220-MHz Proton Magnetic Resonance Spectra of Polymers. II. Polypropylene and Ethylene–Propylene Copolymers

Raymond C. Ferguson

Contribution No. 1746 from the Central Research Department, Experimental Station, E. I. du Pont de Nemours and Company, Wilmington, Delaware 19898.

Received September 14, 1970

ABSTRACT: The 220-MHz pmr spectra of several polyethylenes, polypropylenes having different degrees of stereoregularity, and ethylene–propylene copolymers have been studied, with particular emphasis on possible quantitative applications. The spectra of polypropylenes are detectably affected by the different possible tetrad and pentad sequences of tactic placements. Some of the tetrad (methylene) and pentad (methyl) resonances have been resolved and identified. The multiplicity of possible four- and five-monomer-unit arrangements in less stereoregular polypropylenes, and in ethylene copolymers, produces line broadening and overlap in the spectra which limit quantitative reproducibility and accuracy. Nevertheless, useful estimates of monomer ratios, racemic *vs.* meso dyad placements, and blockiness of monomer sequences can be made.

The high-resolution proton magnetic resonance (pmr) spectra of hydrocarbon polymers are difficultly resolvable because of small chemical shift differences and complex spin–spin coupling patterns. The increased chemical shift dispersion and sensitivity of high-frequency spectrometers have significantly improved the capabilities of pmr spectroscopy for microstructure and quantitative analysis of polymers. This paper covers some applications of 220-MHz pmr spectroscopy to polyethylene, polypropylene, and ethylene–propylene copolymers. The quantitative accuracy of pmr measurements on these polymers is of particular interest, because nmr can, in principle, yield absolute concentration ratios and therefore—if not useful for routine analysis—might nevertheless provide a means of testing or improving the accuracy of empirically calibrated methods, such as infared spectroscopy.

The potential usefulness of pmr for the identification and quantitative determination of branch and end groups in polyethylene[1] is improved at 220 MHz.[2,3] The determination of methyl group concentrations in polyethylene is closely related to the determination of monomer ratios in ethylene–α-olefin copolymers. The discovery of some subtle complications due to tactic placement effects in ethylene–propylene copolymers[3] requires some reexamination of methods developed at 60 MHz.[1,4]

The major interest in the numerous earlier pmr studies of polypropylenes has been the determination of tacticity. The 60-MHz pmr spectra of polypropylenes are poorly resolved, but a number of authors were able to interpret the spectra partially[5–10] and to obtain qualitative or semiquantitative tacticity data.[9] The 100-MHz pmr spectra are more useful,[11–19] but still sufficiently complex to limit the accuracy of tacticity measurements. The spectra of deuterated polymers have been used to determine most of the pmr parameters associated with dyad and triad stereochemical placements,[10,13,15–19] to make improved estimates of stereoregularity, and to deduce the stereochemistry of double bond addition in both isotactic and syndiotactic polymerization.[17] The 220-MHz spectra of highly syndiotactic and highly isotactic polypropylenes are sufficiently well resolved to permit determination or verification of the pmr parameters without the use of deuterated polymers.[2,3] Resolution and assignment of resonances of tetrad configurational sequences have now been reported.[19–21]

Experimental Section

Some of the polyethylene samples studied were Alathon-10 and Alathon-7030 from Du Pont and ASTM sample no. 5–8. ASTM sample no. 5–7 are ethylene–butene-1 copolymers containing approximately 2, 4, and 6 wt % butene-1, respectively. ASTM sample no. 8 is a type I polyethylene (Alathon-34).[22]

Two highly syndiotactic polypropylenes were prepared by polymerization at -78° in *n*-hexane, using a 1:15 molar ratio of VCl_4 and $(C_2H_5)_2AlCl$ as catalyst.[23]

Samples of commercial polypropylenes manufactured by several companies (Hercules, Inc., Dow Chemical Corp., Shell Oil Co., and Eastman Kodak Co.) were obtained. A 10-g powdered sample of Hercules "Profax" polypropylene, Formula 6301, Lot No. 21237 (containing no additives), was extracted 16 hr in a Soxhlet extraction apparatus with boiling spectrograde benzene. The extract (approximately 3%) was recovered by evaporating the solvent under a stream of dry nitrogen. The extracted polypropylene and extract were dried to constant weight in a vacuum oven at 100–120°. Benzene and *n*-heptane extracts of two other commercial polypropylene resins were also studied.[24]

---

(1) R. C. Ferguson, *Kaut. Gummi, Kunstst.*, **11**, 723 (1965); *Rubber Chem. Technol.*, **40**, 385 (1967).

(2) R. C. Ferguson, *Proc. N. Y. Acad. Sci.*, **29**, 495 (1967).

(3) R. C. Ferguson, *Polym. Prepr., Amer. Chem. Soc., Div. Polym. Chem.*, **8**, 1026 (1967).

(4) R. S. Porter, *J. Polym. Sci., Part A-1*, **4**, 189 (1966).

(5) S. Satoh, R. Chujo, T. Ozeki, and E. Nagai, *ibid.*, **62**, S101 (1962).

(6) F. C. Stehling, *ibid., Part A*, **2**, 1815 (1964).

(7) J. C. Woodbrey, *ibid., Part B*, **2**, 315 (1964).

(8) Y. Kato and A. Nishioka, *Bull. Chem. Soc. Jap.*, **37**, 1622 (1964).

