putation scheme given in the Appendix and in Table III, it may be seen that the structural information contained in such polymers is almost precisely complementary to that contained in hemiisotactic polymers. Only three heptads are in fact common to the two polymers: rrmmrr, rmmrrm, and mmrrmm. The remaining 10 are mainly grouped amid the sequences centered on the mr triad, where the information content of the hemiisotactic polymer is very limited. The combined use of the two hemitactic polymers would make it possible to achieve the assignment of 24 out of the 36 heptad signals and of 14 of the 20 hexads.

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## Appendix

The probabilities of triads that center on a disordered carbon (see Figure 4) are

$$\text{mm} = \alpha\beta = M$$

$$\text{rr} = (1 - \alpha)\beta = R$$

$$\text{mr} = \alpha'(1 - \beta) = H$$

$$\text{rm} = (1 - \alpha')(1 - \beta) = K$$

The probability of each dyad placed in a defined position inside the above triads is the sum of the probability of existence of the related triads:

$$(\text{m/r})\text{m} = M + K = A$$

$$\text{m}(\text{m/r}) = M + H = B$$

$$(\text{m/r})\text{r} = R + H = C$$

$$\text{r}(\text{m/r}) = R + K = D$$

where (m/r) means that the second dyad has an undetermined structure.

The probabilities of triads that center on an ordered carbon is the product of the probabilities of the two related dyads. The probability of a general triad is half of the sum of the probabilities of both series of triads (centered on ordered or disordered carbons). For the non-symmetric triad mr, both directions of observation of the chain are to be considered.

The probability of a longer sequence is half of the sum of products of the probabilities of the single blocks, taking into account all the possible ways of formation of that sequence.

This treatment resembles in many respects those proposed by Frisch, Mallows, and Bovey[4] and by Chujo, Kamei, and Nishioka[5] for polymers derived from CHA = CHB monomers, but differs in the choice of the independent probability parameters, which are related to a different way of sequence generation.

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# Resolution of the Carbon-13 Nuclear Magnetic Resonance Spectrum of Hemiisotactic Polypropylene at the Decad and Undecad Level

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ABSTRACT: Hemiisotactic polypropylene was obtained by a two-stage process from *trans*-2-methylpentadiene and its structure determined from its 50.3-MHz $^{13}$C NMR spectrum. The particular distribution of the steric sequences and the choice of suitable experimental conditions made it possible to obtain a spectrum with an unprecedented degree of resolution. Out of 17 well-resolved peaks on the methyl spectrum, 5 are attributed to single nonads and 5 to the following undecads: mmmmmmmmrr, rrmmmmmmrr, rrmmrrmmrr, mmmmrrmmrr, and mmmmrrmmmm. Two signals in the methylene spectrum should be assigned to single decads. The degree of hemiisotacticity of polypropylene ($\alpha = 0.5$, $\beta = 0.96$) and the degree of isotacticity of the starting poly(2-methylpentadiene), obtained by inclusion polymerization in perhydrotriphenylene (96% isotactic dyads), were determined by intensity measurements.

In 1982 we announced the synthesis of a new stereoisomer of polypropylene, for which we proposed the name of hemitactic polypropylene.[1] The distinguishing feature of this polymer is the presence of two different series of tertiary carbon atoms which are constitutionally equivalent and alternate with each other: in the odd series the arrangement of the substituents is precisely defined, while in the even series the arrangement is random. A detailed study of the structure of hemitactic polymers is provided in the article immediately preceding this one,[2] hereafter referred to as part 2, part 1 being ref 1.

