which are more efficient for peripheral protons than for protected main-chain carbons. This is especially true when conditions of solvent, concentration, or temperature are not carefully chosen to minimize such interactions. The result is relatively shorter proton T_2 values and so relatively broader lines.

A 30-MHz ^{1}H nmr study of rubber-carbon black interaction has been reported recently by Kaufman, Slichter, and Davis.[36] These authors conclude that the carbon black, in addition to severely immobilizing rubber chains in the immediate vicinity, also imposes temperature-independent restrictions on the segmental motions of polymer chains farther away. They further conclude that the result of these restrictions is that the ^{1}H nmr line width is subject to only partial motional narrowing, and that this causes line broadening. This kind of description is essentially the same used to interpret the ^{13}C nmr line widths. There is a distinction to be made, however. The ^{13}C line-broadening effect is not temperature independent. The isolation of the ^{13}C spins allows them to avoid some of the more obscuring, intermolecular dipolar interactions which results in narrow lines and thereby permits the detection of the small but important temperature dependence of the line width. The fact that in both experiments the line widths of the filled system are about five times greater than in the unfilled system suggests a comparable spatial factor over which the motional narrowing is incomplete, with the ^{1}H nmr lines broader in an absolute sense because of the smaller average distance to a nearby spin.

Conclusion

The use of ^{13}C nmr to characterize the amorphous region of a solid polymer above the glass-transition temperature is aided by two factors, both of which are absent in ^{1}H nmr experiments: narrow line widths and the absence of spin diffusion. These two factors permit the measurement of individual T_1 and T_2 values for individual carbons, and the interpretation of the differences in terms of structure. The origin of both factors can be traced to the isolation of the ^{13}C spins.

As applied to the analysis of the polyisoprenes, the ability to measure individual T_1 and T_2 values for individual carbons results in the identification of the relative ease of high-frequency segmental motion of the trans chain due to its extended configuration, as well as the difficulty of low-frequency segmental motion of both cis and trans filled polyisoprenes due to spatial restrictions imposed on the bulk polymer by the filler. Comparisons of individual relaxation times also indicate differences between similar carbons in the same chain, and these can be related to deviations from perfect, isotropic behavior for both high- and low-frequency segmental mitoins.

Acknowledgments. The author thanks Dr. E. O. Stejskal, Central Research Department, Monsanto, for many helpful discussions of the interpretation of pulsed nmr spectra of solids and Dr. Rolf Buchdahl and Dr. L. E. Neilsen, Central Research Department, Monsanto, for discussions concerning relaxation processes in polymers.

Methylene Proton Magnetic Resonance of Some Partially Deuterated Polypropylenes

A. Zambelli,* L. Zetta, C. Sacchi, and C. Wolfsgruber

Istituto di Chimica delle Macromolecole del C.N.R., 20133 Milan, Italy.

Received November 30, 1971

ABSTRACT: Several partially deuterated propylene polymers have been studied by pmr. A partial assignment of the methylene hexad proton resonances is tentatively proposed. The high stereoregularity of the *n*-heptane-insoluble fraction of isotactic polypropylene prepared using the HRA $TiCl_3$–$Al(C_2H_5)_2I$ catalyst system and also the methylene proton tetrad resonance assignment have been confirmed.

The use of recent developments in proton magnetic resonance techniques has given much information about the microstructure of poly(α-olefins).[1–17] Detailed information about microstructure is particularly useful in an understanding of the properties of the polymers and the polymerization stereochemistry. This paper describes the results we have obtained by proton magnetic resonance studies of partially deuterated propylene polymers. In particular, we have focused our attention on the methylene resonances of some polypropylenes having different steric regularities and have tried to correlate them with the hexad composition of the polymers. Our results led us to also reconsider the steric regularity of isotactic polypropylene and the previous tetrad assignment.[1,2]

Results

Tetrad Assignment. A complete tetrad methylene assignment was made as shown in Table I in a previous paper.[2]

