Proposed Nomenclature for Di-isotactic Polymers

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INTRODUCTION

With the discovery of certain sterically regular polymers obtained from unsaturated ethylenic monomers with an internal double bond, new problems of nomenclature have arisen because of the need of identifying and distinguishing all the possible tactic structures.   This problem, analogous that encountered with certain vinyl polymers in which an H atom of the CH_2 group of the poly-α-olefin main chain is substituted with a D atom,[1] arises now in the case of the stereoregular polymers of alkenyl ethers, which are derived from monomers of the $CHR{=}CHOR'$ type;[2] in general it applies to all polymers which are derived from monomers of the $CHR{=}CHR'$ type, in which R and R' are atoms or groups different from each other.

For the nomenclature of these polymers it is necessary to take into account the conventions which have been already introduced in the case of vinyl polymers, for which some time ago the names "isotactic" and "syndiotactic" were proposed and are now commonly accepted.[3,4]   As it can be seen from the proposals which were submitted to this Committee at the Nottingham Meeting,[5] an isotactic polymeric structure is characterized by the periodic repetition in the main chain of contiguous or not contiguous groups consisting of a carbon atom with two different substituents

$$
\begin{array}{c}
R_1 \\
| \\
{-}C{-} \\
| \\
R_2
\end{array}
$$
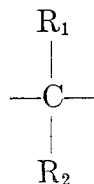
where R_2 can be an H atom, the steric structure of said group being such that, by superimposition of the main chain carbon atoms of two subsequent groups, through translation (which may be followed by rotation) along the chain, their substituents are found to be superimposed.
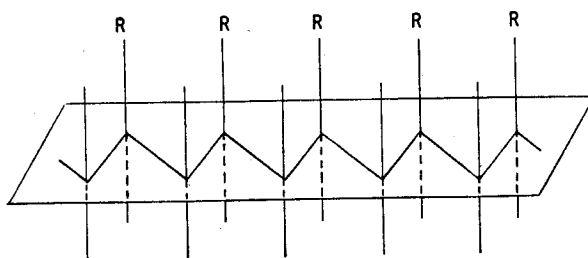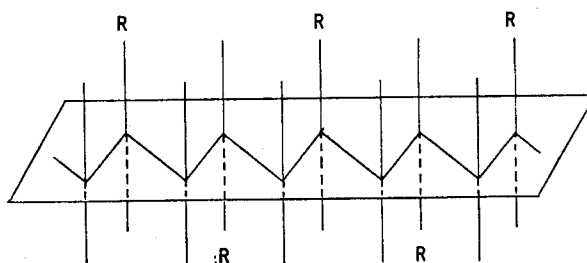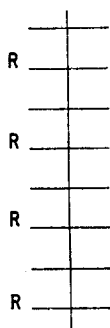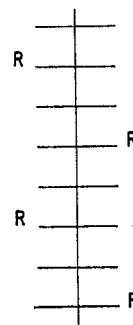
Figure 1.

Figure 2.

Figure 3. Figure 4.

In a syndiotactic structure, on the contrary, this superimposition is not possible for two adjacent groups, but it is observed only for alternate groups.

In the case of vinyl polymers and, in general, of all polymers having an even number of atoms for each structural unit in the main chain, if we suppose the main chain to be stretched in a zigzag fashion on a plane, all the substituents of the same type (R_1 or R_2) belonging to the above mentioned CR_1R_2 group are on the same side of the plane if the structure is isotactic, while they alternate with each other on both sides of the plane of the main chain if the structure is syndiotactic.

These two types of structure are drawn in Figures 1 and 2, for the zigzag representation of the main chain; in Figures 3 and 4 they are drawn according to the Fischer projection.

Obviously, in polymers in the chain of which there is an odd number of atoms for each structural unit (e.g., in the case of isotactic polypropylene oxide[6]), the substituents are on the same side of the plane in which the

$$
\begin{array}{ccccccccc}
 & R & & R & & R & & R & \\
 & | & | & | & | & | & | & | & | \\
-C & - & C & - & C & - & C & - & C & - & C & - & C & - & C - \\
 & | & | & | & | & | & | & | & |
\end{array}
$$

Figure 5.

