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Isotactic Cis-1,4 Poly(1,3-Pentadiene)

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ISOTACTIC CIS-1,4 POLY(1,3-PENTADIENE)

It was foreseeable that cis-1,4 polymers of 1,3-pentadiene, owing to the presence of an asymmetric carbon atom in each monomeric unit, could exist in different stereoisomeric structures; e.g., isotactic, syndiotactic, atactic. Of these possible stereoisomers only the syndiotactic cis-1,4 polypentadiene was known until now (1).

We have recently obtained a new cis-1,4 polymer of 1,3-pentadiene which, on the basis of x-ray analysis, appears to have an isotactic structure of the asymmetric carbon atoms. The new polymer was obtained with the aid of catalysts prepared from $\text{Al}(\text{C}_2\text{H}_5)_3$ and a titanium tetraalkoxide (Al/Ti from 3 to 10) in hydrocarbon solvents.

In a typical run 15 ml. of the trans isomer (99% pure) of 1,3-pentadiene were introduced into a catalyst solution, prepared by reacting at ordinary temperature 0.6 ml. of titanium tetra n-butoxide with 1.8 ml. of $\text{Al}(\text{C}_2\text{H}_5)_3$ in 80 ml. of anhydrous benzene.

After 15 hr. of polymerization at about 0°C . 3 g. of polymer were obtained. In order to remove the less stereoregular low molecular weight macromolecules the crude polymerization product was repeatedly dissolved in benzene and reprecipitated with methyl ethyl ketone; after 3 dissolutions and reprecipitations a polymer was obtained, highly crystalline to x-ray, having m.p. $\sim 44^\circ\text{C}$. (polarizing microscope) and $[\eta]$ 7 dl./g. (in toluene at 30°C .).

The prevailing cis-1,4 enchainment of the new polymer is revealed by the presence in the I.R. spectrum of the molten or dissolved polymer (Fig. 1, solid line) of an intense band at about 13.3μ , characteristic of the cis internal double bonds; far less intense bands are present at 10.35μ , (trans internal double bonds) and at 11μ (vinyl groups).

By assuming, as absorption coefficients for the bands at 10.35, 11, and 13.3μ , the values of 10×10^4 , 12×10^4 , and 6×10^4 moles $^{-1}\text{cm.}^{-1}\text{ml.}$ (2), respectively, we have calculated a cis-1,4 content of 85-90% for the polymer we have isolated. Such a value might be slightly modified when an improved method of analysis is available.

The I.R. spectrum of the new polymer in the crystalline state (Fig. 1, dashed line) shows new bands with respect to the spectrum of the molten or dissolved polymer, the most intense of which are at 13.40, 11.85, 10.80, 9.95μ , while others, less intense, are at 8.85, 8.99, 8.15, 7.60, 6.91μ .

With regard to the differences between the I.R. spectra of the isotactic and the syndiotactic cis-1,4 polypentadienes, these appear small in the spectra of the dissolved or molten polymers, whereas they appear noticeable in the spectra of the two polymers in the crystalline state.