---

(1) A. Zambelli, A. Segre, M. Farina, and G. Natta, *Makromol. Chem.*, **110**, 1 (1967).
(2) F. Heatley and A. Zambelli, *Macromolecules*, **2**, 618 (1969).
(3) A. Zambelli and A. L. Segre, *J. Polym. Sci., Part B*, **6**, 473 (1968).
(4) F. C. Stehling, *ibid., Part A*, **2**, 1815 (1964).
(5) J. C. Woodbrey, *ibid., Part B*, **2**, 315 (1964).
(6) Y. Kato and A. Nishioka, *Bull. Chem. Soc. Jap.*, **37**, 1622 (1964).
(7) J. C. Woodbrey and Q. A. Trementozzi, *J. Polym. Sci., Part C*, **No. 8**, 113 (1965).
(8) W. C. Tincher, *Makromol. Chem.*, **85**, 34 (1965).
(9) S. Ohnishi and K. Nukada, *J. Polym. Sci., Part B*, **3**, 179 (1965).
(10) S. Ohnishi and K. Nukada, *ibid., Part B*, **3**, 1001 (1965).
(11) G. Natta, E. Lombardi, A. L. Segre, A. Zambelli, and A. Marinangeli, *Chim. Ind. (Milan)*, **47**, 378 (1965).
(12) J. Boor, Jr., and E. A. Youngman, *J. Polym. Sci., Part A-1*, **4**, 1861 (1966).
(13) E. Lombardi, A. L. Segre, A. Zambelli, A. Marinangeli, and G. Natta, *ibid., Part C*, **No. 16**, 2539 (1967).
(14) A. Zambelli, M. G. Giongo, and G. Natta, *Makromol. Chem.*, **112**, 183 (1968).
(15) S. Satoh, R. Chujo, T. Ozeki, and E. Nagai, *J. Polym. Sci.*, **62**, S101 (1962).
(16) F. Heatley, R. Salovey, and F. A. Bovey, *Macromolecules*, **2**, 619 (1969).
(17) R. C. Ferguson, *ibid.*, **4**, 324 (1971).

TABLE I
CH_2 PROTON TETRAD CHEMICAL SHIFT[a]

Tetrad	H_{syn}	H	H_{anti}	H_1 and H_2
mmm	0.844		1.233	
mmr	0.886		1.184	
rmr	0.915		1.136	
rrr		1.018		
mrr				1.064; 0.977
mrm		near rrr		

[a] See ref 2 and 3.

This result was achieved by 220-MHz pmr analysis of poly(*cis*-1,2,3,3,3-propylene-d_5), poly(*trans*-1,2,3,3,3-propylene-d_5), and poly(propylene-2-d_1).

Flory and coworkers have proposed a different assignment for the mrm proton resonance.[18] They correlated the experimental chemical shifts found by Heatley and Zambelli[2] with the estimated conformational effects and concluded that their correlations could not be reconciled with the very similar chemical shifts that, according to Heatley and Zambelli, occur for the rrr and mrm tetrads. According to Flory, *et al.*,[18,19] the mrm tetrad resonance should nearly coincide with the resonance of the low-field heterosteric protons of the mrr tetrads; this would be proved by the fact that the peak at 1.064 ppm is more intense than the peak at 0.977 in the spectra of atactic poly(*trans*-1,2,3,3,3-propylene-d_5) and of atactic poly(*cis*-1,2,3,3,3-propylene-d_5).[2,3] Actually, were the two peaks attributable exclusively to the heterosteric (H_1 and H_2) protons of mrr tetrads, they should show equal intensity.[2] Finally, Flory and coworkers[19,20] reported that their calculations of the end-to-end distances in isotactic poly(α-olefins) were inconsistent with the steric purity that some authors[1,13,16,17] determined by pmr analysis. Furthermore, on the basis of the long-range stereochemical effect, they calculated that the mrm resonance in these polymers should be spread between 1.06 and 1.14 ppm (*i.e.*, over the range of the mrr and rmr resonances). They suggested that that was the reason that Zambelli, *et al.*,[1] did not detect the mrm tetrads in the spectrum of isotactic poly(*trans*-1,2,3,3,3-propylene-d_5). Such a spread would reduce the sensitivity of pmr measurements concerning the mrm tetrad compared with the other tetrads.[19] Therefore, isotactic polypropylene, according to Flory, *et al.*, should actually contain at least 5–10% r isolated diads (*i.e.*, mrm tetrads).[19] This point of view should be substantiated also by the fact that the tetrad resonance peaks in stereoregular polymers are sharper than in the atactic ones; in this way, long-range configurational and conformational effects are indicated.[19] Flory's arguments are very important in the consideration of the pmr spectra of polymers and must be considered point by point.

Figure 1 shows the 300-MHz pmr spectrum of a polymer [atactic poly(*cis*-1,2,3,3,3-propylene-d_5)] similar to that investigated by Heatley and Zambelli.[2] In addition to the six main peaks attributed to the tetrads, a low-field wing (marked by an asterisk in Figure 1) of the mmm resonance appears. This wing indicates the presence of some extraneous resonance absorptions; these are present exclusively in the spectra of samples containing some head-to-head:tail-to-tail arranged units. The presence of irregularly arranged units has been detected by ir analysis of fully hydrogenated polymers (a band at 13.3 μ characteristic of sequences of two methylenes).[21]

