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## **Polymerization of Conjugated Diolefins by Homogeneous Aluminum Alkyl-Titanium Alkoxide Catalyst Systems**

### **II. 1,2-Polybutadiene and 3,4-polyisoprene**

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#### SUMMARY:

The polymerization of butadiene and isoprene by homogeneous aluminum alkyl-titanium alkoxide catalysts is reported. Polybutadienes and polyisoprenes prevalently constituted of 1,2 and 3,4 units respectively were obtained. By fractionating the polybutadienes crystalline polymers with a syndiotactic structure were isolated; on the other hand, the polyisoprenes were found to be completely amorphous, probably because of lack of stereoregularity in the polymer chains. Some data concerning the copolymerization of isoprene with 1,3-pentadiene are reported. A discussion of the dependence of the stereospecificity of the catalyst on the nature of the monomer and a model for the stereospecific synthesis of *cis*-1,4 isotactic polypentadiene are included.

#### ZUSAMMENFASSUNG:

Die Polymerisation von Butadien und Isopren mit homogenen Aluminiumalkyl-Titanalkoholat-Katalysatoren wird beschrieben. Dabei wurden Polybutadiene und Polyisoprene, die vorwiegend aus 1,2- bzw. 3,4-Einheiten aufgebaut sind, erhalten. Durch Fraktionierung wurden kristalline Polybutadiene mit syndiotaktischer Struktur isoliert; die Polyisoprene erwiesen sich dagegen als völlig amorph, wahrscheinlich wegen Fehlens von sterischer Regelmäßigkeit in den Polymerketten. Auch einige Daten zur Copolymerisation des Isoprens mit 1,3-Pentadien werden mitgeteilt. Schließlich wird die Abhängigkeit der Stereospezifität des Katalysators von der Natur des Monomeren diskutiert, und es wird ein Modell für die stereospezifische Synthese des *cis*-1,4-isotaktischen Polypentadiens gegeben.

#### *Introduction*

In the preceding paper<sup>1)</sup> the polymerization of 1,3-pentadiene by catalyst obtained from an aluminum trialkyl and a titanium tetra- or trialkoxide was examined. A characterization of the resulting polymers which exhibit a *cis*-1,4 isotactic structure was also included. This paper is concerned with the polymerization of butadiene and isoprene by the

same catalysts. It also discusses the dependence of the stereospecificity upon the chemical nature of the monomer and a model for the formation of *cis*-1,4 isotactic polypentadiene.

### Polymerization of butadiene

Some results concerning the polymerization of butadiene by catalysts prepared from  $\text{Al}(\text{C}_2\text{H}_5)_3$  and a titanium alkoxide are reported in Table 1. The polymers are prevalently constituted of 1,2 units and exhibit on X-ray examination a weak crystallinity due to a syndiotactic structure. Independently of the particular type of aluminum alkyl or titanium alkoxide used all the catalysts have shown a noticeable tendency to give cross-linked polymers. This phenomenon is more evident at higher conversions. Only when operating at low conversion and at rather low temperature (0–10 °C.) it was possible to obtain polymers which can be considered practically free of cross-linking (completely soluble in benzene).

Table 1. Polymerization of butadiene by aluminum alkyl-titanium alkoxide catalysts<sup>a)</sup>

Run	Solvent (ml.)	Titanium compound (moles · 10 <sup>3</sup> )	Al/Ti (molar ratio)	Time of aging of catalyst (min.)	Mono- mer (g.)	Polym. time (hrs.)	Polymer <sup>b)</sup>		
							Yield (g.)	IR analysis (%)	
							1,2	1,4 <i>cis</i>	
1	benzene 30	Ti(O- <i>n</i> -C <sub>4</sub> H <sub>9</sub> ) <sub>3</sub> 0.41	7	30	10	4	0.4	90	10
2	<i>n</i> -heptane 30	Ti(O- <i>n</i> -C <sub>4</sub> H <sub>9</sub> ) <sub>3</sub> 0.34	7	10	10	9	1	98	2
3	benzene 60	Ti(O- <i>n</i> -C <sub>4</sub> H <sub>9</sub> ) <sub>4</sub> 0.44	10	10	10	5	0.8	88	12
4	<i>n</i> -heptane 100	Ti(O- <i>i</i> -C <sub>3</sub> H <sub>7</sub> ) <sub>4</sub> 1,6	6	3	80	8	53	90	10
5	<i>n</i> -heptane 100	Ti(O- <i>n</i> -C <sub>3</sub> H <sub>7</sub> ) <sub>4</sub> 2	7	3	35	16	27	93	7
6	<i>n</i> -heptane 100	Ti(O- <i>n</i> -C <sub>3</sub> H <sub>7</sub> ) <sub>4</sub> 2	7	2	35	5	8	96	4

