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CONSIGLIO NAZIONALE DELLE RICERCHE

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Illuminated table and motion picture film
schematically representing the catalytic
mechanism for the stereospecific polymerization
of propylene

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of the Exposition Universelle de Bruxelles)

ROMA - 1958

The studies carried out by the A. and coworkers within these last five years have allowed to obtain for the first time giant molecules (polymers), starting from small molecules (monomers), corresponding to different architectural models according to a predetermined order.

Before these discoveries, natural giant molecules were known (cellulose, starch, silk, wool, natural rubber) corresponding to a regular repetition of definite structural models, which have had a remarkable importance for mankind since prehistory, as foods and constructional materials.

Men did not succeed before in synthetically producing giant molecules having predetermined ordered structures in the case of vinyl monomers

$\left(\text{CH}_2 = \text{C} \begin{array}{l} \text{H} \\ \text{R} \end{array} \right)$ and diolefinic monomers $(\text{CH}_2 = \text{CH} \cdot \text{CR} = \text{CH}_2)$.

This has now been rendered possible by means of the stereospecific catalytic processes, that is to say processes able to selectively direct polymerization toward the formation of chains having a spatial configuration previously established.

By way of an example, propylene, a typical vinyl monomer,

$\left(\text{CH}_2 = \text{C} \begin{array}{l} \text{H} \\ \text{R} \end{array} \right)$ when polymerization starts can assume two equivalent

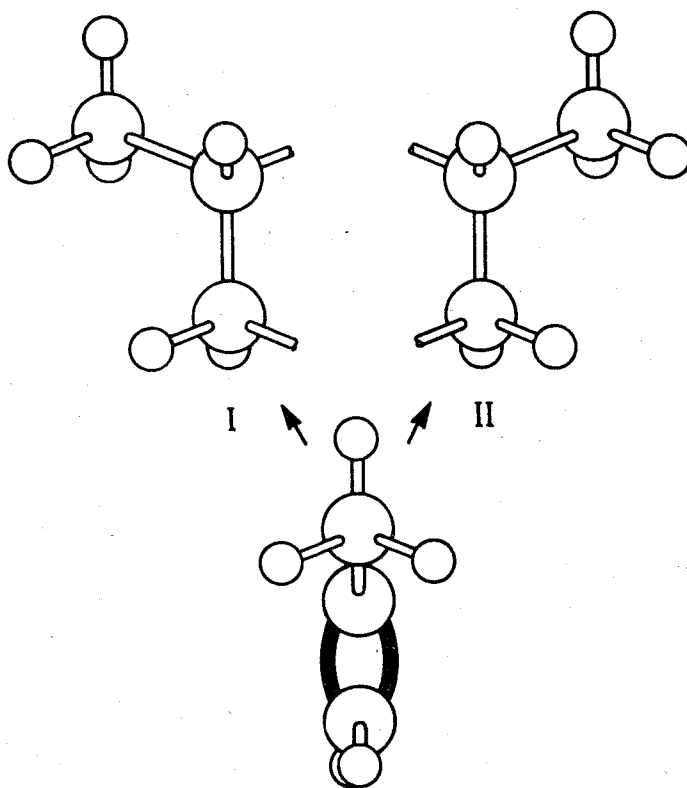
but not superposable spatial configurations as I and II (see fig.).

In the first section of the table one can observe how, when using *non* stereospecific catalysts, polymers consisting of a random succession of monomeric units as I and II are obtained.

The spatial conformation of the resulting chain is shown in the first drawing (top, right) in which only carbon atoms are indicated.

These polymers are amorphous and can not crystallize.

When, on the other hand, stereospecific catalysts are used, ordered



successions of monomeric units, all belonging to the same type, are obtained. In this case the conformation of the resulting chain, as it can be seen in the second drawing (from top, at right) is a very regular one.

The polymers, which have been called by the author « isotactic », are crystalline.

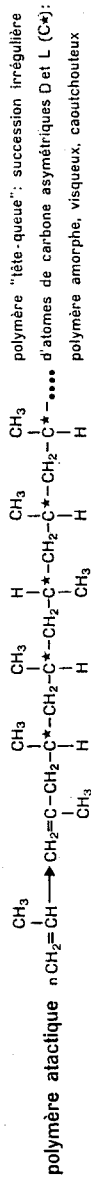
It is possible, at last, to regulate the degree of stereospecificity of the catalyst so as to obtain, at will, polymers which, along their chain bear alternately regular successions of monomeric units all of type I and regular successions of monomeric units all of type II. In this case the resulting polymers have been named by the author « stereoblock- polymers »; they are only partially crystalline (see third drawing from top, right).

In the second section of the table is shown the mechanism, proposed by the author, for the stereospecific polymerization of propylene by means of anionic, coordinated catalysis.

