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Polymerization of Propylene to Syndiotactic Polymer

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SUMMARY:

By the study of differently deuterated homopolymers and copolymers of propylene it is demonstrated that the double bond addition is *cis* in the syndiotactic polymerization of propylene. Furthermore it is confirmed that the addition to the double bond is *cis* also in the isotactic polymerization.

ZUSAMMENFASSUNG:

Durch das Studium von unterschiedlich deuterierten Homopolymeren und Copolymeren des Propylens wird nachgewiesen, daß bei der syndiotaktischen Polymerisation des Propylens *cis*-Addition erfolgt; weiter wird bestätigt, daß auch bei der isotaktischen Polymerisation *cis*-Addition eintritt.

Introduction

Propylene polymerizes to isotactic polymer with *cis* addition to the double bond^{1,2}.

On the contrary, it is not known which type of addition to the double bond occurs in the polymerization of propylene or of any other vinyl monomer to syndiotactic polymer.

By this research we mainly purposed to check up this point of the syndiotactic polymerization mechanism.

Preliminarily we had to interpret more thoroughly the NMR spectrum of syndiotactic polypropylene and to relate its characteristics with the conformational analysis of the polymer.

Then we controlled by NMR analysis also the type of addition to the double bond in isotactic polymerization: the results obtained agreed with previous literature data^{1,2}.

Results

a) *Syndiotactic Polypropylene*

Syndiotactic polypropylene may be described as a succession *abab...* of alternance (or syndiotactic diad) *a* reported in Fig. 1, and of its mirror

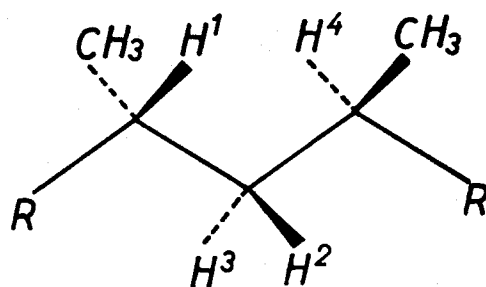
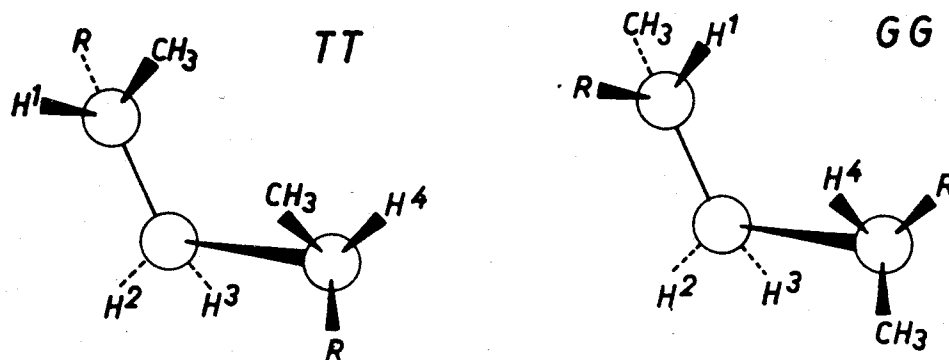
Fig. 1. Alternance *a*

image *b*, each diad sharing the two tertiary carbon atoms with the adjacent ones.

The hydrogens in Fig. 1 are labelled, this labelling being maintained in the whole part of the paper concerning the syndiotactic polymer.

The possible conformers of diad *a* both unstrained and staggered, and therefore with the lowest energy³⁾, are shown in Fig. 2. The notations

Fig. 2. Allowed conformers of alternance *a*

TT and *GG* for the two conformers refer to the internal rotation angle around the bonds adjacent to methylene, by considering skeletal CC bonds ($TT = 180^\circ 180^\circ$, $GG = 300^\circ 300^\circ$ counterclockwise for an observer from the right, by rotating the bond nearest to the observer starting from the eclipsed position).

In the two conformers considered, the coupling constants (J_{ij}) for the different pairs of vicinal hydrogens will be:

$$J_{12} = J_g; \quad J_{13} = J_t; \quad J_{24} = J_t; \quad J_{34} = J_g$$

for conformer *TT*, and

$$J_{12} = J_t; \quad J_{13} = J_g; \quad J_{24} = J_g; \quad J_{34} = J_t$$

for conformer *GG*, where J_t and J_g are the coupling constants when the H-C-C-H internal rotation angle is 180° and $\pm 60^\circ$.

We did not consider methyl hydrogen couplings having no connection with the matter in hand.