<sup>a)</sup> Catalyst prepared by introducing the aluminum alkyl into the solution or suspension (runs 1,2) of titanium alkoxide, and leaving it at room temperature to age for the time indicated. Runs 1–3 were performed in glass vessels (*cf.*<sup>1)</sup>); runs 4–6 in a 500 ml. autoclave, equipped with a thermostat. Polymerization temperature: 0 °C. (15 °C. for run 4).

<sup>b)</sup> 40 to 60% soluble in diethyl ether. The residue after ether extraction (> 95% 1,2 units) exhibits a weak crystallinity of the syndiotactic type.

The crude polymerization products were fractionated by extraction with boiling ether which dissolves the amorphous polymers; the extraction residue is constituted of polymers which exhibit a weak crystallinity of the syndiotactic type (Fig. 1). While on IR examination the crystalline fraction appears to be constituted almost exclusively of 1,2 units, in the ether soluble fraction *cis*-1,4 units (5–15 %) are also present.

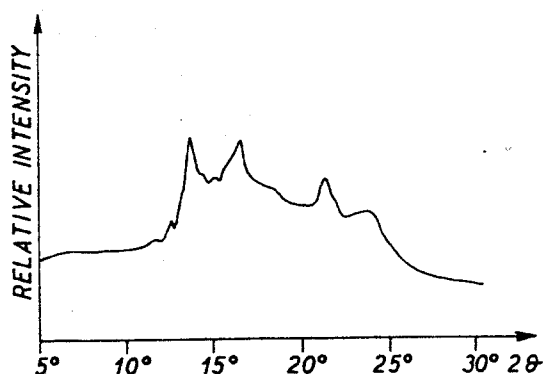


Fig. 1. X-ray powder spectrum ( $\text{CuK}\alpha$ ) registered by a GEIGER counter of a polybutadiene (residue after diethyl ether extraction) obtained by aluminum alkyl-titanium alkoxide systems

The fact that the crystalline fraction shows only a weak crystallinity in spite of its very high 1,2 content (nearly 100 %) probably depends on the low degree of stereoregularity of the polymer chains. However, to a certain degree it could also depend on cross-linking.

Considering the noticeable tendency to give cross-linked polymers, the catalysts obtained from aluminum trialkyls and titanium alkoxides do not appear to be the most suitable for the preparation of 1,2 syndiotactic polybutadiene. As already known such a polymer can be obtained in better yields and with a much higher crystallinity by other catalysts, prepared from aluminum trialkyls and compounds of vanadium<sup>3)</sup>, molybdenum<sup>3)</sup> or cobalt<sup>4)</sup>.

### *Polymerization of isoprene*

Some data concerning the polymerization of isoprene with the  $\text{Al}(\text{C}_2\text{H}_5)_3$ - $\text{Ti}(\text{O}-n-\text{C}_3\text{H}_7)_4$  system are reported in Table 2. Whereas in the polymerization of butadiene cross-linking occurred, this tendency was not observed in the polymerization of isoprene by the same catalyst. In fact, the polymers obtained are completely soluble in benzene at room temperature.

With our experimental conditions (*i.e.*, operating at room temperature and with catalysts aged for periods from a few min. to some hrs.) the opti-

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Table 2. Polymerization of isoprene by the  $\text{Al}(\text{C}_2\text{H}_5)_3\text{-Ti}(\text{O-}n\text{-C}_3\text{H}_7)_4$  catalyst system. Influence of the Al/Ti ratio on polymer yield, molecular weight and 3,4 unit content<sup>a)</sup>

Al/Ti (molar ratio)	Polymer		
	Yield (g.)	$[\eta]$ (100 ml./g.)	IR analysis; 3,4 units <sup>b)</sup> (%)
4	0.94	2.7	94
5	4.6	2.7	94
6	10.7	2.9	95
10	7.56	1.97	91
20	4.23	0.15	83

<sup>a)</sup> Experimental conditions: 100 ml. toluene; 0.5 ml.  $\text{Ti}(\text{O-}n\text{-C}_3\text{H}_7)_4$ ; 30 ml. isoprene (from decomposition of the sulphone, 99.8% pure); catalyst aged for 12 min. at 18°C.; polymerization time and temperature: 8 hrs. at 24°C.