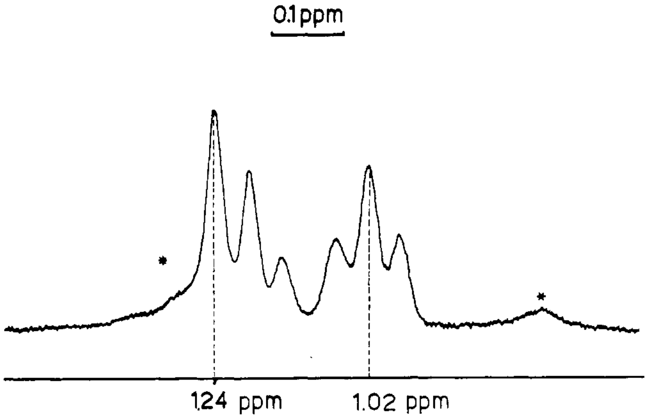
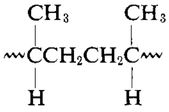


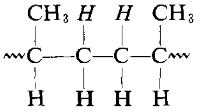
Figure 1. Pmr (300 MHz) spectrum of atactic poly(*cis*-1,2,3,3,3-propylene-d_5) (sample A). The high-field asterisk indicates methyl proton impurities.



$$\begin{array}{cccc} & \mathrm{CH_3} & & \mathrm{CH_3} \\ & | & & | \\ \sim & \mathrm{C} & \mathrm{CH_2CH_2} & \mathrm{C}\sim \\ & | & & | \\ & \mathrm{H} & & \mathrm{H} \end{array}$$

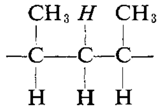
For example, the ir spectra of polypropylene samples prepared in the presence of the same catalysts and under the same conditions as adopted for the preparation of samples A, B, D, and H show the band at 13.3 μ.

The chemical shifts of the different protons of two methylene groups in sequence (*i.e.*, $(CH_2)_2$ protons) should be only slightly different. In particular, the syn and anti protons of the sequence



$$\begin{array}{ccccccc} \mathrm{CH_3} & & H & & H & & \mathrm{CH_3} \\ | & & | & & | & & | \\ \sim\mathrm{C} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{C}\sim \\ | & & | & & | & & | \\ \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} \end{array}$$

(H = syn proton and **H** = anti proton) would reasonably be expected to be only slightly different. However, the absorptions of the low-field wing of the mmm tetrad of Figure 1 are not detected in the spectra of polymers of *trans*-1,2,3,3,3-propylene-d_5 prepared as samples A, D, and H,[22] where the m methylene proton resonances are shifted upfield. This means that the low-field wing absorptions are shifted upfield (to a position obscured by the main peaks) in polymers of *trans*-1,2,3,3,3-propylene-d_5. Such a shift on going from cis to trans monomers is characteristic of the m dyad protons, owing to the mechanism of addition to the double bond.[1,14] In fact, methylene syn and anti protons of m dyads show markedly different chemical shifts



$$\begin{array}{ccccc} \mathrm{CH_3} & & H & & \mathrm{CH_3} \\ | & & | & & | \\ -\mathrm{C} & - & \mathrm{C} & - & \mathrm{C}- \\ | & & | & & | \\ \mathrm{H} & & \mathrm{H} & & \mathrm{H} \end{array}$$

Therefore, it seems reasonable that the observed low-field wing in Figure 1 may be due to the absorptions of anti protons of *m* dyads situated at the central position of tetrads containing irregularly arranged monomers units (*i.e.*, ⌋⌋⌋⌊, ⌊⌋⌋⌋, and similar ones, where ⌋ = $\sim\mathrm{CH_2{-}C(CH_3){-}H}\sim$ ⌊ = $\sim\mathrm{H{-}(CH_3)C{-}CH_2}\sim$).

---

(18) P. J. Flory and Y. Fujiwara, *Macromolecules*, **2**, 315 (1969).
(19) P. J. Flory, *ibid.*, **3**, 613 (1970).
(20) P. J. Flory and J. D. Baldeschwieler, *J. Amer. Chem. Soc.*, **88**, 2873 (1966).
(21) F. Ciampelli and C. Tosi, *Spectrochim. Acta, Part A*, **24**, 2157 (1968).
(22) Unpublished data from our laboratory.

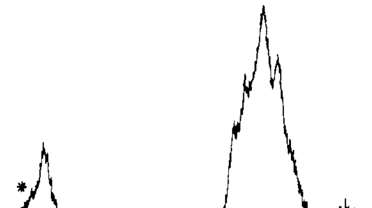
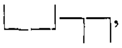


Figure 2. D-decoupled 90-MHz pmr spectrum of atactic poly(propylene-2-d_1) (sample B). The CH_2 resonances are shifted downfield by isotopic effect.

