PPd_4-B, ether insoluble–heptane soluble fraction of poly(propylene-*2,3,3,3-d*$_4$).

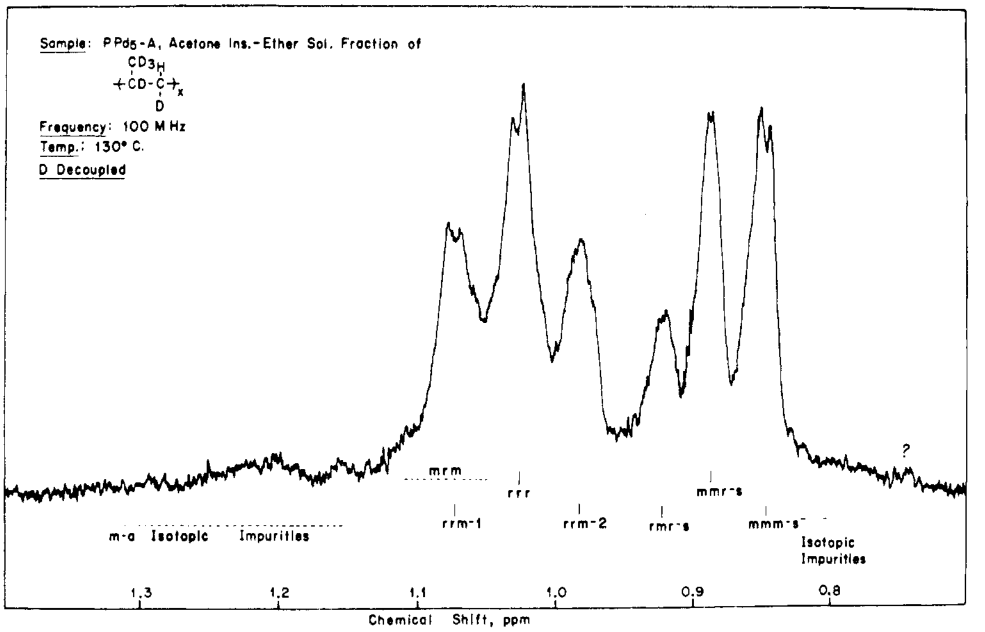


Figure 3. 100 MHz spectrum of PPd_5-A, ether soluble fraction of poly(*trans*-propylene-*1,2,3,3,3-d*$_5$).

in terms of hexad structures, however. Chemical shifts of the tetrad bands determined from 100 and 220 MHz spectra of the various fractions from PPd_5 and PPd_4 are given in Table III. The relative intensities of the six intense bands in Figure 3 were estimated by two methods: (1) from the integral of the spectrum, making no allowance for overlap between bands, and (2) by decomposing the spectrum into six constituent bands, assumed to have a Gaussian shape, using an analog computer. The third and fourth columns in Table III show that the two methods are in fair agreement. The analog computer values, believed to be more accurate, were used in our analysis below. The limits given in the table are average deviations from the mean of duplicate solutions, and they are indicative of the precision rather than the accuracy of the analysis.

Table III shows that the intensity in the *rrm*-1 region is 0.066 ± 0.010 greater than that in the *rrm*-2 region. This difference might be attributed to an unresolved *mrm* band

Table III
Experimental and Calculated Intensities for PPd$_5$-A

H-Type	Chemical shift,[a] ppm	Experimental intensity: No overlap correction	Experimental intensity: Analog computer soln	Calcd intensity for Markoffian chain[b]		Difference
rrm-1	1.080	0.18	0.192 ± 0.005	0.120	0.172	+0.020
mrm	~1.08			0.052		
rrr	1.026	0.24	0.251 ± 0.004	0.275		−0.024
rrm-2	0.978	0.14	0.126 ± 0.005	0.120		+0.006
rmr-s	0.928	0.09	0.076 ± 0.011	0.069		+0.007
mmr-s	0.886	0.16	0.174 ± 0.010	0.207		−0.033
mmm-s	0.847	0.19	0.182 ± 0.003	0.155		+0.027

[a] Conditions: 0.05 g polymer/cm^3 of dichlorobenzene, 130°C, HMDS at 0 ppm. Chemical shifts of *mmm-a*, *mmr-a*, *and rmr-a* in PPd$_4$ are 1.238, 1.194, and 1.151, respectively. Chemical shifts for completely hydrogenated polymer are ~0.04 ppm downfield from these values. [b] $q(m/m) = 0.60$ and $q(r/r) = 0.70$.