$$
\begin{array}{ccccccccc}
 & R & & R & & R & & R & \\
 & | & | & | & | & | & | & | & | \\
-C & -(C) & - & C & -(C) & - & C & -(C) & - & C & -(C) - \\
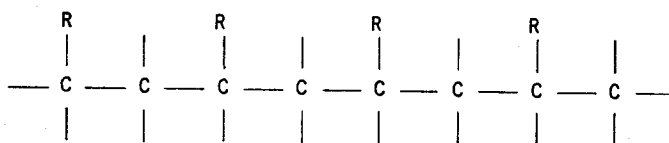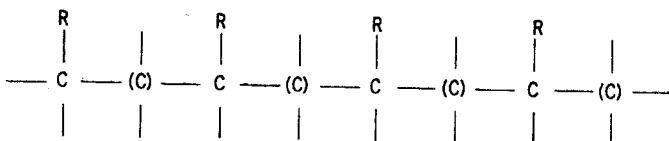 & | & | & | & | & | & | & | & |
\end{array}
$$

Figure 6.

main chain is stretched if the structure is syndiotactic, while they alternate on opposite sides if the structure is isotactic.

A representation sometimes used is obtained by projecting the plane in which the chain is stretched, to a plane normal to the paper, as indicated in Figure 5. This last representation might be taken for a Fischer projection, to which it is typographically analogous; in the case of vinyl polymers the two representations are in fact equivalent. In this particular case the R groups in the isotactic structure are represented on the same side of the chain.

One could, to avoid confusion between this latter representation and the Fishcer projection in the cases where the two representations are not equivalent, distinguish typographically, by printing them in different type faces, or, to make the difference even more marked, by enclosing in parentheses the chain atoms lying on the same straight line, as shown in Figure 6.

DI-ISOTACTIC POLYMERS

Linear polymers of 1,2-substituted ethylenic monomers having different substituents in the 1- and 2-positions can exist in various different simple tactic structures. The case of the tri-substituted ethylenic monomers $CHA{=}CBD$ falls under the more general case of tetra-substituted monomers $CAB{=}CDE$, which, in regard to the possible tactic structures, corresponds to the case of monomer of the $CHR{=}CHR'$ type.

In this case, for the structures in which it is possible to recognize steric regularities of an isotactic type (isotacticity) for each of the sets of tertiary carbon atoms, we propose the name of "di-isotactic structures" (di-isotacticity, di-isotactic polymers, etc.).

To distinguish the two possible di-isotactic structures we propose the name "threo-di-isotactic" for the polymeric structure having, in the case of 1,2-disubstituted ethylenic monomers, all the R and R' substituents on the same side of the plane in which the main chain is zigzag stretched (the R and R' on opposite sides in the Fischer projection); we propose the name "erythro-di-isotactic" for the corresponding polymeric structure having all the R substituents on one side and all the R' substituents on the
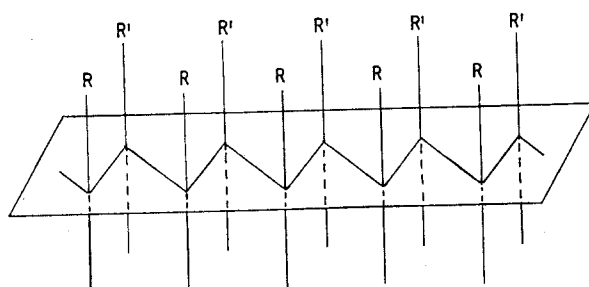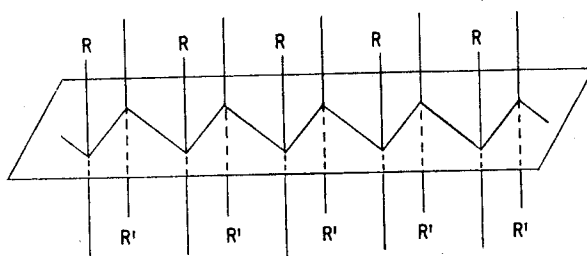
Fig. 7. threo-di-isotactic.
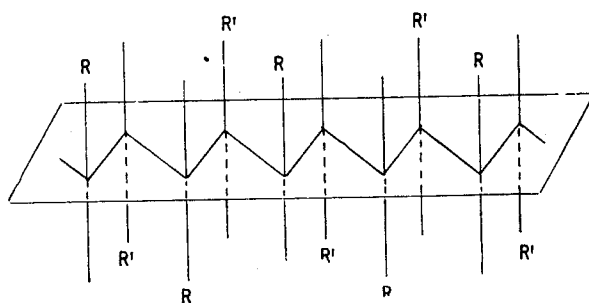

Fig. 8. erythro-di-isotactic.

Fig. 9. di-syndiotactic.

opposite side of the plane in which the main chain is zigzag strecthed (R and R' on the same side in the Fischer projection).

