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Kurzmitteilung

## Polymer of 1,3-Pentadiene with a Cis-1,4 Syndiotactic Structure

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Polymers of 1,3-pentadiene with 1,4 enchainment show two types of steric isomery in each monomeric unit: one type where the double bonds can be cis or trans and the other where the asymmetric carbon atoms can be D or L. Therefore, several regular stereoisomers can be foreseen for such polymers: *e. g.* trans-1,4 or cis-1,4 isotactic and syndiotactic polypentadienes.

From among the possible regular stereoisomers mentioned above, only the trans-1,4 isotactic polypentadiene has been described up to now<sup>1)</sup>.

By polymerizing the trans isomer of 1,3-pentadiene with the aid of various homogeneous catalysts prepared from aluminum alkyl chlorides and 8th group transition metal compounds (*e. g.* cobalt compounds), we recently obtained a new crystalline stereoregular polymer. Its I. R.- and X-ray analyses were indicative of a cis-1,4 syndiotactic structure.

The prevalent cis-1,4 enchainment can be argued from the I. R. spectrum of the polymer, taken either melted or in solution (Fig. 1). In fact, it shows a strong band at about 13.35  $\mu$  (which is typical of the cis-type internal double bonds), and a much less strong band at 10.35  $\mu$  (typical of the trans-type internal double bonds), while it does not show the bands characteristic of vinyl groups (which leads one to exclude the presence of the 3,4 type of monomeric units).

While the band at 10.35  $\mu$  can be assigned to both trans-1,4 and 1,2 units, the band at about 13.35  $\mu$  can be assigned only to cis-1,4 units. The presence of possible 1,2 units, in fact, should give an internal double bond in the side chain, which should be of the trans type (band at 10.35  $\mu$ ) and not of the cis type, since only the trans isomer polymerizes with the aid of the catalysts employed by us.

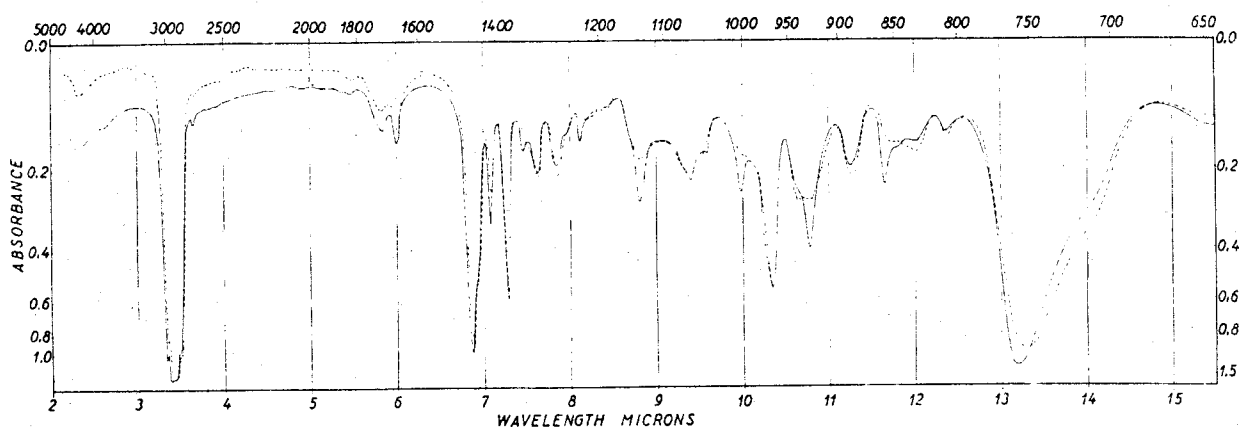


Fig. 1. I. R. spectra of the cis-1,4 syndiotactic polypentadiene (—) in the solid state, and (- - -) in the molten state

By assuming the value  $10 \cdot 10^4 \text{ mole}^{-1} \cdot \text{cm}^{-1} \cdot \text{ml.}$  as the absorption coefficient<sup>2)</sup> for the band at  $10.35 \mu$ , independently of the fact that this band is originated by either 1,2 or trans-1,4 units, we have assigned to the polymer obtained by us a cis-1,4 content of the order of 85–90 % (calculated by difference to 100)\*).

The I. R. spectrum of the solid polymer (annealed for some hours at  $30\text{--}35^\circ\text{C.}$ ), if compared with the spectrum of the polymer either melted or in solution, shows some variations of frequency and intensity, and also it shows the appearance of new bands that can be attributed to the crystalline state of the polymer.

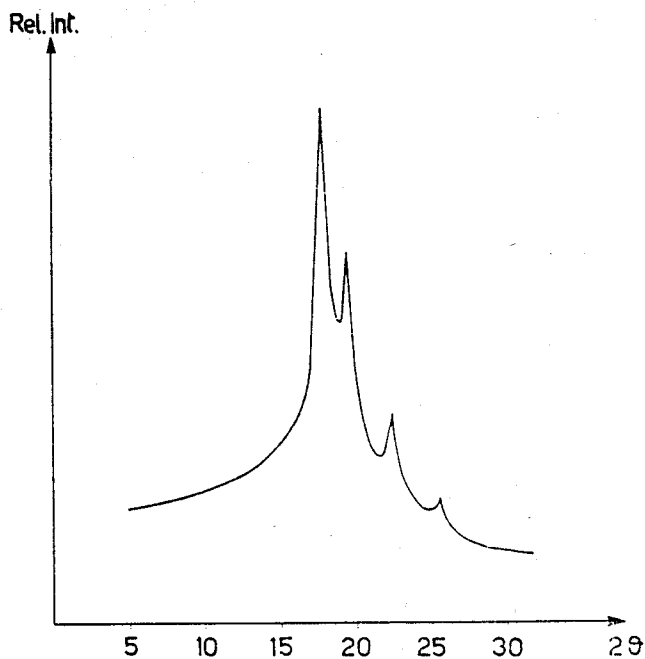


Fig. 2. X-ray powder spectra ( $\text{CuK}\alpha$ ), registered by a GEIGER counter, of cis-1,4 syndiotactic polypentadiene

\*) Such a value might be slightly modified when a more precise method of analysis is available.

