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by

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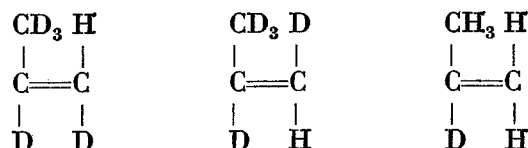
NMR Data on the Stereoregularity of Polypropylene

By A. ZAMBELLI, A. L. SEGRE, M. FARINA, and G. NATTA

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SUMMARY:

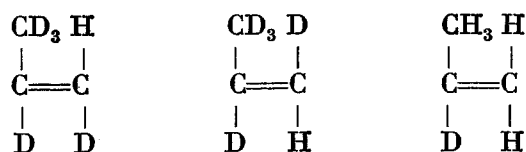
NMR spectra of isotactic, predominantly syndiotactic, and atactic polymers of the following deuterated propylenes have been run on a Varian HA 100 spectrometer:



It was thus possible to indicate a lower limit for the steric purity of isotactic polypropylene, to establish that all permanences always derive from the *cis*-opening of the monomer units, and to obtain evidence for the influence of tetrads on the NMR spectrum of methylenic protons.

ZUSAMMENFASSUNG:

Die NMR-Spektren von isotaktischen, vorwiegend syndiotaktischen und ataktischen Polymeren der hier angegebenen deuterierten Propylene wurden mit einem Varian-HA100-Spektrometer aufgenommen.



Dadurch war es möglich, eine untere Grenze für die sterische Reinheit von isotaktischem Polypropylen anzugeben; ferner wurde gesichert, daß alle Permanenzen stets von der *cis*-Öffnung der Monomereinheiten herrühren; schließlich konnten Hinweise für den Einfluß von Tetraden auf das NMR-Spektrum der Methylenprotonen gefunden werden.

Introduction

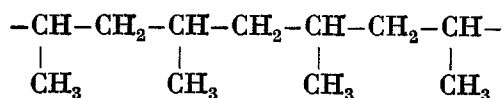
In these last years, several papers have been published that contributed to the interpretation of the NMR spectra of polypropylenes exhibiting different steric structures¹⁻¹⁰). Thus, by examining the spectrum of the methyl groups, the presence of isotactic, heterotactic, and syndiotactic triads (*ddd* or *lll*, *ddl* or *lld*, *dld* or *ldl* sequences) can be evidenced in the various polymers; however, the quantitative determinations of the triads

are still inaccurate owing to the insufficient resolution of the spectrometers. On the contrary, some methods have been proposed for the determination of the amount of permanences and alternances (*dd* or *ll*, *dl* or *ld* sequences). Such methods consider the spectrum of methylenic protons, which, to a first approximation, were supposed to be little influenced by the structure of the *tetrads* *).

Table 1. Nomenclature of tetrads

1. <i>ido</i> alternance	
2. <i>gluco</i> alternance	
3. <i>manno</i> alternance	
4. <i>allo</i> permanence	
5. <i>altro</i> permanence	
6. <i>galacto</i> permanence	

*) Due to reasons of symmetry, it is convenient to analyse the spectrum of methylenes in terms of *tetrads*. A tetrad consists of the following structural unit:



With this basic unit one can also define the effect of the methyl groups that are second neighbours to the central CH_2 -group¹¹). A permanence, as well as an alternance, can be at the center of 3 types of tetrads. By analogy with aldohexoses, we propose for the 6 tetrads the names reported in Table 1, together with the FISCHER-ROSENOFF projections of tertiary carbon atoms.

Obviously, the absolute configurations of tetrads have not been taken into account. In order to distinguish the chemical shift of the non-equivalent methylenic hydrogens of permanences, we define as *syn* the hydrogens lying in the same half-space as the methyls, when performing the zig-zag planar projection of the macromolecules, and as *anti* the hydrogens lying in the opposite half-space.

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On this subject we reported^{9,10} the NMR spectrum of a highly crystalline sample of isotactic poly-2.3.3.3-d₄-propylene; it consisted of only two doublets, thus showing, in our opinion, a very high stereoregularity.

