

A NEW POLYMER OF 1,3-PENTADIENE HAVING A 1,2-SYNDIOTACTIC STRUCTURE

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Abstract—*Trans* 1,3-pentadiene has been polymerized to a 1,2-polymer which is largely syndiotactic. The polymerization can be performed in aliphatic solvents at about 20° using a catalyst prepared from $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$ and cobalt triacetylacetonate. X-ray and infra-red examinations show that the polymer can be crystalline. Differences between the effects of cobalt catalysts in aliphatic and aromatic solvents are discussed.

ALTHOUGH several types of stereoregular polymers are foreseeable for 1,3-pentadiene, only three have been obtained and characterized up to now, i.e. the *trans*-1,4 isotactic,⁽¹⁾ the *cis*-1,4 isotactic,^(2, 3) and the *cis*-1,4-syndiotactic^(3, 4) polymers. In this communication we report the preparation and properties of a new polymer of 1,3-pentadiene, which is constituted of 1,2 monomeric units* (up to 98 per cent) and which exhibits a detectable stereoregularity of syndiotactic type.

The new polymer has been obtained by polymerizing the *trans* isomer† of 1,3-pentadiene with catalysts prepared from $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$ and cobalt triacetylacetonate (CoA_3) in aliphatic solvents, at about 20°. A typical polymerization run is as follows: $2 \cdot 10^{-3}$ moles (0.25 ml) of $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$ are introduced into a solution of CoA_3 ($2 \cdot 2 \cdot 10^{-6}$ moles) in 20 ml of *n*-heptane, then 5 ml of 1,3-pentadiene (*trans* isomer, purity 99 per cent) are added. After 10 hr of polymerization at 20°, 2.35 g of solid polymer are obtained.

The predominant 1,2-structure of the monomeric units is deduced from the position of the band of the methyl groups in the i.r. spectrum. This band is at about $1,377 \text{ cm}^{-1}$ in the spectrum of the new polymer, while it is known⁽³⁾ that in the spectra of 1,4 poly-pentadienes (e.g. *trans*-1,4 isotactic, *cis*-1,4 isotactic or syndiotactic polymers) it is at about $1,372 \text{ cm}^{-1}$.‡ The double bonds of the side chains are all of the *trans* type (band at 966 cm^{-1}), as one would expect from the fact that the *trans* isomer of pentadiene has been polymerized.

The 1,2 polypentadiene obtained by us, in the unstretched state, was found to be amorphous by X-ray examination at room temperature, however, fibers of the polymer examined in the stretched state at about 20° gave a diffraction spectrum, from which an

* We call 1,2 units those derived from the polymerization of the vinyl group of 1,3-pentadiene. Other authors, who call 1,3-pentadiene 1-methyl-1,3-butadiene, indicate these units as 3,4.

† The *cis* isomer does not polymerize, under the conditions examined.

‡ A paper on the i.r. methods of analysis of the various stereoregular polypentadienes will be published shortly by F. Ciampelli.

identity period along the chain axis of $5.1 \pm 0.05 \text{ \AA}$ was calculated. Such an identity period, considering that the monomeric units are 1,2, is what one would expect for a polymer with a planar conformation of the chain, having a stereoregularity of the syndiotactic type (for a polymer having a 1,2 isotactic structure an identity period of about 6.5 \AA or higher would be expected).

Infra-red spectra of the dissolved and the solid polymer respectively, registered at room temperature, appear identical, and this fact is generally accepted as indicative of lack of crystallinity. However if films of the polymer are examined in the stretched state, at room temperature, spectra are obtained which have new bands. These new bands are particularly intense in spectra of films examined at low temperature (about -75°), even in the unstretched state. Evidently the new bands are attributable to the presence of a crystalline phase, which forms at low temperature or, in the stretched state, even at room temperature. The positions of the most intense of these bands (Fig. 1) are as follows: $910; 934; 988; 1014; 1140; 1178; 1340 \text{ cm}^{-1}$.