absorbing in the *rrm*-1 region as suggested by Flory and Fujiwara.[3] The intensity of the *mrm* tetrad, designated by (*mrm*), so estimated agrees within experimental error with the value estimated from the intensity sum rule. Thus, substituting the analog computer values in Table III into the necessary intensity relation gives[27]

$$(mrm) = 0.5(mmr) + (rmr) - 0.5(rrm)$$

and taking $(rrm) = 2(rrm\text{-}2)$ we obtain $(mrm) = 0.037 \pm 0.021$. Also, (*mrm*) estimated by assuming the polymer to be a Markoffian chain with dependence on first neighbors only is also in agreement with the above estimates. The relative intensities calculated using this model with conditional probabilities $q(m/m) = 0.60$ and $q(r/r) = 0.70$ are given in the fifth column of Table III. Here $q(m/m)$ is the conditional probability that an *m* dyad is succeeded by another *m* dyad and $q(r/r)$ is the conditional probability that an *r* dyad is succeeded by another *r* dyad. The conditional probabilities were chosen to give a fit to the observed intensities. The last column shows that the calculated and experimental intensities are in fair agreement. The value of (*mrm*) obtained by this procedure is 0.052.

The fact that three different methods yield similar estimates, i.e., 0.066 ± 0.010, 0.037 ± 0.021, and 0.052, for (*mrm*) suggests that the *mrm* band indeed absorbs in the *rrm*-1 region. On the other hand, Zambelli, et al., proposed that unequal intensities in the *rrm*-1 and *rrm*-2 regions of their spectra were caused by the presence of non-head-to-tail, or irregular, structures.[15] However, ir spectra of our PP-A sample, the fully hydrogenated analog of the PPd$_5$-A sample, showed no 750 cm^{-1} band, a band which is characteristic of the irregular structure $CH(CH_3)\cdot CH_2CH_2CH(CH_3)$.[25] If 1% of the methylene groups in the polymer had existed in this structure, they would have been detected under the conditions of our analysis.

Methyl groups in irregular structures absorb at ~0.74 ppm,[15] and there is a weak unidentified band at this position in Figure 3 as well as in Figure 2. We do not believe that irregular structures are the source of this band in our spectra, however. The Pd$_4$ and Pd$_5$ monomers contained only small amounts of methyl hydrogen isotopic impurity, 0.8 and 1.8%, respectively. From the ir results less than ~1% of the monomer groups in the polymers would be expected to exist in irregular structures. Accordingly, the band intensity at 0.74 ppm arising from this source should be undetectably small.

Although the 750 cm^{-1} band was indeed undetectably small in the ir spectrum of PP-A, a weak band at 723 cm^{-1} indicated that 1–2% of methylene groups present existed in $(CH_2)_{n\geq4}$ sequences. Such long methylene sequences are probably caused by displacement and subsequent polymerization of ethylene from metal alkyl catalyst by propylene.[28] From model compound spectra, it appears that such long sequences would absorb in the *m-a* region.[14] This is supported by the fact that methylene groups in polyethylene under our experimental conditions absorb in the *m-a* region, at 1.22 ppm. Consequently, we believe that $(CH_2)_{n\geq4}$ sequences are probably not the cause of the unequal intensities in the *rrm*-1 and *rrm*-2 regions in Figure 2.

Whereas our results favor assigning the *mrm* tetrad to the *rrm*-1 region, the approach we have used to make this assignment is generally similar to the one used by HZ,[12,15] who arrived at a different conclusion. They concluded that the *mrm* absorption coincides with the *rrr* absorption. Both of these assignments rely critically on the accuracy of experimental intensity measurements to determine indirectly the intensity of the *mrm* band using the intensity sum rule. The experimental intensity measurements are subject to errors of unknown magnitude because of incomplete band resolution and complications caused by isotopic impurities. Furthermore, there is some uncertainty in the concentration of non-head-to-tail propylene units and copolymerized ethylene units in the deuteriopolypropylene, as well as in the location of the NMR bands that would derive from such structures. Consequently, we believe that neither the HZ assignment nor the one that we favor is firmly established.

***mmr* and *rmr* Assignment.** Our assignment of the *mmr-s* and *mrm-s* bands is consistent with the intensity sum rule, as shown in the previous section. The assignment is also supported by the fact that the intensities were fitted to a simple structural model, i.e., the Markoffian chain discussed above. This procedure did not assign the corresponding anti protons. However, the corresponding anti protons can be identified with certainty in spectra of PPd$_4$ fractions, particularly of PPd$_4$-A, where the *mmr* and *rmr* spectra appear as AB quadruplets. Further support for the assignment of the *mmr-a* and *-s* bands is also supplied by epimerization experiments discussed later.

