

Nuclear Magnetic Resonance Analysis of Some Deuterated Polypropenes

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Synopsis

High resolution 60 and 100 Mc. NMR spectra have been obtained for a series of deuterated polypropenes with compounds of the highest sterical purity used. The fundamental parameters of the spectra (chemical shifts and coupling constants) have been accurately determined and compared with previous results available in the literature. The results may be applied to quantitative estimates of the stereoregularity of polymers not deuterated by the NMR method.

Introduction

The problem of the analysis of the NMR spectrum of the propylene polymers has received wide attention in literature;¹⁻⁵ the first result obtained was the interpretation of the spectra of both crystalline isotactic and syndiotactic polypropylenes. Attempts were also made to analyze head-to-tail sterically disordered, or not perfectly ordered polypropylenes.

Having surveyed the NMR data concerning polypropylene in solution, we herein propose to characterize both crystalline isotactic and syndiotactic polypropylenes. For this purpose, it was decided to examine polymers that have the highest possible sterical purity; these were obtained in the presence of highly stereospecific catalytic systems, isotactic and syndiotactic, respectively.^{7,8}

Moreover, we have also studied head-to-tail polypropylenes with a sterically disordered or not perfectly ordered structure, in order to obtain information on the stereoisomeric composition of the polymers, with regard to the content in permanences and alternances of steric configuration⁵ and to their distribution in the macromolecules (mechanical mixtures of isotactic and syndiotactic polymers, stereoblock polymers, atactic polymers).

Results Obtained

Isotactic 2,3,3,3-*d*₄ Polypropene.⁷ As shown in Figure 1, the spectra of the raw highly isotactic polymer (sample A), obtained with the aid of the catalytic system $\gamma\text{-TiCl}_3\text{-Al}(\text{C}_2\text{H}_5)_2\text{I}$, its heptanic extract (sample B), and

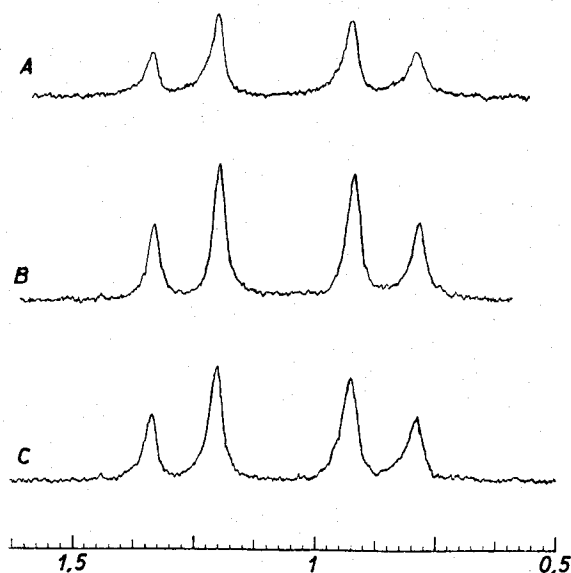


Fig. 1. NMR spectra of isotactic 2,3,3,3- d_4 polypropene: (A) raw polymer; (B) heptanic extract; (C) heptanic residue.

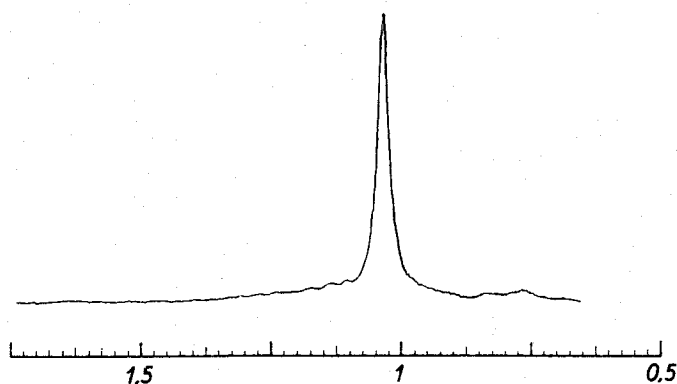


Fig. 2. NMR spectrum of raw syndiotactic 2,3,3,3- d_4 polypropene (sample D).

