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**Di-Isotactic Polymers of *cis*- and *trans*- β -Chloro-Vinyl Ethers
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Di-Isotactic Polymers of *cis*- and *trans*- β -Chloro-Vinyl Ethers and Factors Determining their Steric Configurations

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SUMMARY:

Some *cis*- and *trans*- β -chlorovinyl alkyl ethers were polymerized in a stereospecific way, with the obtainment of crystalline polymers.

The steric structures of poly(*cis*-) and poly(*trans*- β -chloro vinyl butyl ethers) are different one from another, and more precisely of the *erythro* and *threo* di-isotactic type respectively. These results demonstrate a steric polymerization mechanism, which is identical in both forms, with a *cis* opening of the double bond.

Moreover some aspects of the stereospecific polymerization mechanism of mono-olefinic monomers are discussed. Beside the type of opening of the double bond (*cis* or *trans*), determining the steric ratios inside each monomeric unit, also the mode of attack of the monomer to the chain is considered here. It can take place on one or on the other of the two enantiomer faces (D or L) of the monomer in a constant or in an alternated way. Such a *steric attack* determines the structural relationships between subsequent monomeric units.

ZUSAMMENFASSUNG:

Einige *cis*- und *trans*- β -Chlorvinyl-alkyläther sind stereospezifisch polymerisiert worden, wobei kristalline Polymere erhalten wurden. Die sterischen Strukturen des Poly-*cis*- und des Poly-*trans*- β -chlorvinylbutyläthers unterscheiden sich darin, daß der erstere eine *erythro*- und der letztere eine *threo*-di-isotaktische Struktur besitzt. Diese Ergebnisse beweisen, daß in beiden Fällen eine *cis*-Addition an die Doppelbindung stattfindet; d.h., daß der sterische Polymerisationstyp für die beiden Formen identisch ist.

Es werden außerdem einige Gesichtspunkte des Mechanismus der stereospezifischen Polymerisation von mono-olefinischen Monomeren diskutiert. Außer dem Typ der Öffnung der Doppelbindung (*cis* oder *trans*), der die sterischen Verhältnisse im Innern der einzelnen Monomereinheiten bestimmt, wird die Art des Angriffs des Monomeren auf die Ketten in Betracht gezogen. Dieser kann auf der einen oder auf der anderen Seite der beiden enantiomorphen Flächen (D oder L) des Monomeren in konstanter oder in alternierender Weise stattfinden. Dieser *sterische Angriff* bestimmt die strukturellen Beziehungen zwischen aufeinanderfolgenden Monomereinheiten.

Introduction

The stereospecific polymerization of bi-substituted 1,2-olefins, which has already been the subject of our publications, represents a field of considerable interest since it has allowed us to define a new class of stereo-

regular polymers and to better understand the problems of such polymerizations, providing data, which are also partly extensible to the stereospecific polymerization of α -olefins. In one of our publications¹⁾, we reported the synthesis of polymers, obtained with stereospecific processes of the coordinated-anionic type, having a new type of regular structure from $1d_1$ *cis*- and *trans*-propylenes. Such structures, characterized by the presence of a steric isotactic regularity for each of its series of the tertiary carbon atoms in the chain, were defined by us di-isotactic. In order to differentiate the two possible structures of this type we adopted the prefixes "*erythro*" and "*threo*"²⁾, according to their specific meanings in organic chemistry, for substances of low molecular weight.

Although there is only a negligible difference between the various physical properties (melting point, X-ray diffractions, *etc.*), the regularity of the disposition of the deuterium atoms for each of the two new types of polymers obtained, seems evident from the fact that poly-(*cis*-propene $1d_1$) and poly-(*trans*-propene $1d_1$) have IR spectra definitely different from each other and from those polymers obtained from *cis-trans* mixtures. This might suggest that in the stereospecific polymerization of *cis*- and *trans*-propylenes $1d_1$, (and consequently in α -olefin polymerizations carried out with the same stereospecific heterogeneous catalysts), we have a constant type of opening of the olefinic double bond.