The determination as accurate as possible of the steric purity of isotactic polypropylene has acquired interest after the recent research of FLORY and co-workers on "the chain dimensions of sterically regular macromolecules and on their temperature coefficients"^{12,13}. According to these authors^{12,13}, the experimental data are consistent with the theoretical calculations only if one admits the presence in highly crystalline isotactic polymers of at least 5 % of isolated, randomly distributed alternances. In their opinion¹⁴, the NMR spectrum of isotactic poly-2.3.3.3-d₄-propylene only consisted of two doublets, not because of the high steric purity of the polymer, as we suggested^{9,10}, but because the chemical shift of the methylenic protons of isolated alternances was displaced with respect to the position found in syndiotactic polymers and coincides accidentally with one of the 4 lines we have reported. In other words, the isotactic macromolecules should consist of sequences of the ...*ddddllll*... type.

This fact, whenever proved, would involve considerable consequences. First of all, the proposed interpretation of the X-ray crystal structure of the polymer¹⁵ ought to be modified. In the second place, the presence of such *manno* alternances would be a suggestion, although not a proof, that the stereospecificity of the isotactic polymerization is not caused by the asymmetry of the active centers, but by the configuration of the last polymerized monomer unit, while the presence of isolated couples of *gluco* alternances in isotactic macromolecules would have the opposite meaning (see Table 2). For these reasons, we decided to complete our NMR data in order to attain an unequivocal interpretation of the spectrum of isotactic poly-2.3.3.3-d₄-propylene and, more generally, to evidence the influence of the structure of the tetrads on the spectrum of the methylenic protons.

Table 2. Sequences of tetrads for the two simplest cases of steric irregularities in isotactic macromolecules

Case A *)



1. *allo* permanence

2. *altro* permanence

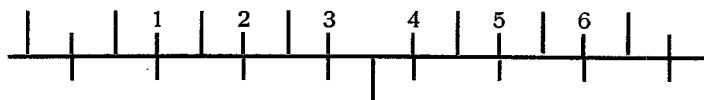
3. *manno* alternance

4. *altro* permanence

5. *allo* permanence

*) Numbers refer to central CH₂-group of tetrad.

Case B*)



1. *allo* permanence
2. *altro* permanence
3. *gluco* alternance

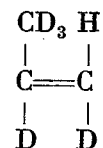
4. *gluco* alternance
5. *altro* permanence
6. *allo* permanence

*) Numbers refer to central CH₂-group of tetrad.

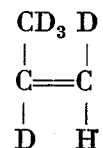
Results

Figs. 1–3 report the 100 Mc NMR spectra of isotactic (a), substantially atactic (b), and prevailing syndiotactic (c) polymers of the following monomers:

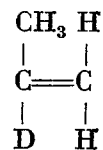
- 1) *cis*-1.2.3.3.3-d₅-propylene
(Figs. 1a, 1b, 1c)



- 2) *trans*-1.2.3.3.3-d₅-propylene
(Figs. 2a, 2b, 2c)



- 3) 2d₁-propylene
(Figs. 3a, 3b, 3c)



Figs. 1a and 2a show, by comparison, the 100 Mc NMR spectrum (dashed line) of isotactic poly-2.3.3.3-d₄-propylene, run under the same conditions.

Discussion

1. Steric purity of isotactic polypropylene

On the condition that the hypotheses of FLORY and BALDESCHWIELER¹⁴⁾ are correct, a singlet should be detected at $\nu = 0.802$ ppm or at $\nu = 0.936$ ppm in spectrum 1a, or else a singlet at $\nu = 1.193$ ppm or at $\nu = 1.328$ ppm in spectrum 2a; the singlet area should obviously be at least 5 % of that of the main peaks, definitely higher than the sensitivity of our analysis, which is better than 2 % (see experimental part). As this does not occur, we must, on the contrary, conclude that the polymers examined by us did not contain alternances with whatever arrangement for more than

2 %. We note that in order to remove any doubt on these conclusions, arising from the broadening of the peaks due to H—D coupling and from the isotopic effect on the chemical shifts, we have examined the isotactic polymers of both *cis*- and *trans*-1.2.3.3.3-d₅-propylene.

