CONSIGLIO NAZIONALE DELLE RICERCHE

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Models of chain portions of crystallizable polymers having regular structure, obtained by stereospecific polymerization of vinylic and diolefinic monomers

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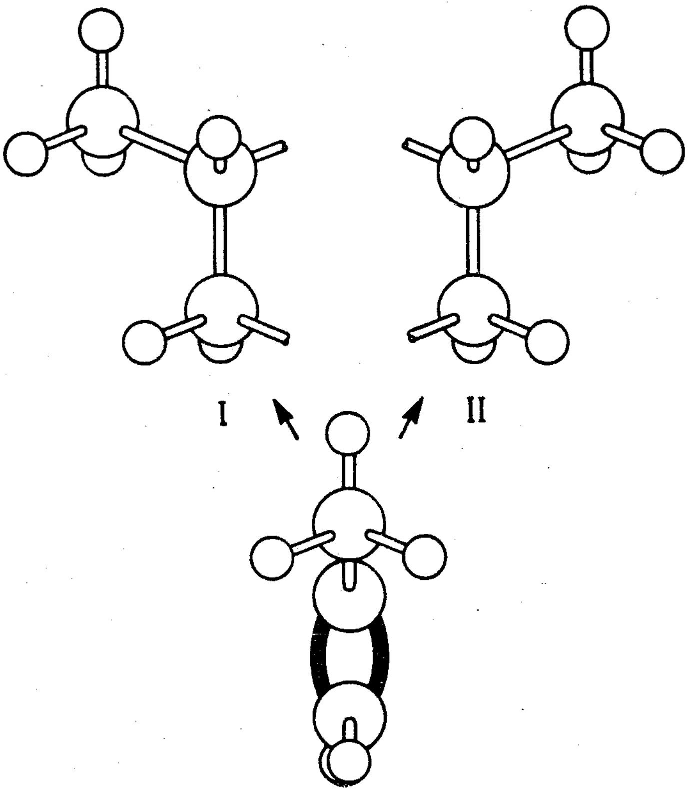
Only by means of stereospecific catalysis the polymerization of vinyl monomers $\left(CH_2{=}C\begin{smallmatrix}\diagup H\\ \diagdown R\end{smallmatrix}\right)$ and of diolefinic monomers ($CH_2{=}CH{-}CR{=}CH_2$) has been possible, so as to obtain polymeric chains having a spatially ordered structure and therefore presenting outstanding properties.

Among the most interesting and significant polymers, some models are described hereinbelow.

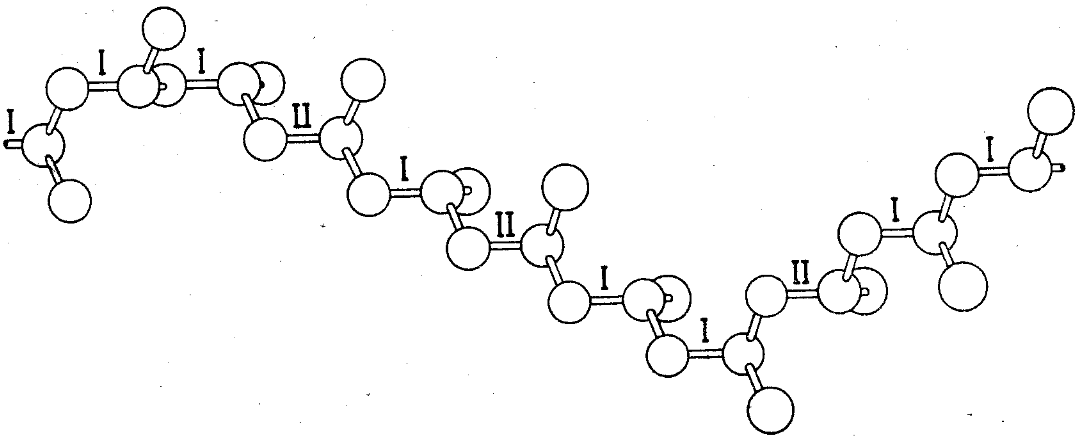
1) Vinyl polymers.