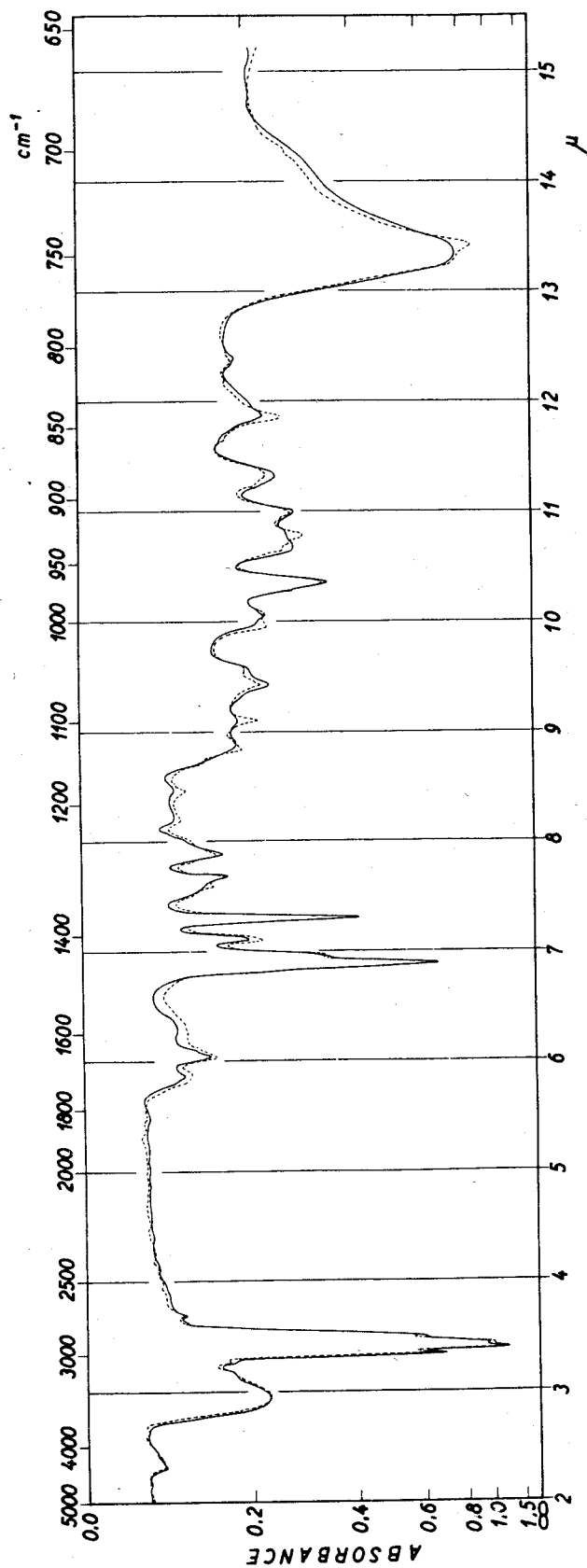


Fig. 1. I.R. spectra of a sample of cis-1,4 isotactic polybutadiene in the solid state (dashed line) and in the molten state (solid line).

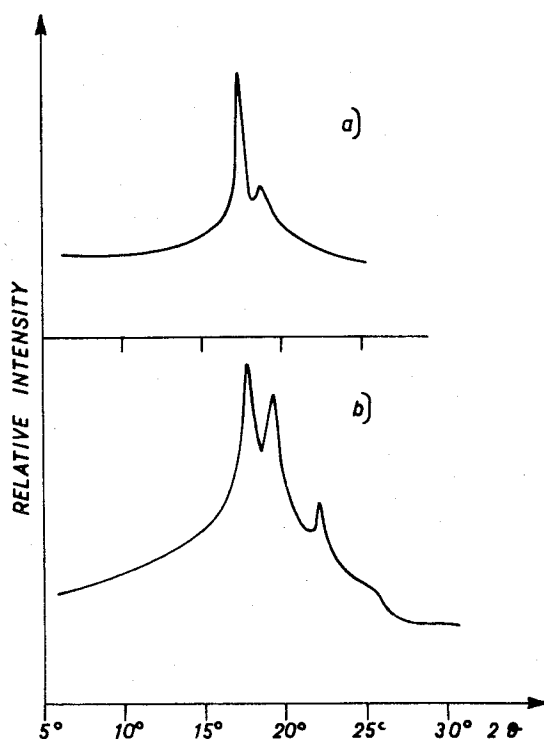


Fig. 2. X-ray powder spectra ($\text{CuK}\alpha$), registered with a Geiger counter, of samples of cis-1,4 polypentadienes: (a) isotactic, (b) syndiotactic.

Noteworthy in the spectra of the two polymers in the crystalline state is the different position of the band of the cis double bonds, which is at about 13.2μ in the case of the syndiotactic and at about 13.4μ in that of isotactic polymer (whereas in the spectra of the molten or dissolved polymers this band is at about 13.3μ both for isotactic and syndiotactic polypentadiene).

The structural regularity of the new polymer, which is revealed by the differences between the I.R. spectra of the solid and the molten polymer, is also confirmed by the x-ray spectrum, which shows the presence of a crystalline structure. From the examination of the x-ray Geiger spectrum (Fig. 2a), it has been observed that the most intense maxima correspond to layer distances $d = 5.17$ and 4.71 \AA ; such distances are very close to those observed for the most intense maxima of the syndiotactic polymer (Fig. 2b), but the ratios between the corresponding diffraction intensities are different in the two polymers.