In the light of the discussion reported in part 2 we now propose the adoption of a more precise name for the new polymer, so as to specify that an isotactic succession exists between the tertiary carbons of the odd (ordered) series. Henceforth, the term *hemiisotactic* will be used for this polymer instead of the more general term hemitactic. Hemiisotactic polypropylene (hit-PP) differs from the other partially ordered polypropylenes as yet known. These have a low degree of stereoregularity, while in the hemiisotactic polypropylene we find the ordered superimposition of an almost perfect stereoregularity on a com-

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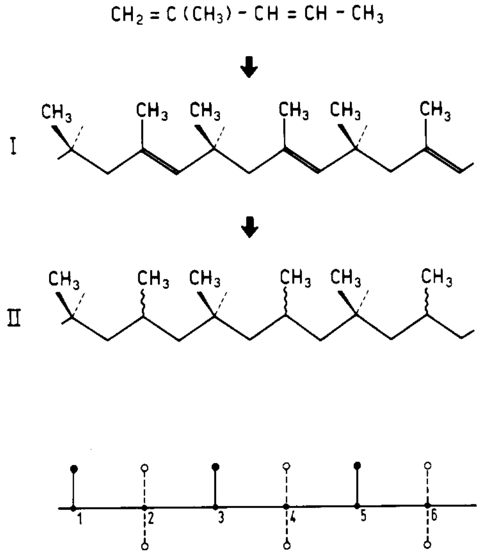
**Scheme I**



pletely random arrangement. This leads to a quite novel distribution of stereosequences which is almost eloquently expressed in the $^{13}$C NMR spectrum. As we shall see below, hemiisotactic polypropylene is an excellent means of investigation, permitting an unprecedented depth in the interpretation of the spectrum of polypropylene.

## Experimental Section

Poly(1,3-dimethyl-*trans*-1-butenylene) (or poly(2-methylpentadiene)) (I) was obtained by inclusion polymerization in perhydrotriphenylene (PHTP) by means of two techniques: direct $\gamma$-irradiation (0.5 Mrad, room temperature) of the inclusion compound between PHTP and *trans*-2-methylpentadiene (Fluka, >98%)[3] or by addition of the monomer to preirradiated PHTP.[4] Polymerization occurred at room temperature. The polymer was obtained free from the matrix by extraction with hot pentane. Yields were 30–70 mg/g, depending on polymerization conditions.

Hydrogenation was carried out on 200-mg samples of polymer I by using *p*-toluenesulfonylhydrazide in mesitylene (50 mL) at 140 °C (three 4-g additions during 40 h) in a way similar to that described in the literature.[5,6] The reaction was considered to be complete when the $^1$H NMR spectrum revealed less than 0.5% unsaturation. After repeated precipitations with methanol, 150 mg of a product (hemiisotactic polypropylene II), soluble in $CHCl_3$, was recovered.

IR spectra were performed on a Nicolet MX-1 FT instrument, DSC measurements with a Mettler TA 2000, and GPC analyses, on a Waters instrument equipped with six Ultrastyragel columns ($10^5$ Å, $10^4$ Å × 2, $10^3$ Å × 2, and 500 Å; 72 000 theoretical plates) in $CH_2Cl_2$ at room temperature; $^1$H NMR analyses were performed with a Varian XL 200 instrument in $CDCl_3$ at room temperature.

$^{13}$C NMR spectra of hit-PP were run on a Varian XL 200 at 50.3 MHz under the following conditions: 25 °C; 2% w/v in $CDCl_3$; 4000-Hz sweep width; 16 000 transients: 2-s acquisition time; 8-s delay time; 90° pulse angle; 0.25 Hz/point. Chemical shifts are expressed as ppm from $Me_4Si$. No processing functions were applied to obtain the spectrum reported in Figures 3–5. Best-fitting iterations were performed on a UNIVAC 1100/80 by a program written in Fortran IV; details will be reported in another paper.[7]

## Synthesis and Structural Determination of Hemiisotactic Polypropylene

The synthesis of hit-PP is outlined in Scheme I. It takes place in two stages:[1] the first involves the formation of an unsaturated polymer, isotactic poly(1,3-dimethyl-*trans*-1-butenylene) (or isotactic 1,4-*trans*-poly(2-methylpentadiene)) (I), in which the configuration of the asymmetric atom is exactly defined; the second stage involves hydrogenation of the double bond under nonisomerizing conditions, with the formation of the second center of stereoisomerism having a random configuration.