II. Quantitative Measurements of Stereoregularity. Although the precise location of the *mrm* tetrad was not completely defined, the preceding assignment shows that all the *r* centered tetrads absorb in the central region and all the *m* centered tetrads absorb in the outer regions of the methylene spectrum. This conclusion is confirmed by intensity measurements made on PPd$_4$-C, a heptane insolu-

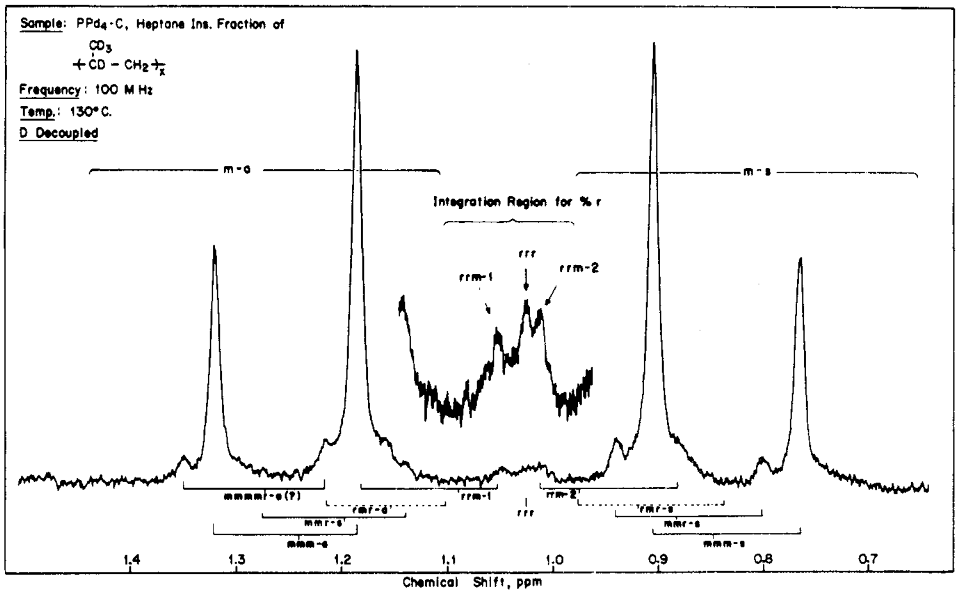


Figure 4. 100 MHz spectrum of PPd$_4$-C, heptane insoluble fraction of poly(propylene-*2,3,3,3-d$_4$*).

ble fraction whose 100 MHz spectrum is shown in Figure 4. The monomer from which the polymer was made contained 0.8% methyl hydrogen isotopic impurity. Upon polymerization the methyl hydrogen absorbs in the *m-s* region. After the electronic integral of the spectrum had been corrected for this absorption, the syn to anti methylene hydrogen intensity ratio was found to be 1.006, with a standard deviation, σ, of 0.025 in six determinations. The fact that this ratio is so close to unity means that there is no *r* band ($<\sim$1% intensity) buried in one or the other of the two *m* regions of the spectrum. The absence of other spurious unresolved bands in these regions for this sample is thus also demonstrated. We can therefore make quantitative measurements of the degree of stereoregularity with confidence in their validity.

Measurements made under various conditions show the PPd$_4$-C sample has 5.0% *r* dyads. The spectrum in Figure 4 was obtained at 100 MHz with deuterium decoupling, and the region over which the electronic integral was taken to estimate the *r* content is shown. This region does not include the two outer members of the *rrm* AB quadruplet. The uncorrected percent *r* value so obtained was 5.0%, with σ = 0.3%. Because the ratio of the intensities of the AB quadruplet bands at 100 MHz is 0.12:1.0:1.0:0.12, this precedure underestimates the *r* dyads by at most 0.12 × 5.0%, i.e., 0.6%, for this sample. A corrected percent *r*, obtained by adding half this value, is 5.3%. The maximum possible bias introduced by this correction procedure is 0.3%. Measurements with no deuterium decoupling gave a corrected value of 4.8% *r*, with σ = 1.02%. At 220 MHz there is very little overlap between *r* and *m* bands and 5.0% *r* was obtained, with σ = 0.41%. Thus, the three estimates obtained under various conditions, 5.3, 4.8, and 5.0% *r*, are in good agreement with each other.