By comparing the spectrum of sample A (Figure 1) with that of poly(*trans*-1,2,3,3,3-propylene-d_5) prepared in the presence of the same catalyst and under the same synthesis conditions, common peaks have not been distinctly detected except for those attributable to protons of r-centered tetrads.[22] Therefore, the resonance of $(CH_2)_2$ protons, which are undoubtedly present in the samples under examination (as revealed by ir analysis of analogous nondueterated samples), should be obscured by the peaks of the r-centered tetrads. Thus, the difference detected by Flory between the intensities of the peaks at 1.077 and 0.990 ppm, partially attributed to heterosteric protons of mrr tetrads, might not be due at all to mrm tetrads, as suggested, but to $(CH_2)_2$ protons or to the presence of r-centered tetrads containing irregularly arranged units (*i.e.*, , , etc.).

That this hypothesis is correct seems indicated by the fact that if the tetrad composition of the polymer shown in Figure 1 is calculated according to Flory's assignment, neglecting the low-field wing of mmm tetrads, the results disagree with the intensity sum rule.[23] In fact, assuming a Lorentzian line shape and neglecting the low-field wing of the mmm tetrads, the relative areas of the peaks obtained by using a Dupont 310 curve resolver are: $A_1 = 0.30$, $A_2 = 0.18$, $A_3 = 0.08$, $A_4 = 0.14$, $A_5 = 0.20$, and $A_6 = 0.10$, where A_1, A_2, etc., are normalized peak areas of the spectrum of Figure 1, numbered from left to right.

According to Flory's assignment, the tetrad mole fractions of the polymer are: (mrm) $= A_4 - A_6 = 0.04$, (rrr) $= A_5 = 0.20$; whereas (mmm) $= A_1 = 0.30$, (mmr) $= A_2 = 0.18$, (rmr) $= A_3 = 0.08$, and (mrr) $= 2A_6 = 0.20$ both according to Flory[18] and to Heatley and Zambelli.[2] In the opinion of the latter authors, rrr tetrad resonances and mrm tetrad resonances have nearly coincident chemical shifts; therefore, they cannot be measured directly, but are obtained from the relationship

$$(\text{rrr}) + (\text{mrm}) = A_5$$

and the intensity sum rule

$$2(\text{mrm}) + (\text{mrr}) = 2(\text{rmr}) + (\text{mmr})$$

In such a case

$$(\text{mrm}) = (\text{rmr}) + [(\text{mmr}) - (\text{mrr})]/2 = 0.07$$

$$(\text{rrr}) = A_5 - (\text{mrm}) = 0.13$$

In that case, the inequality between A_4 and A_6 should be due to the $(CH_2)_2$ protons and/or to the protons of r-centered tetrads containing irregularly arranged units; as suggested in this paper, the mole fraction of such protons should be

$$A_4 - A_6 = 0.04$$

By taking the molar fractions of tetrads determined by Flory's assignment, one obtains

$$2(\text{rmr}) + (\text{mmr}) - 2(\text{mrm}) - (\text{mrr}) = 0.06$$

instead of zero, as required by the intensity sum rule. However, this might be only a deceptive discrepancy. Actually, one might admit that A_6 (and not A_4) comprises, in addition to half of the protons of mrr tetrads, also the $(CH_2)_2$ protons and the protons of the r-centered tetrads containing irregularly arranged units. As a matter of fact, on the basis of the data described so far, the previous hypothesis that the $(CH_2)_2$ protons are obscured by the peak of area A_4 is arbitrary.

However, the alternative hypothesis that A_6 instead of A_4 is partially due both to the $(CH_2)_2$ protons and to the r-centered tetrads containing irregularly arranged units is contradicted by the spectrum of atactic poly(propylene-2-d_1) reported in Figure 2. This polymer contains irregularly arranged monomer units as did sample A. This is shown by ir analysis and is also suggested by the presence of a broad highfield methyl resonance peak shown at *ca.* 0.75 ppm in Figure 2. Owing to H_1–H_2 geminal coupling (H_1 and H_2 are heterosteric protons of mrr tetrads, necessarily present in equal amounts) the H_1 and H_2 resonances are split in this spectrum, and so one observes the presence of an extraneous absorption (marked by an asterisk in Figure 2) as a low-field wing of the r-centered tetrad peak. Such a low-field wing explains why the A_4 and A_6 peaks of Figure 1 have different intensities, but it cannot reconcile the discrepancy of the intensity sum rule with the tetrad composition determined by Flory's assignment. In fact, if the absorptions of the methylene protons of the $(CH_2)_2$ sequences and of r-centered tetrads containing irregularly arranged units were obscured by the A_6 peak in the spectrum of Figure 1, a high-field wing of the peak due to the r dyads of Figure 2 should be also observed. (Compared with the spectrum of Figure 1, chemical shifts of methylene protons are shifted downfield by an isotopic effect.)