(9) J. C. Woodbrey and Q. A. Trementozzi, *J. Polym. Sci., Part C*, **No. 8**, 113 (1965).

(10) W. C. Tincher, *Makromol. Chem.*, **85**, 34 (1965).

(11) S. Ohnishi and K. Nukada, *J. Polym. Sci., Part B*, **3**, 179 (1965).

(12) S. Ohnishi and K. Nukada, *ibid., Part B*, **3**, 1001 (1965).

(13) G. Natta, E. Lombardi, A. L. Segre, A. Zambelli, and A. Marinangeli, *Chim. Ind. (Milan)*, **47**, 378 (1965).

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

(15) E. Lombardi, A. Segre, A. Zambelli, A. Marinangeli, and G. Natta, *ibid., Part C*, **No. 16**, 2539 (1967).

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

(17) A. Zambelli, M. G. Giongo, and G. Natta, *ibid.*, **112**, 183 (1968).

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

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

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

(21) F. Heatley, R. Salovey, and F. A. Bovey, *ibid.*, **2**, 619 (1969).

(22) The ASTM samples were kindly supplied by Dr. C. D. Lewis, Chairman, Task Group on Infrared Measurement of Branching in Polyethylene (Section VII-H, ASTM D-20), and are described in a distribution cover letter, Jan 27, 1967.

(23) Kindly synthesized and provided for study by Dr. R. D. Lipscomb, Central Research Department, E. I. du Pont de Nemours and Co.

(24) These extracts were supplied by Dr. T. E. Dye, Textile Fibers Department, E. I. du Pont de Nemours and Co.

A number of experimental ethylene–propylene copolymers were kindly provided by Dr. W. K. Witsiepe, Elastomer Chemicals Department, E. I. du Pont de Nemours and Co.

Samples of the *n*-alkane series, C_5 to C_{12}, eicosane, and the series $(CH_3)_2CH(CH_2)_nCH(CH_3)_2$, $n = 0$–3, were obtained from Chemical Samples Co., Columbus, Ohio.

The 220-MHz pmr spectra were run on a Varian Associates HR-220 nmr spectrometer. Polymer solvents employed were redistilled Eastman practical-grade *o*-dichlorobenzene (*o*-DCB), bp 180° (760 mm), and hexachloro-1,3-butadiene (HCBD), bp 95° (20 mm), containing no impurities detectable in the pmr spectra. The spectra were calibrated *vs.* hexamethyldisiloxane (HMDS) internal, and $\delta^* = 0$. The chemical shift of HMDS *vs.* tetramethylsilane is somewhat solvent and temperature dependent, but the δ-scale values can be approximated by adding 0.04 ppm to the δ^*-scale values.

Polyethylene. The $(CH_2)_n$ protons of polyethylene are effectively (though not rigorously) magnetically equivalent, and a singlet resonance is observed. The line width of molten polyethylene is typically on the order of a few hertz at 140°, decreasing to about 2 Hz at 170°. In addition to the $(CH_2)_n$ resonance at δ 1.29 (estimated shift from tetramethylsilane, external), other groups readily detectable at the 1% level[2] are $-CH_3$, δ 0.88; $-CH{=}CH_2$, δ 4.89, 4.95, 5.76 (J(trans) = 17, J(cis) = 10 Hz); $-CH{=}CH-$, δ 5.39; $>C{=}CH_2$, δ 4.69; $=CHCH_2-$, δ 5.39, 2.00.

Aside from the usual difficulties in measuring the intensity ratios of weak *vs.* strong lines, determination of the relative intensities of the olefinic *vs.* $(CH_2)_n$ resonances appears to be straightforward. However, multiscan averaging with a computer is generally needed for adequate S/N, even on neat samples.

Quantitative measurement of the methyl resonance is more difficult, because of incomplete resolution from the wing of the $(CH_2)_n$ line and the $(^{13}CH_2)_n$ satellite resonance (Figure 1). The resolution in this region of the spectrum was improved by running the samples as solutions in HCBD or *o*-DCB at 150°. A concentration of 25% w/v in HCBD appeared to give an optimum compromise between resolution and S/N.

The intensity ratios of the $(CH_2)_n$, $(^{13}CH_2)_n$, and CH_3 resonances were measured on single scan as well as multiple scan spectra. Multiple scan spectra were useful because of the improved S/N and also because it was possible to record the CH_2 line and the $^{13}CH_2$ satellite and methyl resonances at different output levels with accurately known ratios, for more accurate measurement of the relative areas by planimetry. The $^{13}CH_2/CH_2$ intensity ratios were consistently 10–15% low and poorly reproducible, possibly because of nonlinear spectrometer response and/or uncertainties in estimating the shape of the wings of the $(CH_2)_n$ line.

The effect of the above errors can be minimized by measuring the relative intensities of the CH_3 and the sum of the two $^{13}CH_2$ satellite resonances. The methyl group concentration is given by the relationship

$$[CH_3]/100[CH_2] = (1.1)(^2/_3)(\text{area } CH_3/\text{area } ^{13}CH_2)$$

where 1.1% is the natural abundance of ^{13}C; the integrals are measured by planimetry. In spite of the uncertainties in estimating line shapes and overlap corrections, the nmr analyses on standard samples are in reasonable agreement with the methyl group concentrations found by infrared analyses (Table I).