The coupling constants ($\overline{J_{ij}}$) for each pair of vicinal hydrogens, averaged for the two conformers in rapid conversion will therefore be ⁴⁾:

$$\begin{aligned}\overline{J_{12}} &= \overline{J_{34}} = P_{TT}J_g + P_{GG}J_t \\ \overline{J_{13}} &= \overline{J_{24}} = P_{TT}J_t + P_{GG}J_g\end{aligned}$$

where P_{TT} and P_{GG} are the probabilities of the two conformers. We observe that

$$\overline{J_{13}} - \overline{J_{12}} = (J_t - J_g)(P_{TT} - P_{GG})$$

and that $P_{TT} - P_{GG}$, $J_t - J_g$ are both certainly positive; therefore protons H^2 and H^3 cannot be magnetically equivalent, although presenting the same chemical shift.

For hydrocarbons, relationship $J_t - J_g > 0$ is general⁵⁾; $P_{TT} - P_{GG} > 0$ because in the unperturbed chain the two conformers are isoenergetic, but the sequences of two or more *TT* conformers are allowed, whereas the sequence of two *GG* conformers is never allowed as it provokes strong non bonded interactions³⁾.

The case $P_{TT} - P_{GG} = 0$ might occur only in the solid state for perfectly spiralized macromolecules that may be described by the sequence $(TT)(GG)(TT)(GG)^* \dots$; on the other hand the case $P_{TT} = 1, P_{GG} = 0$ would occur, still in the solid state, for perfectly planar zig-zag macromolecules, which may be described by the sequence $(TT)(TT)(TT) \dots$

In solution (being the chains less perturbed) it will always be:

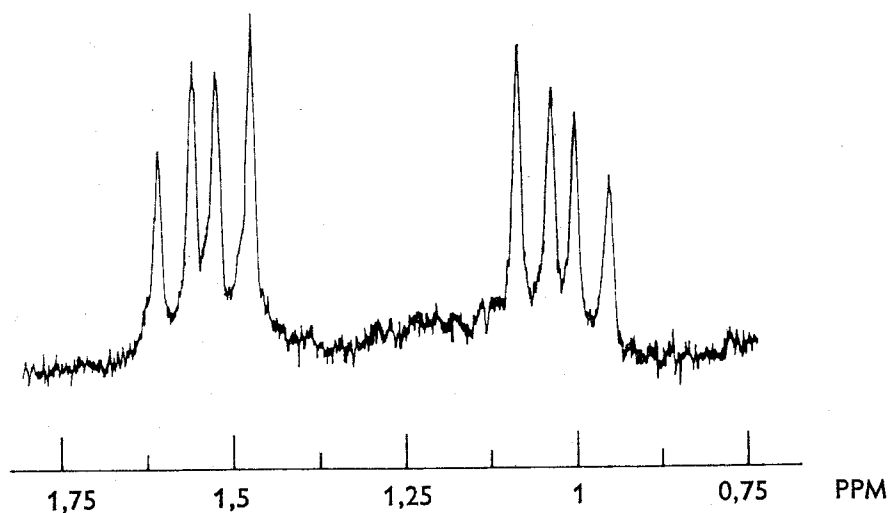
$$1 > P_{TT} - P_{GG} > 0.$$

Therefore, the spectra that early led⁶⁾ to the statement that $\overline{J_{12}} = \overline{J_{13}}$ must be considered as deceptively simple.

In fact, the 100 Mc NMR spectrum under deuterium decoupling conditions of a syndiotactic polymer of *trans* 1.3.3.3 d_4 propylene reported in Fig. 3 clearly shows that $\overline{J_{13}} \neq \overline{J_{12}}$ and may be interpreted as having AA'BB' symmetry with

$$\begin{aligned}J_{AB} (\equiv \overline{J_{12}} = \overline{J_{34}}) &= 4.8 \text{ cps} & J_{AA'} &= 0 \\ J_{AB'} (\equiv \overline{J_{13}} = \overline{J_{24}}) &= 8.3 \text{ cps} & J_{BB'} &= 0 \\ \delta_A &= 1.537 \text{ ppm} \\ \delta_B &= 1.027 \text{ ppm}\end{aligned}$$

^{*)} This corresponds to the assumption that the first alternance of the sequence is *b*. By assuming it to be *a*, the *GG* pairs should be changed into *G'G'*, where $G'G' = 60^\circ 60^\circ$. In this section, both conformations, *GG* of *a* and *G'G'* of *b*, are indicated as "GG conformers", any distinction being unnecessary.

Fig. 3. NMR spectrum of syndiotactic poly *trans* 1.3.3.3 d_4 propylene

where the statement $J_{AB} \equiv \overline{J_{12}} = \overline{J_{34}}$ and $J_{AB'} \equiv \overline{J_{13}} = \overline{J_{24}}$ is a consequence of the performed conformational analysis.

The symmetry of the spectrum of Fig. 3 shows that the polymer of *trans* 1.3.3.3 d_4 propylene is di-syndiotactic¹⁾.