On the other hand, Flory[18,19] also suggested that the chemical shift of r dyads isolated between isotactic blocks should be particularly sensitive to long-range steric effects on local conformation. Hence, dyads $(\text{m})_x\text{r}(\text{m})_y$ (where x and y = 1, 2, 3, 4, . . . , n) should be spread within the chemical shift range of rmr tetrads and the chemical shift of the low-field proton of mrr tetrads (*i.e.*, between 1.077 and 1.144 ppm at the most). Were this hypothesis correct, the tetrad chemical shift assignment by Flory might once again be reconciled with the intensity sum rule. In fact, in that case, quantitative tetrad determination would be practically impossible. Actually, the absorptions respectively of mrm and rmr and the low-field one of mrr tetrads could not be separated by any means.

In principle, we certainly must agree that the chemical shift of an r dyad in a $(\text{m})_x\text{r}(\text{m})_y$ sequence depends on the values of x and y and, to be absolutely rigorous, the stereochemical configuration of the entire chain must also be stipulated.[19] However, it must be admitted that the incremental chemical shift range difference for such r dyads decreases with increasing x and y until the resonances coalesce for values of x and y greater than a given number n. Flory estimates n as being very high, on the basis of the conformational analysis of $(\text{m})_x\text{r}(\text{m})_y$ segments with x and y of variable

---

(23) H. L. Frisch, C. L. Mallows, and F. A. Bovey, *J. Chem. Phys.*, 45, 1505 (1966).

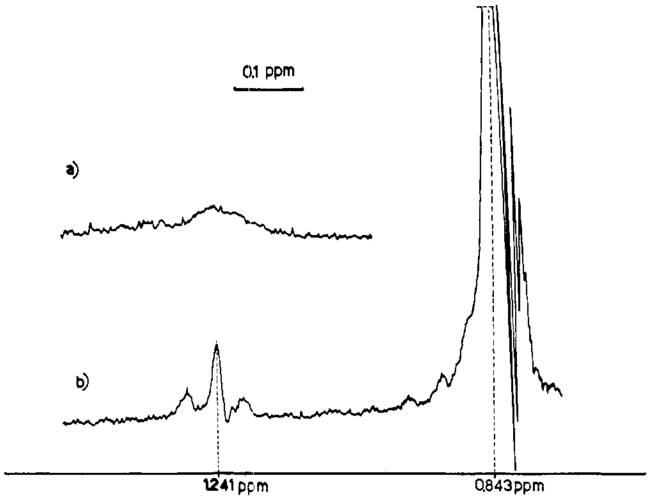


Figure 3. Pmr (90 MHz) spectrum of isotactic poly(*trans*-1,2,3,3,3-propylene-d_5) (sample C): (a) undecoupled, (b) D decoupled.

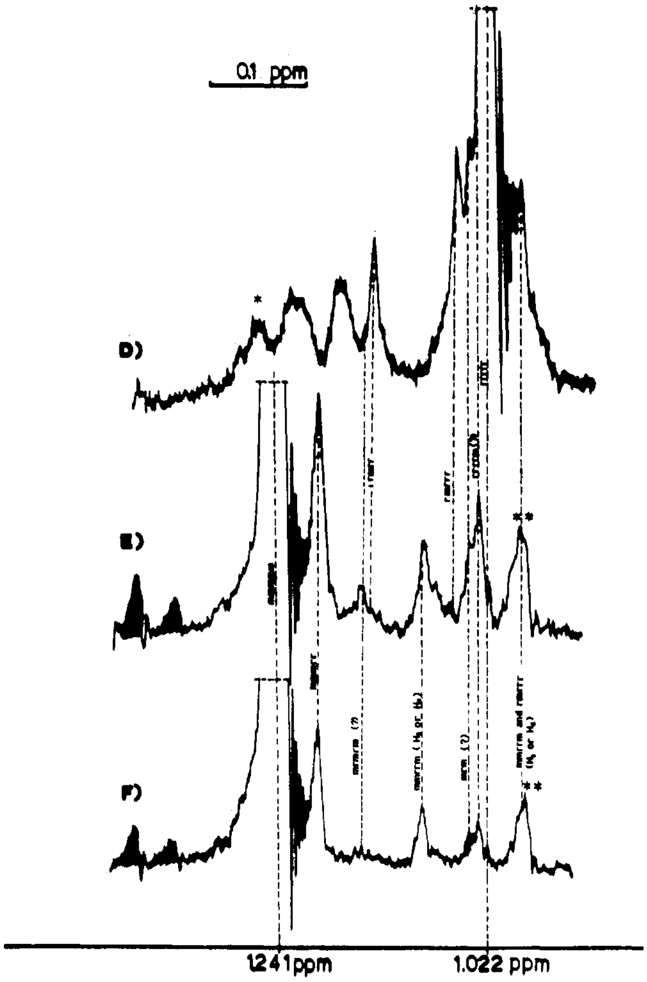


Figure 4. D-decoupled 90-MHz pmr spectra of poly(*cis*-1,2,3,3,3-propylene-d_5): (D) primarily syndiotactic, (E) primarily isotactic, (F) more isotactic than E (shaded peaks are due to solvent impurities). The double asterisk indicates peak overlapped with solvent impurities.