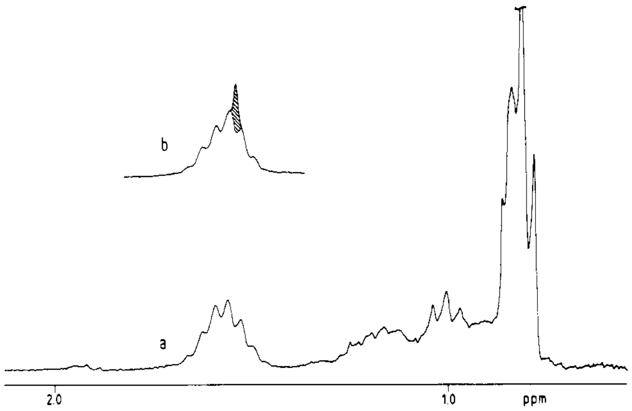


**Figure 1.** (a) $^1$H NMR spectrum of hit-PP; (b) C*H* spectrum of a sample containing same residual unsaturation (shaded area).

The starting polymer I was obtained by radical polymerization of *trans*-2-methylpentadiene included in the crystal lattice of perhydrotriphenylene (PHTP). The degree of constitutional and steric regularity observed in the inclusion polymerization of conjugate dienes in PHTP is known to be very high;[3,4,8-11] this ensures the virtually complete absence of extraneous structures. In the specific case of the unsaturated polymer I, which is crystalline and high-melting, its very limited solubility in all common solvents even at high temperatures makes an accurate structural determination troublesome. To increase its solubility we prepared samples of a copolymer containing small amounts of 4-methylpentadiene by the same technique. In this way we succeeded in obtaining the X-ray fiber spectrum[3] and the $^{13}$C NMR spectrum.[11] Both experiments agree in attributing a 1,4-trans isotactic structure to I. As already pointed out elsewhere[1,11] the obtainment of hit-PP is in itself an independent and direct demonstration of the structure of I.

Conversion from I to II was achieved with diimide generated in situ by thermal decomposition of tosylhydrazide, a method widely employed in noncatalytic hydrogenation of unsaturated polymers.[5,6,12] The reaction runs at a higher temperature than usual (140 °C); initially the reaction proceeds in a heterogeneous phase; the hydrogenated product is soluble under these conditions, and this facilitates completion of the reaction. The best samples do not contain traces of residual unsaturation and of aromatic and sulfur-containing impurities.

Typical $\bar{M}_v$ values, determined by intrinsic viscosity in toluene at 30 °C by using the relationship proposed by Danusso and Moraglio[13] for atactic polypropylene, are approximately 150 000. The $\bar{M}_w/\bar{M}_n$ ratio, determined by GPC and referred to polystyrene, is 1.5.

The IR spectrum corresponds in its main features to that of an atactic polypropylene. The presence of residual unsaturated monomer units is revealed by $^1$H NMR spectroscopy as a small singlet (=C(C$H_3$)—) overlapping the C$H$(CH$_3$) multiplet of hit-PP (Figure 1).

As was mentioned briefly in part 1, the hemiisotactic structure of II is demonstrated by examination of the methyl region in the $^{13}$C NMR spectrum recorded at 140 °C in *o*-dichlorobenzene (Figure 2). Under such conditions the spectrum is known to be sensitive to pentads, which appear well separated from one another, except for mmrm and rmrr, whose chemical shifts almost coincide. A perfectly atactic polypropylene gives rise to nine signals divided into groups of three signals, with a succession of intensities of 1:2:1:2:4:2:1:2:1.