A di-syndiotactic polymer (Fig. 4 a) may be obtained (from the *trans* monomer used by us or indifferently from the *cis* monomer) only if the

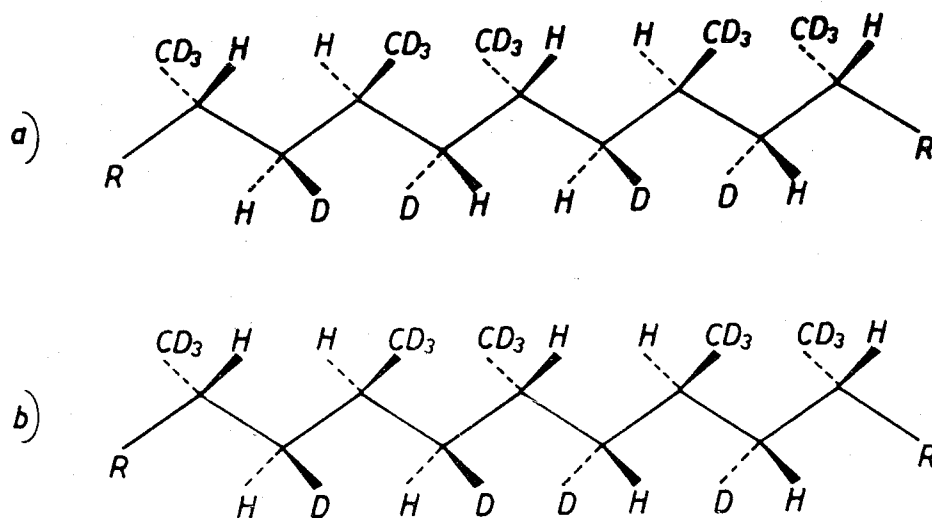


Fig. 4. a) Di-syndiotactic polymer
b) Polymer syndiotactic only with regard to tertiary C atoms

double bond opening is constant^{1,7)}. Instead, were the double bond opening casually *cis* or *trans*, a polymer like that of Fig. 4 b would be always obtained.

To confirm the above data we calculated again, obtaining a sufficient agreement with the experimental spectrum (Fig. 5), the spectrum of

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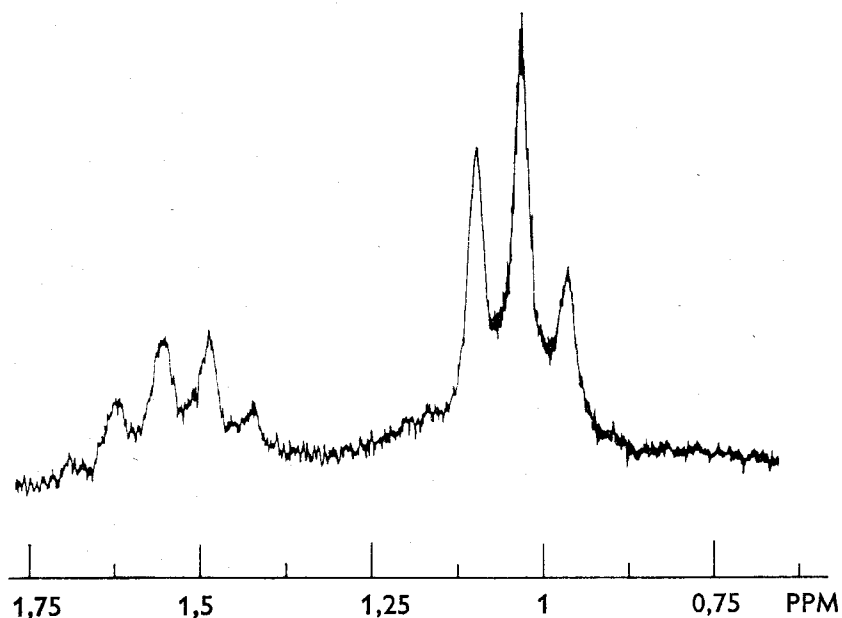


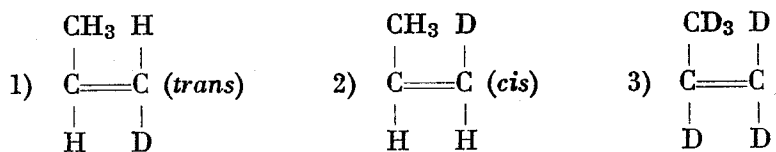
Fig. 5. NMR spectrum of syndiotactic poly 3.3.3 d₃ propylene

syndiotactic poly-3.3.3-d₃ propylene as having symmetry AA'B₂B₂' (instead of A₂B₄⁶⁾) with the following parameters:

$$\begin{aligned} \delta_A &= 1.537 \text{ ppm}; & \delta_B &= 1.027 \text{ ppm} \\ J_{AB} &= 4.8 \text{ cps}; & J_{A'B} &= 8.3 \text{ cps} \\ J_{AA'} &= 0 & J_{BB'} &= 13.5 \text{ cps} \end{aligned}$$

As to geminal coupling $J_{BB'}$, we have arbitrarily chosen the value of the corresponding geminal coupling that may be detected in the spectrum of isotactic polypropylene⁶⁾.