Propylene, a typical vinyl monomer $\left(CH_2{=}C\begin{smallmatrix}\diagup H\\ \diagdown CH_3\end{smallmatrix}\right)$ when head-to-tail polymerization starts can assume two equivalent but not superposable configurations, namely:



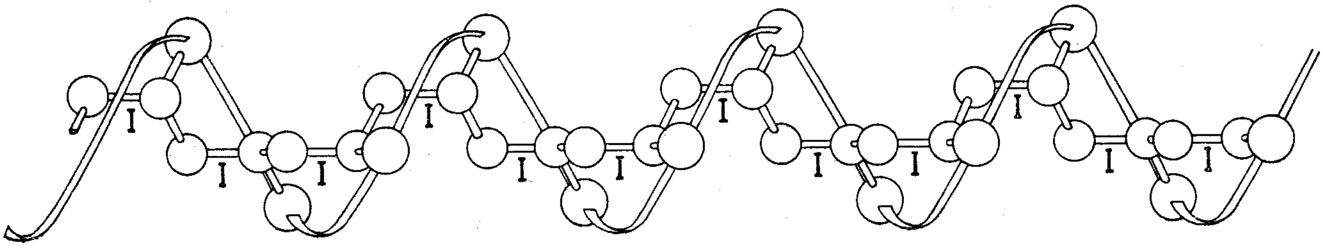
As it is possible to see from the figure, owing to the presence of a tertiary carbon atom with tetrahedral orientation of the four chemical bonds, one configuration is the mirror image of the other one.

By statistical succession of monomeric units of the two types, polymers are obtained, the chain of which has a disordered spatial structure such as (only carbon atoms are drawn):

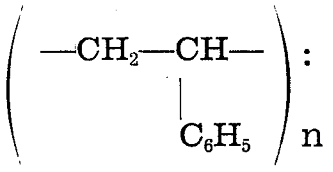


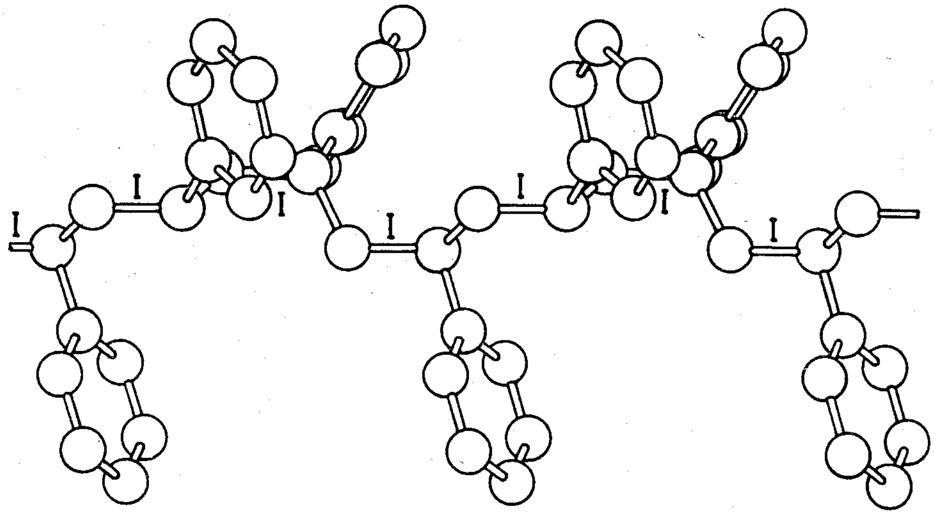
It had not been possible heretofore, that is to say before the discoveries of the A. and his co-workers, to direct the polymerization reaction, starting from vinyl monomers, in such a way so as to obtain along the chain, monomeric units all belonging to the same type.

