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Crystalline Alternating Copolymers of Ethylene-Butene-2 and Ethylene-Cyclopentene

by

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In a preceding paper[1] concerning the research works carried out at this Institute on the stereospecific catalysis, we described the synthesis of the crystalline ethylene-*cis*-butene-2 and ethylene-cyclopentene alternating copolymers, having the formulas:

In the preliminary discussion on the possible structures of these copolymers, it had been admitted, on the basis of the identity period, that the main chain has a conformation of the A_3BA_3C type (BUNN's terminology)[2].

For this structure of the main chain a *threo*-syndiotactic disposition of the methyl groups in the ethylene-*cis*-butene-2 copolymer appeared to be the most probable, owing to a higher distance among the encumbrant CH_3-groups. However, with a relatively small difference in the conformational potential energy[3], always with a A_3BA_3C model of the chain, containing within the identity period, as in the previous case, the monomeric units, it is possible to give different space positions to the methyl groups, which can be distinguished henceforth only by detailed structural studies. For instance, a A_3BA_3C structure of the chain is also compatible with an *erythro*-isotactic succession, corresponding to what can be foreseen for a succession of enantiomorphous anticlined units[4]. More detailed structural calculations have favoured this last model (which differs from

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the one previously considered only in the disposition of a methyl group); the local *t2c* symmetry around the axis of the chain of the ethylene-cyclopentene copolymer[4] is also compatible with an *erythro*-isotactic model and is due to a phenomenon of statistical vicariance among the chains.

At the present state of our research, we believe that the structure is *erythro*-isotactic. The ethylene-2-butene copolymer crystallizes in the space group $P2_1/b$ (a unique axis) with the constants $a = 10.92 \pm 0.10$ Å, $b \sin\alpha = 5.94 \pm 0.05$ Å, $c = 9.15 \pm 0.10$ Å, whereas the orthorhombic unit cell of the ethylene-cyclopentene copolymer has the following constants: $a = 8.76 \pm 0.10$ Å, $b = 7.83 \pm 0.10$ Å, c (chain axis) $= 9.02 \pm 0.10$ Å.

A satisfactory mode of packing of the macromolecules of the ethylene-2-butene copolymer with distances between non-bonded carbon atoms all greater than 4 Å has been found only for a A_3BA_3C *erythro*-isotactic structure. The accordance between calculated and observed intensities is promising at this stage of the research. In Fig. 1 a model of the conformation of the chain is shown.

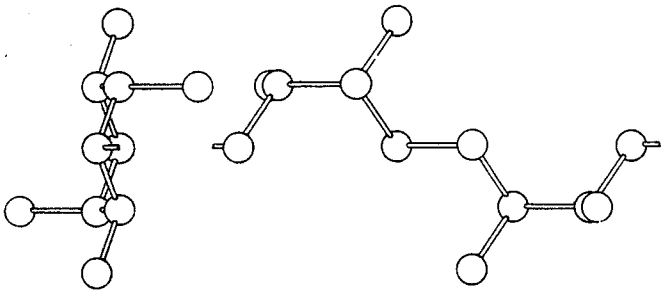

Fig. 1. Conformation of a A_3BA_3C-chain type with *erythro*-isotactic structure

Such a structure would agree with a *cis*-opening of the double bond; this type of opening was observed by us both in the *erythro* and in the *threo*-di-isotactic polymers (of the chloromethoxyethylene type) obtained, however, by stereospecific cationic polymerization.

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