Addition to the Double Bond during the Syndiotactic Polymerization of Vinylic Monomers

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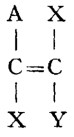
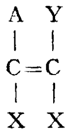
STARTING from *cis*- and *trans*-1,2-disubstituted vinylic monomers, Natta, Farina, and Peraldo[1] first obtained two different di-isotactic polymers (*erythro* and *threo*) and a third polymer, isotactic with respect to one substituent and atactic with respect to the other. Thus it was possible to establish the type of addition to the double bond occurring during the isotactic polymerization of propene.[2] This method is general for isotactic polymerization, but cannot be used to establish how the double bond opens during the syndiotactic polymerization.

In fact, starting from both *cis*- or *trans*-monomers, the same di-syndiotactic polymer could always be obtained, provided that the addition is always constant (*cis* or *trans*); however, a polymer, syndiotactic only with respect to one substituent and atactic with respect to the other one, could be obtained if the double bond undergoes a random *cis*- or *trans*-opening.[1,3] We have established that the addition to the double bond is *cis* also in syndiotactic polymerization of propene[4] by a more general method. Let us consider the monomers, (I) and (II), where $A \neq X$, $Y \neq X$, and a third vinylic monomer (III), which does not contain the substituent X.

When monomers (I) + (III) and (II) + (III) are copolymerized, it is always possible to obtain copolymers in which most units derived from (I) and (II) respectively, have two adjacent units derived from (III), provided that the reactivity ratio products $r_{I} \cdot r_{III}$ and $r_{II} \cdot r_{III}$ are not too high and a suitable excess of (III) is used. When the monomers differ only by isotopic substitutions, $r_{I}r_{III} \simeq 1 \simeq r_{II}r_{III}$, then a large excess of monomer (III) is not required.

(I)

$$\begin{array}{cc} A & X \\ | & | \\ C & \!\!=\!\! C \\ | & | \\ X & Y \end{array}$$

(II)

$$\begin{array}{cc} A & Y \\ | & | \\ C & \!\!=\!\! C \\ | & | \\ X & X \end{array}$$

Copolymers (I) + (III) and (II) + (III) are always different from one another provided that the type of addition to the double bond is constant. In fact (in zig-zag planar projection), the vicinal X's are *gauche* in the (III)–(I)–(III) sequences and *trans* in the (III)–(II)–(III) sequences if the addition is *cis*, whereas the opposite situation occurs when the addition is *trans*. The structures of the syndiotactic copolymers of the suitably deuteriated propenes used were determined by n.m.r.[4]

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[1] G. Natta, M. Farina, and M. Peraldo, *Atti Accad. naz. Lincei, Rend. Classe Sci. fiz. mat. nat.*, 1958, **5**, 424; *Chimica e Industria*, 1960, **42**, 255.
[2] T. Miyazawa and T. Ideguchi, *J. Polymer Sci., Part B, Polymer Letters*, 1963, **1**, 389.
[3] C. L. Arcus, *J. Chem. Soc.*, 1955, 2801.
[4] A. Zambelli, M. G. Giongo, and G. Natta, in the press.

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