It is also known^{16,17}) that the isotactic polymerization of propylene takes place by *cis*-opening; therefore, spectra 1a and 2a respectively correspond to those of the *anti*- and *syn*-protons of *allo* permanences. The band at $\nu \approx 1.26$, hardly detectable in Fig. 2a, is then due to the presence of *cis*-1.2.3.3.3-d₅-propylene in *trans*-1.2.3.3.3-d₅-propylene used in the preparation of the polymer. In fact, its area, determined by averaging several spectra, is about 2–3 % of that of the main peak; this value coincides with that foreseen for the *anti*-protons, on the basis of the purity of the starting monomer (determined independently by IR analysis) by supposing a 100 % *cis*-addition to the double bond during the polymerization and the absence of a considerable isomerization of the monomer.

2. Influence of the structure of the tetrads on the NMR spectrum of the methylenic protons

The validity of the conclusions drawn in the previous section is independent of the actual chemical shift of the methylenic protons of isolated alternances because no hypothesis had to be put forward on this regard.

A second problem is to establish to what extent the different tetrads may be evidenced by NMR analysis. In order to obtain high concentrations of tetrads of different type, it is convenient to examine either atactic polymers, or in general products with the lowest steric regularity. The spectra reported in Figs. 1b and 2b (approximately atactic polymers) are of immediate evidence and show that the structure of the tetrads does not influence the chemical shift of the alternances to such an extent as to give a complete superposition with *syn*- and *anti*-protons. No clear influence of the structure of tetrads can be detected in Figs. 1b and 2b because of the H—D geminal coupling. However, a comparison between the spectra reported in Figs. 3a, 3b and 3c suggests that *anti*-protons of *altro* permanences or of *galacto* permanences (or both) have a chemical shift of 0.04 ppm higher than that of the *anti*-protons of *allo* permanences.

On the other hand, the corresponding *syn*-protons have a lower chemical shift by 0.04 ppm. The geminal coupling constant is unvaried (13.5 cps). The different types of alternances cannot unambiguously be distinguished in the spectrum 3b. Better results on the tetrad analysis will