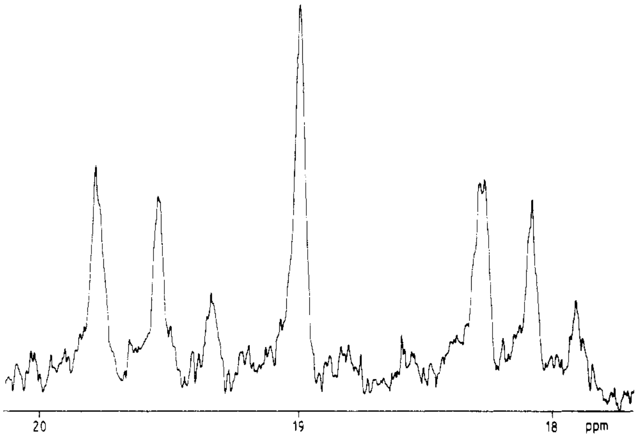


**Figure 2.** High-temperature $^{13}$C NMR methyl spectrum of hit-PP.

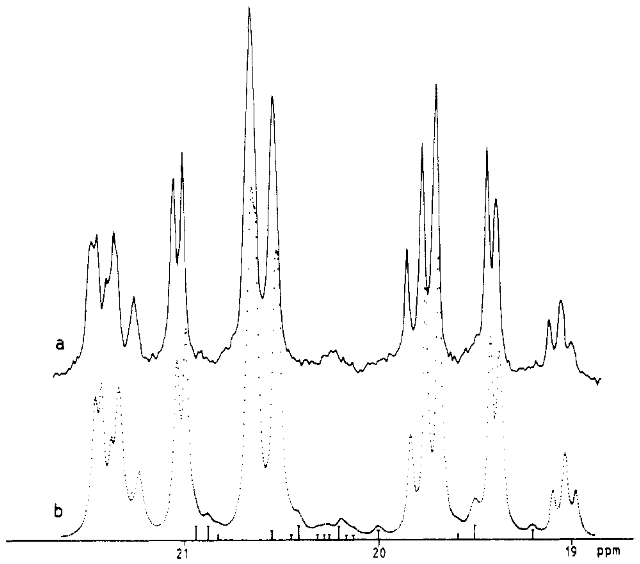


**Figure 3.** High-resolution $^{13}$C NMR methyl spectrum of hit-PP (50.3 MHz, room temperature): (a) experimental; (b) calculated with $\beta = 0.96$ and $\alpha = 0.50$. Vertical lines indicate the chemical shift and intensity of the "forbidden" heptads.

The spectrum of II has only seven signals, which coincide with seven of the preceding ones. The missing signals correspond to pentads rmrr, mmrm, and rmrm, which are prohibited in hemiisotactic polymers. In addition, the relative intensities of the signals are close to calculated values,[1,2] and precisely (starting downfield) 3:2:1:4:0:0:3:2:1.

Further proof can be obtained by examination of the methylene spectrum. The signals present in polymer II lie between 44.2 and 45.5 ppm, while a common atactic polypropylene presents almost double the range. The outer signals, which are absent in our spectrum, are due to hexads mrmrm, mrmrr, rrmrr, and mrrrm downfield, and to rmrmr, mmrmr, and mmrmm upfield, all of which are prohibited in hit-PP.[14,15]