its heptanic residue (sample C) can be superimposed. We note that the spectra of the heptanic extract and of the heptanic residue do not generally coincide; the behavior exhibited by samples B and C is a consequence of the particular catalytic system used. The pattern consists of two doublets and it is interpreted as an AB type spectrum with parameters $\delta_{AB} = 0.392$ ppm and $\tau_{AB} = 13.5$ cps. The results are in agreement with previous data in the literature. We have also verified that a departure from an AB type interpretation of the spectrum (unequal splitting of the two doublets) as observed by Stheling¹ is only a spurious effect due to too large an intensity of the radio frequency field.

Syndiotactic 2,3,3,3- d_4 Polypropylene.⁸ From the corresponding spectrum (Fig. 2, sample D) it is seen that the two protons of the methylenic group are equivalent and have a chemical shift of 1.035 ppm with respect to the hexamethyldisiloxane (HMDS).

Additional information on the spectrum of the isotactic polymer can be obtained from the analysis of two diisotactic polymers, that is, the 1- d_1

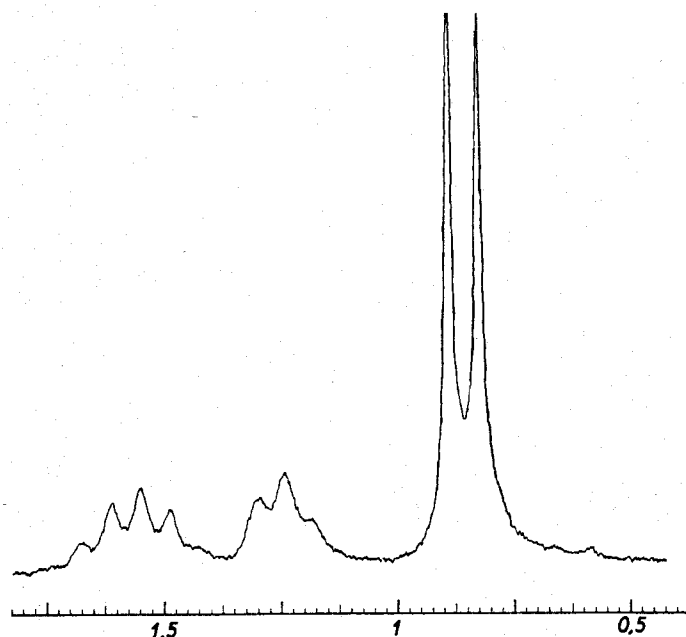
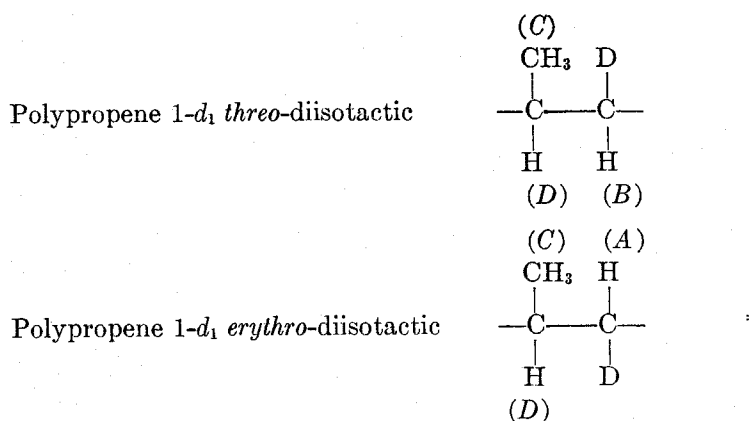


Fig. 3. NMR spectrum of heptanic residue of 1- d_1 -*threo*-diisotactic polypropene (sample *E*).

threo-diisotactic and the 1- d_1 *erythro*-diisotactic polypropene (samples *E* and *F*, respectively). These two polymers have been studied by Natta, Farina, Peraldo⁹⁻¹¹ and by Miyazawa and Ideguchi.¹² Following their assignment it is possible to identify by NMR the two nonequivalent protons of the methylene group of the isotactic polymer. Referring to the notation for a zig-zag planar projection of the chain, we can label the different protons as:



From their spectra (Figs. 3 and 4), one obtains for the *threo* form: $\nu_D = 1.575$ ppm, $\nu_B = 1.261$ ppm; for the *erythro* form we have: $\nu_D = 1.575$ ppm, $\nu_C = 0.856$ ppm, and $\nu_A = 0.869$ ppm. ν_A is obtained as a difference from the spectra of the 2,3,3,3- d_4 isotactic polypropene. It is interesting to note that the arithmetic mean value of ν_A and ν_B does not coincide with the value of $\nu_{A=B}$ (methylenic protons) for the syndiotactic polypropene.

* This labelling of the protons will be used throughout this work, the methylenic protons of syndiotactic polymers being labelled $A = B$.

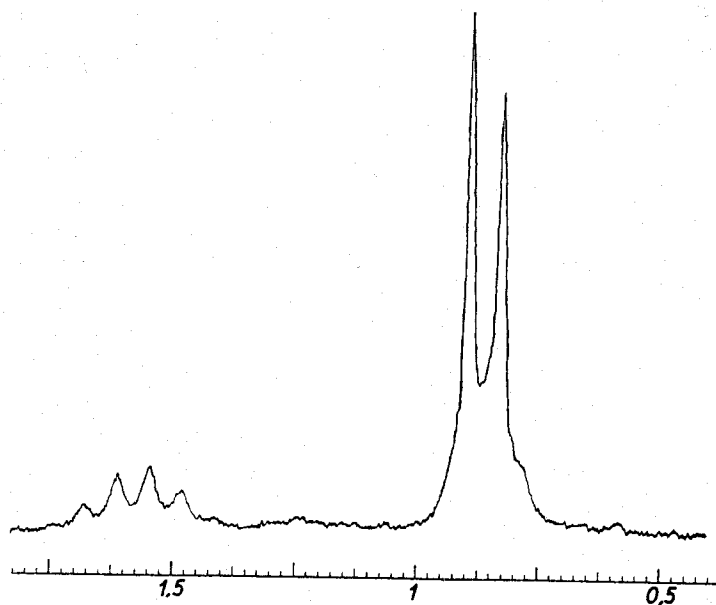


Fig. 4. NMR spectrum of heptanic residue of 1-*d*₁-erythro-diisotactic polypropene (sample *F*).

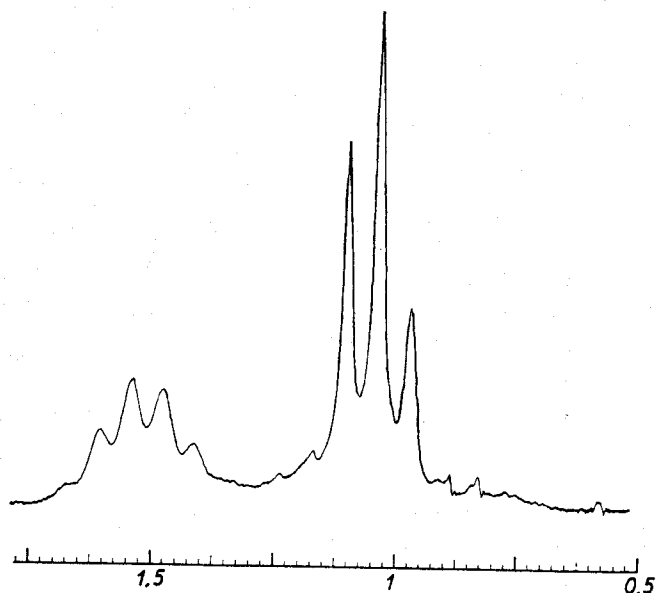


Fig. 5. NMR spectrum of raw syndiotactic 3-3-3-*d*₃-polypropene (sample *G*).

No theoretical calculation of the chemical shift for the *A* and *B* protons of the isotactic 2,3,3,3-*d*₄ polypropene has been attempted in this work.