We established the type of addition to the double bond by syndiotactic copolymerization of the monomers



The monomers above copolymerize with a random distribution of the different monomer units, being, apart from the isotopic effect which is negligible for our purposes:

$$K_{11} = K_{12} = K_{21} = K_{22} = K_{13} = K_{31} = K_{23} = K_{32} = K_{33}$$

where K's are the kinetic constants of addition among the different monomers.

Thus, by copolymerizing an excess of monomer 3 with a defect of monomer 1 and 2, respectively, two copolymers will be obtained (1 + 3 and 2 + 3), in which most units deriving from 1 or 2 will be adjacent to two units deriving from monomer 3.

The opening being constant, pairs of monomers 1 + 3 and 2 + 3 will yield two different copolymers, A and B, in which the hydrogen-containing monomer units will be situated as shown in Fig. 6 in planar zig-zag projection, or in the mirror situations.

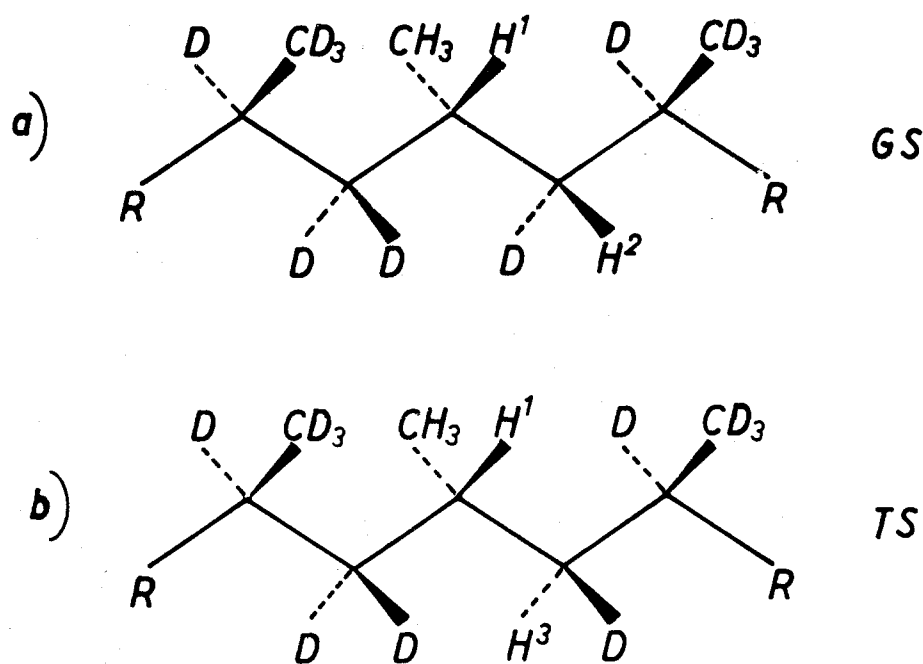


Fig. 6. a) *GS* copolymer. b) *TS* copolymer

As can be seen, the two copolymers are different. In Fig. 6a there are only the two hydrogens H^1 and H^2 placed on the same side of the plane containing the chain in zig-zag projection, while in Fig. 6b there are only the H^1 and H^3 hydrogens situated on opposite sides.

To make a distinction between the two products, we shall call *GS* (*gauche syndiotactic*) copolymer A, and *TS* (*trans syndiotactic*) copolymer B, with reference to the internal rotation angles $H-C-C-H$ in the conformers *TT* of the alternances (see Fig. 2).

A copolymer *GS* will be obtained by copolymerization of monomers 1 + 3 and a copolymer *TS* by copolymerization of monomers 2 + 3 if the double bond opening is *cis*, whereas if the opening is *trans*, copolymer *TS* will be obtained from monomers 1 + 3 and copolymer *GS* from monomers 2 + 3 (Fig. 7).