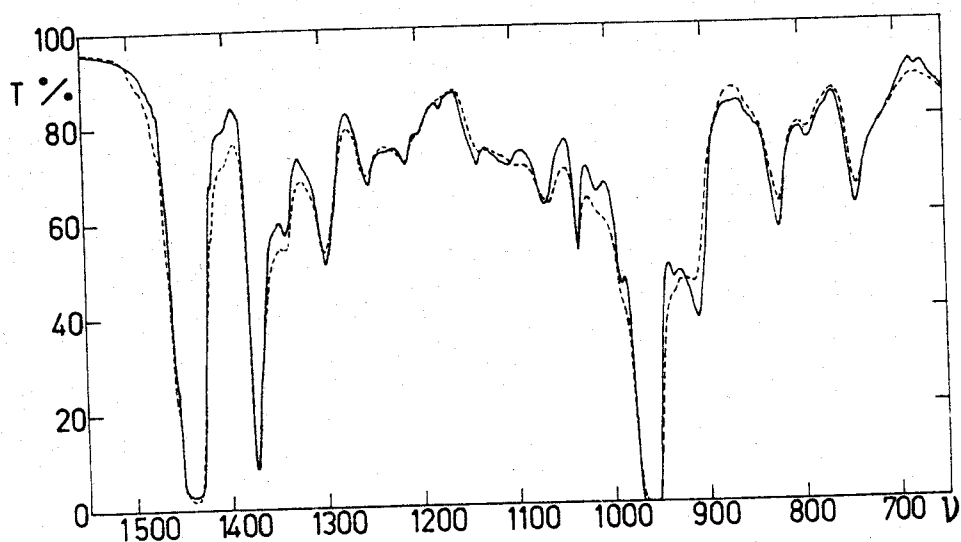


FIG. 1. Infra-red spectra of a sample of 1,2-syndiotactic polypentadiene, in the stretched state (continuous line: -75° ; broken line: $+20^\circ$).

The fact that the reflections in the X-ray fiber spectrum are not very sharp indicates that the structural regularity of the new polymer is rather low. This is confirmed by the absence of a well defined melting point.* Since the content of 1,2 units of the polymers examined is rather high (about 98 per cent), the low structural regularity is to be attributed to a low regularity of steric type, that is, to the fact that the macromolecules contain only relatively short chain-segments having a syndiotactic structure.

The polymerization temperature has an influence on the polymer structure. In fact, the polymers obtained at room temperature have a content in 1,2 units of about 98 per cent, while those obtained at 0° and -10° have a 1,2 unit content of about 95 and 90 per cent respectively (the remaining units being mostly *cis*-1,4).

It is interesting to observe that the $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}-\text{CoA}_3$ system, which in aliphatic solvents gives 1,2 polypentadienes, as shown above, gives *cis*-1,4 polypentadienes when

* The crystallinity bands which appear in the spectrum of the stretched polymer at low temperature, remain, at low temperature, also when the stress is removed. On raising the temperature gradually, these bands disappear completely between 0° and $+10^\circ$. Such an interval therefore may be considered as the melting range of the crystalline phase of the polymer.

used in aromatic solvents.^(4, 8) This noticeable change in the structure of the polymer when varying the nature of the hydrocarbon solvent is rather surprising and is difficult to interpret. In the case of di-olefin polymerization by alkyl derivatives of alkali metals it has been already observed that the polymerization solvent has some influence on the polymer structure. It is well known that isoprene is polymerized by butyl lithium in hydrocarbon solvents to predominantly *cis*-1,4 polymer,⁽⁵⁾ while in diethyl ether or tetrahydrofuran a predominantly 3,4 polymer is formed.⁽⁶⁾ Similarly, in the polymerization of butadiene by the same system, 1,4 polymers are obtained in hydrocarbon solvents (aliphatic or aromatic), and 1,2 polymers are obtained in THF.⁽⁷⁾ The case of the polymerization of pentadiene by the $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}-\text{CoA}_3$ system appears to be different, because here the polymer structure changes even when different types of hydrocarbon solvents, aliphatic and aromatic respectively, are used.