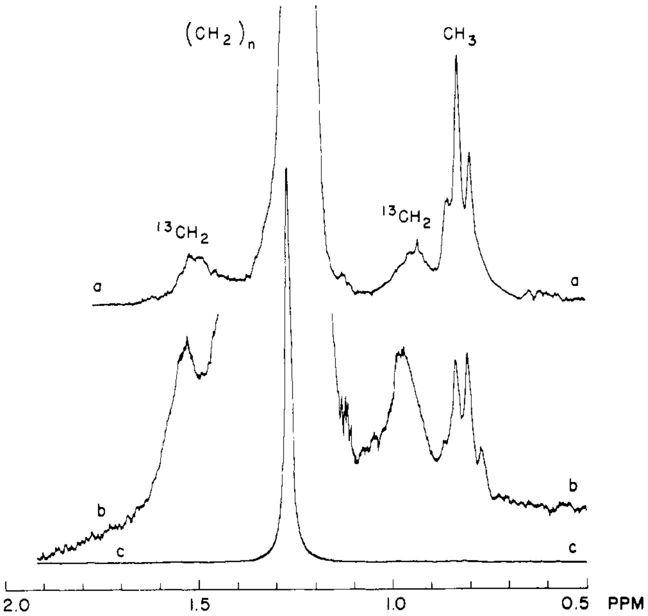

Figure 1. Partial 220-MHz pmr spectra of two polyethylenes, 25% w/v in hexachloro-1,3-butadiene at 145°: (a) ASTM sample no. 8; (b and c) ASTM sample no. 5. The signal amplitude control was reduced 20-fold in recording (c).

In principle, nmr might be able to distinguish between methyl branches and longer alkyl branches because of the doublet *vs.* triplet multiplicity and chemical shift differences of the methyl resonances. However, careful measurements of the chemical shifts in a selection of normal and of branched alkanes indicate that the chemical shift difference between a branch methyl *vs.* a branch ethyl CH_3 would be on the order of 4 Hz, *i.e.*, less than the vicinal coupling constant, J = 6–7 Hz. The spectrum of ASTM sample no. 5 (Figure 1b), which is an ethylene–butene-1 copolymer, was expected to have a triplet methyl resonance, as observed for ASTM no. 8 (Figure 1a). The observed CH_3 pattern in Figure 1b in fact appears to consist of two triplets with a chemical shift difference of *ca.* 6 Hz, indicating the presence of at least two nonequivalent methyl group environments. However, in most of the samples studied, little or no fine structure was resolved.

TABLE I
METHYL GROUPS IN POLYETHYLENE

Sample	CH_3/100 C atoms Nmr	 Ir[a]
ASTM no. 5	0.46 (σ = 0.08)	0.45
ASTM no. 7	1.56	2.1
ASTM no. 8	1.45	1.61

[a] ASTM standard method D2238.

Polypropylene. The 220-MHz spectra of several commercial crystalline polypropylenes and of the residues and hot solvent extracts of some of these have been obtained. Hexachloro-1,3-butadiene (HCBD) and *o*-dichlorobenzene (*o*-DCB) were used as solvents; both give good quality spectra at 150–170°. The chemical shifts differ somewhat in HCDB *vs.* *o*-DCB solutions, but the effect was too small to permit resolution and identification of additional resonances. Thus, most of the studies were made with *o*-DCB solutions.

The most highly isotactic polypropylenes studied were the residues from exhaustive hot solvent extraction. These samples gave sharp, well-resolved spectra (Figure 2), typically indicating ≤1% *r*-dyads.[25]

The spectra of the whole polymers were slightly broader, the resolution typically being comparable to that of the 220-MHz spectrum of isotactic polypropylene published by Heatley, *et al.*[21] The spectra of the commercial polypropylene resins, including samples from different manufacturers, were all essentially identical. The whole polymers had about 2% *r*-dyad placements.

The fractions extracted with hot benzene or *n*-heptane were significantly less stereoregular, and the spectra, *e.g.*, Figure 3, were more noticeably broadened. The observed *r*-dyad concentrations were on the order of 10–20%.

The spectra of the "syndiotactic" polypropylenes (Figure 4) and of so-called "atactic" polypropylenes (Figure 5) were not as well resolved. The systematic increase in line broadening with

---

(25) The notation *r* for racemic (syndiotactic) and *m* for meso (isotactic) dyads of H. L. Frisch, C. L. Mallows, and F. A. Bovey [*J. Chem. Phys.*, **45**, 1505 (1966)] will be used. The method of measuring dyad placements will be discussed later.

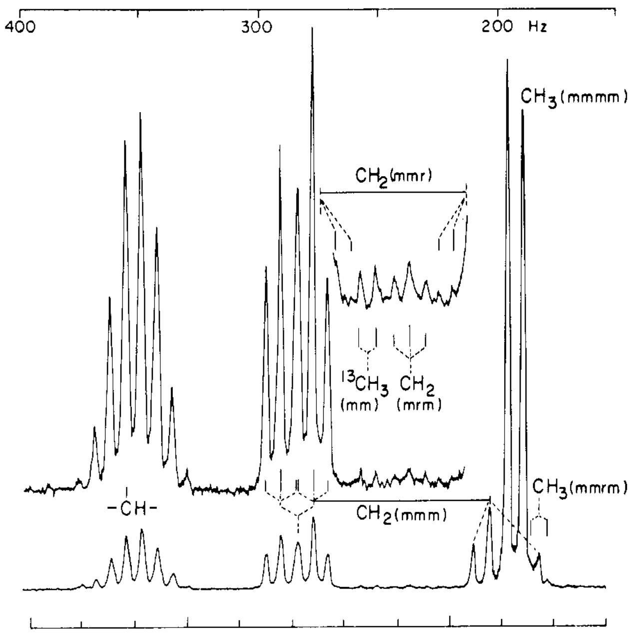

Figure 2. 220-MHz pmr spectrum of benzene-insoluble residue from exhaustively extracted Hercules "Profax" polypropylene. 10% w/v solution in *o*-dichlorobenzene at 145°. Internal reference, hexamethyldisiloxane.