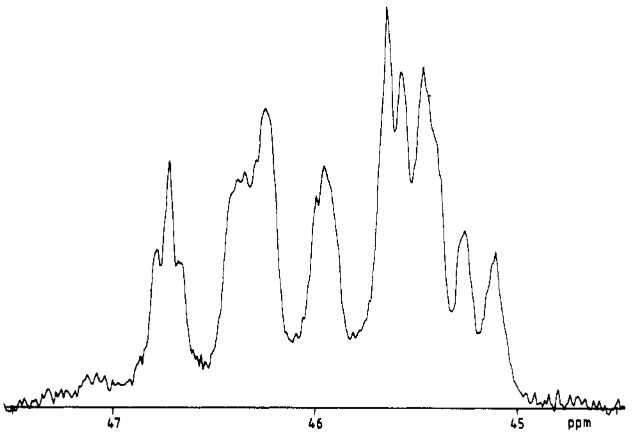


**Figure 4.** High-resolution $^{13}$C NMR methylene spectrum of hit-PP.

**Table I**
**Quantitative Evaluation of the Methyl Region of the $^{13}$C NMR Spectrum of hit-PP at the Pentad Level**

| | | intensity | | | | |
|---|---|---|---|---|---|---|
| | | | calcd for $\alpha = \alpha' = 0.5$ and $\beta =$ | | | |
| peak | pentad | exptl | 1 | 0.97 | 0.96 | 0.95 |
| 1–5 | mmmm | 2.86 | 3 | 2.852 | 2.804 | 2.755 |
| 6, 7 | mmmr | 2.02 | 2 | 2.056 | 2.074 | 2.090 |
| 8, 9 | rmmr, mmrr | 4.72 | 5 | 4.796 | 4.728 | 4.665 |
| | mmrm, rmrr, rmrm | 0.65 | 0 | 0.416 | 0.554 | 0.690 |
| 10–12 | rrrr | 2.87 | 3 | 2.852 | 2.804 | 2.755 |
| 13, 14 | mrrr | 1.97 | 2 | 2.056 | 2.074 | 2.090 |
| 15–17 | mrrm | 0.91 | 1 | 0.972 | 0.962 | 0.955 |

**Table II**
**Assignment of the Methyl Carbon Region of the $^{13}$C NMR Spectrum of hit-PP[a]**

| | chem shift, ppm | | |
|---|---|---|---|
| peak | exptl | calcd | sequence |
| 1 | 21.46 | 21.461 | mmmmmmmm |
| 2 | 21.43 | 21.427 | mmmmmmmmrr |
| 3 | 21.38 | 21.380 | rrmmmmmmrr |
| 4 | 21.34 | 21.337 | mmmmmmrr |
| 5 | 21.24 | 21.234 | rrmmmmrr |
| 6 | 21.04 | 21.044 | mmmmmmrrmm |
| | | 21.034 | mmmmmmrrrr[b] |
| 7 | 20.99 | 20.990 | rrmmmmrrmm[b] |
| | | 20.990 | rrmmmmrrrr |
| 8 | 20.64 | 20.69 | mmrrmmrrmm |
| | | 20.67 | mmrrmmrrrr |
| | | 20.654 | mmmmrrmm |
| | | 20.64 | rrrrmmrrrr |
| | | 20.629 | mmmmrrrr |
| 9 | 20.53 | 20.531 | rrmmrrmm |
| | | 20.511 | rrmmrrrr |
| 10 | 19.83 | 19.833 | mmrrrrmm |
| 11 | 19.75 | 19.755 | mmrrrrrr |
| 12 | 19.68 | 19.684 | rrrrrrrr |
| | | 19.684 | mmrrrrrrrr |
| | | 19.684 | mmrrrrrrmm |
| 13 | 19.42 | 19.419 | rrmmrrrrrr |
| | | 19.419 | rrmmrrrrmm[b] |
| 14 | 19.37 | 19.374 | mmmmrrrrrr[b] |
| | | 19.366 | mmmmrrrrmm |
| 15 | 19.10 | 19.097 | rrmmrrmmrr |
| 16 | 19.04 | 19.033 | mmmmrrmmrr |
| 17 | 18.98 | 18.976 | mmmmrrmmmm |

[a] Chemical shifts of sequences centered on the rmmr pentad are ill-defined. [b] Assignment of sequence is derived from preliminary calculations done by Ferro.[20]

## Analysis of the $^{13}$C NMR Spectrum at Room Temperature

The solubility of hit-PP at room temperature in common NMR solvents prompted us to search for conditions of higher spectral resolution. As a matter of fact, Schilling and Tonelli[15] reported data indicating a widening of the spectral range of both $CH_3$ and $CH_2$ of polypropylene as the temperature decreases. The same trend was observed by Provasoli and Ferro in the spectrum of a low-molecular-weight model compound.[16] The $^{13}$C NMR spectrum of the methyl region of hit-PP, as recorded in a dilute $CDCl_3$ solution (2% w/v), is shown in Figure 3: it presents 17 exceptionally sharp peaks and shows a sensitivity reaching the nonad level or even beyond, bearing in mind