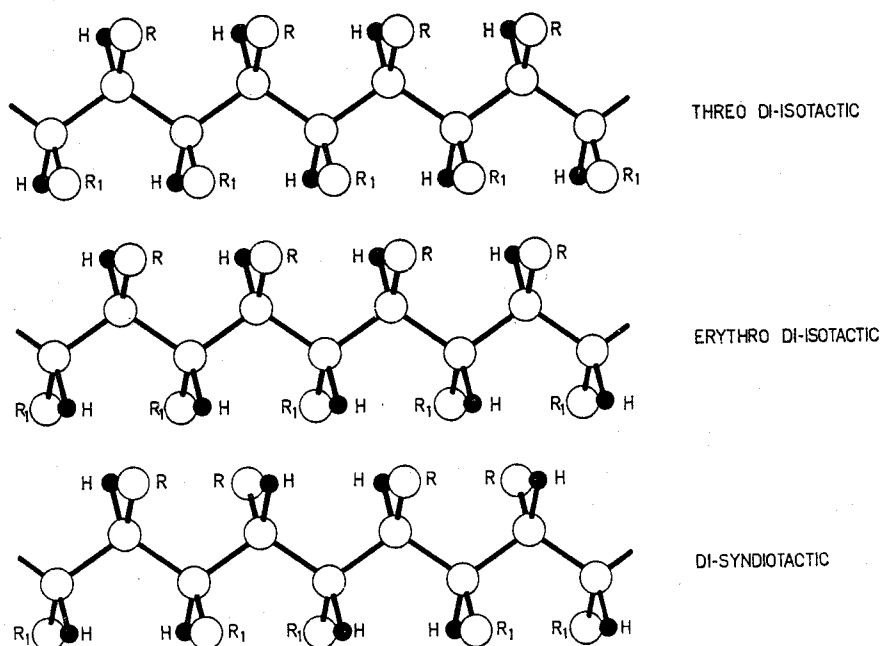


Fig. 1. Zig-zag planar projections of *threo*-di-isotactic, *erythro*-di-isotactic and di-syndiotactic polymeric structures

In addition to the *erythro* and *threo*-di-isotactic structures we had also foreseen the possibility of the existence of di-syndiotactic stereoregular polymers. Their preparation, starting from deuterio-substituted propylenes and employing processes already used in the preparation of syndiotactic polypropylene, is presently the object of one of our research problems.

In Fig. 1 the *erythro* and *threo* di-isotactic structures and also the "di-syndiotactic" structure are represented schematically for a monomer of the general formula $\text{CHA}=\text{CHB}$.

The polymers mentioned here are hydrocarbon-type polymers. Later on, however, we obtained *threo*-di-isotactic crystalline polymers from some *trans*-alkenyl ethers (*trans*-alkyl 2-alkoxy-ethylenes)³⁾.

These polymers were obtained in a different way from the previous ones, with polymerization processes acting by a cationic mechanism. They represented the first examples of crystalline stereoregular polymers of a di-isotactic type, formed from disubstituted monomers of the formula $\text{CHA}=\text{CHB}$, in which also from a reactivity point of view the unsaturation was not of a vinyl type. Furthermore these products were obtained with catalysts differing from the ZIEGLER-type catalysts, since the latter are poisoned by oxygen atoms present in the monomer. In the case of alkenyl ethers only the *trans*-monomer has given crystalline polymers of the "*threo*" type structure, while with the polymerization of the *cis*-isomer we obtained only amorphous polymers for which we could not observe a regularity of structure.

In this note we refer to our further studies of monomers of the formula $\text{CHA}=\text{CHB}$ which have enabled us to obtain crystalline polymers of a different structure, by employing respectively the *cis*- and the *trans*-isomer of such monomers as β -chloro-vinyl-ethers (1-chloro-2-alkoxy ethylenes). They confirm some of our predictions which were advanced from our work on vinyl polymers and provide new examples of stereospecific syntheses of a new class of stereoregular polytactic polymers, obtained with cationic catalysts.

From our results we have come to consider in more detail some of the geometric aspects of stereospecific polymerization processes.