The concentration of *r* dyads in polymers which do not contain deuterium cannot be accurately estimated at 100 MHz because of extensive overlap between *r* and *m* methylene absorption bands. However, overlap is considerably reduced at 220 MHz and almost eliminated at 300 MHz. Measurements were made at 220 MHz on several heptane insoluble fractions from commercial PP, as well as on an unfractionated polymer, C-5. The results, together with several literature values, are given in Table IV. Our C-5 sample was also examined by ^{13}C NMR, and the value obtained from an analyses of the methyl pentad bands is also given in the table.[30] The ^{1}H and ^{13}C NMR values were in excellent agreement, 6.6 and 6.8% respectively.

Table IV
Percent *r* Dyads in Polypropylene and Deuteriopolypropylene from ^{1}H NMR Measurements

Sample description	Ref	% *r*
Commercial PP, benzene insol fraction	14	1
Commercial PP, heptane insol fraction	13, 21	1.3
C-3 heptane insol fraction	This work	1.8
C-4 heptane insol fraction	This work	1.8
PPd$_4$-C, heptane insol fraction	This work	5.0
C-5 unfractionated	This work	6.6,[a] 6.8

[a] ^{13}C NMR value.

Inspection of Table IV shows that the *r* dyad concentration in the heptane insoluble fractions ranges from 1 to 5%. Whether the breadth of the range arises from the use of different catalysts, the details of the separation procedures, or other causes is not known. The *r* content of the deuteriopolypropylene lies at the extreme upper end of the range. If the melting point of the deuteriopolypropylene were greater than that of PP having the same structure, this observation could be readily explained. This seems improbable, however, because the melting point of perdeuteriopolyethylene is known to be smaller than that of polyethylene.[31]

III. Identification of *rrm* Spectrum in Polypropylene. Triad Assignments. The preceding assignments based on deuteriopolypropylenes are very helpful in interpreting the more complex spectra of PP. The spectra of *rrr*, *mrm*, and *rrm* tetrads are of particular interest in trying to see whether structures I or II apply to predominantly isotactic PP. The *rrr* tetrad is found in predominantly syndiotactic PP, and the CH$_2$ spectrum has the appearance of a triplet although it is a "deceptively simple" spectrum with unequal vicinal coupling constants.[11] The *mrm* tetrad should also appear as a triplet[13] similar to the *rrr* triplet. The *rrm* multiplet would be expected to be more complex

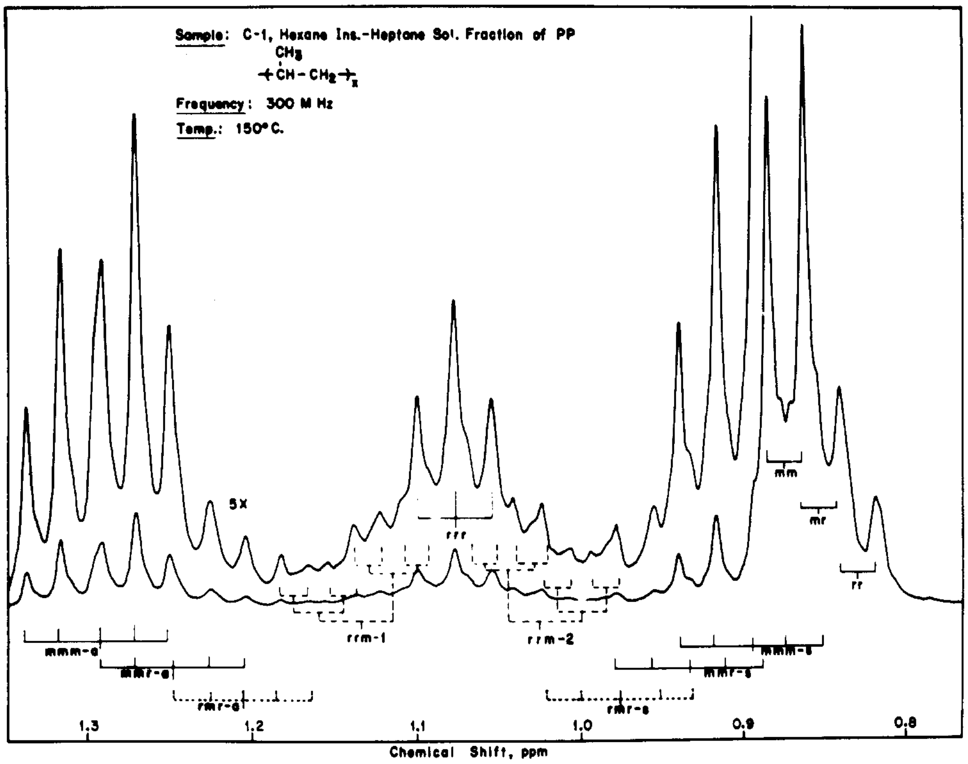


Figure 5. 300 MHz spectrum of C-1, a hexane insoluble–heptane soluble fraction from PP.

because of the nonequivalent methylene hydrogens in this tetrad.