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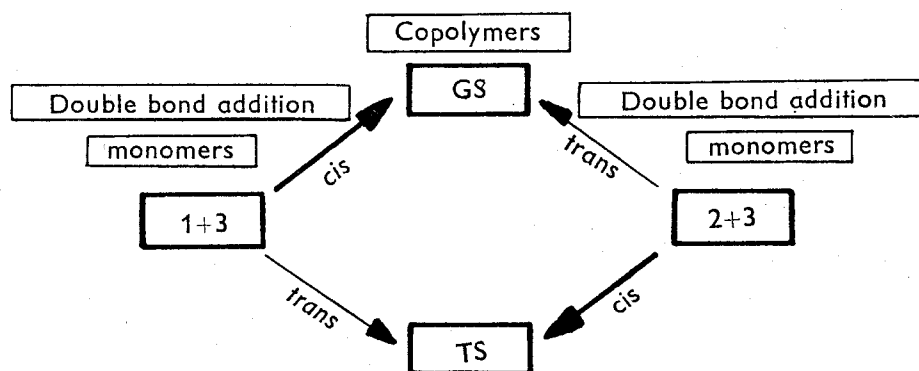


Fig. 7. Steric relationships monomers-copolymers vs. the addition to the double bond

In the case of the monomers considered the structure of the two copolymers may be easily established by NMR analysis. In fact, as we have seen,

$$\overline{J}_{12} = 4.8 \text{ cps}$$

$$\overline{J}_{13} = 8.3 \text{ cps}$$

The NMR spectra of the copolymers prepared from C_3D_6 (80 %) and the minor comonomers (20 %) are reported in Figs. 8 and 9. The values of

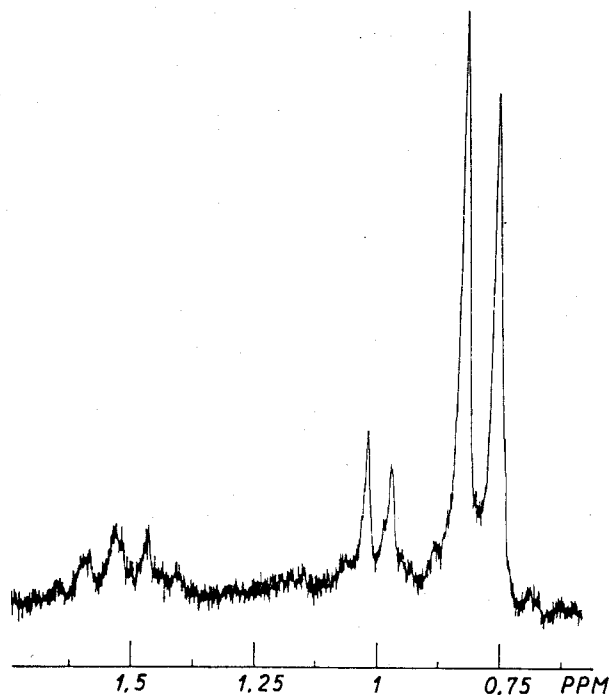


Fig. 8. NMR spectrum of the syndiotactic copolymer 1 + 3 (GS)

the vicinal coupling constants that may be drawn simply on inspection of the parts of the spectra considered concerning the methylenic protons show that the copolymer GS is obtained from 1 + 3, while the copolymer

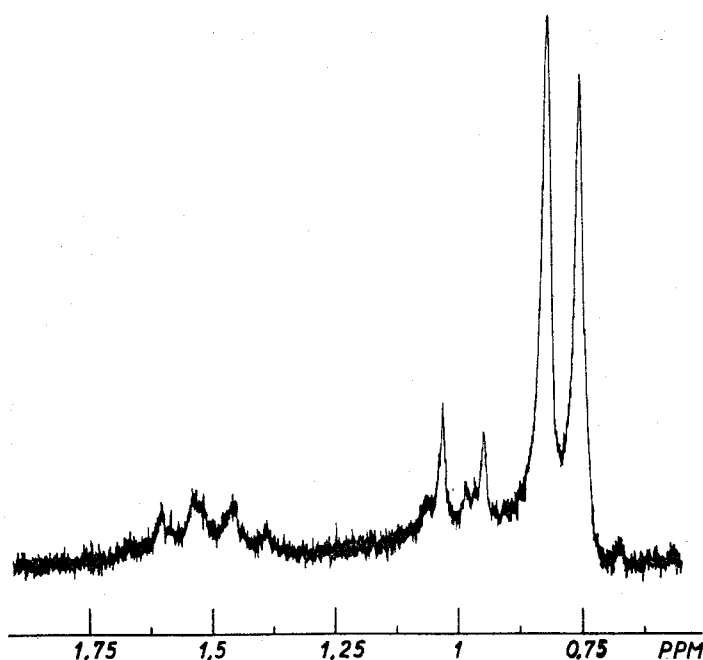


Fig. 9. NMR spectrum of the syndiotactic copolymer 2 + 3 (TS)

TS from 2 + 3. It is therefore established that the double bond addition in the polymerization of propylene to syndiotactic polymer is of the *cis* type in the presence of the catalyst used by us (see experimental part)*).

b) *Isotactic Polypropylene*

By arbitrarily fixing the orientation of the macromolecules from left to right and by observing them from the right, isotactic polypropylene may be described as a mixture of macromolecules consisting of *aa...* or *bb...* successions of permanences (or isotactic diads), *a* and *b* being mirror images, and each permanence sharing the tertiary C with the adjacent ones.