By reducing the degree of deuteration of the starting monomer, it is possible to determine experimentally the values of the coupling constants J_{AD} , J_{BD} , and $J_{(A=B)D}$, respectively, for the isotactic and syndiotactic polymers. The spectrum of Figure 5 (sample *G*)⁸ refers to the syndiotactic 3-3-3-*d*₃ polypropene. It consists of a triplet for the equivalent protons *A* and *B* and of a quintet for the *D* protons. In first approximation, it can be treated as an A_2X_4 first-order spectrum, having the fundamental parameters $J_{(A=B)D} = 6.5$ cps, $\nu_D = 1.575$ ppm, and $\nu_{A=B} = 1.035$ ppm.

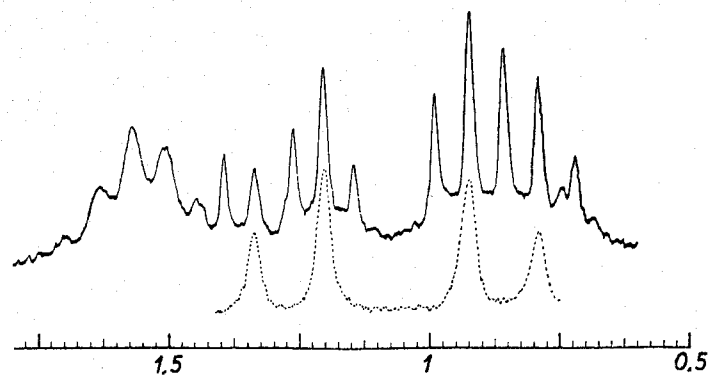


Fig. 6. NMR spectrum of heptanic residue of isotactic 3-3-3- d_3 -polypropene (sample *H*).

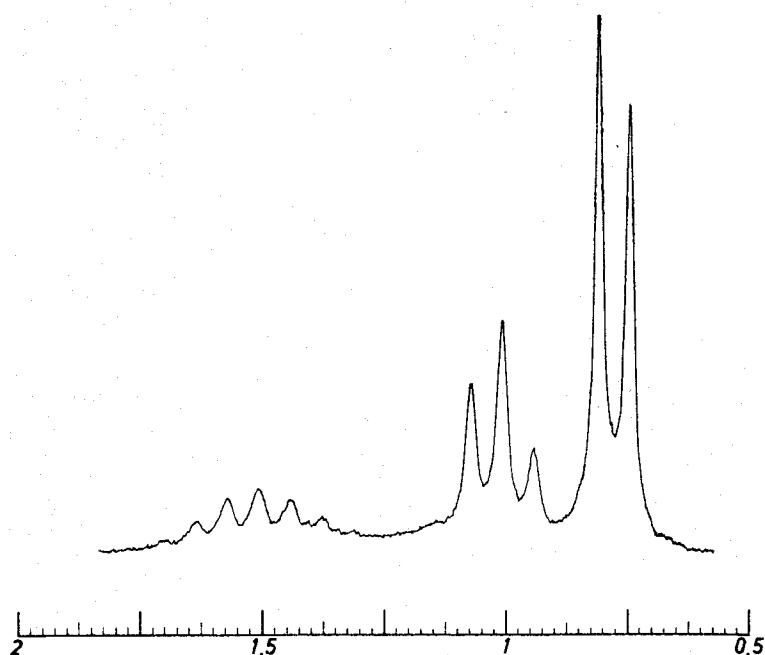


Fig. 7. NMR spectrum of a raw syndiotactic polypropene (sample *L*).

The spectrum of Figure 6 (sample *H*)¹ refers to the isotactic 3,3,3- d_3 polypropene; it consists of three quintets which can be directly interpreted as a first-order spectrum of the $A_2X_2Y_2$ type by superimposing the AB spectrum of the 2,3,3,3- d_4 isotactic polypropene. The fundamental parameters are: $J_{AD} = 7$ cps, $J_{BD} = 6$ cps; $\nu_D = 1.575$ ppm, $\nu_A = 0.869$ ppm, $\nu_B = 1.261$ ppm.