decreasing stereoregularity has been observed in the study of other homopolymers and copolymers, and is due to chemical shift, not viscosity, effects.[26] Comparison of the spectra of these diverse samples confirmed that the methylene and methyl resonances are detectably affected by tetrad and pentad sequence arrangements, respectively.[19–21]

Tetrads. Heatley, *et al.*,[20] made complete tetrad methylene assignments consistent with the 100-MHz[19] and 220-MHz[20] spectra of atactic polymers of *cis*- and *trans*-propylene-*1,2,3,3,3-d*$_5$, and with 220-MHz spectra of isotactic polypropylene.[21] The intensity relations for the isotactic polypropylene indicated about 2% *r*-dyads, occurring predominately as isolated *syndiotactic* placements breaking long *isotactic* sequences.

Flory[27] has reinterpreted these published spectra, challenged the *mrm* assignments, and elaborated earlier arguments[28,29] that isotactic polypropylenes must have considerably more than 2% *r*-dyads. He argues that the *mrm* and *rrr* resonances should not have the nearly equal chemical shifts assigned by Heatley, *et al.*, and assigns the δ^* 1.068 triplet in the isotactic polypropylene spectra to the *rrr* tetrad. To rationalize his estimate of higher *r*-dyad concentrations than are shown by the spectra, Flory argues that the *mrm* resonances must be broadened beyond detectability by long-range conformational effects.

The conflicting assignments and interpretations have been tested by comparison of computer simulations with the observed spectra. Subspectra for the various *n*-ad sequences were calculated by suitable approximations of the "cyclic dimer" model (1,3-dimethylcyclobutane), and combined with intensity weighting, to produce Lorentzian line shape plots of trial spectra; details of the computer methods and results will be published separately.[30] The nmr parameters best fitting all the spectra of this work are summarized in Table II. These parameters, except for differences in reference zero (HMDS, internal, in this work), are in close

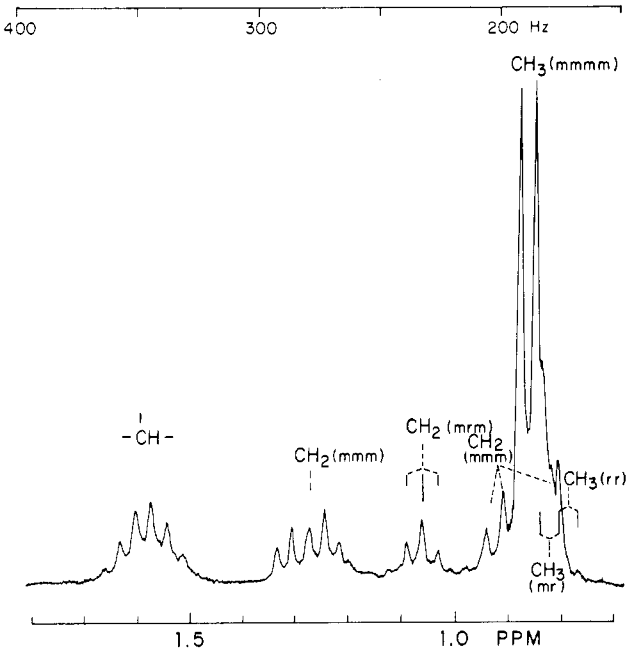

Figure 3. 220-MHz pmr spectrum of benzene-soluble extract of Hercules "Profax" polypropylene. Same conditions as for Figure 2.

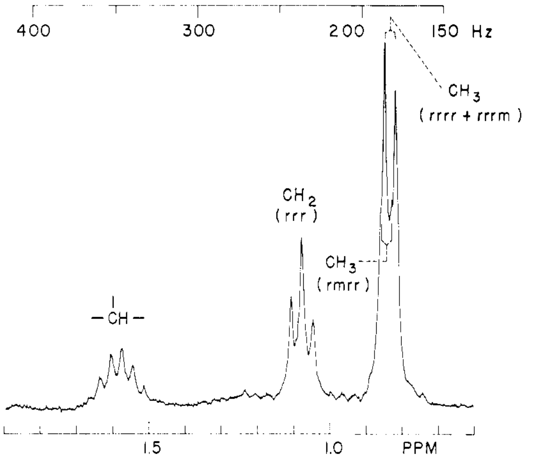

Figure 4. 220-MHz pmr spectrum of highly syndiotactic polypropylene. Same conditions as for Figure 2.

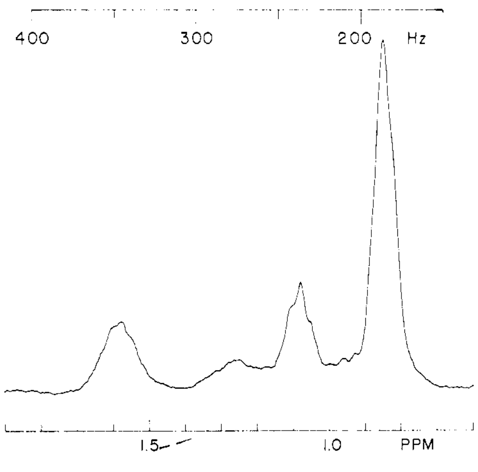

Figure 5. 220-MHz pmr spectrum of Eastman "Epolene" (atactic) polypropylene. 5% w/v solution in *o*-dichlorobenzene at 155°. Internal reference, hexamethyldisiloxane.