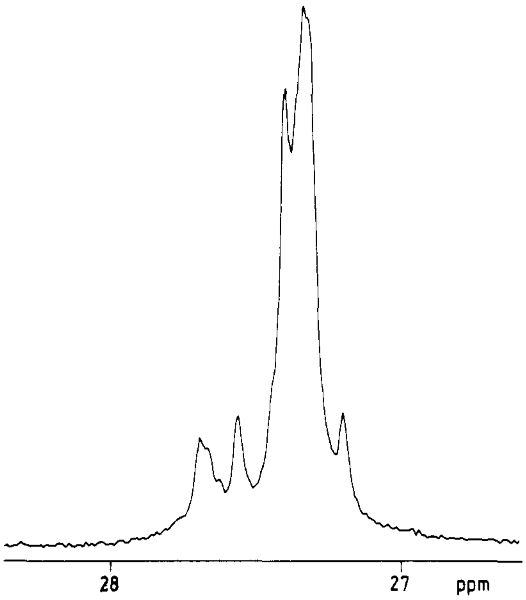


**Figure 5.** High-resolution $^{13}$C NMR methyne spectrum of hit-PP.

that only 14 heptads are expected. In its turn, the methylene spectrum (Figure 4) shows 11 peeks and it is to be interpreted at the octad and decad level. The methyne spectrum (Figure 5), which is notoriously much less detailed, shows five peaks interpretable at the pentad level.

Comparison with the high-temperature spectrum allows us to collect the 17 $CH_3$ signals into groups corresponding to the permitted pentads (Tables I and II). Thus, peaks 1–5 correspond to the sequences centered on the mmmm pentad, 6 and 7 on mmmr, 8 and 9 on both rmmr and mmrr, 10–12 on rrrr, 13 and 14 on rrrm, and 15–17 on mrrm. Besides higher resolution, a major difference with respect to the high-temperature spectrum consists in the overlap of rmmr signals with the mmrr ones that agree with the trend reported by Schilling and Tonelli.[15] Integration of the groups of signals corresponding to the single pentads yields values that practically coincide with the expected ones if we overlook weak peaks in the region between 20.35 and 19.95 ppm, due to chemical and steric impurities. Further mention of this point will be made further on.

Interpretation of the low-temperature spectrum was carried out on the basis of both the selection rules and the distribution of the sequence intensities proper to hemiisotactic polymers (see in particular Tables II and III in part 2) and also of the chemical shift values as computed by Tonelli for heptads at 20 °C.[17]

The most interesting point of the spectrum is the group of signals 15–17. It is assigned to the pentad mrrm: due to the selection rules discussed in part 2, such a pentad only gives rise to one heptad (mmrrmm) that splits into three nonads with relative intensities 1:2:1. This pattern is well verified in the spectrum in which peak 16 is roughly equal to the sum of peaks 15 and 17. The further application of the selection rule shows that each nonad generates only one undecad: hence, this is the level at which sequences are recognized. *Peak 16 is confidently attributed to mmmmrrmmrr.* Intensity criterium is not applicable to the remaining two peaks; but *we assigned undecad rrmmrrmmrr to peak 15 and undecad mmmmrrmmmm to peak 17* on the basis of the observations done by Zambelli and Gatti[18] and by Ferro et al.[19] Both sequences have a notable stereochemical interest: the latter corresponds to the most probably defect in isotactic polypropylene, under the well-confirmed hypothesis of steric control by a chiral catalyst; the former stands for a complex stereoregular sequence, common to hemiisotactic and hemisyndiotactic polymers.