It is interesting to note that more refined calculations of the fundamental parameters J and ν , as obtained from undeuterated polypropenes, agree with the present values.

Finally, from the spectra of the diisotactic polymers we obtain $\nu_{CH_3} = 0.856$ ppm and $J_{(CH_3)D} = 6.5$ cps. From the spectrum of a syndiotactic 1-2-2- d_3 polypropene (sample *I*) we obtain in this case $\nu_{CH_3} = 0.801$ ppm, and from the spectrum of a syndiotactic polypropene with a very high degree of crystallinity, we found $J_{(CH_3)-D} = 6.5$ cps also for the syndiotactic polymer.

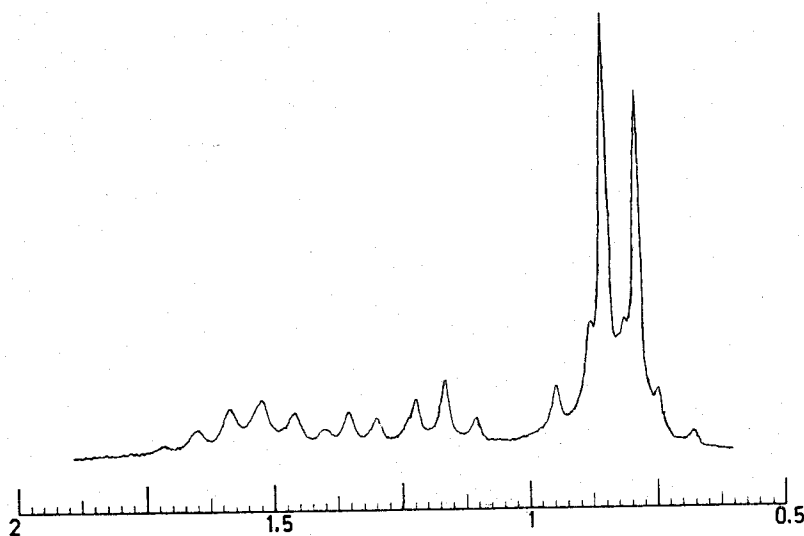


Fig. 8. NMR spectrum of the heptanic residue of a thermally degraded isotactic polymer (sample *M*).

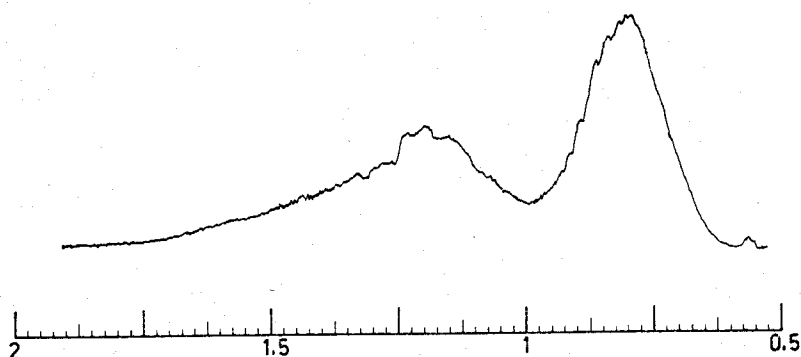
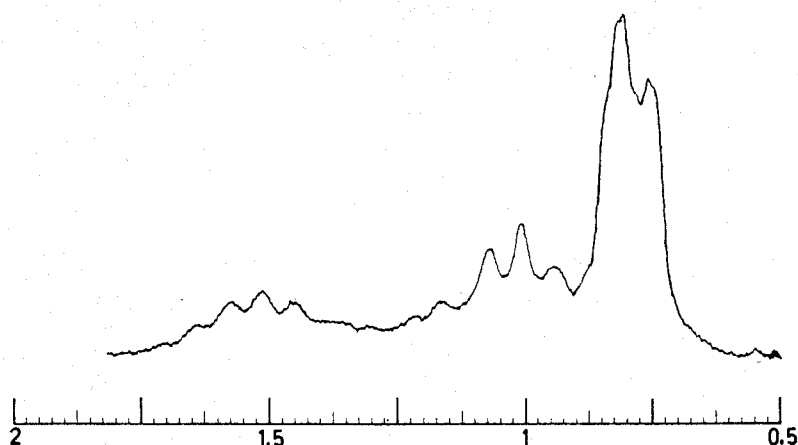
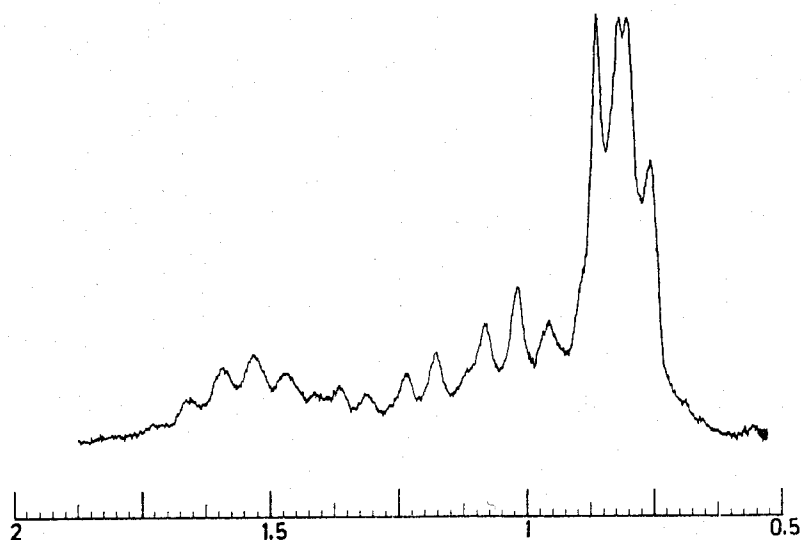