length and on admitting the validity of a particular criterion of quantitative correlation among chemical shift, chain interactions, and conformation. The validity of Flory's analysis and of the ensuing results could be experimentally tested by the determination of the end-to-end distance of isotactic polypropylene.[18,20] The experimental data of Flory might be explained only by admitting that this polymer contains at least 5–10% syndiotactic dyads isolated among isotactic blocks (mmmrmm. . .mrmm. . .).[20] On the other hand, Zambelli, *et al.*,[1] did not detect dyads of this type by nmr in the deuterated samples investigated. According to Flory, the samples studied by Zambelli, *et al.*, also must have contained 5–10% r dyads isolated among isotactic blocks ($m_x rm_y$) and these authors failed to detect them because of the decrease in the sensitivity in the nmr analysis due to the spreading of the chemical shifts. In order to check this point, we have reexamined the same sample of isotactic poly(*trans*-1,2,3,3,3-propylene-d_5), already studied five years ago by Zambelli, *et al.* (sample C, Figure 3).[1] The spectrum of this polymer shows no extraneous absorption in the chemical shift range indicated by Flory for the $(m)_x r(m)_y$ syndiotactic dyads, except those due to the *m anti* proton isotopic impurities. Sixty deuterium-decoupled spectra were time averaged in order to raise sensitivity sufficiently. In the range of chemical shifts indicated by Flory, the following resonances were noticed (Figure 3): (1) a sharp peak at 1.241 ppm due to the impurities of *cis*-1,2,3,3,3-propylene-d_5 in the *trans*-1,2,3,3,3-propylene-d_5 used[1] and (2) two peaks of width at half-height 1.7 Hz at 1.120 and 1.273 ppm, and a perfectly flat base line.

That the two peaks at 1.120 and 1.273 ppm are not solvent impurities was shown by their broadening when the spectrum was repeated under the same conditions but without deuterium decoupling. It is possible that they were due to deterioration (partial oxidation) of the 5-year-old sample. In any case, broad peaks were absent and the sum of the areas of the two observed signals represented less than 2% of the area of the main peak.

In addition to this negative evidence that entirely contrasts with what was proposed by Flory, there is equally valid positive evidence. In Figures 4 and 5 are shown the pmr spectra of samples of prevailingly isotactic poly(*cis*-1,2,3,3,3-propylene-d_5) with variable steric regularity (samples E, F, and G). As shown by the comparison of the spectra of the different samples, the peaks of mmm, mmr, rmr, mrr, and rrr tetrads become sharper with increasing mole fraction of mmm tetrads. For the polymer with the highest steric regularity (sample F of Figure 4), the widths at half-height of the peaks of mmr and mrr tetrads are no broader than that of mmm tetrads. Under such conditions it can be hardly admitted that mrm tetrads are spread to the extent foreseen by Flory.[19] In any case, owing to the sharpness of the peaks of unambiguous assignment, the relative areas may be accurately measured without considerable error, even admitting a spreading of the resonances of $(m)_x r(m)_y$ groups. The amount of mrm tetrads may be measured indirectly by using the intensity sum rule. For example, sample F of Figure 4 shows the following steric irregularity content: (mmr) = 0.054, (rmr) = 0.022, (mrr) = 0.064, and (mrm) = $^1/_2$[(mmr) + 2(rmr) − (mrr)] = 0.017. Hence, not even the sample considered can contain a mole fraction of 0.05–0.1 mrm tetrads (which is the lowest amount that Flory believes necessarily present) and at the same time satisfy the intensity sum rule. Thus, the conclusion must be drawn that any attempt at a rigorous correlation between spatial distribution of the macromolecule segments and the chemical shifts is, at best, premature.

Even in the case of isotactic polypropylene, such a relatively simple problem as the calculation of the chemical shifts of syn and anti protons has not been solved so far, even though the