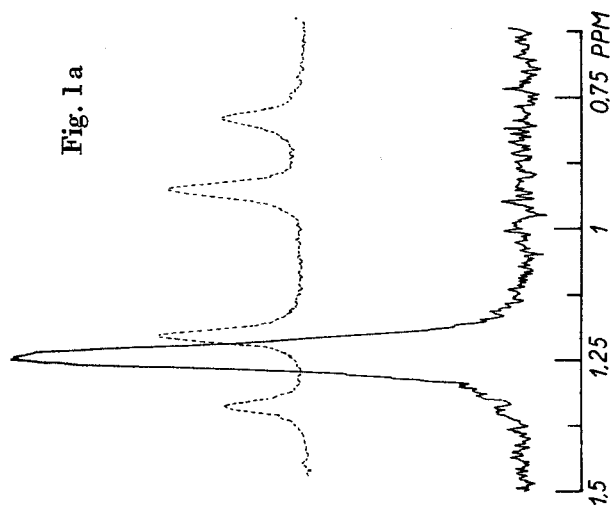


Fig. 1b

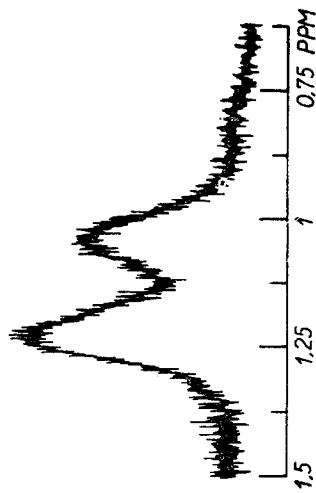


Fig. 1c

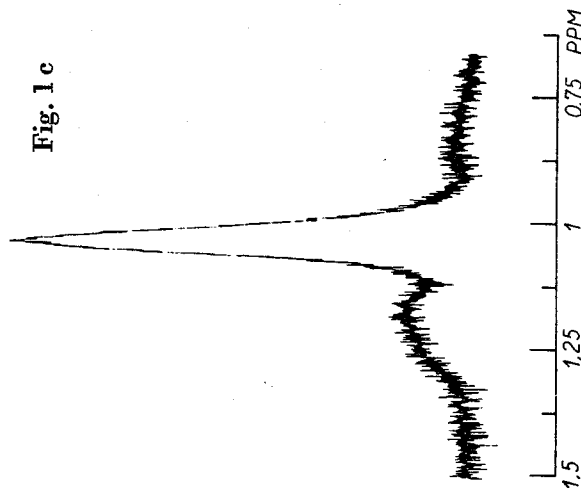


Fig. 2a

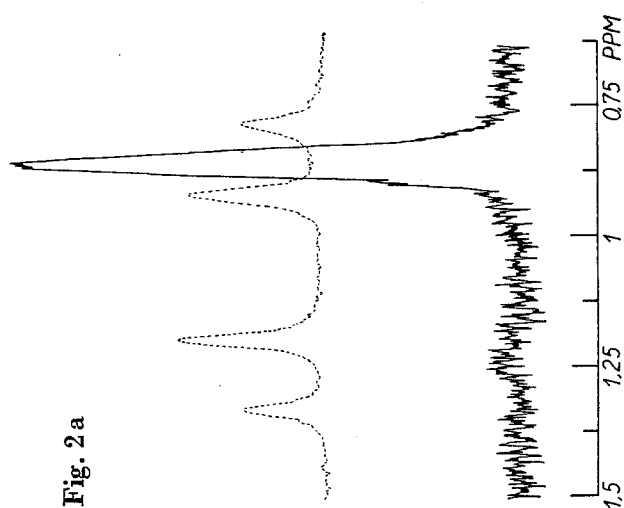


Fig. 2b

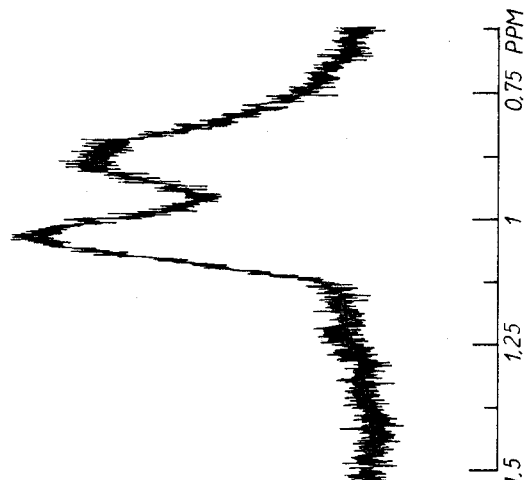
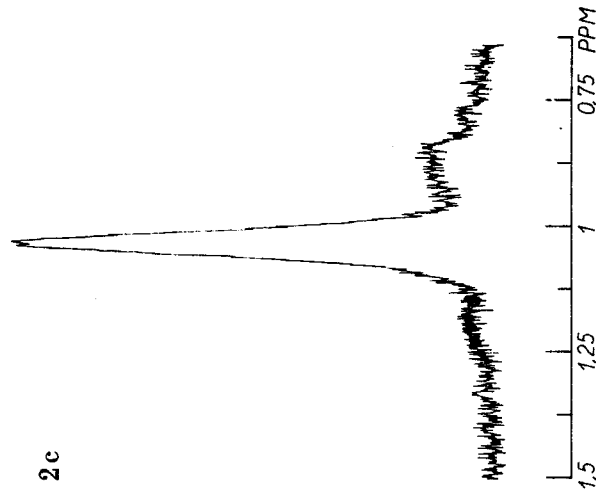


Fig. 2c



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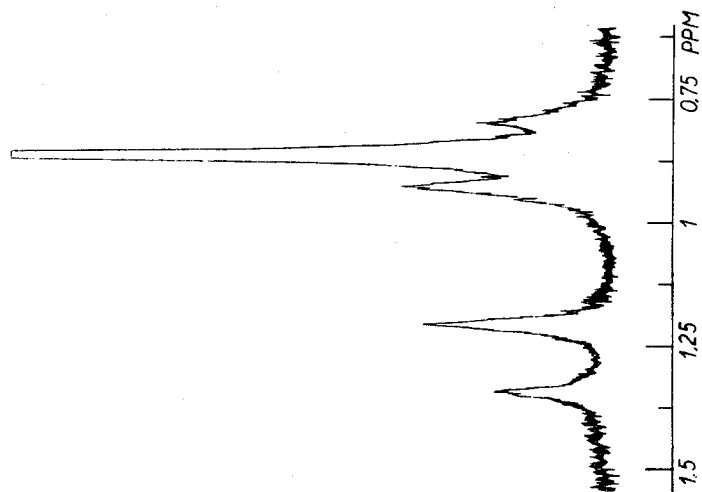