---

(26) R. C. Ferguson, *Macromolecules*, **2**, 237 (1969).

(27) P. J. Flory, *ibid.*, **3**, 613 (1970).

(28) P. J. Flory and Y. Fujiwara, *ibid.*, **2**, 315 (1969).

(29) P. J. Flory and J. D. Baldeschwieler, *J. Amer. Chem. Soc.*, **88**, 2873 (1966).

(30) R. C. Ferguson, to be published.

TABLE II
NMR PARAMETERS FOR VARIOUS *n*-AD SEQUENCES IN POLYPROPYLENES

	Chemical shift, ppm				Coupling constant,[d] Hz			
n-ad	CH_3(M)	H_A	$H_B(H_{A'})$	H_X	J_{MX}	J_{AB}	J_{AX}	J_{BX}
Pentads								
mmmm	0.871[a]			1.597[a]	6.56[a]		6.9[a]	6.1[a]
mmrm	0.824[a]				6.56[a]		(6.9)	(6.1)
mrrm	0.788[a]				(6.56)		(8.0)	(5.0)
(*r*)*mr*(*r*)	0.841[b]				(6.56)		(6.9)	(6.1)
(*r*)*rr*(*r*)	0.830[b]			1.589[b]	6.56[b]		(8.0)	(5.0)
Tetrads								
mmm		0.888[a]	1.286[a]			−13.6[a]	6.9[a]	6.1[a]
mmr		0.951[a]	1.242[a]			(−13.6)	(6.9)	(6.1)
rmr		0.974[c]	1.194[c]			(−13.6)	(6.9)	(6.1)
mrm		1.068[a]	1.068[a]			(−13.6)	(8.0)	(5.0)
mrr		1.038[c]	1.117[c]			(−13.6)	(8.0)	(5.0)
rrr		1.075[b]	1.075[b]			(−13.6)	(8.0)	(5.0)

[a] New estimates from the isotactic polypropylene spectra (*o*-DCB solutions, HMDS internal). HCDB solutions gave different shifts: *mmmm*, δ_{CH_3}* 0.833, δ_{CH}* 1.530; *mmrm*, δ_{CH_3}* 0.790; *mrrm*, δ_{CH_3}* 0.744; *mmm*, δ_A* 0.841, δ_B* 1.215; *mmr*, δ_A* 0.903, δ_B* not resolved; *mrm*, δ_A* = $\delta_{A'}$* 1.027. [b] New estimates from the syndiotactic polypropylene spectra. (*r*) in the pentad assignments indicates that the tetrads having *one m* replacing *r* probably contribute to the resolved methyl doublets. [c] From polypropylene-d_5 spectra;[20] reference zero adjusted. [d] Values in parentheses were assumed for the computer runs. The coupling constants J_{AX} = 8.0 and $J_{A'X}$ = 5.0 (=J_{BX} above) for *r*-centered tetrads are from Heatley, *et al.*,[21] and are approximately the values found for deuterated polymers.[17]

agreement with those of Heatley, *et al.*, and the methylene shifts are within experimental error of Flory's estimates except for *mrm*.

Trial spectra were calculated for several limiting models: A, Bernoulli trial (random *r*-dyad placements); B, all *r*-dyads isolated, *i.e.*, ...*mmmrmmm*... (interpretation of Heatley, *et al.*); C, all *r*-dyads in groups, *i.e.*, ...$mmmr_nmmm$..., $n \geq 3$ (Flory assumption); D, same as C, except with additional isolated *r*-dyads producing no detectable *mrm* pattern (both Flory assumptions).

The triad and tetrad probabilities for these models were calculated for several values of P_m, the probability of an *m*-dyad placement, employing well-known relationships.[25] For models A and B, with $P_m \geq 0.8$, the methyl group shifts were assigned $\delta_{mm}^* = 0.871$, $\delta_{mr}^* = 0.824$, and $\delta_{rr}^* = 0.788$. The best match to the spectrum of the most isotactic polypropylene (Figure 2) was obtained with $P_m = 0.99$; $P_m = 0.98$ gave a good fit to the spectra of the whole polymers.[30]

The tetrad probabilities of models A and B are not distinguishably different at low *r*-dyad concentrations. However, model A gave significantly better agreement with the spectrum of the extract (Figure 3); $P_m \approx 0.15$.

No satisfactory matches to Figures 2 and 3 were obtained with model C.[30] For $n \geq 3$ and $P_m > 0.8$ the probabilities are $P_{mm} \gg P_{rr} \geq P_{mr}$ and $P_{mmm} \gg P_{rrr} \geq P_{mrr} = P_{mmr}$. To approximate the observed methyl patterns, *n* must be large, and the triad shifts must be assigned in the unusual order $mm < rr < mr$. The calculated methylene patterns matched poorly, the observed patterns being inconsistent with $P_{mrr} = P_{mmr}$ The methylene patterns of the isotactic samples (*e.g.*, Figure 3 and Figure 1 of ref 21) show a detectable *mmr*, but no *mrr*, pattern. If we assume that *n* is large, neither *mmr* nor *mrr* would be detectable, so this model fails.