Isotactic polypropylene, discovered by the A., is characterized by the fact that all the monomeric units along the chain possess the same steric configuration:



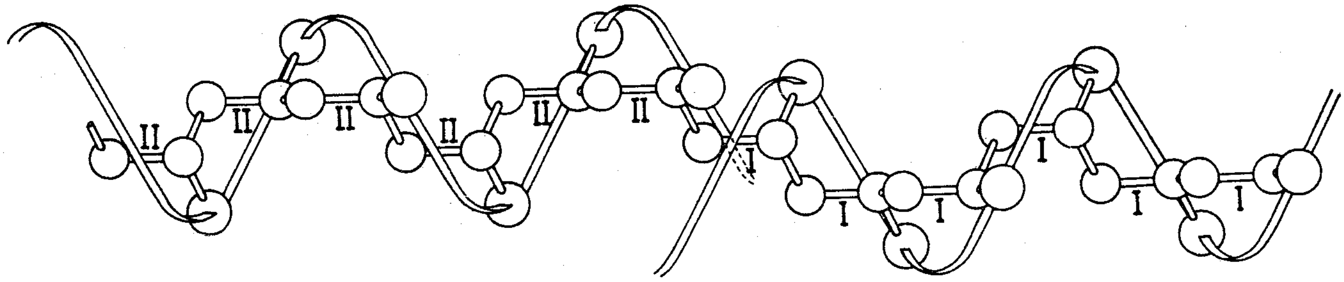
Isotactic polypropylene (contrary to the atactic one, previously known) is a crystalline polymer; it has a high melting point, excellent mechanical properties and can give origin to highly resistant textile fibers and to transparent films.

Also isotactic polystyrene  $\left(\begin{array}{c} -CH_2-CH- \\ \qquad\quad | \\ \qquad\quad C_6H_5 \end{array} \right)_n$:



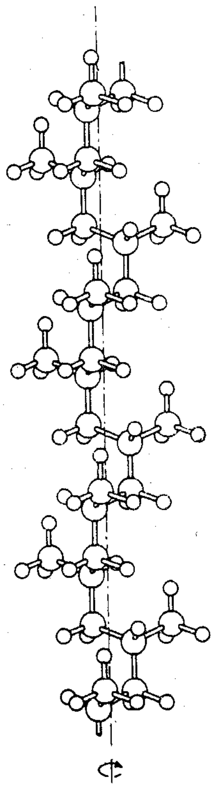
contrary to the previously known type, can crystallize owing to the regularity of its chain and melts ad 230-240° C (446-464° F), that is to say 140-150° C (284-302° F) above the softening point of the corresponding atactic polymer.

Furthermore it is possible to direct the stereospecific polymerization reaction so as to obtain, from time to time, some inversions in the isotactic order:

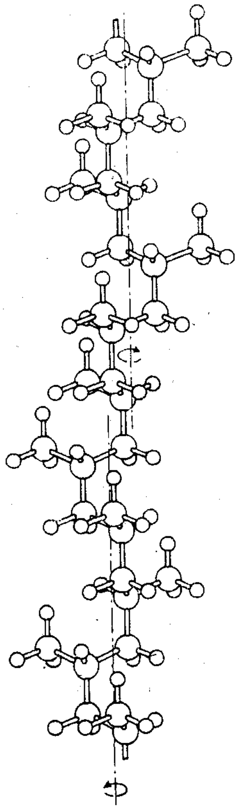


The resulting polymers, called by the A. « stereoblock-polymers », are less crystalline than the corresponding isotactic ones and their properties are intermediate among those of rubber and those of crystalline polymers.

In the pavilion are shown models of chain portions of spatially ordered isotactic polypropylene, which can assume in crystals the configuration of a right helix (model n. 1) or left helix (model n. 3); of isotactic polystyrene (model n. 4); of stereoblock polypropylene (model n. 2).