Fig. 3 a

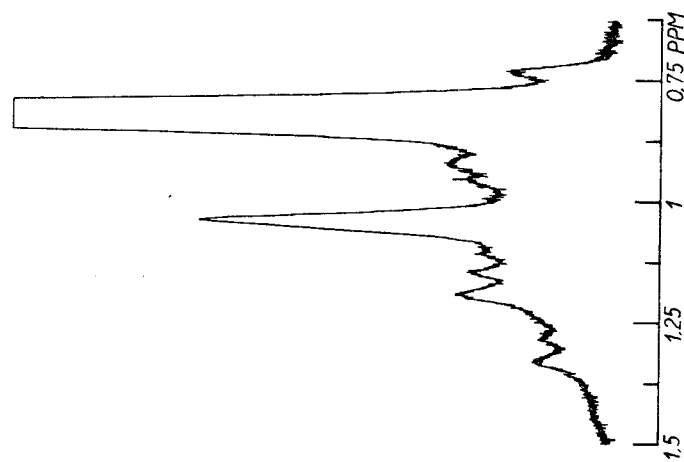


Fig. 3 b

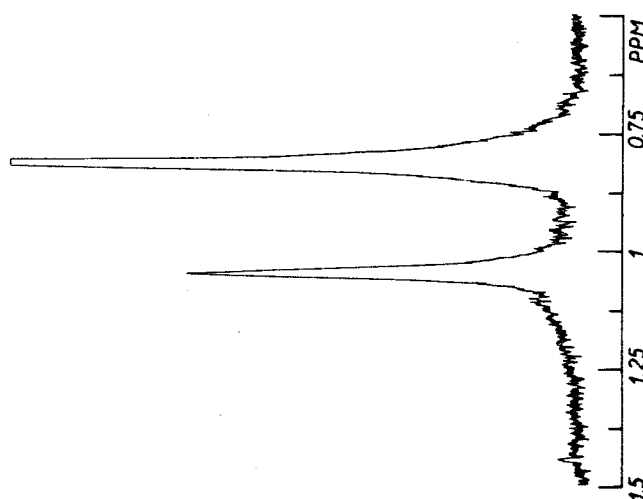


Fig. 3 c

Fig. 1. a) NMR spectrum of isotactic poly-*cis*-1.2.3.3.3- d_5 -propylene, b) atactic poly-*cis*-1.2.3.3.3- d_5 -propylene, c) prevailing syndiotactic poly-*cis*-1.2.3.3.3- d_5 -propylene

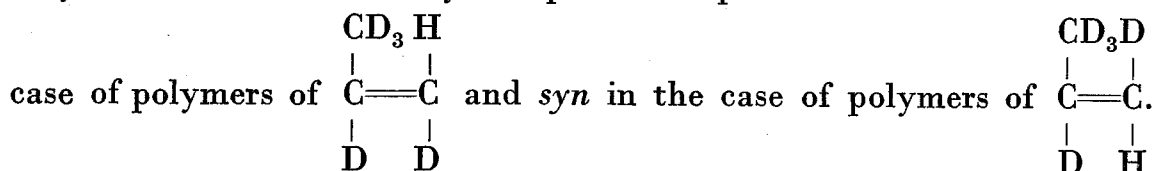
Fig. 2. a) NMR spectrum of isotactic poly-*trans*-1.2.3.3.3- d_5 -propylene, b) substantially atactic poly-*trans*-1.2.3.3.3- d_5 -propylene, c) prevailing syndiotactic poly-*trans*-1.2.3.3.3- d_5 -propylene

Fig. 3. a) NMR spectrum of isotactic poly-2- d_1 -propylene, b) substantially atactic poly-2- d_1 -propylene, c) prevailing syndiotactic poly-2- d_1 -propylene

be probably obtained by deuterium decoupling. The peak at $\nu \approx 0.70$ ppm in Fig. 3b is presumably due to the presence of head-to-head units, which can also be observed by IR analysis.