Obviously we will only consider permanences *a* (Fig. 10). The hydrogens in Fig. 10 are labelled, the same labelling being used in the whole part of this paper concerning the isotactic polymerization.

*) The area (A) of the doublet concerning methylenic protons in Fig. 8 does not only represent the methylenic protons (H_{313}^2) of the sequences of monomeric units 313.

Actually

$$A \propto \sum_{n=1}^{\infty} \frac{1}{n} H_{3(1)n}^2$$

because only the summation considered comprises all the H^2 only coupled with H^1 in alternances *a* considered, and therefore useful for the determination of the type of addition to the double bond. Just for the sake of simplicity we uniquely considered in the discussion sequences 313. Analogous considerations are valid for the doublet concerning methylenic protons H^3 in Fig. 9.

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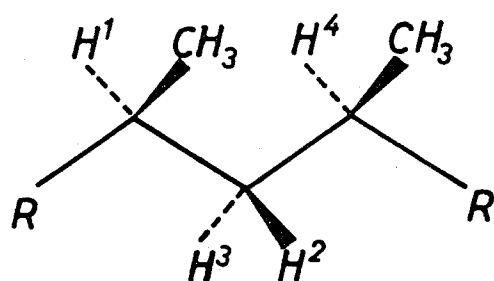


Fig. 10. Permanence *a*

A permanence *a* may give rise in solution³⁾ to the conformers shown in Fig. 11.

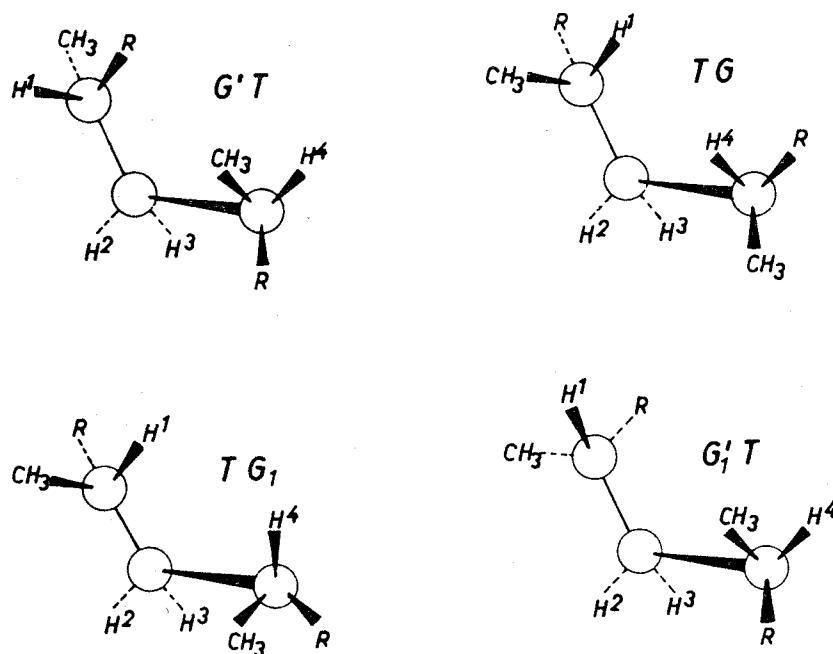


Fig. 11. Allowed conformers of permanence *a*

Conformers *G'T* and *TG* are isoenergetic and isoentropic³⁾. Conformers *TG*₁ and *G*₁'*T* are also isoenergetic and equally probable, but possess a higher energy than the former, approaching eclipsed conformations.

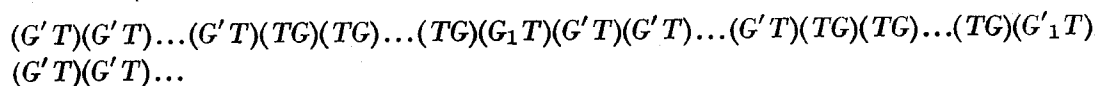
Table 1. Vicinal coupling constants for the conformers of permanences

Con- former	J_{ij}	Con- former	J_{ij}	Con- former	J_{ij}	Con- former	J_{ij}
<i>G'T</i>	$J_{12} = J_g$	<i>TG</i>	$J_{12} = J_t$	<i>TG</i> ₁	$J_{12} = J_t$	<i>G</i> ₁ ' <i>T</i>	$J_{12} = J_G$
	$J_{13} = J_t$		$J_{13} = J_g$		$J_{13} = J_g$		$J_{13} = J_G$
	$J_{24} = J_t$		$J_{24} = J_g$		$J_{24} = J_G$		$J_{24} = J_t$
	$J_{34} = J_g$		$J_{34} = J_t$		$J_{34} = J_G$		$J_{34} = J_g$

The symbol J_G indicates the vicinal coupling constant when the internal rotation angle H-C-C-H is about $\pm 120^\circ$.