The *rrm* tetrad was concentrated and identified in sample C-1, whose 300 MHz spectrum is shown in Figure 5. A first-order interpretation of the *rrm* spectrum is given by the dashed lines. A triplet at the *rrr* chemical shift position is superimposed on the *rrm* spectrum. The chemical shift difference between the *rrm*-1 and *rrm*-2 hydrogens is similar to that in the deuteriopolypropylenes and the coupling constants characterizing the spectrum are 13.5, 8.9, and 4.3 Hz. The 13.5 Hz value is equal to the geminal methylene coupling constant in *m* dyads.[8] The vicinal coupling constants, 8.9 and 4.3 Hz, are equal within experimental error to the 8.3 and 4.8 Hz values found for the *rrr* tetrad.[11] These observations strongly support our identification. Near equality of the vicinal coupling constants in the *rrm* and *rrr* tetrads is to be expected from conformation considerations.[32]

The *rrm* spectrum was also generated by epimerizing highly isotactic PP. This procedure generates free radicals that abstract tertiary hydrogen atoms from PP molecules. We believe that the planar polymer radical thus formed can, in turn, abstract another hydrogen atom from other molecules in the system. When it does so the reaction site can revert to its original configuration, or it can convert to the opposite configuration. In the former case the chain configuration is unchanged whereas in the latter case two contiguous *r* placements flanked by long *m* sequences are generated, as exist in structure II. If this reaction occurs at random along the chain and the reaction is carried to small conversion, no other structures should be generated.

The sample which was epimerized was a heptane insoluble fraction of PP with ~2% *r* and a DSC melting peak at 162°C. The spectrum of the sample before epimerization showed only very weak bands in the *r* methylene portion of the spectrum. However, Figure 6 shows that the spectrum of the isomerized sample, which had 13% *r* and a broad DSC melting peak at 126°C, has relatively intense bands in this region. The spectrum in the *r* methylene region of Figure 6 corresponds very closely to the *rrm* spectrum in Figure 5.

The epimerization reaction should also generate *mmr* tetrads but no *rmr* tetrads. The spectrum in Figure 6 is in accord with this expectation. The *mmr-s* bands are badly overlapped, but some *mmr-a* bands relatively free of overlap can be seen. This supports the MMR assignment previously derived from the deuteriopolymers.

The epimerization reaction would be expected to generate both *rr* and *mr* triads. Our interpretation of the methyl region is given in Figure 6, where the *mr* and *rr* triads chemical shifts are shown 0.022 and 0.047 ppm upfield from the *mm* triad, respectively. This interpretation is supported by the fact that the *rr* doublet was 0.045 ppm upfield from the *mm* doublet in mixtures of predominantly isotactic and predominantly syndiotactic PP. Our methyl band assignments are also in agreement with Woodbrey's conclusion that the *mr* triad lies midway between the *mm* and *rr* triads.[6] However, our assignment disagrees with the methyl pentad assignment given by Ferguson.[14] In a pentad interpretation, we place the *mmrm* and the *mrrm* pentads generated in the epimerization reaction at 0.022 and 0.047 ppm upfield from the *mmmm* pentad. Ferguson's assignment was based on a comparison of methyl intensity measurements with intensities calculated for various assumed models for the structure of the polymer chain. It is difficult to make accurate measurements of the relative intensities of methyl bands in PP because of severe overlap, and we believe our assignment is more firmly established. For example, he tentatively assigned the *mrrm* pentad to a position 0.083 ppm upfield from the *mmmm* pentad. However, our epimerized sample, which undoubtedly contains *mrrm* pentads, shows no band at this position.