Fig. 9. NMR spectrum of a polypropene obtained by cationic polymerization (sample *N*).

The main features which appear from the results obtained on the partially deuterated polymers are that no overlapping occurs in the spectrum of the syndiotactic form, while for the isotactic form there is overlapping between the proton H_A of the methylenic group and the protons of the CH_3 group. In Figures 7 and 8 we report the spectra of the syndiotactic and isotactic polypropene (samples *L* and *M*). For comparison in Figures 9, 10, and 11 are reported the spectra of a polypropene obtained by cationic polymerization¹³ (sample *N*) and of anionic polypropenes with different degree of stereoregularity (samples *P* and *Q*). An interesting result is the appearance of an additional doublet in the CH_3 part of the spectrum, of sample *P*, which was first ascribed by Woodbrey³ to the heterotactic methyl group.

The problem now remains to correlate the properties of such intermediate types of spectra and the description of the polymer in terms of its degree of stereoregularity. Obviously, the nature of the CH_2 group depends on the relative position of the $-CH_3$ groups attached to the two adjacent tertiary carbon atoms, that is, we can describe a CH_2 group as being asso-

Fig. 10. NMR spectrum of sample *P*.Fig. 11. NMR spectrum of sample *Q*.

ciated to the permanence or alternance* of the steric configuration of the two adjacent tertiary carbon atoms. It follows that one can measure the relative amount of the CH_2 group of the two types simply if a calibrating curve is available; this curve can be constructed by analyzing different mechanical mixtures of pure isotactic and pure syndiotactic polymers. For this purpose, one can select a suitable part of the spectrum in the CH_2 region. By comparison of the spectra of the isotactic and syndiotactic polypropylenes we note that, for calibrating purposes, a suitable choice can be the ratio between the height (or the area) of the peak centered at 1.01 ppm, (A_{101}), which belongs exclusively to the CH_2 group of syndiotactic polymer, and that of the peak centered at 0.94 ppm, (A_{94}), which belongs at the same time to the CH_2 group of syndiotactic polymer and to the methylenic proton *A* of isotactic polymer. We note that the difference in frequency of the two components of the peak A_{94} is within the limits of

* For the nomenclature used see reference 5.