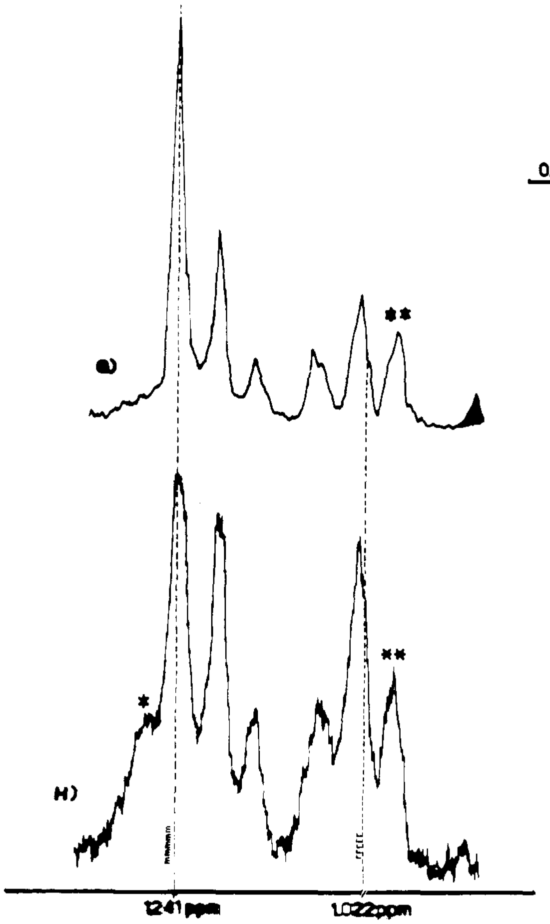


Figure 5. D-decoupled 90-MHz pmr spectra of samples G and H. The double asterisk indicates peak overlapped with solvent impurities.

shifts of such protons differ more widely than those of tetrad protons.[24]

It also seems hazardous to attempt to evaluate the steric purity of vinyl polymers by rheological and thermoelastic methods. Even more questionable is any generalization based on the measurements done by Flory on samples of unknown steric regularity. However, since we have not examined by nmr the samples used by Flory, we cannot comment on the number of isolated r dyads they contained.

Also, as has already been observed by other authors,[16] the arguments which led Flory to state that the samples studied by Zambelli, *et al.*,[1] contained 5–10% isolated r dyads are unknown. In fact their rheological properties have never been investigated. Furthermore, it seems evident that the long-range stereochemical influence on the chemical shift has been much overestimated by Flory, *et al.*[18,19] Perhaps a more refined calculation might bring about a closer agreement between the information obtained by solution-property and thermoelastic measurement and that obtained by pmr studies.

Hexads. As observed by Flory and coworkers, the CHD tetrad reasonances of the published spectra[1-3] are sharper in stereoregular polymers than in the stereoirregular ones. Obviously, we must agree that this is due to a steric effect operating over a distance greater than that of the tetrads. We also agree that for the "utmost rigor, the stereochemical configuration of the entire chain must be stipulated."[19] However, at a certain distance, this rigor becomes redundant.

Table II
Tentatively Proposed CH_2 Proton Hexad Resonances

		Chemical shift[a]		
Tetrads	Hexads	H_{anti}	H	H_1 and H_2
mmm	mmmmm	1.241		
	mmmmr rmmmr	1.233		
mmr	mmmrr	1.198		
	mmmrm rmmrm rmmrr	1.182		
rmr	rrmrr	1.144		
	mrmrm rrmrm	1.137, 1.152		
mrr	mmrrm			0.990, 1.090
	rmrrr			0.990, 1.060
	mmrrr rmrrm			1.077
mrm	mmrmm rmrmm rmrmr		1.034,[b] 1.042[b] 1.04–1.05	
rrr	rrrrr		1.022	
	mrrrm rrrrm		1.034,[b] 1.042[b]	

[a] In parts per million referred to HMDS as internal standard. [b] Uncertain assignment between mrm and rrr tetrads.

We have compared the D-decoupled 90-MHz spectra of several poly(*cis*-1,2,3,3,3-propylenes-d_5) having different microstructures (Figures 4 and 5). The peaks of the tetrads are more or less partially resolved into resonances that individually seem sharp, like the main resonances (...mmm... or ...rrr...) of stereoregular polymers. The total number of resonance peaks in the spectra is such that they may be correlated with the hexad composition of the polymers.

Therefore, it seems reasonable to postulate that the stereochemical effects of sequences higher than hexads are negligible. According to this hypothesis, a partial hexad assignment may be attempted by comparison of the spectra, and by assuming that the Heatley–Zambelli tetrad assignment is correct.

The resonances of mmr and mrr ($H_1 + H_2$) tetrads of the isotactic sample F are *ca.* 1-Hz wide and have equal intensity. The intensity ratio and line sharpness may be explained by the presence in the sample of pairs of r dyads between isotactic blocks

...mmmrrmmm...

The sharpness of the peaks is due to the fact that, as far as the chemical shifts are concerned, such dyads and the terminal m dyads of the isotactic blocks are all in the same long-range steric environment. Consequently, the peaks at 1.198 ppm should be due to the mmmrr hexads and those at 1.090 and at 0.990 ppm to the heterosteric H_1 and H_2 protons of the mmrrm hexads (see Table II).

In the syndiotactic sample D, the peaks of the rmr and mrr tetrads appear sharp. In this case, the sharpness and intensity ratio may be easily explained by considering the typical steric defects of the syndiotactic polymers to be isolated isotactic dyads (...rrrmrr...).[25] Therefore, the resonance at 1.144 ppm should be due to the anti protons of the rrmrr hexad and resonances at 1.060 and at 0.990 ppm to the heterosteric protons of the rrrmr hexad. It is noteworthy

---

(24) F. A. Bovey in "NMR-Basic Principles and Progress," Vol. 4, Springer Verlag, Heidelberg, 1971, p 1.