Furthermore we propose the name "di-syndiotactic" for the structures in which it is possible to recognize steric regularities of a syndiotactic type for the two sets of tertiary carbon atoms. Those structures are drawn in Figures 7–9 according to the zigzag representation, and in Figures 10–12 according to the Fischer projection.

It is worthy of noting here that polymerization of pure stereoisomeric forms of CHR=CHR' monomers can yield two types of di-isotactic polymers (erythro or threo), depending on the monomeric form employed (cis or trans), while, on the contrary, only one product with di-syndiotactic structure is obtained.

The terminology which we have used is in accordance with the current nomenclature for polymers having simple isotactic or syndiotactic structure.

As regards the particular use of the prefixes "erythro" and "threo," which are commonly used to define the relative steric configuration of two
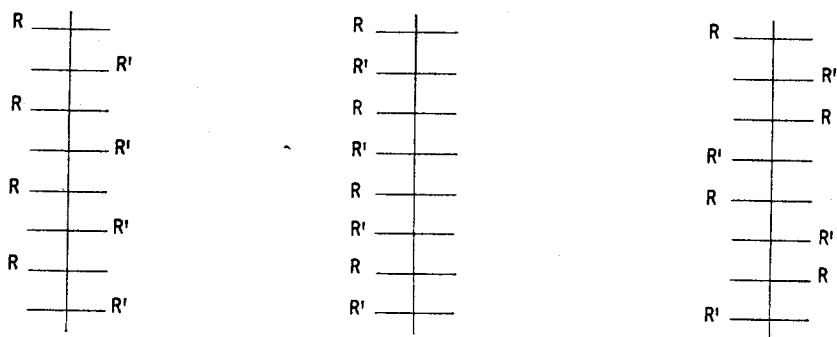
Fig. 10. threo-di-isotactic.   Fig. 11. erythro-di-isotactic.   Fig. 12. di-syndisotactic.

C atoms in a molecule, we feel that it is legitimate to extend to high polymers the definition reported by Newman;[7] according to this definition, "erythro" denotes that diastereomer which, when observed in the Newman representation in one of its eclipsed forms, presents superimposed at least two sets of substituents which are equal or similar; "threo" denotes the opposite isomer.

If one applies those terms in the field of polyolefins, one sees that the known relations between structure of the olefinic monomer (cis or trans), type of opening of the double bond (cis or trans) and the resulting structure (erythro or threo), are valid.

Generalizing the use of the prefixes erythro and threo in the definition of the relative steric positions of the two sets of substituents R and R' bound to different atoms of the chain, we can define as erythro-di-isotactic a polymer which, in the Fischer projection, has all the R and R' substituents (which may or may not be contiguous) on the same side of the chain; we can then define as threo-di-isotactic a polymer which in the Fischer projection has all the R substituents on one side and all the R' substituents on the opposite side of the chain. Finally we can define as di-syndiotactic a polymer which, in the Fischer projection, has both R and R' substituents alternately on opposite sides of the chain.*

As we have already observed for the isotactic structures in the zigzag representation, in a threo-di-isotactic polymer the R and R' substituents are on the same side of the plane (or in opposite sides in a erythro-di-isotactic polymer) only for a particular type of structural unit, i.e., —CHR—CHR'—.

The possibility of partially ordered structures also exists; in some cases their nomenclature can be easily derived. For instance, the polymer which is obtained by copolymerization with stereospecific catalysts of a mixture (in 1:1 molar ratio) of cis- and trans-1-deutero-1-propene has an isotactic structure with respect to the CH—CH₃ group and an atactic structure with respect to the CHD group; thus its name is (1-atactic, 2-isotactic) poly(1-deutero-2-methylethylene).

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* The definitions of the erythro and threo structures of $1d_1$ polypropylene, reported in ref. 8, are inverted with regard to the original work.[1] However, the figures in ref. 8 are correct, as can be seen from our Figures 5 and 17.

POLYMERS OF OLEFINS HAVING TWO IDENTICAL SUBSTITUENTS

A particular case of tactic polymers is observed when the two substituents R and R' of the ethylenic monomer are equal; the structural unit is thus reduced to the —CHR— group and we have only one atom in the chain for each structural unit. In accord with our general definition, an isotactic polyalkylidene can be depicted in the zigzag representation as in Figure 13, which would be equivalent in the Fischer projection to the representation in Figure 14; a syndiotactic polyalkylidene, can be depicted in the zigzag representation as in Figure 15 and in the Fischer projection as in Figure 16.