Peak 12 is attributed to heptad rrrrrr, peak 11 to mrrrrr, and peak 10 to mrrrrm. The internal intensity ratio of these signals agrees to a first approximation with that predicted (6:4:2 expressed as 1/64 of total area). More careful examination shows that in reality *peaks 10 and 11 must be attributed to nonads mmrrrrmm and mmrrrrrr,* if we take into account the fact that all the other nonads formally originating from the corresponding heptads are forbidden in hit-PP.

Signals 13 and 14 (area 4:4) must be attributed to heptad rrrrmm: their splitting is due to the differing chemical shifts of the four nonads, or better undecads, that they contain, which all have equal intensity; two of these converge in signal 13 and two in signal 14.

Attribution of peaks 6 and 7 (area 4:4) to the undecads originating from heptad mmmmrr is achieved in just the same way as for peaks 13 and 14. Any other hypothesis, considering contributions deriving from heptad rrmmrr, is to be excluded on an intensity basis—in such a case the sum of the areas of signals 6 and 7 ought to be equal to that of signals 1–5—as also on the basis of the chemical shift values as computed by Tonelli.[17]

In their turn, signals 1–5 (area 3:2:1:4:2) are attributed to the five sequences derived from the isotactic pentad, and precisely *peak 1 is attributed to nonad mmmmmmmm, peak 2 to undecad mmmmmmmmrr, peak 3 to undecad rrmmmmmmrr, peak 4 to nonad mmmmmmrr, and peak 5 to nonad rrmmmmrr.* Comparison between the spectrum of isotactic and syndiotactic sequences shows a better resolution in the former region: peak 12 (syndiotactic heptad) is single and very sharp, whereas at lower field the isotactic heptad splits into three signals. The extreme sensitivity of this spectral region toward the steric structure of polypropylene gives rise, in samples with lower steric purity, to an apparent widening of isotactic signals, which could be erroneously attributed to an intrinsically larger line width.

In striking contrast to the details observed in the outer areas of the methyl spectrum, the central zone contains two signals only, 8 and 9, gathering together all the permitted mr-centered nonads and the residual mm-centered heptad. The intensity ratio between signals 8 and 9 (area 12:8) shows that the rrmmrr sequence contributes almost exclusively to signal 8. On the basis of Tonelli computed data, *both nonads mmmmrrmm and mmmmrrrr converge in the peak 8 and nonads rrmmrrmm and rrmmrrrr in the peak 9.*

The analysis of the methylene spectrum leads to interesting observations, too. Main peaks are confined between 45.0 and 46.8 ppm; the assignment of signals is developed at hexad level but octad and even decad resolution is apparent. Intensity of the experimental peaks roughly follows the pattern 0.5:1:0.5:2:2:2:2:1:3:1:1, whereas theory predicts unity values for every octad.

Peaks 4–6 are assigned respectively to hexads rrmmr, rrrrr, and rrmmm according to Tonelli.[15,17] Moving toward high field, three peaks (7–9) are observed covering a total area 6/16, corresponding to six octads. Peak 7 is assigned to hexad rmmmm according to Tonelli[17] and Zambelli,[14] while peaks 8 and 9, whose relative area is 1:3, are to be assigned to four octads derived from the hexads mrrmm and mmmmm. Signals 10 and 11 are certainly due to single octads rrrrmmm and rrrrmmr. In this case we are not able to determine the precise correlation between signals and octad structure.

In the end, peaks 1–3 all belong to the sequences centered on the hexad rrrrm. Fractionary value of the intensity clearly indicates *that peaks 1 and 3 are sensitive to the decad structure.* Their assignment to the sequences mmrrrrmmm, mmrrrrmmr, rrrrrmmm, or rrrrrmmr is still an open problem.

## Quantitative Evaluation of the Spectrum

A line-shape analysis, carried out by a least-squares procedure,[7] enabled us to describe the spectrum reported in Figure 3 as the sum of 17 Lorentzian peaks and to obtain the best values of chemical shift and intensity for each peak. At a next stage all 28 permitted nonads were considered, with intensity corresponding to the values computed in part 2. The spectrum was optimized with respect to the chemical shift of each component. As a matter of fact, only 24 simple signals, each corresponding to a single nonad (or undecad) or to a group of nonads lying in the range of 0.005 ppm, were necessary in order to achieve a satisfactory result (Table II). Our data represent a possible test for chemical shift computation at a higher level of sequence length.