IV. Structure of Stereoregular Polypropylenes and Deuteriopolypropylenes. The spectrum of the heptane insoluble fraction, PPd$_4$-C, given in Figure 4, shows three small peaks in the *r* region. The central peak position coin-

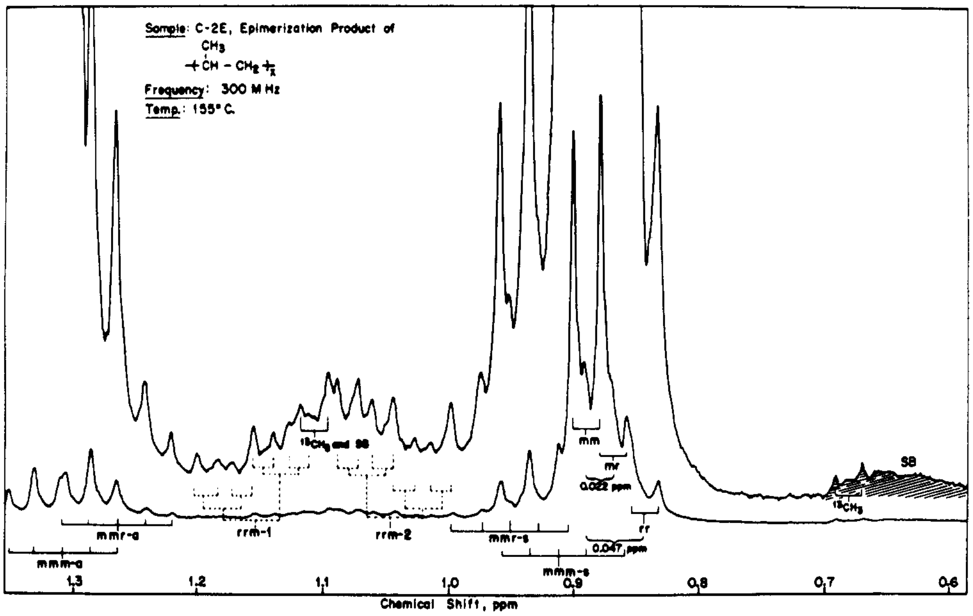


Figure 6. 300 MHz spectrum of C-2E, an epimerization product of PP.

cides with the *rrr* chemical shift. However, in view of the uncertainty in the *mrm* assignment, this band could possibly be the *mrm* tetrad. The two flanking peaks are the central peaks in the *rrm* AB quadruplet. Thus, neither structures I nor II adequately describe this polymer, which was made with a titanium halide and metal alkyl catalyst. As shown by Zambelli et al. predominantly isotactic fractions of poly(*cis*-propylene-*1,2,3,3,3-d*$_5$) made with VCl$_3$–Al(C$_2$H$_5$)$_2$Cl catalyst also show the *rrm* band as well as a band at the *rrr* position.[15]

The structure of stereoregular polymers that do not have deuterium substituents is more difficult to establish because of the greater complexity of the spectra. Our own spectra of such PP fractions do not have sufficient resolution and signal-to-noise ratio to establish the structures contained therein. However, 220 MHz spectra of highly stereoregular fractions of PP have been reported and interpreted by others.[13,14] As described below, we disagree with the interpretation that has been given to these spectra. Our conclusion that these spectra have been inaccurately interpreted is based on (1) the demonstration that the *rrm* tetrad is difficult to detect in 220 MHz spectra, and (2) our methyl band assignments derived from epimerized PP.

Heatley, Salovey, and Bovey concluded that structure I was the dominant structure in the heptane-insoluble fraction of a commercial PP that they examined.[13] This conclusion was based on the 220 MHz spectrum which is reproduced in part in Figure 7, curve A. Their interpretation is shown in the figure. This conclusion rests mainly on the apparent triplet labeled *mrm*. The *rrm* tetrad was eliminated from consideration because it does not have a triplet spectrum, and it was assumed that the *rrr* structure was improbable in a chain composed very largely of *m* dyads. A small doublet 0.05 ppm upfield from the intense *mm* triad was attributed to the *mr* triad. Ferguson, whose spectrum of a benzene insoluble fraction of a commercial PP is very similar to that given in Figure 7, curve A, arrived at the same conclusion using similar arguments.[14]

The 220 MHz spectrum of C-1 over the *r* methylene region is also given in Figure7, curve B. Our spectrum has been shifted laterally to make the anti and syn *mmm* peaks in the two curves coincide. As noted above, the 300 MHz spectrum of this sample given in Figure 5 shows a sizable *rrm* absorption in addition to a triplet at the *rrr* chemical shift position. Curves A and B in Figure 7 show that the band shapes in the *r* methylene region are similar. This strong similarity suggests that the *rrm* tetrad may be present but may have been overlooked in the curve A sample. This contention is supported by an examination of the methyl region. We believe that the small doublet observed by these investigators 0.05 ppm upfield from the *mm* doublet is not the *mr* triad. Our methyl assignment based on epimerization experiments places the *mr* triad significantly downfield from this position. Rather, we believe that the small doublet they observed 0.05 ppm upfield from the *mm* triad is the *rr* triad, which occurs 0.047 ppm upfield from the *mm* triad in our assignment. Presence of the *rr* triad requires the presence of *rrm* or *rrr* tetrads in the sample.