3. Some remarks on double bond opening

From the examination of the spectra 1a, 1b, 1c, and 2a, 2b, 2c, we may observe that the methylenic protons of permanences are *anti* in the



Therefore, the methylenic groups of permanences $\left(\begin{array}{c} \text{CH}_3 \text{ H} \quad \text{CH}_3 \\ | \quad | \quad | \\ -\text{C}-\text{C}-\text{C}- \\ | \quad | \quad | \\ \text{H} \quad \text{H} \quad \text{H} \end{array} \right)$ derive

from monomer molecules whose opening was *cis*, independently of the predominant structure of the polymers. It is generally accepted that the growing chains of poly- α -olefins are bound to the catalytic complex through a methylenic group; this means that when the $(n+1)^{\text{th}}$ monomer unit enters into the chain in the same configuration as the n^{th} , the opening of the double bond of the n^{th} is of the *cis*-type.

4. Contributions to the quantitative analysis of the microtacticity of polypropylene

From the spectra reported one can determine the amount of diads with a fairly good accuracy. The presence of at least two additional doublets in the spectrum 3b shows that the methods of analysis of the diads on non-deuterated polymers^{9,10)} are strictly valid only for mechanical mixtures of isotactic and syndiotactic polymers; when applied to stereoblock or atactic polymers, the method underestimates the number of permanences; however, the error will rapidly decrease with increasing *allo* permanences and with decreasing *altro* and *galacto* permanences. Therefore, the NMR analyses of non deuterated polymers are highly sensitive to the possible presence of alternances in highly isotactic polymers. The same cannot be said as to the presence of permanences in prevailingly syndiotactic polymers.

Conclusion

The data reported confirm that highly crystalline isotactic polypropylene contains more than 98 % of permanences. Obviously, we do not have

clear evidence whether the alternances which are present in lower amount than the sensitivity of our analysis are randomly distributed or not.

In many isotactic polymers of propylene characterized by not very high crystallinity, the detected alternances were not distributed at random¹⁸⁾ and not always isolated. However, these results, concerning polymers with intermediate steric regularity, cannot be extrapolated to highly stereoregular isotactic polymers. The methylenic groups of alternances are originated from *cis*-type opening, not only in highly isotactic, but also in substantially atactic and prevailingly syndiotactic chains.

We also think that we have demonstrated NMR analysis to be the most direct and suitable method for the configurational study of the polymers. *Anti*-protons of the *altro* or of the *galacto* permanences, or of both, are shifted upfield by 0.04 ppm and *syn*-protons undergo the same downfield shift with respect to the chemical shift of the corresponding protons of *allo* permanences.

Experimental Part

Preparation of bromopropenes

a) *d*₅-1-Bromopropenes. By photochemical deuterobromination of *d*₄-propene¹⁹⁾, a mixture of *cis*- and *trans*-bromopropene was obtained. The two isomers were separated by GLC. Purity of *cis*-isomer 99.9%. Purity of *trans*-isomer 99.7%.

b) 2-Bromopropene was prepared by dehydrobromination of 1,2-dibromopropane²⁰⁾ and separated from 1-bromopropenes by fractionation and GLC (lowest purity 99.9%).

Preparation of deuterated propenes

As described in literature²¹⁾, bromopropenes were reacted with Li in *n*-butyl ether at -25°C. By subsequent hydrolysis with H₂O or D₂O, different monomers were obtained. *Cis*- and *trans*-*d*₅-1-bromopropenes were stored at -78°C in the dark, and used within the shortest possible time after GLC separation.