<sup>b)</sup> The remaining units are prevalently *cis*-1,4.

imum Al/Ti molar ratio is 6–7 with regard to the polymer yield. At this ratio also the highest 3,4 content and the highest molecular weights are obtained.

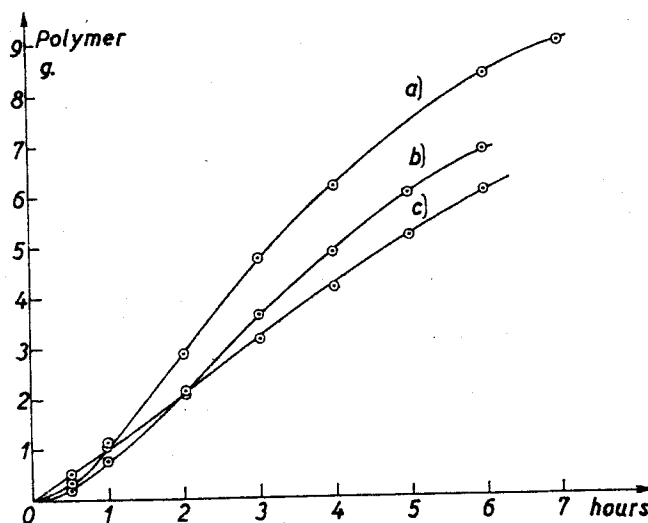
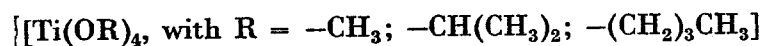


Fig. 2. Polymerization of isoprene by an  $\text{Al}(\text{C}_2\text{H}_5)_3\text{-Ti}(\text{O-}n\text{-C}_3\text{H}_7)_4$  catalyst. Variation of the amount of polymer with polymerization time. Experimental conditions: 155 ml. toluene; 0.75 ml.  $\text{Ti}(\text{O-}n\text{-C}_3\text{H}_7)_4$ ; 2.25 ml.  $\text{Al}(\text{C}_2\text{H}_5)_3$ ; 45 ml. isoprene (from sulphone); catalyst aged at 20°C., for a) 20 min., b) 1 hr., c) 3 hrs.; polymerization temperature 24°C.

Fig. 2 shows plots representing the variation of the amount of polymer with polymerization time, for catalysts aged for different lengths of time. In the case of unaged or briefly aged catalysts the curves present an initial inflexion, indicative of an induction period; this disappears for catalysts aged for about 3 hrs. The induction period is presumably due to

the fact that the catalyst forming reaction is slow and that the formation of the catalyst continues after the addition of the monomer.

The different titanium alkoxides employed



gave practically identical results.

From the data of Table 2 a rapid decrease of the molecular weight with increasing Al/Ti ratio is observed. This fact presumably depends on a transfer of the growing chains by the aluminum trialkyl or a species derived from it. Actually, in polymerizations performed using  $\text{C}^{14}$  labelled  $\text{Al}(\text{C}_2\text{H}_5)_3$  (Table 3) it has been observed that the  $\text{C}^{14}$  content in the polymer increases with the decrease of the molecular weight. This phenomenon appears similar to that found in the case of the polymerisation of  $\alpha$ -olefins<sup>5)</sup>.

Table 3. Polymerization of isoprene by the  $\text{Al}(\text{C}_2\text{H}_5)_3\text{-Ti}(\text{O-}n\text{-C}_3\text{H}_7)_4$  catalyst system<sup>a)</sup>  
Variation of polymer  $^{14}\text{C}$  activity on the Al/Ti ratio

Al/Ti (molar ratio)	Polymer <sup>b)</sup> (g.)	$[\eta]$ (100 ml./g.)	Polymer activity (counts/min.)
6	1.5	1.27	47
9	2.57	0.56	70
12	2.38	0.37	100
15	2.04	0.35	115

a) Experimental conditions: 30 ml. toluene; 10 ml. isoprene (PHILLIPS „polymerization grade”); 0.2 ml.  $\text{Ti}(\text{O-}n\text{-C}_3\text{H}_7)_4$  (isoprene was added to the toluene solution of  $\text{Al}(\text{C}_2\text{H}_5)_3$ , then  $\text{Ti}(\text{OR})_4$  was introduced). Polymerization time and temperature: 9 hrs. at 25 °C.

b) IR analysis: 90–95% 3,4 units.