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The structural regularity of the new polymer is revealed by its X-ray spectrum (Fig. 2), which is rich in sharp reflections, characteristic of a high degree of order.

The fiber spectrum reveals an identity period along the chain axis of  $8.50 \pm 0.05 \text{ \AA}$ ; this means that the repetition unit contains at least two monomeric units.

By assuming *a priori* a head-to-tail enchainment, the possible chain models satisfying the principle of the minimum internal energy and of the equivalence of monomeric units, are, in this case, those shown in Fig. 3.

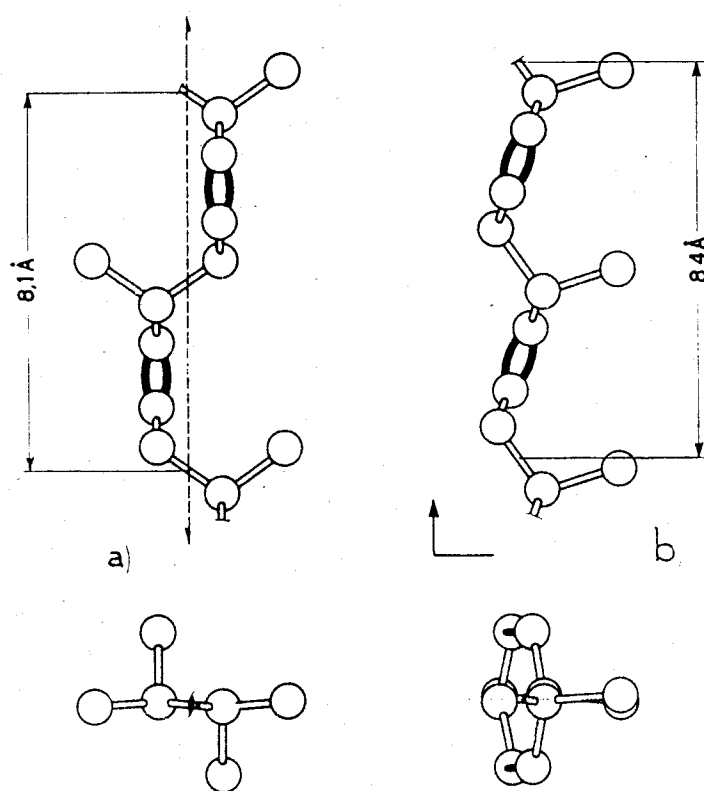


Fig. 3. Chain models of, (a), a hypothetical cis-1,4 isotactic, and, (b), the cis-1,4 syndiotactic polypentadiene (side and end views). The symmetry elements characteristic of the two chain models, (a screw twofold axis for model *a*, and a glide plane for model *b*), are also shown

Assuming that the interatomic distances and the valence angles are normal, then the two models would show repetition periods of  $8.1 \text{ \AA}$  (model *a*) and of  $8.4 \text{ \AA}$  (model *b*)<sup>3)</sup>; evidently, the identity period found experimentally is in good agreement with that of model *b*.

The symmetry element connecting the two monomeric units contained in the repetition period is a screw twofold axis in model *a*, and a glide plane along the chain in model *b*. Owing to the nature of these symmetry ele-

ments, one must necessarily deduce that the succession of the tertiary carbon atoms is isotactic in model *a*, and syndiotactic in model *b*.

The behaviour of the diffracted intensity on the first two layers of the fiber spectra further proves that the chain of the *cis*-1,4 polypentadiene obtained by us is syndiotactic (model *b*). In fact, it can be observed that the overall value of the diffracted intensity on the second layer is much higher than on the first one. This ascertainment is well interpreted by model *b*, because in it, six from among the ten carbon atoms forming the repetition unit appear to be nearly superposed along the direction of the chain axis, at a distance of  $c/2$  ( $c$  = repetition period); therefore, these atoms cannot contribute to the diffraction on the first layer, but they can do so on the second layer. Obviously, this remark cannot be applied to the alternative model *a*.

The melting temperature of the sterically purer *cis*-1,4 syndiotactic polypentadiene, which we obtained, is of about 52–53°C. (by polarized-light microscope).

By varying the catalysts it was also possible to obtain polymers with a lower melting temperature (42–43°C.), depending on their lower steric purity.

A particular interest of *cis*-1,4 polypentadiene obtained by us lies on the fact that this is the first ditactic polymer with a syndiotactic structure, derived from a diolefin monomer.

The melting temperature of the *cis*-1,4 syndiotactic polypentadiene, in the less sterically pure polymers, is only a little higher than that of natural rubber. This finding and the conformations of the chains, due to *cis*-1,4 enchainment, permit foreseeing for this polymer good elastomeric properties, which will be described in another paper.

<sup>1</sup>) G. NATTA, L. PORRI, P. CORRADINI, G. ZANINI, J. Polymer Sci. **51** (1961) 463.

<sup>2</sup>) Average value taken from the literature: see, for instance: H.L. McMURRY, V. THORNTON, Analyt. Chem. **24** (1952) 318.

<sup>3</sup>) G. NATTA, P. CORRADINI, Suppl. nuovo Cimento **XV**, 111 (1960).