Preparation and Polymerization of β -Chlorovinyl Ethers

The synthesis of β -chlorovinyl ethers was accomplished by dehydrohalogenation of the corresponding α,β -dichloroethyl alkylethers with diethylaniline. The experimental details, conditions used for the sepa-

ration of the *cis*- and *trans*-isomers, physical constants and infra-red spectra of the monomers are given in another publication⁴).

The polymerization of β -chlorovinyl ethers was carried out in an inert, moisture-free atmosphere, employing cationic catalysts such as boron-fluoride etherate, ethyl aluminium dichloride, or diethyl aluminium chloride. A high degree of stereospecificity is obtained by operating at a low temperature (-75°C .) with an inert solvent (toluene).

The following is a typical polymerization procedure. A sample of 5.6 g. of β -chlorovinyl butylether, having more than 96% *cis*-isomer, was dissolved in 10 ml. of anhydrous toluene and was then slowly added at -75°C . to a solution of 0.25 g. of $\text{AlCl}_2\text{H}_5\text{Cl}_2$ in 30 ml. of toluene, kept under dry nitrogen in a flask equipped with a stirrer. After 15 hrs. the reaction was stopped by the addition of methanol thus allowing the polymer to coagulate. A white, fibrous polymer, soluble in benzene and chloroform but insoluble in acetone, was obtained quantitatively. The intrinsic viscosity, determined in toluene at 30°C ., was $0.8 \cdot 100 \text{ ml./g}$.

When a stretched film was examined by X-ray, a spectrum, typical of crystalline and oriented fibers, resulted. Utilizing the polarizing microscope one can observe the disappearance of a weak dichroism at temperatures higher than 200°C . accompanied by some decomposition.

Other monomers of this class, polymerized according the above-described method, are: *trans*- β -chlorovinyl butylether and *trans*- β -chlorovinyl isobutylether (to crystalline polymers), *cis*- β -chlorovinyl isobutyl ether and *cis*- and *trans*- β -chlorovinyl ethylethers (to polymers which did not result crystalline on X-ray examination).

In Figs. 2, 3, and 4 are reported the infrared spectra of some poly(1-chloro-2-alkoxy ethylenes). These are spectra of films of polymers obtained by evaporation of CS_2 or CHCl_3 solutions on NaCl , and they are very

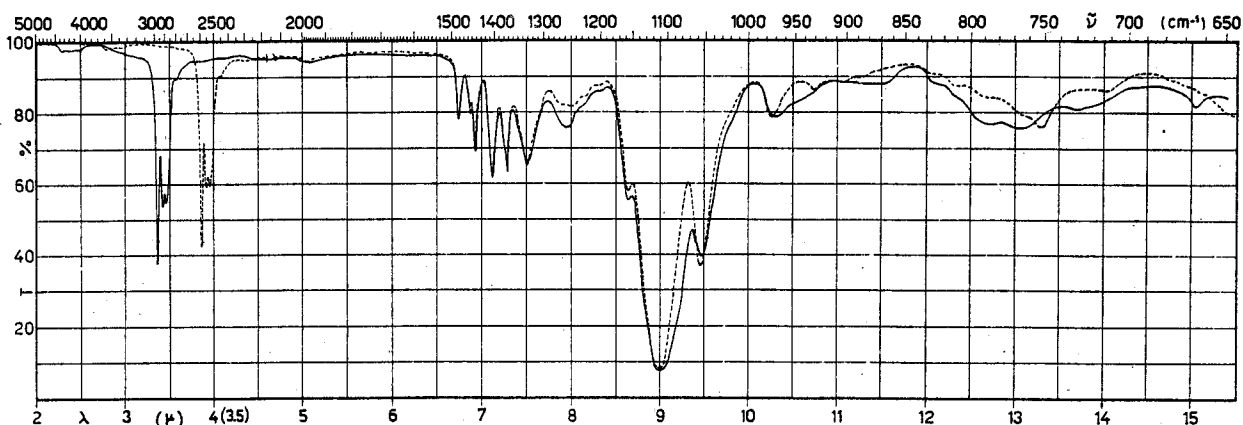


Fig. 2. Infrared spectra of
 ——— poly(1-chloro-2-ethoxy ethylene *cis*)
 - - - - poly(1-chloro-2-ethoxy ethylene *trans*)