1



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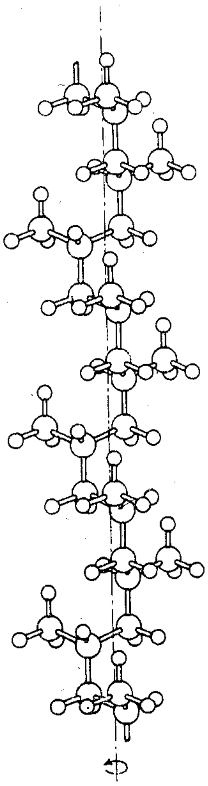

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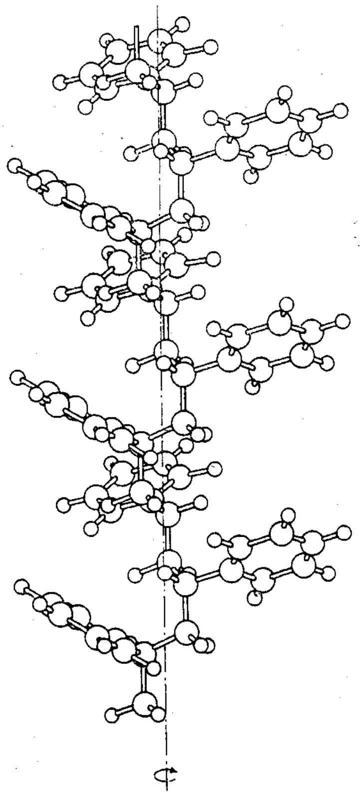

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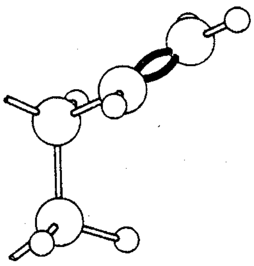
2) Diolefinic polymers.

Butadiene $\overset{1}{C}H_2=\overset{2}{C}H—\overset{3}{C}H=\overset{4}{C}H_2$, a typical diolefinic monomer, can assume when polymerization starts four different spatial configurations, two configurations (I-II), with 1-2 enchainment, equivalent but not superposable, and two configurations (III-IV) with 1-4 enchainment, namely:



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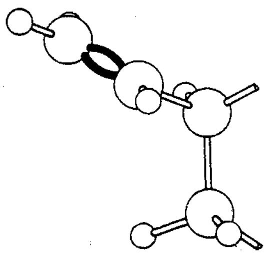

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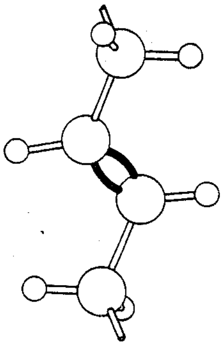
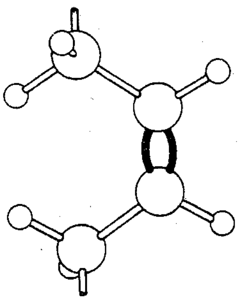