An analogous treatment was also carried out at the hexad and octad levels for the $CH_2$ spectrum. A more detailed discussion of the simulation of the spectrum of hit-PP will be given in a forthcoming publication.[7]

A further problem concerns the evaluation of the degree of hemiisotacticity of polymer II. As extensively reported in part 2, the distribution of sequences depends upon three probability parameters, termed $\alpha$, $\alpha'$, and $\beta$. In chemical terms $\beta$ corresponds to the isotactic dyad content in the starting poly(2-methylpentadiene) (I), and $\alpha$ and $\alpha'$ correspond to the probability that hydrogen will be added on one or on the other diastereotopic face of the double bond, in isotactic and syndiotactic dyads, respectively.

The examination undertaken so far implicityly supposed that $\beta = 1$ and $\alpha = 0.5$ (ideal hemiisotactic polymer). To verify deviations from these assumptions we compared the relative intensities of certain signals with those computed for the corresponding sequences as $\alpha$ and $\beta$ move from ideal values.[2] The expected intensity ratio between pentads mmmm and rrrr (or mmmr and mrrr), changing the value of $\alpha$ from 0.49 to 0.51, passes from 0.910 to 1.098 (or from 0.960 to 1.041); the observed value is 0.997 (or 1.023) (see Table I). We may thus state that no selectivity exists in hydrogenation with diimide and that polymer II is perfectly ideal from this point of view ($\alpha = 0.500 \pm 0.003$).

As regards $\beta$, evidence indicating a nonunity value lies in the presence of a series of weak peaks, in particular at 47.05, 20.95, and 19.42 ppm, and of a wide plateau between peaks 9 and 10 in the methyl spectrum. It must however be taken into account that in this region the residual unsaturation present in hit-PP could give a small contribution (the chemical shift of the methyl signal in homopolymer I is 20.13 ppm). Using Tonelli's data we attributed the signal at 47.05 ppm to hexads rrmrr and mrrrm. Intensity as computed by the formulas reported in part 2 indicates that $\beta$ should have a value of $\geq 0.96$.

The same $\beta$ value is obtained by comparing the signal intensities with the pentad probabilities in the methyl spectrum (Table I). In Figure 3 we report the final refinement of the spectral analysis, carried out by introducing all permitted nonads and the most significant forbidden heptads. The chemical shits assumed for these last sequences were deduced from the Tonelli data.[17]

From this discussion we can conclude that polymer II is almost pure hemiisotactic polypropylene. As a consequence poly(2-methylpentadiene) (I) is an almost pure isotactic polymer (more than 96% of isotactic dyads). The latter finding is particularly significant, both with regard to the method whereby it was obtained and with regard to the implications it has concerning the degree of steric control in PHTP inclusion polymerization.

As a final observation, it would seem worthwhile to stress the fact that the distribution of the hemitactic polymer sequences, expressed here in the terms $\alpha$, $\alpha'$, and $\beta$, cannot be expressed by means of the common schemes of Markov chains, in terms of m and r. For example, the following values of the conditional probabilities of second-order Markov chains exactly reproduce the tetrad distribution[21]

$$p_{\rm mmm} = 0.6667; \qquad p_{\rm mrm} = 0; \qquad p_{\rm rrm} = 1;$$
$$p_{\rm rrm} = 0.3333$$

yet nonetheless at the pentad level, nonnegligible deviations from the distribution calculated by means of our scheme are to be observed, and the differences increase as the length of the sequences examined increases. Only a knowledge of the chemical history of the product (method of synthesis and the possible further transformations) makes it possible to formulate correct hypotheses for the statistical interpretation of the polymer structure.

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