Purity of the monomers. Sensitivity of NMR measurements

The monomers in the gaseous state were examined by IR analysis. The isotopic impurities of the monomers due to randomly distributed H atoms were too low to allow a satisfactory analysis. Their order of magnitude can be roughly calculated from the purity of D₂O used in all stages of the synthesis (99.7%). The presence was observed of *trans*-1,2,3,3,3-*d*₅-propene (~1%) in *cis*-1,2,3,3,3-*d*₅-propene and of *cis*-1,2,3,3,3-*d*₅-propene (~2.5%) in *trans*-1,2,3,3,3-*d*₅-propene. The higher purity of the *cis*-isomer is probably due to the higher stability of *cis*-1-bromopropene to isomerization, especially during the reaction with Li.

The presence of *cis*-1,2,3,3,3-*d*₅-propene (2.5%) in *trans*-1,2,3,3,3-*d*₅-propene was especially proved by the presence of two absorption bands at 448 and 446 cm⁻¹ on a fairly well defined base line in the IR spectrum, and confirmed by two other bands, characteristic of

cis-monomer which, although not well separable from the absorptions characteristic of the *trans* isomer, are clearly detected at about 1165 cm^{-1} . The presence of *trans*-1.2.3.3.3- d_5 -propene ($\sim 1\%$) in *cis*-1.2.3.3.3- d_5 -propene is observed around 710 cm^{-1} although with far lower accuracy.

As shown from the spectrum of Fig. 2a, the presence of *anti*-hydrogens is detectable at $\nu = 1.261\text{ ppm}$, whereas *syn*-hydrogens are not detectable in the spectrum of Fig. 1a. Therefore, 2% can be assumed as sensitivity limit of the NMR analyses relating to the spectra of Figs. 1a and 2a.

Polymerization

The polymerization conditions, reported in Table 3 were adopted for all 3 monomers. The catalytic system $\text{TiCl}_3\text{--Al}(\text{C}_2\text{H}_5)_2\text{I}$ was checked because at 0°C it does not promote isomerization of the monomers. The X-ray crystallinity²²⁾ of isotactic polymers was 80%; the IS²³⁾ of a sample of syndiotactic polypropylene prepared under the same conditions was 2.8.

Table 3. Polymerization conditions

Attempted polymer type	<i>n</i> -Heptane (cm ³)	Catalyst system [moles] · 10 ⁻³			Monomer (cm ³)	Temp. (°C)	Time (h)
Isotactic	15	TiCl_3HRA 4	$\text{Al}(\text{C}_2\text{H}_5)_2\text{I}$ 4	—	300	0	6
Atactic	15	VCl_4 1	$\text{Al}(\text{C}_2\text{H}_5)_3$ 5	—	300	-78	20
Syndiotactic	15	VCl_4 1	$\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$ 5	anisol 1	300	-78	4

Isomerization control

After polymerization of *cis*-1.2.3.3.3- d_5 -propene, the residual monomer ($\sim 80\%$) contained $\sim 1.4\%$ of *trans*-monomer (determined by IR analysis). Therefore, under the operating conditions adopted the isomerization of the monomers was negligible during the preparation of isotactic polymers.

NMR analysis

The polymers, dissolved at 150°C in *o*-dichlorobenzene (30–50 mg polymer/1 ml) containing hexamethyldisiloxane ($\sim 3\%$) as internal reference, were examined by a HA100 Varian spectrometer. The isotactic polymers examined were residues of the extraction in boiling *n*-heptane. The other polymers were examined without fractionation.

Note added in proof

In the meantime, the above results were improved by running the NMR spectra of the polymers under deuterium decoupling conditions.

For example, the widths of the peaks of isotactic and syndiotactic polymers of CD_3CDCHD isomers, measured halfway, are reduced to less than 1 cps. This fact increases both sensitivity and resolution.

Under the same conditions, each spectrum of the atactic polymers of CD_3CDCHD consists of two groups of three peaks spaced out by $\sim 3\text{ cps}$ (as it could be foreseen by the knowledge that the tetrads are 6).

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Also in the spectra of predominantly syndiotactic polymers of CD_3CDCHD , the presence of all six possible tetrads could be evidenced.

On the contrary, no other peaks appeared in the NMR spectra of isotactic polymers, which were not due to isotopic impurities.

We may conclude that our evaluation of a steric purity of at least 98% for isotactic polypropylene is more prudent than realistic.

We wish to thank Dr. M. PERALDO for performing the IR analysis of the monomers.

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