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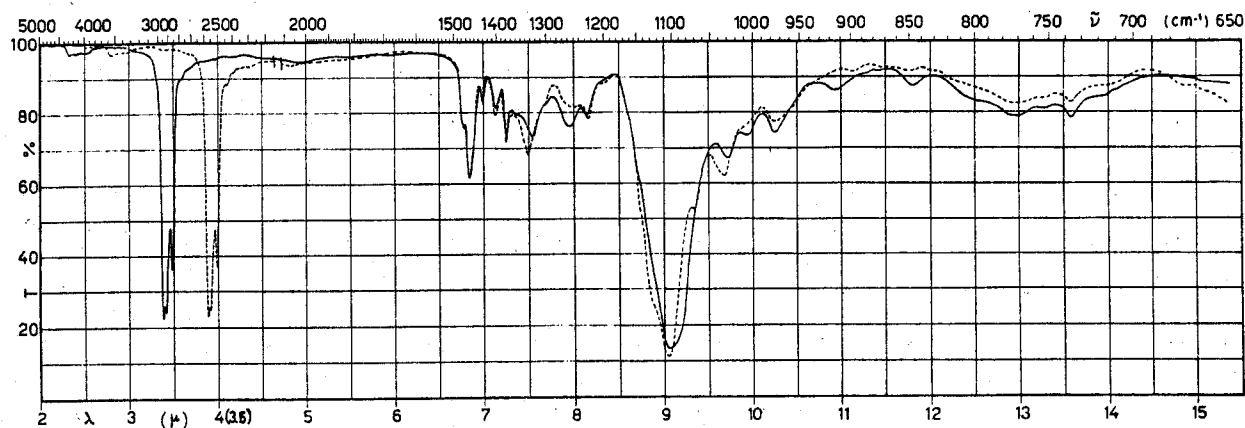


Fig. 3. Infrared spectra of
—— poly(1-chloro-2-butoxy ethylene *cis*)
- - - - poly(1-chloro-2-butoxy ethylene *trans*)

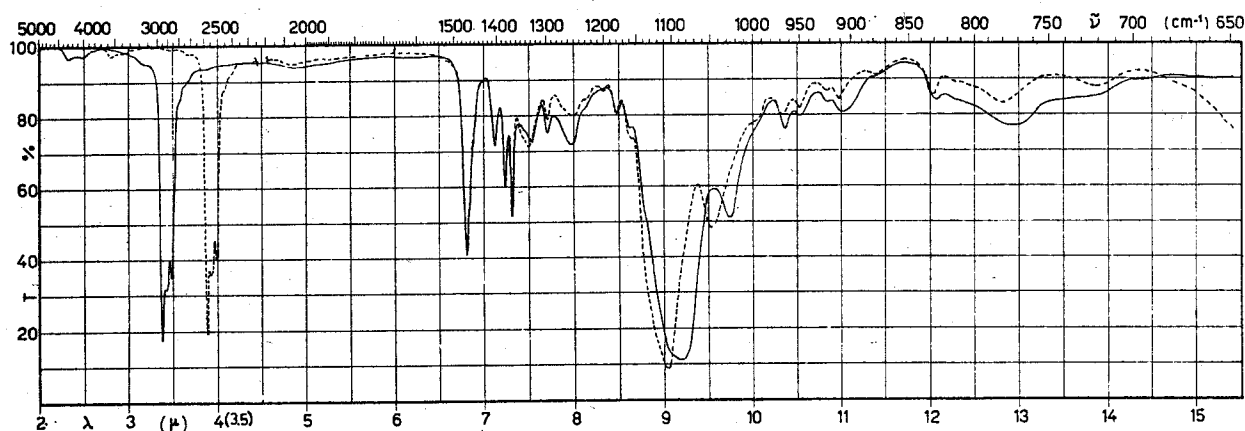


Fig. 4. Infrared spectra of
—— poly(1-chloro-2-isobutoxy ethylene *cis*)
- - - - poly(1-chloro-2-isobutoxy ethylene *trans*)

similar to those of the same polymers in solution. A certain regularity can be noticed in the differences existing between the spectra of polymers obtained from *cis*-isomers and those obtained from the *trans*-isomers.