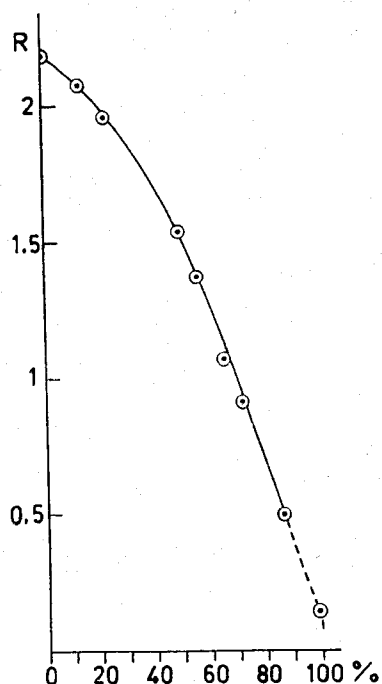


Fig. 12. Index of alternance and permanence. The abscissa is the wt.-% of isotactic polymer. Since the calibration was carried out using the ratio between the heights of the bands, respectively, at 1.01 ppm and 0.94 ppm (and not the areas that can be hardly measured) R is greater than 0 even for the purest isotactic polypropylene; actually, though the band at 1.01 ppm is absent, the base line does not go back to 0.

resolution of the instrument. For the ratio $R = A_{101}/A_{94}$ we propose the name of index of alternance and permanence. For samples that are not true mechanical mixtures, this index can be used to make semiquantitative comparisons. The calibrating curve, which has been constructed by mixing different amounts of samples L and M , is reported in Figure 12. Our choice has been based on spectra obtained at 100 Mc./sec.; a different choice, due to a lower degree of resolution of the CH_2 part of the spectrum, was previously given⁵ for spectra at 60 Mc./sec.

The accuracy, which can be attributed to the values of the index of alternance and permanence, is a sensitive function of the degree of resolution of the spectra; a possible improvement can be obtained by varying, for instance, the nature of the solvent.

The second piece of information that can be deduced from the NMR spectra is the relative amount of different types of CH_3 groups, which can be described as being of the syndiotactic, isotactic, and heterotactic types. So far, we have not succeeded in obtaining sufficient resolution to determine quantitatively their relative amounts because of the partial overlapping of the H_A proton, and because the presence of the heterotactic CH_3 groups broadens this part of the spectrum. We are trying to improve the experimental techniques. Nevertheless, one can use the available qualitative information to assess the stereoblock or atactic character of some polypropenes.

As an example, we take the spectra of samples *P* and *Q*. Sample *P* is the boiling ethyl ether-soluble fraction of a polymer obtained in the presence of the catalytic system $\beta\text{-TiCl}_3\text{-Ga}(\text{C}_2\text{H}_5)_3$ at 70°C . and by operating under the conditions described in the experimental part. Sample *Q* is the portion of the same raw polymer which is insoluble in boiling ethyl ether and soluble in boiling *n*-heptane. The index of alternance and permanence gives, respectively, 51 and 58% of permanences, while the spectrum of the CH_3 groups indicates the presence of a large amount of heterotactic methyl groups in sample *P* and of a comparable amount of isotactic and syndiotactic methyl groups with a very little amount of heterotactic methyl groups in sample *Q*.

The x-ray analysis confirms that sample *P* is amorphous, while sample *Q* exhibits both a typical syndiotactic and isotactic crystallinity,¹⁴ independent of the fact that the index of alternance and permanence does not differ too much for the two samples.

Experimental Studies

NMR Spectra. The NMR spectra were taken at 100 Mc./sec. on polymers solutions of constant concentration, that is, 30 mg. of polymer dissolved in 0.6 cc. of a solution containing orthodichlorobenzene (94 vol.-%) HMDS (6%). The operating temperature was $110 \pm 1^\circ\text{C}$. Referring to an HA 100 Mc./sec. Varian spectrometer the running conditions for field sweep operation were as follows: frequency response 2, radio frequency attenuator 30 db., sweep time 250 sec., and sweep width 250 cps, carefully controlled between runnings with a frequency meter; the signal was locked on the HMDS peak.