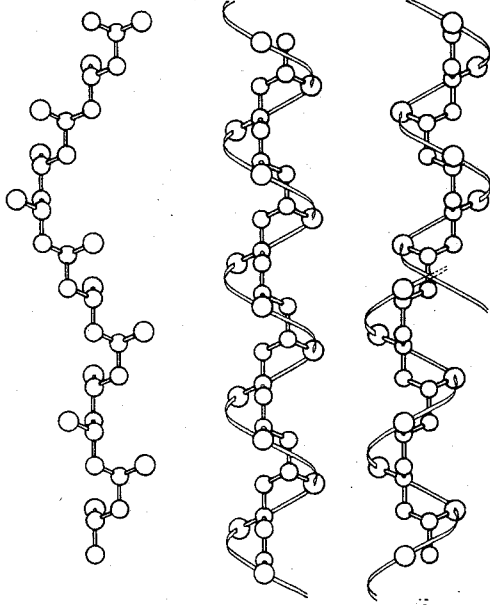
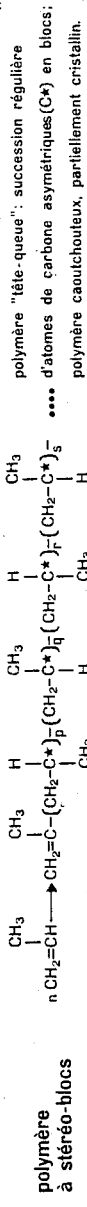
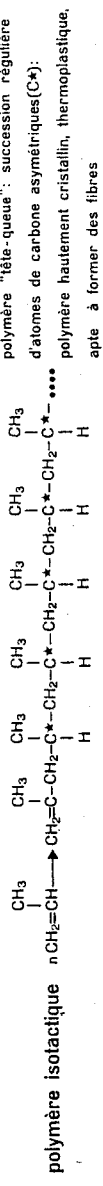
On the edges of a crystalline support having a layer structure (compound of a transition metal), active centers are formed by surfacial reaction with a metal alkyl. These active centers behave as catalyst in a stereoselective way, that is to say, allowing the addition on themselves of successive monomeric units to form the polymeric chain of a giant molecule, always and only according to one of the two possible configurations (I) and (II).

POLYMÉRISATION CATALYTIQUE "tête-queue" DU PROPYLÈNE PAR CATALYSE ANIONIQUE COORDONÉE

1° par les catalyseurs non stéréospécifiques :

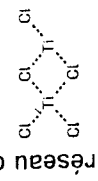
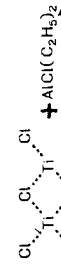
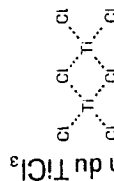
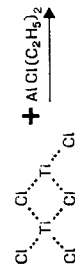


2° par les nouveaux catalyseurs stéréospécifiques :

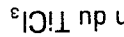
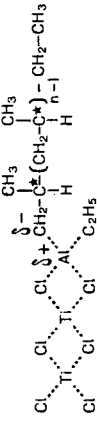


POLYMÉRISATION STÉRÉOSPÉCIFIQUE PAR CATALYSE ANIONIQUE COORDONÉE

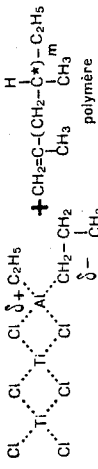
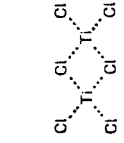
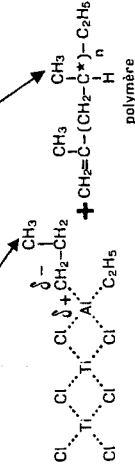
formation de centres actifs stéréospécifiques (complexes polymétalliques) sur la surface du cristal



croissance des chaînes du polymère isotactique



amorçage de nouvelles chaînes et arrêt des chaînes



réseau cristallin du TiCl₃

réseau cristallin du TiCl₃

réseau cristallin du TiCl₃

réseau cristallin du TiCl₃

The four stages of the polymerization process are illustrated in a detailed way, namely:

- formation of the active centers,
- addition of propylene (chain growth),
- chain termination,
- initiation of a new chain.

The mechanism of coordinated anionic catalysis appears evident from the fact that a particular form of carbon atom, rich in electrons (carbon anion) is involved; it coordinates itself to catalytic electron-deficient complexes having a structure of the type shown.

The propylene units, polarized under the strong polar effect of the

$$\begin{array}{c} \text{CH}_3 \\ | \\ \text{CH}_2 = \text{CH} \\ \delta - \quad \delta + \end{array}$$

crystal surface in the sense $\text{CH}_2 = \text{CH}$, arrange themselves one after the other in the bond between the carbon and the complex anion, thus forming new carbon anions able to react subsequently.

The coordinated anionic catalysis has brought to new classes of plastic materials, of synthetic fibers, of elastic rubbers and has allowed for the first time the synthesis of polymers having regular spatial configuration, heretofore known only in nature (rubber and gutta-percha).

Film.

The motion picture film shown nearby represents in a very evident way how propylene monomers can assume, under polymerization conditions, the two different spatial configurations previously mentioned and produce polymeric chains having an ordered spatial structure, called « isotactic ».

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