Structure of Polymers

A study of the crystalline structure of the polymers so prepared was done by P. CORRADINI and P. GANIS. It revealed interesting conclusions⁵⁾, which we summarize briefly here. The poly(*trans*-1-chloro-2-isobutoxy ethylene) has an identity period of $20.8 \pm 0.20 \text{ \AA}$, with a helicoidal type of chain spaced at $10/3$. Poly(*trans*-1-chloro-2-butoxy ethylene) possesses an helical structure spaced at $3/1$ with an identity period of $6.5 \pm 0.10 \text{ \AA}$.

The study on the conformation of such polymers has permitted to assign a threo-di-isotactic structure to these products, analogous to that already attributed to poly(*trans*-methyl isobutoxy ethylene)³).

The X-ray examination of poly(*cis*-1-chloro-2-butoxy ethylene) allows to determine a helical structure of type 4/1 with an identity period of 8.6 ± 0.10 Å. Corresponding to such a structure are angles of internal rotation of $\sim 90^\circ$ and $\sim 180^\circ$.

A study of the change of the internal energy for the isolated chain, as a function of such angles, both for the *threo* and for the *erythro* configuration, has permitted us to attribute an *erythro*-type structure to poly(*cis*-1-chloro-2-butoxy ethylene). The energy curve shows indeed a minimum, which is properly accentuated for angles of rotation close to those found experimentally. This structure is further proved by the FOURIER transforms, elaborated by optical methods.

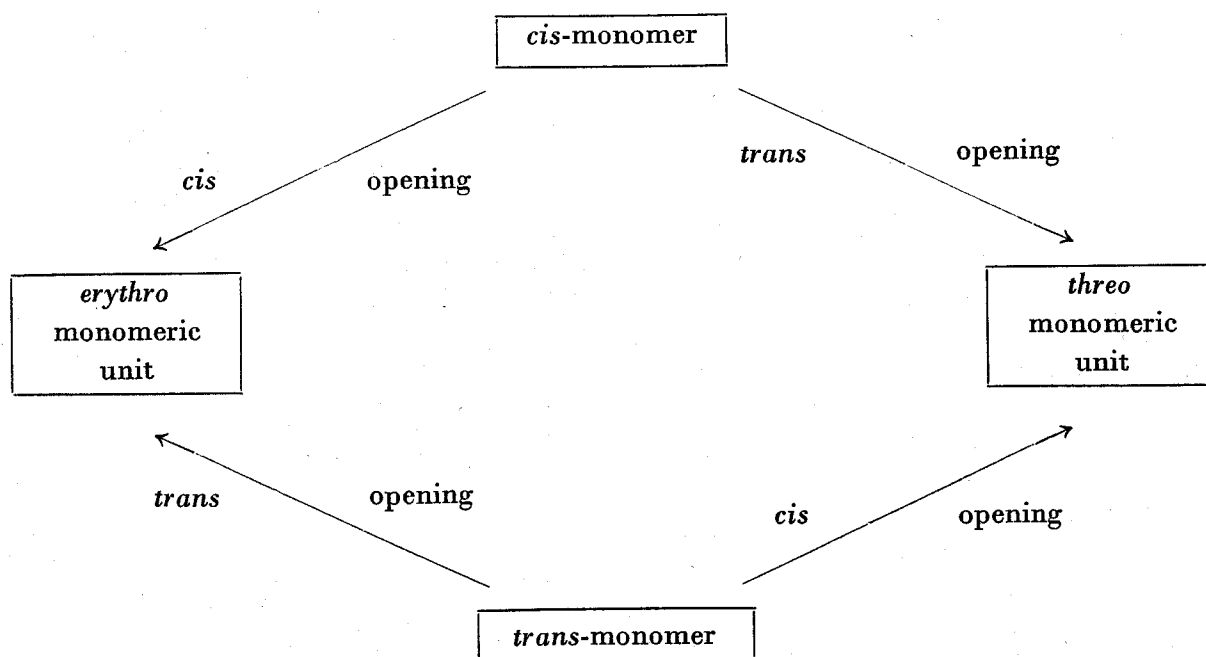
The conclusions reported, in fact, can be considered as reliable, because in all the cases in which a complete determination of the crystalline structure was made, chain configurations and conformations were found, which correspond to those foreseen on the basis of the energetic considerations mentioned above.