Table 1 reports the coupling constants (J_{ij}) concerning the vicinal hydrogens directly bound to skeletal carbons in the different conformers.

According to CORRADINI and ALLEGRA³⁾, the conformers of permanences *a* may follow one another in a chain as



any other possibility leading to strong non bonded interactions. Thus for every passage from the clockwise helix $(TG)(TG)\dots$ to the counterclockwise one $(G'T)(G'T)\dots$, a conformer G_1T or a conformer $G_1'T$ must exist; therefore, if the probability to have an inversion from the clockwise helix to the counterclockwise one in correspondence of a permanence *a* is *P*, the probabilities of existence of the different conformers will be:

$$P_{G_1T} = P_{G_1'T} = \frac{P}{2}$$

$$P_{G'T} = P_{TG} = \frac{1-P}{2}$$

The coupling constants (J_{ij}) between the pairs of vicinal hydrogens directly bound to skeletal carbons averaged for the rapid interconversion of the conformers will be

$$\overline{J_{12}} = \frac{1}{2} J_t + \frac{1-P}{2} J_g + \frac{P}{2} J_G = \overline{J_{24}}$$

$$\overline{J_{13}} = \frac{1}{2} J_g + \frac{1-P}{2} J_t + \frac{P}{2} J_G = \overline{J_{34}}$$

We observe that $\overline{J_{12}} - \overline{J_{13}} = \frac{P}{2} (J_t - J_g)$ is necessarily positive since $P > 0$

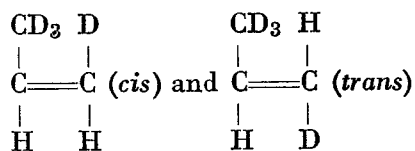
$$J_t - J_g > 0.$$

Actually *P* should be zero only if the considered macromolecules (*aaa...*) in solution, consisted of only one segment of counterclockwise helix followed by only one segment of clockwise helix, or by only one segment of helix: both these hypotheses contrast with measurements of mean square end to end distance and with the IR spectra of the melt polymer⁸⁾.

Therefore, by comparing $\overline{J_{12}}$ (bigger) and $\overline{J_{13}}$ (smaller) we may identify H^2 (*syn* hydrogen according to our previous definition⁹⁾) and H^3 (*anti* hydrogen).

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In order to establish the type of double bond opening in isotactic polymerization of propylene we analysed the isotactic polymers of



The NMR spectrum of the isotactic poly *cis* 1.3.3.3 d₄ propylene (Fig. 12) has nearly A₂X₂ symmetry with the following parameters: $\delta_A = 1.560$ ppm, $\delta_X = 0.857$ ppm, $J_{AX} = 7$ cps.

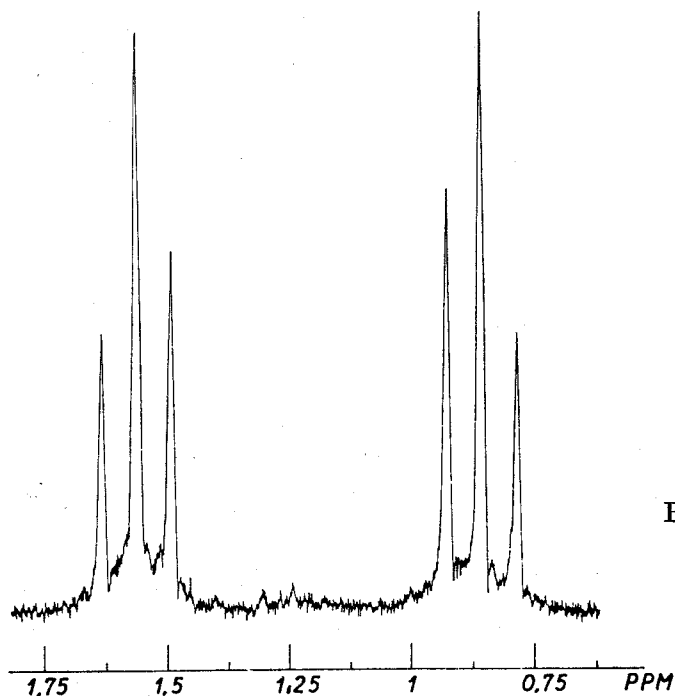


Fig. 12. NMR spectrum of isotactic poly *cis* 1.3.3.3 d₄ propylene

The NMR spectrum of the isotactic poly *trans* 1.3.3.3 d₄ propylene (Fig. 13) has A₂B₂ symmetry with the following parameters: $\delta_A = 1.560$ ppm, $\delta_B = 1.248$ ppm, $J_{AB} = 5.7$ cps.