Table 4. Influence of the polymerization temperature on the structure of the polyisoprenes obtained by the  $\text{Al}(\text{C}_2\text{H}_5)_3\text{-Ti}(\text{O-}n\text{-C}_3\text{H}_7)_4$  system<sup>a)</sup>

Polym. temp. (°C.)	3,4 units (%)
25	94
0	97
-10	99

a) Al/Ti molar ratio = 6.

With regard to the characteristics of the polymer, the average 3,4 unit content of the products obtained at 20–25 °C. and with an Al/Ti molar

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ratio of 6-7 is about 94-95%, the remaining units being prevalently *cis*-1,4. A certain influence of the polymerization temperature on the polymer structure has been observed, the 3,4 unit content being higher the lower the temperature. Polymerizing at a temperature below 0°C. and at an Al/Ti ratio of about 6, crude polymers constituted of 99-100% 3,4 units have been obtained (Table 4).

The 3,4 polyisoprenes were found to be amorphous on X-ray examination, even those constituted almost exclusively of 3,4 units. Even on examining the polymers at low temperature and under stretching no crystallinity was detected. Furthermore, no difference has been noticed between the IR spectra of the solid and dissolved polymers (Fig. 3); this fact is usually considered indicative of a non regular conformation of the chains in the solid state.

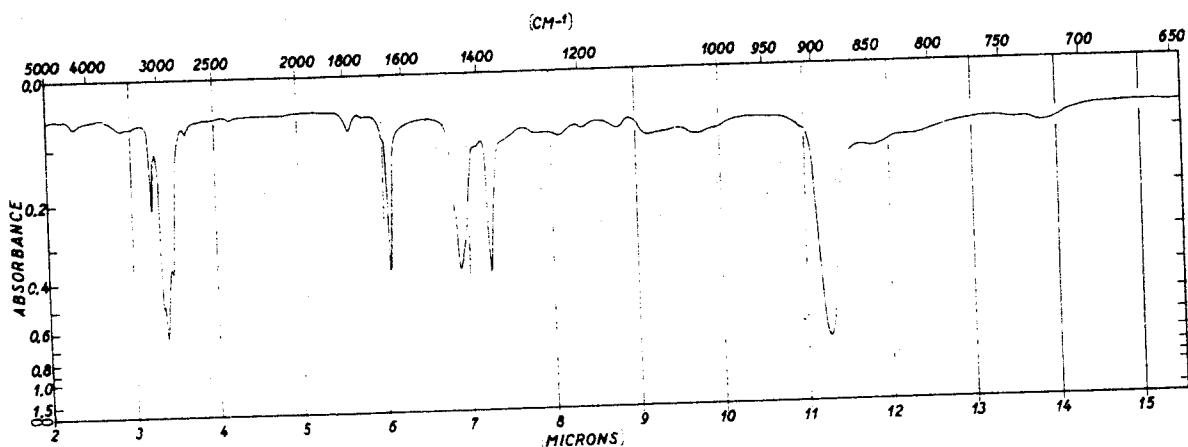


Fig. 3. IR spectrum of a polyisoprene obtained by aluminum alkyl-titanium alkoxide systems

The lack of crystallinity may be attributed to different factors:

- the polymers are atactic, that is, they show disorder in the distribution of the configurations of the asymmetric carbon atoms in the chains;
- the polymers possess a certain stereoregularity, probably of low degree; however, the regular conformation of the stereoregular chain sections, and hence the formation of the crystalline lattice, is hindered by steric factors, due to the presence of the bulky isopropylidene group in the side chain.

Although the latter hypothesis cannot be completely ruled out, it seems more probable that the lack of crystallinity of the polymers is attributable to lack of stereoregularity along the chains.