General Considerations on the Steric Aspects of Addition Mechanism of Monoolefinic Monomers

It has already been pointed out by ARCUS⁶) that, from a steric point of view, polymerization processes could be described in terms of the relative presentation of the monomers and of the type of addition of the ethylenic double bond in the monomer itself.

The opening of the double bond, *cis*- or *trans*- or the addition *cis*- or *trans*- on the double bond, determines the way in which new bonds are formed in relation to the plane of the six atoms which form the unsaturated planar system and defines the steric relationships within a 1,2-bisubstituted monomeric unit of formula $-\text{CHA}-\text{CHB}-$, according to the following scheme²).

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It must be observed, however, that such considerations are related to the final result of all the steps in the addition process and not just to that of the monomer to the growing chain-catalyst system. The above-scheme refers to a monomeric unit within the chain, bound to other monomeric units on either side*).

The steric relations between the neighboring monomeric units are determined by the manner in which the new monomers are joined to the growing chain. The molecule of an olefinic compound which has no asymmetric substituents, possesses at least one plane of symmetry (that on which are the two unsaturated atoms and those four which are directly bound to them), which divides the molecule into two parts, not superimposable in types such as: $\text{CHA}=\text{CH}_2$, $\text{CHA}=\text{CHB}$, *trans*- $\text{CHA}=\text{CHA}$ and $\text{CAD}=\text{CBE}$. In such cases one could affirm that the two halves of the molecule are enantiomorphous and they possess those known properties of optical antipodes. In particular the reactivity of the two faces toward

*) The intermediate steps, might have a different, more complex steric course: in particular, the terminal carbon atom, bound to the catalytic system, at the moment of a new monomer addition, could or could not undergo an inversion of its own configuration. For example, a *cis*-addition to the chain-catalyst system, results in *cis*, only if the addition of the successive entering monomers takes place without an inversion of the configuration of the atom under consideration. In a contrary case the ultimate result is analogous to that of a *trans*-addition. These considerations gain ground on the basis of numerous examples in organic chemistry. The synthesis of α,β -glycols from olefins, for example, carried out in the presence of peracids follows a *trans*-route, even if the intermediate epoxide, in many cases isolable, is obtained by *cis*-addition. The hydration which follows in the reaction occurs by WALDEN inversion.

a reagent which does not have optical stereoisomeric centers, (and in a symmetric environment) will be identical (addition of halogens, hydrohalogen acids, etc.), while toward an asymmetric reagent their reactivity will be different. An addition, on one or on the other of the two faces will lead in such a case to diastereoisomeric compounds. The two faces can be conventionally designated as the D and L faces. In the *cis*-isomers of those monomers having a formula $\text{CHA}=\text{CHA}$, the two forms are identical; in such a case however, one can still observe in each face a local asymmetry around each of the unsaturated semi-atoms which are enantiomers and they also can be conventionally designated as D and L.

In a stereospecific polymerization, the attack will take place on a determined atom (I in Fig. 5) on just one side of the entering monomer and not on the other side (or just on the half of a certain sign of either equal unsaturated atoms in the case of *cis* $\text{CHA}=\text{CHA}$ monomers).