In such cases it may be convenient sometimes to use a system of nomenclature for the polymer deriving from the monomer employed. For instance, according to what we previously said, the structure shown in Figures 13 and 14 could be named erythro-di-isotactic poly(1,2-di (R) ethylene), while the structure shown in Figures 15 and 16 could be named threo-di-isotactic poly(1,2-di (R) ethylene).

Referring to what has been already observed in connection with the possibility of confusion between the Fischer projection and the particular zigzag representation indicated, e.g., in Figure 5, it is interesting to consider the example of an isotactic polyalkylidene. In this last representation its structure is drawn as in Figure 17; the same drawing in the Fischer projection stands for a syndiotactic polyalkylidene. The confusion disappears when the form of representation proposed in Figure 18 is used.
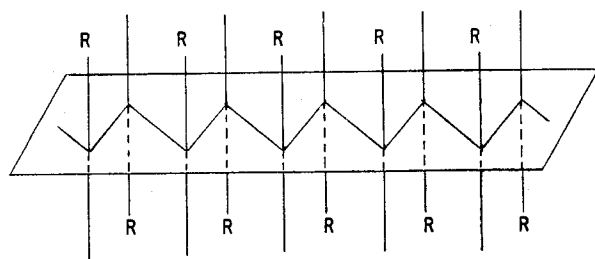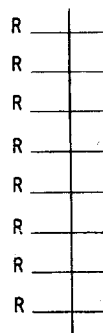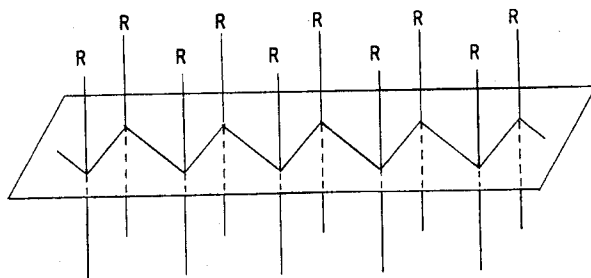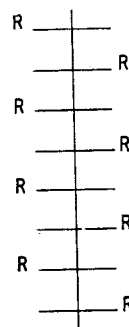

Figure 13.

Figure 14.

Figure 15.

Figure 16.

$$
\begin{array}{cccccccc}
\overset{\displaystyle R}{|} & & \overset{\displaystyle R}{|} & & \overset{\displaystyle R}{|} & & \overset{\displaystyle R}{|} & \\
-\,C\,- & C\,-- & C\,- & C\,- & C\,- & C\,- & C\,- & C\,- \\
\underset{\displaystyle R}{|} & & \underset{\displaystyle R}{|} & & \underset{\displaystyle R}{|} & & \underset{\displaystyle R}{|} &
\end{array}
$$

Figure 17.

$$
\begin{array}{cccccccc}
\overset{\displaystyle R}{|} & & \overset{\displaystyle R}{|} & & \overset{\displaystyle R}{|} & & \overset{\displaystyle R}{|} & \\
-\,C\,- & (C)\,-- & C\,- & (C)\,- & C\,- & (C)\,-- & C\,- & (C)\,- \\
\underset{\displaystyle R}{|} & & \underset{\displaystyle R}{|} & & \underset{\displaystyle R}{|} & & \underset{\displaystyle R}{|} &
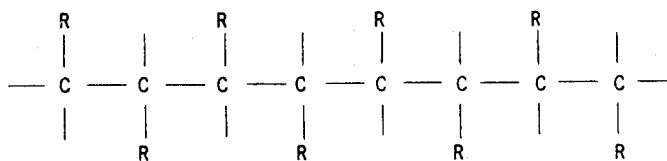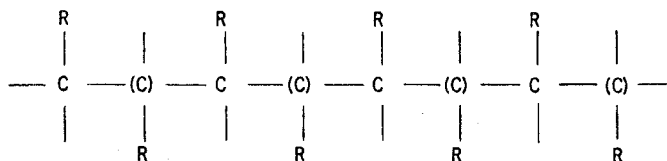\end{array}
$$

Figure 18.

Briefly, we may say that designations isotactic and syndiotactic can be used to define the steric relations of between structural units, while the terms erythro and threo can be used to define the steric relations within a given structural unit.

The discovery of new stereoregular structures, which we have called di-isotactic, illustrates the general nature of the concepts of taxis and iso-taxis.

Finally, we believe that the proposed definitions can be extended also to nonolefinic linear polymers.

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