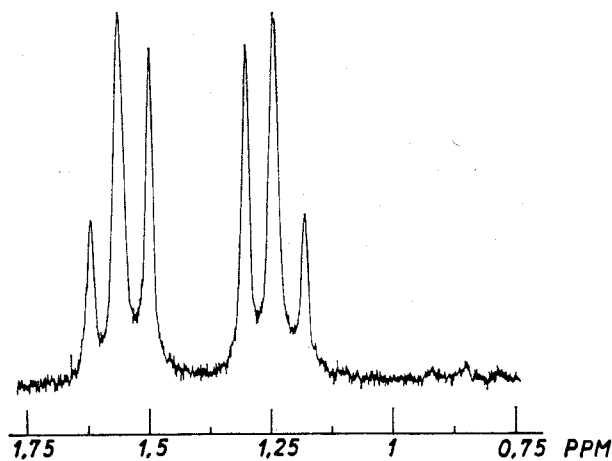


Fig. 13. NMR spectrum of isotactic poly *trans* 1.3.3.3 d₄ propylene

J_{AX} (= 7 cps) $>$ J_{AB} (= 5.7 cps) shows that the *syn* hydrogens (H^2 in Fig. 10) are present only in poly *cis* 1.3.3.3 d_4 propylene and the *anti* hydrogens (H^3 in Fig. 10) are present only in poly *trans* 1.3.3.3 d_4 propylene.

We can therefore confirm^{1,2)} that the addition to the double bond is *cis* also in the isotactic polymerization.

Experimental Part

Polymerizations

The catalyst system for the syndiotactic polymerization was $VCl_4-Al(C_2H_5)_2Cl$ -Anisol at $-78^\circ C$ ¹⁰⁾ in *n*-heptane; for the isotactic polymerization, the catalyst was $\delta-TiCl_3-Al(C_2H_5)_2I$ at $0^\circ C$ in *n*-heptane¹¹⁾.

Monomers

Deuterated monomers were prepared starting from Mg_2C_3 , PBr_3 , D_2O and H_2O according to literature^{9,12-14)}.

Isotopic purities were established by mass spectrography ranging between 96 and 99%.

The steric purity of *cis* and *trans* isomeric monomers was controlled by NMR to be always higher than 95%.

NMR spectra

were run at $130^\circ C$ for syndiotactic polymers and at $150^\circ C$ for the isotactic ones under deuterium decoupling conditions. All the examined polymers had been dissolved in *o*-dichlorobenzene containing hexamethyldixyloxane (5% by volume) as internal reference. Concn. of the polymers ranged from 50 to 100 mg/ml of solvent.

A Varian HA 100 spectrograph and a heteronuclear spin decoupler SD 60B NMR Specialities externally locked by an oscillator Hewlett Packard 204 B were used.

Calculations of the spectrum reported in Fig. 5 were performed by Laokoon 3 program¹⁵⁾.

Parameters were not refined due to the band width of ~ 2 cps.

Conclusion

The addition to the double bond is of the *cis* type also in the syndiotactic polymerization of propylene.

The *cis* type addition refers to the overall stereochemical mechanism, *i.e.* when the monomer unit $(C_3H_6)_1$ is inserted in the chain.

The meaning of it may be that also the addition of $(C_3H_6)_1$ on the transition metal-carbon bond is *cis* or that the addition is *trans* followed by configuration inversion of the methylene of $(C_3H_6)_{1-1}$.

From a merely formal point of view, the two possibilities are equivalent.

However, by accepting that the polymerization is anionic coordinated^{10,16)} the second hypothesis must be rejected.

Actually in the usual S_N2 reactions the leaving group is *trans* to the nucleophile, this fact causing an inversion of configuration¹⁷⁾.

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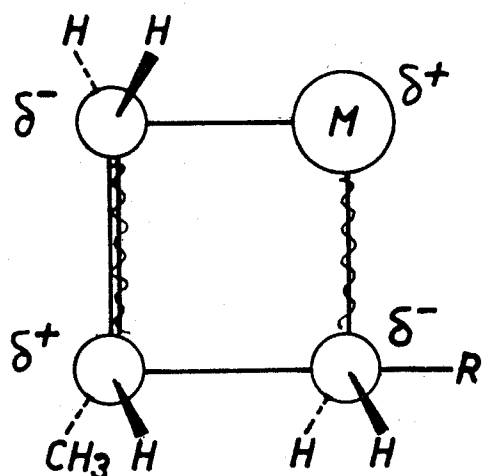


Fig. 14. Intermediate state before double bond opening. The bonds that break during addition are crossed out. The disposition of the substituents on the C belonging to the four-centered complex is arbitrary

On the contrary, in this case the intermediate four centered complex may pass to final state only by cleavage of a *cis* bond with respect to the bond that forms (Fig. 14), and this should involve configuration retention.

We wish to thank Dr. A. L. SEGRE for running the spectra of the samples and Dr. M. FARINA for helpful discussions.

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