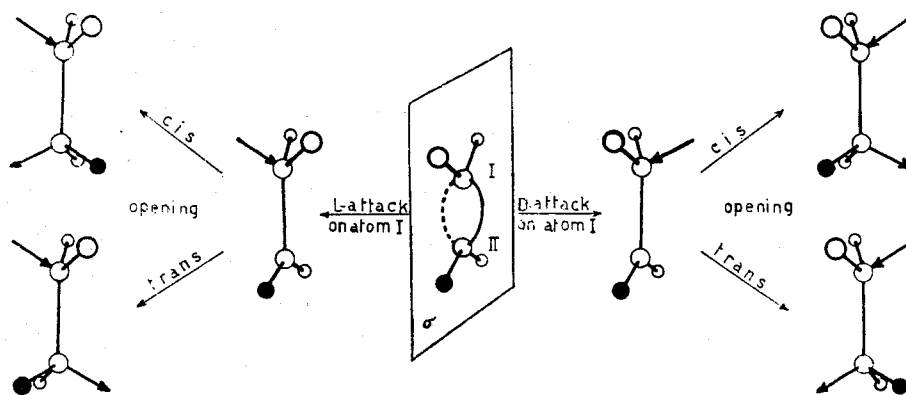


Fig. 5. Scheme of a D(L) attack on a monoolefinic monomer

We can then speak of a D(L) attack to the chain and as a consequence of it we can speak of a constant or alternating *steric attack* when such an attack occurs always on the same side or alternately on one or the other side, respectively. The steric course of addition, so defined, determines unequivocally the sign of the entering monomeric unit, (or at least of the carbon atom, which was first bound to the growing chain in the case of a non-constant opening). We can write therefore the unequivocal relationships:

- (1) constant steric attack \rightarrow isotactic polymeric structure
 alternating steric attack \rightarrow syndiotactic polymeric structure

In Table I are summarized the steric relationships between the structures of the monomer and of the polymer as a function of the opening and steric attack for those olefinic 1,2-bisubstituted monomers with the formula $\text{CHA}=\text{CHB}$.

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Table 1. Steric relationships between the structures of the monomer and of the polymer

Monomer	Type of opening	Steric attack	Structure of the polymer
<i>cis</i>	<i>cis</i>	constant	<i>erythro</i> di-isotactic
<i>trans</i>	<i>trans</i>	constant	<i>erythro</i> di-isotactic
<i>trans</i>	<i>cis</i>	constant	<i>threo</i> di-isotactic
<i>cis</i>	<i>trans</i>	constant	<i>threo</i> di-isotactic
<i>cis</i>	<i>cis</i>	alternating	di-syndiotactic
<i>cis</i>	<i>trans</i>	alternating	di-syndiotactic
<i>trans</i>	<i>cis</i>	alternating	di-syndiotactic
<i>trans</i>	<i>trans</i>	alternating	di-syndiotactic

Since it might be useful to speak of the position of the monomer, with respect to the growing chain or to the catalyst, it is also convenient to define a D(L) mode of *steric approach* and a constant or alternating mode of *steric approach*, in a perfect parallel way as it was done for the *steric attack*.

In the above-reported steric considerations, the terms "constant" and "alternating" are referred to that side of the monomer which participates in the reaction; while in a previous paper⁷⁾ they stood for the relative position of certain substituents in the monomer which is to be added and of the same substituents in the monomer already added. The so understood "constant" and "alternating" presentations correspond to the way of presentations [I] and [I'] proposed by ARCUS⁶⁾. An identical relative position is however possible by exposing one molecule to the other from either side of the plane of the adding monomer. Such an ambiguity was implicitly eliminated by specifying the *cis*- or *trans*-type of addition.

One can see that the „mode of presentation" [I] of ARCUS with *cis*-addition and that [I'] with *trans*-addition correspond in both cases to an alternating *steric approach* and to an alternating *steric attack* (thus a syndiotactic structure is obtained). Analogously the "mode of presentation" [I] with *trans*-addition and that of [I'] with *cis*-addition correspond in both cases to a constant *steric approach* and to a constant *steric attack* and to an isotactic structure. The steric attack has the advantage of determining the steric relationship between neighbouring monomeric units, regardless of the type of opening, which in its turn determines unequivocally the steric relationship within the monomeric unit.