Reagent Preparation. For the preparation of the reagents and of the differently deuterated propenes, we refer to a previous publication.⁵ Tri-

TABLE I

Sample	Catalytic system or reference	Fraction
<i>A</i>	7	Raw
<i>B</i>	7	Heptanic extract
<i>C</i>	7	Heptanic residue
<i>D</i>	8	Raw
<i>E</i>	9	Heptanic residue
<i>F</i>	9	Heptanic residue
<i>G</i>	8	Raw
<i>H</i>	7	Heptanic residue
<i>I</i>	8	Raw
<i>L</i>	8	Raw
<i>M</i>	$\gamma\text{-TiCl}_3\text{-Al}(\text{C}_2\text{H}_5)_2\text{I}$ at 70°C .	Heptanic extract of de- graded heptanic residue
<i>N</i>	13	
<i>P</i>	$\beta\text{-TiCl}_3\text{-Ga}(\text{C}_2\text{H}_5)_3$ at 70°C .	Ethyl ether extract
<i>Q</i>	$\beta\text{-TiCl}_3\text{-Ga}(\text{C}_2\text{H}_5)_3$ at 70°C .	Heptanic extract

ethyl gallium was prepared from gallium trichloride and triethylaluminum.¹⁴

Polymerization Runs. In Table I we give the catalytic systems used or the corresponding references.

For the determination of the calibrating curve, the mechanical mixtures of isotactic and syndiotactic polypropylene were prepared from sample *L* (a raw syndiotactic polymer with an IR syndiotactic index⁸ of 2) and from sample *M*. In order to improve the solubility of the isotactic polymer, the sample used was prepared in the presence of the catalytic system γ -TiCl₃-Al(C₂H₅)₂I at 70°C.; subsequently it was thermally degraded. Sample *M* is the boiling ethyl ether-insoluble and boiling *n*-heptane-soluble fraction of the degraded polymers. The NMR spectra of sample *M* and of the not degraded isotactic polymer do not show any appreciable difference.

Conclusions

With the present state of resolution of the NMR spectra, it is possible to measure, for a given head-to-tail polymer of propylene, the index of alternance and permanence; moreover, from the part of the spectrum belonging to the CH₃ group, it is possible to confirm¹⁵ the presence of stereoblocks. Quantitative estimates are more difficult and a further improvement of the experimental techniques is under study.

The NMR results confirm that the different fractions, which can be obtained from raw polymers (obtained by Ziegler-Natta polymerization) by extraction with a series of solvents at increasing boiling points have generally a different degree of stereoregularity. In particular, the steric regularity of the heptanic extract is comparable with the steric regularity of the heptanic residue only in a few special cases (see, for instance, the spectra of samples *A*, *B*, and *C*, obtained only with a particular catalytic system).

As is confirmed in another work,¹⁵ the heptanic extracts of the raw polymers obtained from catalytic systems consisting of TiCl₃ in the four modifications (α , β , γ , δ) and of organometallic compounds of Al, Ga, and Be, are generally stereoblock polymers which sometimes show x-ray crystallinity of both syndiotactic and isotactic types.

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Résumé

Des spectres à haute résolution à 60 et 100 Mc de résonance nucléaire magnétique ont été obtenus pour une série de polypropylènes deutérés utilisant des composés de pureté stérique la plus élevée. Les paramètres fondamentaux des spectres (les constantes des shifts chimiques et de couplage) ont été déterminés avec précision et comparés avec des résultats préalablement disponible dans la littérature. Les résultats peuvent être appliqués pour estimer quantitativement la stéréorégularité de polymères non-deutérés par la méthode de résonance nucléaire magnétique.

Zusammenfassung

60- und 100-MHz-NMR-Hochauflösungsspektren wurden für eine Reihe deuterierter Polypropene an Verbindungen höchster sterischer Reinheit erhalten. Die grundlegenden Parameter der Spektren (chemische Verschiebung und Kopplungskonstanten) wurden genau bestimmt und mit früheren, in der Literatur vorhandenen Ergebnissen verglichen. Die Ergebnisse können zur quantitativen Bestimmung der Stereoregularität nicht-deuterierter Polymerer durch die NMR-Methode verwendet werden.