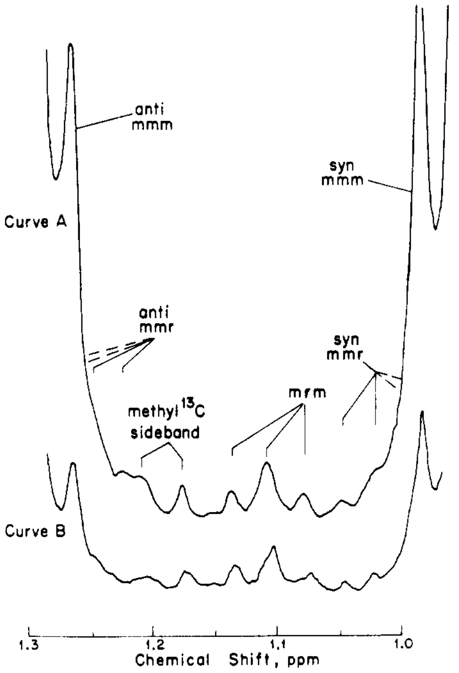


Figure 7. 220 MHz spectra of PP fractions. Curve A: heptane insoluble fraction at 10% w/v concentration at 140°C, taken from ref 13. Curve B: sample C-1, hexane insoluble–heptane soluble fraction at 5% w/v concentration at 130°C.

Thus, the tetrad bands observed in the spectra of these stereoregular PP samples are not necessarily different from those that have been identified in stereoregular deuteriopolypropylenes.

The ^{13}C NMR spectrum of the heptane-insoluble fraction obtained from PP made with a $TiCl_3$–$Al(C_2H_5)_2I$ catalyst has also been reported, and a complete ^{13}C methyl pentad assignment was proposed.[21] This assignment led to the conclusion that this sample conforms to structure I. By contrast, our independent ^{13}C methyl pentad assignment, based in part on epimerized polypropylenes,[30] leads to the conclusion that this sample conforms closely to structure II. The ^{13}C NMR methyl pentad band assignment which led others to conclude that the structure of the heptane-insoluble fraction of PP made with a $TiCl_3$–$Al(C_2H_5)_2I$ catalyst conforms to structure I has been withdrawn and a different band assignment[33] demonstrated which agrees with our conclusions from ^{13}C studies of epimerized polymer.[30]

V. Conclusions. Our use of deuteriopolymers and epimerization experiments has been a fruitful approach to the assignment of ^{1}H NMR bands in polypropylene. We have thus confirmed the *mmm, mmr, rmr, rrm,* and *rrr* tetrad assignments proposed by Flory and Fujiwara[3a] and Heatley and Zambelli. Although our results favor the Flory–Fujiwara *mrm* assignment, the exact location of the *mrm* tetrad has not been firmly established by ourselves nor by other spectroscopists. However, this tetrad absorbs in the *r* methylene region of the spectrum, and the uncertainty in its precise location does not limit the accuracy of stereoregularity determinations. Such determinations made on the heptane insoluble fraction of several PP and deuteriopolypropylene polymers gave an *r* dyad content ranging from 1 to 5%.

Stereoregular fractions of deuteriopolypropylene have a complex structure, containing *rrm* as well as *rrr* and/or *mrm* tetrads. Published spectra of the heptane-insoluble fraction of commercial PP are not necessarily inconsistent with the tetrads that we and Zambelli et al. have found in deuteriopolypropylenes.

Acknowledgment. The assistance of T. Hines, S. H. Killian, J. O. Brewer, and Herschel Williams is greatfully acknowledged. We also acknowledge helpful discussions with N. F. Chamberlain, J. J. R. Reed, C. S. Speed, and H. J. Wristers. The 220 and 300 MHz spectra were run by Lou Cary of Varian Associates.

References and Notes

(1) (a) Exxon Chemical Company; (b) Amoco Chemicals Corporation.

(2) I. Ando and A. Nishioka, *Polym. J.*, **2**, 161 (1971).

(3) (a) P. J. Flory and Y. Fujiwara, *Macromolecules*, **2**, 327 (1969); (b) P. J. Flory, *ibid.*, **2**, 613 (1970).

(4) F. C. Stehling, *J. Polym. Sci., Part A*, **2**, 1815 (1964).

(5) J. C. Woodbrey and Q. A. Tremontozzi, *J. Polym. Sci., Part C*, **8**, 113 (1965).