III

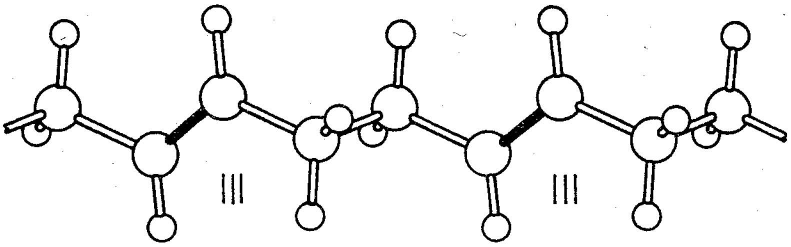


IV

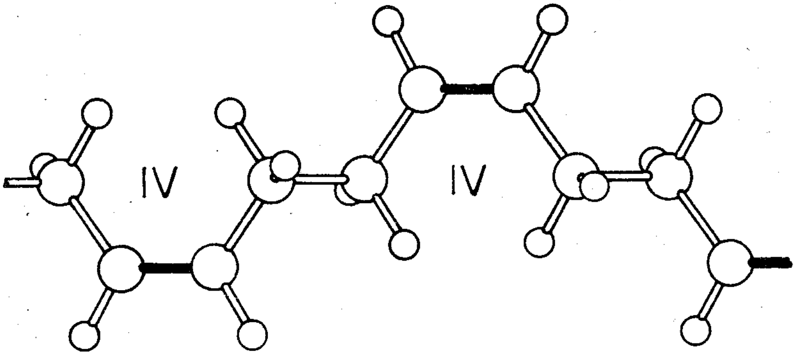
The up to now known polymers, incapable of crystallization, were formed by an irregular enchainment of monomeric units in their four possible configurations, of the following type:

(I) (I) (III) (II) (II) (IV)(III) (IV) (IV) (I)

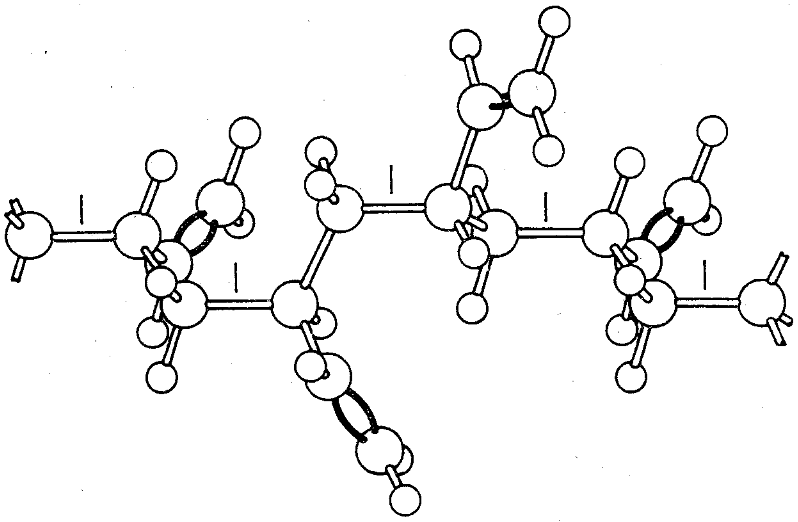
It has now been possible to polymerize butadiene so as to obtain four pure stereoisomers respectively formed by regular successions of monomeric units all belonging to type (III) (1-4 trans polybutadiene):



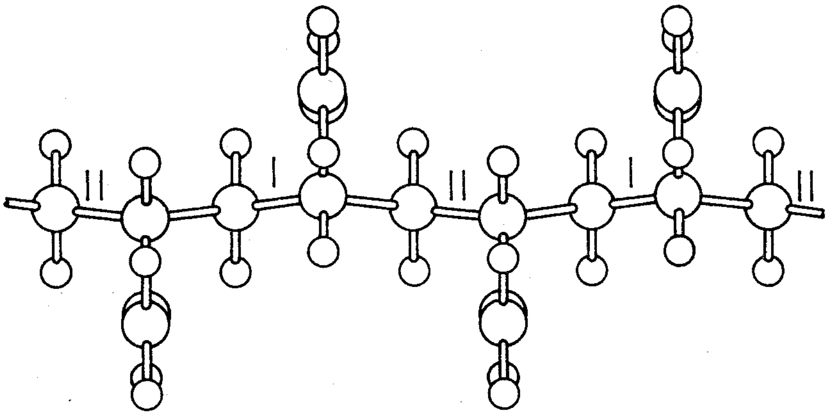
or by regular successions of monomeric units all belonging to type (IV) (1-4 cis polybutadiene):



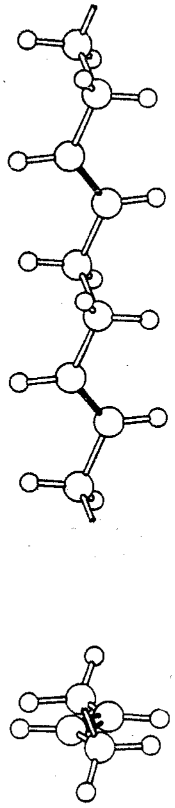
or by regular successions of monomeric units all belonging to type (I) or to type (II) (1-2 isotactic polybutadiene):



or by regular successions of monomeric units alternatively belonging to type (I) and to type (II) (1-2 syndiotactic polybutadiene):



The polymers thus obtained, the structures of which are shown under n. 5, 6, 7, 8 models, have quite different properties, and different also from those of the previously known atactic polymers.