From the fiber spectrum of the new polymer an identity period of about $8.15 \pm 0.05 \text{ \AA}$. was measured, which is slightly smaller than that of the syndiotactic polymer ($8.50 \pm 0.05 \text{ \AA}$). In a previous communication (1) on the basis of a conformational analysis of the chains of the

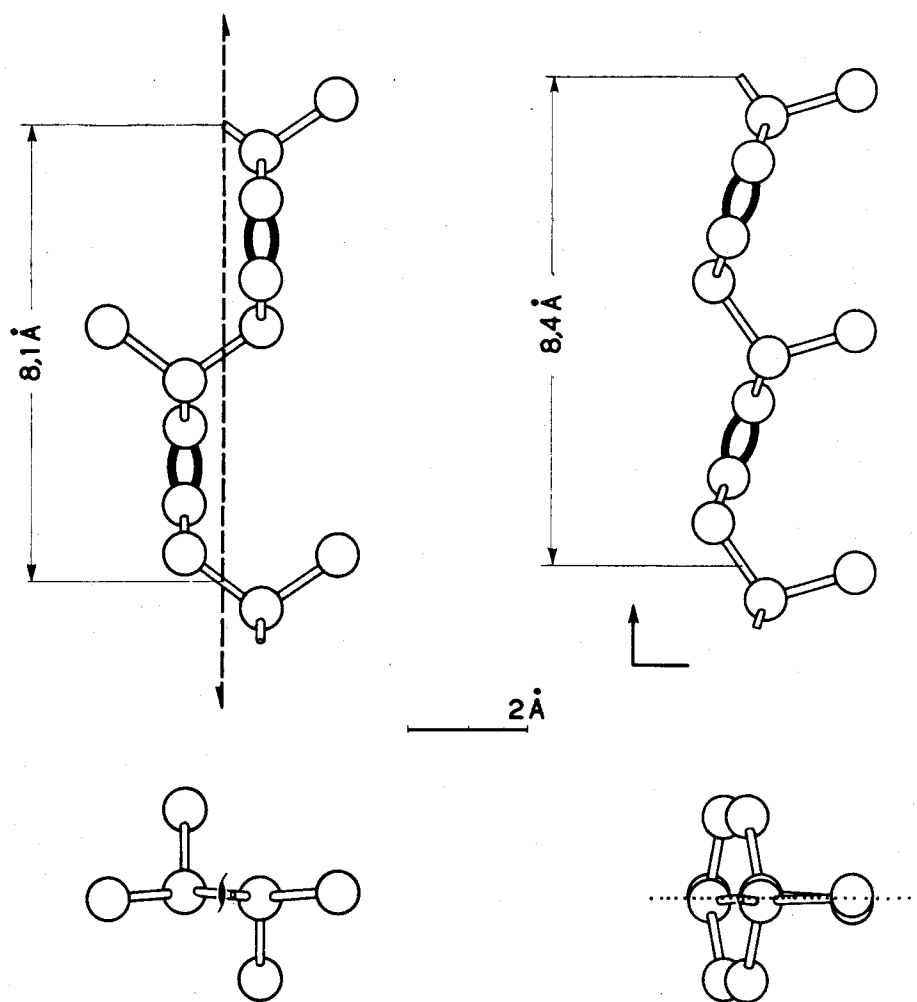


Fig. 3. Chain models of the cis-1,4 isotactic (left) and the cis-1,4 syndiotactic polypentadienes.

cis-1,4 polypentadienes, we foresaw that the identity period of the cis-1,4 isotactic polypentadiene, at that time unknown, could have been about 8.1 Å., which is very close to that actually found. We assume, therefore, for the cis-1,4 isotactic polypentadiene in the crystalline state, a chain model shown in Figure 3, already reported in our previous communication (1). Such a model is characterized by the presence of a screw twofold axis, while the chain model of the cis-1,4 syndiotactic polypentadiene is characterized by a glide plane (1).

The isotactic structure of the new polymer is further confirmed by the behavior of the x-ray diffracted intensity on the non equatorial layers of the fiber spectrum. In the spectrum of the isotactic polymer the amount of the total intensity diffracted on the first layer is about the same as that on the 2nd, whereas in the spectrum of syndiotactic polymer it is much lower, as already reported (1). Also the total intensity diffracted

on the 3rd layer is higher for the isotactic than for the syndiotactic polymer. Such data can be interpreted by taking into account that, in the syndiotactic model, six among the carbon atoms which constitute the repetition unit are nearly superimposed along the direction of the chain axis at a distance of $c/2$ (c = identity period) and cannot therefore appreciably contribute to the diffraction on the layers characterized by an odd l index; this does not occur in the case of isotactic polymer.

The two *cis*-1,4 polymers of 1,3-pentadiene constitute the first example of ditactic polymers, obtained from the same diolefinic monomer, with respectively isotactic and syndiotactic structure.

The elastomeric properties of the new polymer, which appear interesting, will be reported in a subsequent communication.

References

- (1) Natta, G., L. Porri, A. Carbonaro, F. Ciampelli, and G. Allegra, *Makromol. Chem.*, 51, 229 (1962).
- (2) Average values taken from the literature. See, for example, H. L. McMurray and V. Thornton, *Anal. Chem.*, 24, 318 (1952).

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