In the case of vinyl type monomers ($\text{CH}_2=\text{CHR}$) if they are bound by the end of the growing chain with the group CHR, then scheme 1) is valid, even if the opening is not constant. If instead they were bound

first to the CH_2 group, then we could have a sterically regular structure, even with an irregular steric attack, provided there were a compensation between the irregular type of attack and the opening.

Conclusions

The obtainment of two different di-isotactic polymers on polymerizing β -chlorovinyl ethers, having between them a steric ratio *erythro-threo* from *cis-trans* isomers, shows in this case as well as that given for propylenes ld_1 ¹⁾ an identical type of polymerization mechanism for the two isomers.

Following our previously exposed scheme we can also say in the case under consideration that the polymerization mechanism follows a steric course of a constant attack and *cis*-opening. Once determined the influence of geometric factors such as type of opening and steric attack there remains to be examined the relationship of the various catalysts to the chemical nature of the monomer in stereospecific polymerizations.

The first di-isotactic polymers were obtained from α -olefin (propylene ld_1) and required the use of heterogeneous catalysts consisting of a complex of a metallo-organic compound on the surface of a transition metal halide. The constancy of steric attack is dependent in this case on the activated adsorption of the monomer on the solid surface corresponding to an active centre. The first step is probably connected with a dative bond, to which are directed the π electrons of the α -olefin double bond and the 3d orbitals of the transition metal. Such an adsorption phase is influenced by steric factors and it is easily understandable how the molecule can bind itself in a determined steric attack which along with the specific opening of the double bond induces a definite orientation of the CHR and CDH group when a certain (*cis*- or *trans*-) isomer of the monomer is used.

In the case of substituted vinyl ethers the presence of atoms containing free electron pairs prevents, as previously reported, the use of heterogeneous catalysts employed in the polymerization of mono-olefinic hydrocarbons; on the other hand the presence of an oxygen atom joined to a carbon of the double bond increases the electron density of the latter, resulting in higher reactivity toward cationic processes and in less reactivity with those processes of an anionic nature. For this reason di-isotactic polymers of substituted vinyl ethers were obtained with more or less mild cationic catalysts (boron fluoride etherate, monoalkyl aluminum dichloride, *etc.*). The stereospecificity obtained with soluble catalysts is due to the basic character of the monomer which allows a direct

coordination, even in the homogeneous phase, with the catalyst. It is also possible that the catalyst reacts in its dimeric form and that the two electron-rich groups (the oxygen or the chlorine atom and the double bond) are simultaneously brought together in the first stage of the complex formation of the monomer with the catalyst to which is bound the growing polymeric chain, by the replacement of the eventual dative bond left between the oxygen of the last monomeric unit of the polymer chain and the catalyst. If the coordination of the new monomeric unit occurs in a constant steric approach and if it is followed by the same type of opening (*e.g.* *cis*-) of the double bond, then the formation of the di-isotactic polymer, starting with a pure (*cis*- or *trans*-) isomer of the monomer is easily comprehensible. The fact that the *cis*-isomers of the alkenyl ethers (1-alkyl-2-alkoxy ethylene) did not give any crystalline polymers, contrary to the *cis*- β -chlorovinyl buthyl ether, may be explained by different reasons. While the absence of crystallinity might not be due to a lack of steric order, as is demonstrated in the case of the absence of crystallinity of isotactic poly-orthomethoxy styrene, which becomes crystalline after its hydrogenation⁸⁾, it might be due to the hard packing of the molecules in the crystal. A second reason could be the presence of a methyl group in place of a chlorine atom, which might not allow a direct and unique (from a steric point of view) coordination of *cis*-isomer of the monomer with the catalytic complex — a condition necessary for obtaining a stereoregular polymer. Although the presence of a second polar group (in the case of chloro vinyl ethers), could facilitate the packing of the chains in the crystals, thus enhancing crystallization, we do not have sufficient data at present to conclude whether the polymers obtained from the *cis*-isomers of the alkenyl ethers are completely or not stereoregular.

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