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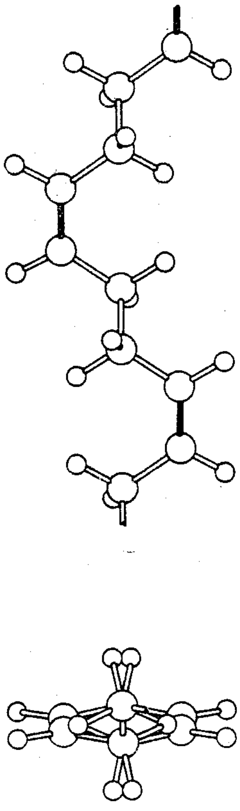

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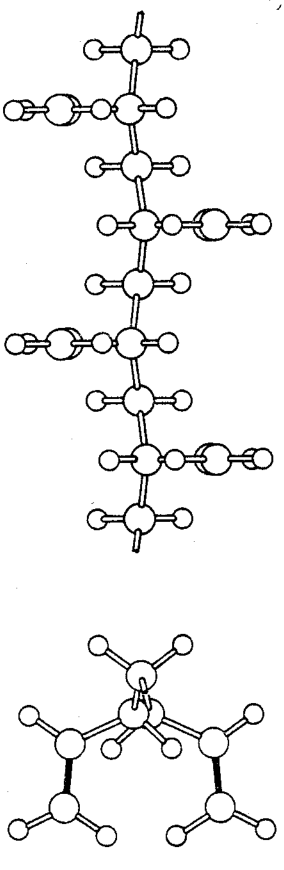

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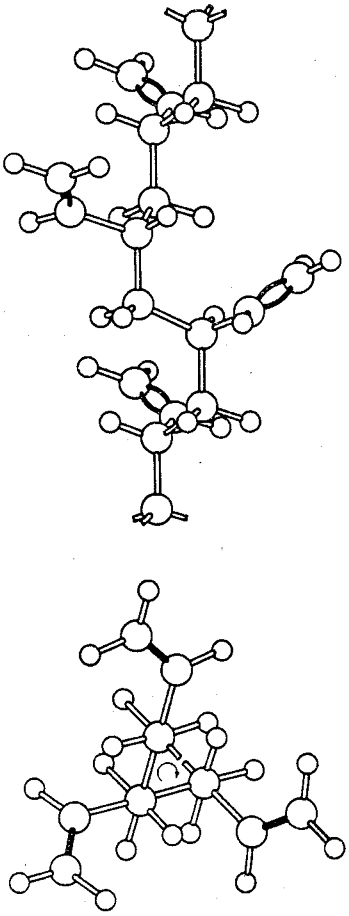

8

By way of example, and this is shown by samples, polybutadiene having the 1-4 cis enchainment can crystallize under stretch and possesses a structure quite similar to that of natural rubber. It can be vulcanized and can give a product having good elastic properties, which can compare with those of natural rubber.

On the contrary, polybutadiene having the 1-4 trans enchainment is a thermoplastic material, similar to natural guttapercha.

The 1-4 trans polybutadiene melts at 140° C and shows another 1st order transition point at 65° C. At this temperature there is a reversible transformation of the crystalline structure into another modification. The latter crystalline modification has a shorter identity period along the polymer chain. A sample of the oriented polymer when heated, reversibly contracts with the possibility of production of mechanical work, behaving therefore very similar to a living muscle.

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