For model D, the assumptions most consistent with the observed spectra are that *n* is large and thatt he *mmr* pattern is due to randomly placed *r*-dyads. Thus, the *mmr* intensity provides an independent estimate of these *r*-dyads. The methyl resonances place further constraints on acceptable trial solutions. For the isotactic polymers studied in this work, the concentration of *r*-dyads must be less than 5%; higher concentrations would have been revealed by decreased relative intensity of the *mmm* pattern and a different methyl resonance pattern.

The spectrum of the syndiotactic polymers (Figure 4) was most nearly approximated by a Bernoullian trial, with $P_m = 0.15$; the two strongest methyl doublets were assigned $\delta_{rr}^* = 0.830$ and $\delta_{mr}^* = 0.841$. The general appearance of the methylene regions was reproduced moderately well, but with differences indicating that Bernoullian statistics were not strictly applicable and/or that further refinement of the tetrad parameters would be needed. The changes would be small, however, and not alter the assignments in Table II.

The triplet at δ^* 1.068 in the spectra of isotactic polypropylenes must therefore be due to the *mrm* tetrad. The *r*-dyad concentrations found, using the results for model A, were 1% for the extracted polypropylene (Figure 2), about 2% for the commercial polypropylene resins, and about 15% for the extract (Figure 3).

It is perhaps surprising that the *mrm* and *rrr* shifts are so nearly equal. However, Flory's assumption that *only* the *mrm* tetrad would be subject to significant broadening is no less surprising, and in fact itself leads to inconsistencies in interpretation of the spectra of the isotactic polypropylenes when all of the necessary *n*-ad relationships, and methyl as well as methylene patterns, are analyzed.

The major reason for Flory's claim that the isotactic polypropylenes must have 5–20% *r*-dyad placements was to fit calculated mean-square end-to-end distances with various measured values reported in the literature.[27] It should be noted, however, that in the only documented case in which the nmr and mean-square end-to-end distances were measured on the same sample, the results were consistent with 2% *r*-dyads.[21]

Triads and Pentads. The chemical shifts of the methine and methyl resonance are expected to be sensitive to triad and/or pentad sequences. Because of spin–spin coupling to seven adjacent protons, the methine resonance is approximately an octet, with $J \approx 6.5$ Hz. The tacticity effects are apparently small, and not resolvable because of the high multiplicity. The *mm*- and *rr*-triad methine shifts were estimated from the spectra of highly isotactic and syndiotactic polymers, respectively.

The methyl shifts are more sensitive to tacticity effects, and the failure of a single set of triad shifts to fit the spectra of all samples is best explained by pentad effects. Because of the high stereoregularity of the isotactic polypropylenes, the assignment of the *mmmm* and *mmrm* shifts as in Table II and Figure 2 is unambiguous. The high-field line of a weaker doublet, labeled *rr* in Figure 3, was detected in the spectra of some of the whole polymers and their extracts; the tentative pentad assignment is *mrrm*. The associated *mmmr* and *mmrr* pentad resonances were not resolved. The lower stereoregularity of the "syndiotactic" polymers makes pentad assignments more difficult, but *rrrr*, *rrrm*, and *rmrr* must make major contributions; tentative assignments are indicated in Figure 4 and Table II.

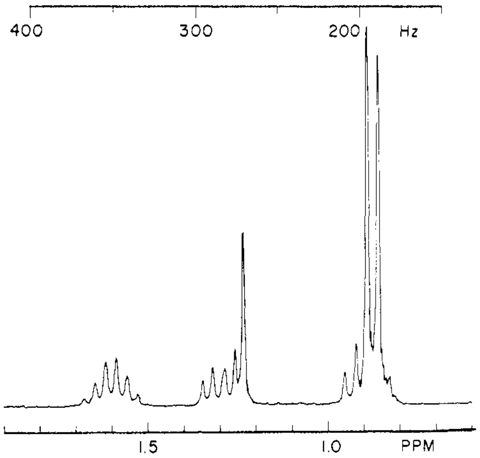

Figure 6. 220-MHz pmr spectrum of 10:90% by weight mixture of polyethylene and isotactic polypropylene. Same conditions as Figure 2.

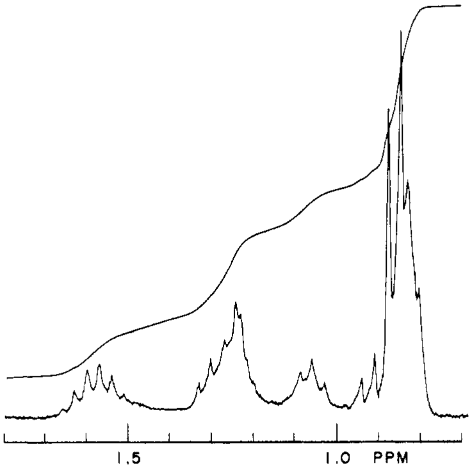

Figure 7. 220-MHz pmr spectrum of an ethylene–propylene copolymer containing about 10 wt % ethylene. Same conditions as for Figure 2.