(25) A. Zambelli, G. Gatti, C. Sacchi, W. O. Crain, Jr., and J. D. Roberts, *Macromolecules*, 4, 475 (1971); A. Zambelli in ref 24, p 102.

that the higher field protons of mrrmm and rrrmr hexads have practically coincident chemical shifts. The other broader peaks indicate the presence of the anti protons of unresolved hexads due to atactic blocks along with the predominantly syndiotactic chains.

The spectrum of sample G of Figure 5, a disordered polymer in which m dyads prevail over r dyads, shows a more or less evident splitting of all tetrad peaks into hexad peaks showing on average the usual sharpness, like the mmmmm and rrrrr hexads in the stereoregular polymers.

The lower field peak of the mrr tetrads is split into three components for the heterosteric H_1 or H_2 proton of the mmrrm hexads at 1.090 ppm, and for the rmrrr hexads at 1.060 ppm; the third type of mrr-centered hexads (mmrrr or rmrrm or both) appear at 1.077 ppm. Similarly, the peak at 1.152 ppm of sample G might be assigned to the anti protons of the mrmrm hexads because it is present also in the spectrum of sample E of Figure 4; actually, in this prevailingly isotactic sample, rmr tetrads should most likely occur between isotactic dyads. The third peak at 1.137 ppm of sample G could arise from rrmrm.

Owing to the proximity of the rrr and mrm tetrad resonances, the possible hexads in this region of the spectrum are

rrrrr	mmrmm
mrrrr	mmrmr
mrrrm	rmrmr

Apart from the obvious assignment of the rrrrr hexads at 1.022 ppm by comparison with sample D, no further hexad assignment seems possible in this region for the peaks at 1.034 and 1.042 ppm. A similar splitting appears in the spectra of more disordered samples of Figure 5.

The peaks of the mmm tetrads of sample G show a partial splitting probably due to the mmmmm, mmmmr, and rmmmr hexads. The rmmmr and rmmmm hexad anti proton resonances seem to occur at slightly higher field compared to mmmmm protons. This seems to be shown also by an examination of the position of the broad peak of mmm tetrads in the spectrum of sample D (syndiotactic) of Figure 4.

In the spectra of samples D and H, other methylene proton resonances appear at low field. Such resonances, pointed out in the previous section, are typical of polymers containing chemical inversion (*i.e.*, head-to-head or tail-to-tail arranged monomer units) and their assignment has been already discussed.

Conclusions

Methylene proton magnetic resonance allows the partial description of the steric structure of propylene polymers as being successions of hexads having distinguishable chemical shifts. The line widths of hexad resonance peaks are of the same order of magnitude as the main resonances of the sterically pure (isotactic and syndiotactic) polymers. Therefore, a significant effect on the CH_2 proton chemical shifts of sequences longer than hexads can be neglected. The broadening proposed by Flory[18] of the mrm tetrads when isolated between isotactic blocks seems to be excluded.

Experimental Section

Deuterated monomers were prepared as described in previous papers.[1,13] Samples A, E, F, and G were obtained by fractional crystallization from a rough polymer prepared using the VCl_3–$Al(C_2H_5)_2Cl$ catalyst system in *n*-heptane at 15°. Samples B and H were prepared using the VCl_4–$Al(C_2H_5)_3$ catalyst system in *n*-heptane at −78°. Sample C was obtained after extraction by boiling *n*-heptane of a whole polymer prepared using the $TiCl_3HRA$–$Al(C_2H_5)_2I$ catalyst system in *n*-heptane at 15°. Sample D was prepared using the VCl_4–$Al(C_2H_5)_2Cl$–anisole catalyst system in *n*-heptane at −78°. More detailed descriptions of the different polymerization types have been reported in previous papers.[1,13,18]

Pmr spectra were recorded with a Bruker HFX-90 spectrometer under deuterium-decoupling conditions at a sweep width of 1 and 2 Hz/cm, and were time averaged using a Fabri-Tek 1074 a 4096-channel computer. The sweep rate was 40 μsec in every case. Spectra were recorded at 130°, and the temperature was checked with the ethylene glycol calibration sample.

The polymers were dissolved in *o*-dichlorobenzene containing hexamethyldisiloxane (5% by volume) as internal reference. Concentration of the polymers ranged from 15 to 30 mg/ml of solvent. The spectrum of atactic poly(*cis*-1,2,3,3,3-propylene-d_5) was recorded with a Varian Associates HR-300 nmr spectrometer at 150° (without decoupling).

Acknowledgment. We wish to thank Dr. L. F. Johnson for taking the nmr spectrum of poly(*cis*-1,2,3,3,3-propylene-d_5).