In previous papers the polymerization mechanism of conjugated di-olefins by Co catalysts in aromatic solvents was examined.⁽⁸⁾ The conclusions reached from these studies were as follows:

- (a) when the $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$ -cobalt compound system is prepared in aromatic solvents, two molecules of arene co-ordinate to the cobalt of the catalytic centre, with formation of a cation of the type $[\text{Co}(\text{arene})_2]^+$;
- (b) the monomer, before its incorporation into the growing polymer chain as a *cis*-1,4 unit, co-ordinates to Co through the two double bonds, in the *cis* conformation. The co-ordination of the monomer occurs by displacing the co-ordinated arene.

From these conclusions two main differences are immediately made evident between the features of the cobalt catalysts in aliphatic and in aromatic solvents respectively, in the polymerization of pentadiene. The first difference concerns the catalyst structure. In pure aliphatic solvents, the cation $[\text{Co}(\text{arene})_2]^+$ cannot form, and therefore the catalyst complex obtained in this solvent is in some respect different from that obtained in benzene. It could be that in aliphatic solvents the co-ordination around the cobalt is not octahedral as in benzene. The second difference concerns the mode of co-ordination of pentadiene to Co before its incorporation into the growing chain. Since in aliphatic solvents 1,2 monomeric units are obtained, the co-ordination of the monomer most probably occurs through the vinyl group only, and not through both the double bonds as in benzene.

In order to explain the different stereospecificities of the polymerizations in aliphatic and aromatic solvents respectively it is therefore necessary to clarify why the co-ordination occurs by the two double bonds in an aromatic solvent, and by the vinyl group only in an aliphatic solvent.

A tentative explanation of this phenomenon is as follows. The co-ordination of a di-olefin to a transition metal by the two double bonds presumably occurs in two steps, (a) the co-ordination of the vinyl group and (b) the co-ordination of the remaining double bond.

Our opinion is that in benzene the change from (a) to (b) is rather rapid due to the pre-existing co-ordination of the arene. In an aliphatic solvent, probably because of the different steric situation around Co in this solvent, such a passage would be much slower and consequently the monomer, after the co-ordination to Co by only the vinyl group, would enter the growing chain as a 1,2 unit.

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Resume—On a polymérisé le trans 1,3 pentadiène en un polymère 1,2 lequel est syndiotactique. On peut faire la polymérisation en milieu solvant aliphatique vers 20° en utilisant un catalyseur préparé à partir de $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$ et du triacétylacétonate de cobalt. Les examens aux rayons X et par infra rouge montrent que le polymère peut avoir une structure cristalline. On examine les différences obtenues avec le catalyseur au cobalt en milieux aliphatiques et aromatiques respectivement.

Sommario—Il trans 1,3-pentadiene è stato polimerizzato a polimero 1,2 sindiodattico. La polimerizzazione può avvenire in solventi alifatici a circa 20° con un catalizzatore preparato con $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$ e triacetilacetato di cobalto. Gli esami ai raggi X ed infrarossi indicano che il polimero può essere cristallino. Le differenze tra i risultati ottenuti con i catalizzatori al cobalto nei solventi alifatici e aromatici rispettivamente sono pure oggetto di discussione.

Zusammenfassung—Trans-1,3-Pentadien wurde zu einem weitgehend syndiotaktischen 1,2-Polymer polymerisiert. Die Polymerisation kann in aliphatischen Lösungsmitteln bei etwa 20° unter Verwendung eines Katalysators aus $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$ und Kobalttriacetylacetonat durchgeführt werden. Röntgenographische und Infrarotuntersuchungen haben gezeigt, daß das Polymer kristallin sein kann. Die unterschiedliche Wirkung von Kobaltkatalysatoren in aliphatischen und aromatischen Lösungsmitteln wird besprochen.