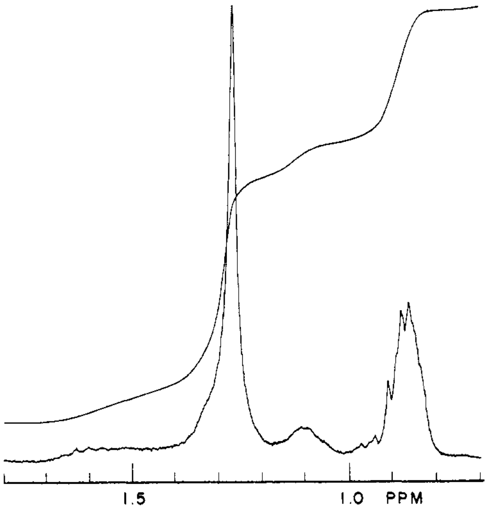

Figure 8. 220-MHz pmr spectrum of an ethylene–propylene copolymer containing about 36 wt % ethylene. Same conditions as for Figure 2.

Ethylene–Propylene Copolymers. The nmr spectra of ethylene–propylene copolymers are strongly dependent on the monomer ratios and are also significantly affected by the tactic placements of propylene dyads and by the sequence distributions of the two monomers.

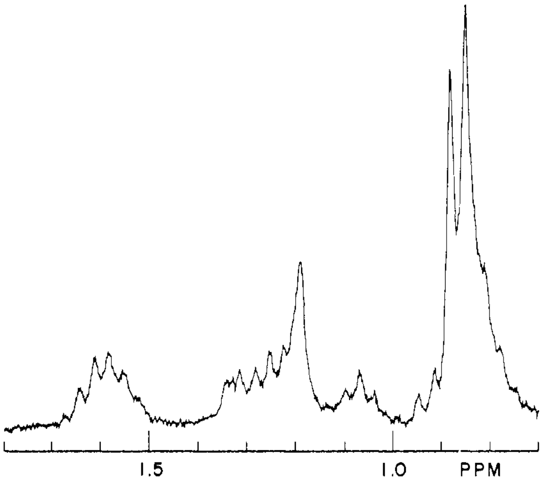

Figure 9. 220-MHz pmr spectrum of the benzene-soluble extract from a commercial crystalline polypropylene resin. Same conditions as for Figure 2.

Figure 6 is the 220-MHz spectrum of a mixture of 10% polyethylene–90% isotactic polypropylene (by weight); this blend can serve as a prototype of a block copolymer. The singlet resonance of the long-chain methylene sequences is clearly evident at δ^* 1.23, and relatively low concentrations of polyethylene (*ca.* 1–2 wt %) or equivalent concentrations of long ethylene blocks are detectable.

In contrast, Figures 7 and 8 are the spectra of ethylene–propylene copolymers, containing about 10 and 36 wt % ethylene, in which the distribution of ethylene appears to be essentially random. These two copolymers were prepared by essentially the same procedure, but with different monomer ratios in the feed. Interestingly, the hot solvent extracts of one of the commercial polypropylene resins produced spectra (Figure 9) having an excess CH_2 intensity corresponding to about 10% ethylene and closely resembling Figure 7.

At low ethylene concentrations, tactic placement effects are still evident in the methyl and methylene regions of the spectra, and qualitative or semiquantitative statements, at least about dyad

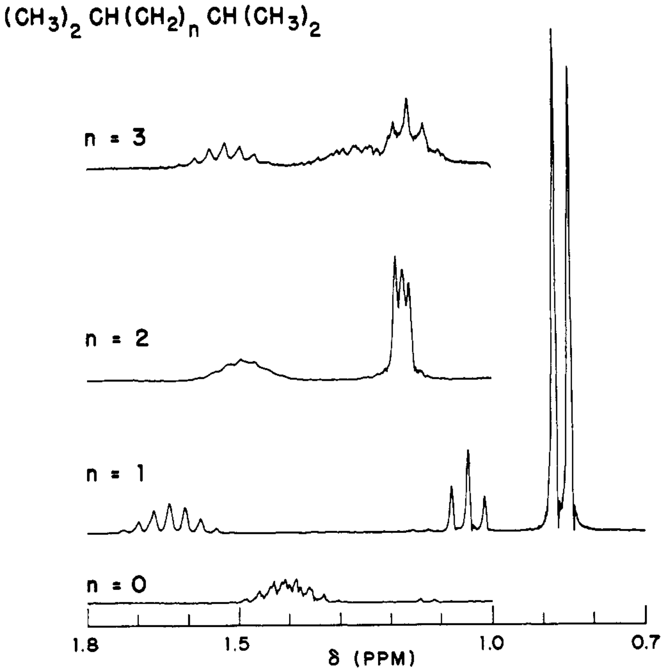

Figure 10. 220-MHz pmr spectra of $(CH_3)_2CH(CH_2)_nCH(CH_3)_2$ as neat liquids at 23°. Internal reference: tetramethylsilane. The methyl group doublets were at approximately the same frequency in all cases and are omitted, except for $n = 1$.

placements, can be made. In Figures 7 and 9, for example, the chemical shift of the strongest doublet corresponds to the *mmmm*-pentad (or *mm*-triad). With increasing ethylene content, the methyl resonances in general shift upfield, overlap badly, and become unassignable. The characteristic methylene dyad or tetrad patterns persist to a higher ethylene content. The *r*-dyad (probably mainly *mrm*-tetrad) methylene triplet and portions of the *m*-dyad (mainly *mmm*-tetrad) ABX_2 methylene pattern are observable in Figures 7 and 9, and the contributions of propylene dyad resonances can be inferred from the intensity distributions in Figure 8.