(6) J. C. Woodbrey, *J. Polym. Sci., Part B*, **2**, 315 (1964).

(7) W. C. Tinchner, *Makromol. Chem.*, **85**, 34 (1965).

(8) E. Lombardi, A. Segre, A. Zambelli, A. Marinangeli, and G. Natta, *J. Polym. Sci., Part C*, **16**, 2539 (1967).

(9) A. Zambelli, A. Segre, M. Farina, and G. Natta, *Makromol. Chem.*, **110**, 1 (1967).

(10) A. Zambelli and A. Segre, *J. Polym. Sci., Part B*, **6**, 473 (1968).

(11) A. Zambelli, M. G. Giongo, and G. Natta, *Makromol. Chem.*, **112**, 183 (1968).

(12) F. Heatley and A. Zambelli, *Macromolecules*, **2**, 618 (1969).

(13) F. Heatley, R. Salovey, and F. A. Bovey, *Macromolecules*, **2**, 619 (1969).

(14) R. C. Ferguson, *Macromolecules*, **4**, 324 (1971).

(15) A. Zambelli, L. Zetta, C. Sacchi, and C. Wolfsgruber, *Macromolecules*, **5**, 440 (1972).

(16) L. F. Johnson, F. Heatley, and F. A. Bovey, *Macromolecules*, **3**, 175 (1970).

(17) L. F. Johnson, *Anal. Chem.*, **43**, 28A (1971).

(18) W. O. Crain, Jr., A. Zambelli, and J. D. Roberts, *Macromolecules*, **4**, 330 (1971).

(19) A. Zambelli, G. Gatti, C. Sacchi, W. O. Crain, Jr., and J. D. Roberts, *Macromolecules*, **4**, 475 (1971).

(20) Y. Inoue, A. Nishioka, and R. Chujo, *Makromol. Chem.*, **152**, 15 (1972).

(21) A. Zambelli, D. E. Dorman, A. I. R. Brewster, and F. A. Bovey, *Macromolecules*, **6**, 925 (1973).

(22) J. C. Randall, *J. Polym. Sci., Polym. Phys. Ed.*, **12**, 703 (1974).

(23) J. Boor, Jr., and E. A. Youngman, *J. Polym. Sci., Part A-1*, **4**, 1861 (1966).

(24) G. J. Listner, U.S. Patent 3,511,824.

(25) G. Bucci and T. Simonazzi, *J. Polym. Sci., Part C*, **7**, 203 (1964).

(26) Y. Fujiwara and P. J. Flory, *Macromolecules*, **3**, 43 (1970).

(27) H. L. Frisch, C. L. Mallows, and F. A. Bovey, *J. Chem. Phys.*, **45**, 1565 (1966).

(28) A. D. Ketley and J. D. Moyer, *J. Polym. Sci., Part A*, **1**, 2467 (1963).

(29) A. Segre, *Macromolecules*, **1**, 93 (1968).

(30) J. R. Knox and F. C. Stehling, to be published. Our method for assigning the ten ^{13}C methyl pentads is as follows. The *mmmm* and *rrrr* pentads correspond to the most intense peaks in highly isotactic and highly syndiotactic PP, respectively. Lightly epimerized isotactic PP should have three weak peaks with the ratios 2:2:1 given by the *mmmr, mmrr,* and *mrrm* pentads, respectively. The least intense peak is assigned to *mrrm*. Lightly epimerized syndiotactic PP should have three weak peaks with the ratios 2:2:1 given by the *rrrm, mmrr,* and *rmmr* pentads. The least intense peak is assigned to *rmmr*. The band which is common to both the epimerized isotactic PP and the epimerized syndiotactic PP is assigned to *mmrr*. The third band in the epimerized isotactic PP is then assigned to *mmmr*, and the third band in the epimerized syndiotactic PP is assigned to *rrrm*. Pentads unassigned by this procedure, i.e., *mmrm, rrmr,* and *mrmr*, may be assigned in spectra of atactic PP using the necessary pentad intensity relations. Our assignment, reading from low field to high field, is *mmmm, mmmr, rmmr, mmrr, (rmrr), (mmrm), (mrmr), rrrr, rrrm,* and *mrrm*. Pentads not enclosed in parentheses are unequivocally established, whereas those shown in parentheses are considered as tentative.

(31) F. C. Stehling, E. Ergos, and L. Mandelkern, *Macromolecules*, **4**, 672 (1971).

(32) P. J. Flory, private communication.

(33) A. Zambelli, P. Locatelli, G. Bajo, and F. A. Bovey, *Macromolecules*, **8**, 687 (1975).