A study of the spectra of homologous series of normal and branched alkanes, and in particular of the series $(CH_3)_2CH(CH_2)_n$-$CH(CH_3)_2$ (Figure 10), was helpful in understanding the complexity of and in defining some of the limitations on the use of the spectra of the copolymers. In general, the methylene resonance patterns for $X(CH_2)_nX$, where X is methyl or methine, vary considerably in position and multiplicity, for $n = 1$–5, but approach a predominantly singlet character for $n \geq 5$. 2,4-Dimethylpentane ($n = 1$, Figure 10) is apparently a good model for syndiotactic polypropylene. As n increases, the methylene resonances shift downfield and become more complex, especially for $n = 3$. Note that the methine group also shifts somewhat unpredictably.

Quantitative applications of ethylene–propylene copolymer spectra are therefore subject to greater difficulties than realized earlier. Porter[4] has reported the use of an empirically calibrated monomer ratio determination, based on the incremental intensity increase of a singlet in the methylene region of the 60-MHz spectra. This "singlet" however, being due mainly to the longer methylene sequences, underestimates the $(CH_2)_n$ groups for $n = 2$–5, particularly the $n = 3$ (isolated ethylene) sequences. The method must also be somewhat sensitive to the tacticity of propylene dyads.

An *approximate* method of analysis employs the integrals of four regions of the 220-MHz spectra: region A, δ^* 1.82–1.45, assigned to CH groups; region B, 1.45–1.16, assigned to $0.5CH_2$ of propylene *m*-dyads + CH_2 of propylene attached to ethylene + $2CH_2$'s of ethylene; region C, 1.16–1.00, assigned to CH_2 of propylene *r*-dyads; and region D, 1.00–0.77, assigned to $0.5CH_2$ of propylene *m*-dyads + CH_3. The following relationships apply

$$A/k = [P] \qquad (1)$$

$$B/k = xy[P] + 2(1 - x)[P] + 4[E] \qquad (2)$$

$$C/k = 2x(1 - y)[P] \qquad (3)$$

$$D/k = xy[P] + 3[P] \qquad (4)$$

where [E] and [P] are the mole fractions of ethylene and propylene, x is the fraction of propylene units attached head to tail to another propylene, y is the fraction of these units in *m*-dyads, and k is a constant including the solution concentration and spectrometer variables. Solution of these equations, with the constraint $[E] + [P] = 1$, gives the monomer ratio; a quantity (x) related to the distribution of ethylene and propylene runs, and the fraction of propylene dyad placements which are meso (y).

The method has the following limitations: (1) the electronic integrals of the four regions are not clearly separated and the choice of break points is somewhat arbitrary; (2) it is assumed that all propylene units polymerize 1,2 and head to tail, and (3) corrections for ^{13}CH satellite resonances are neglected. Tests of this method with various copolymer samples have given results in approximate agreement with an empirically calibrated infrared method.

The estimates of x and y are more strongly affected by the random and systematic errors than is the monomer ratio estimate. Although the analysis is, in principle, applicable over the entire monomer ratio range, the estimates of x and y become unreliable as the ethylene content is increased above 15 wt %. As the ethylene content increases, the effects of x and y decrease, and as the composition approaches 100% polyethylene, the analysis is simplified by the approximation $x \approx 0$ and solving the pair of simultaneous equations (1) + (2) + (3) and (4).

As suggested earlier, at low ($\leq 10\%$) ethylene content, the position and shape of the $(CH_2)_n$ resonance qualitatively distinguish random from block copolymers; *e.g.*, compare Figures 6 and 7. Interestingly, the prominent $(CH_2)_n$ resonance at δ^* 1.20 in the polypropylene extract, Figure 9, is 0.03–0.05 ppm upfield from the corresponding resonances in the copolymers or the polypropylene–polyethylene blend. The unusual position of this resonance indicates the presence of other structural arrangements, *e.g.*, $(CH_2)_2$ from head-to-head polymerization, $(CH_2)_4$ from isolated 1,3 polymerization, or (more likely) $(CH_2)_n$ groups near branches or chain ends.

Conclusions

The chemical shifts in the 220-MHz pmr spectra of polypropylene and ethylene–propylene copolymers are detectably affected by the structural arrangements of four- and five-monomer sequences. Tactic placement effects dominate the spectra of head-to-tail polypropylenes, and some of the characteristic tetrad methylene and pentad methyl resonance patterns have been resolved and identified. The multiplicity of arrangements arising for four- and five-monomer sequences results in a rapid decrease in spectral definition with decreasing stereoregularity. The chemical shifts of the methyl resonances are affected by pentads to the extent that unambiguous quantitative estimates of triad placements are not possible. The fractions of *r*- and *m*-dyad placements can be determined reliably from the methylene resonance patterns of highly stereoregular polypropylenes, and can be estimated for less stereoregular samples, in spite of overlap of some of the tetrad methylene patterns.

The 220-MHz spectra of ethylene–propylene copolymers are strongly affected by tacticity and monomer sequence distributions. Because of considerable overlap in the spectra, monomer ratio analyses are not absolute, unambiguous, or highly reproducible. At low ethylene content, qualitative or semiquantitative estimates of tactic placements of propylene dyads and "blockiness" of ethylene sequences can be made. In the limit of low propylene content, or in polyethylene, the total methyl group concentration can be estimated.

Acknowledgments. The author thanks Drs. C. D. Lewis, R. D. Lipscomb, W. K. Witsiepe, and T. E. Dye for the polymer samples they contributed. Most of the experimental work was done by Mr. F. W. Barney. Infrared analyses were made by Miss C. J. Hermann.