*Copolymerization of isoprene with pentadiene*

In order to demonstrate whether the catalytic complexes which give *cis*-1,4 polypentadiene are the same as those which give 3,4 polyisoprene the copolymerization of isoprene with pentadiene was examined. If a copolymer were obtained in which the isoprene units were 3,4 and the pentadiene units *cis*-1,4, this would demonstrate that the same catalytic center is effectively able to give different structures to the units derived from the two different monomers.

The results of a typical copolymerization run are reported in Table 5. The copolymer was fractionated and the various fractions were examined by X-ray and IR. In each fraction the isoprene units were prevalently 3,4, while the pentadiene units were prevalently *cis*-1,4. No fraction was found to be crystalline on X-ray. This fact makes it very probable that the pentadiene units are copolymerized with the isoprene units; if the copolymerization products were a mechanical mixture of the two homopolymers a crystallinity due to *cis*-1,4 isotactic polypentadiene should be observed, considering that in the polymerization products the pentadiene units were prevalent ( $\sim 80\%$ ).

The copolymerization of butadiene with pentadiene was also examined, but in this case the characterization of the products was found to be much more difficult by the fact that cross-linking occurs.

Table 5. Copolymerization of isoprene with 1,3-pentadiene by the  $\text{Al}(\text{C}_2\text{H}_5)_3\text{-Ti}(\text{O}-n\text{-C}_4\text{H}_9)_4$  catalyst system<sup>a)</sup>

Fractions examined <sup>b)</sup>	Amount (g.)	[ $\eta$ ] (100 ml./g.)	X-ray exami- nation	IR Analysis			Iso- prene <sup>c)</sup> (%)
				Pentadiene (%)			
				<i>cis</i> -1,4	<i>trans</i> -1,4 and 1,2	3,4	
Crude product	1.3	1.85	amorphous	38.3	33.0	10.5	18.2
Fraction I	0.06	—	amorphous	22.5	53.0	12.0	12.5
Fraction II	0.42	0.61	amorphous	38.8	33.0	10.6	11.0
Fraction III	0.33	1.48	amorphous	39.0	33.0	10.3	17.4
Fraction IV	0.42	2.38	amorphous	39.0	31.8	10.8	18.9
Fraction V	0.55	2.6	amorphous	41.0	28.0	10.9	20.2

a) Polymerization conditions: 80 ml. benzene; 0.3 ml.  $\text{Ti}(\text{OC}_4\text{H}_9)_4$ ; 0.9 ml.  $\text{Al}(\text{C}_2\text{H}_5)_3$ ; 9.5 g. pentadiene (*trans* isomer, 98%); 4.1 g. isoprene (PHILLIPS "polymerization grade"). Time of aging of the catalyst: 15 min. at 20°C. Polymerization time and temperature: 50 hrs. at 20°C.

b) For fractionation conditions, cf. experimental part.

c) Almost exclusively as 3,4 units.



*Discussion*

*Dependence of the stereospecificity on the chemical nature of the monomer*

An unexpected result of the polymerizations is that the catalyst which gives 3,4 amorphous polyisoprene or 1,2 syndiotactic polybutadiene gives, in the case of pentadiene, a polymer having a *cis*-1,4 isotactic structure, that is having a completely different type of addition and stereoregularity. To our knowledge differences of this type in the structure of polydiolefins obtained by the same catalyst have not been observed previously. In the case of the stereospecific polymerization of butadiene and isoprene (the 2 diolefins most intensively studied until now) some differences in the steric composition of the corresponding polymers obtained by the same catalyst have already been observed; such differences, however, were not of sufficient magnitude to alter the prevailing type of structure which was the same in both polymers.

The different behaviour of pentadiene, with respect to butadiene and isoprene, is not restricted to the polymerization by the aluminum alkyl-titanium alkoxide catalysts examined in this paper. In preliminary runs we have in fact observed that other catalysts which give 1,2 syndiotactic polybutadiene (*e.g.*, the  $\text{Al}(\text{C}_2\text{H}_5)_3$ -molybdenyl or vanadyl alkoxide systems) give polymers of pentadiene which also are prevailingly *cis*-1,4.

It is now generally admitted that in the case of catalysts obtained from metal alkyls and transition metal compounds, the incorporation of the monomer in the growing chain is preceded by coordination of the monomer to the transition metal. The question arises whether the different structure of polypentadiene, with respect to polybutadiene or polyisoprene, depends on different types of coordination of the monomers.

In the case of butadiene or isoprene it seems reasonable to assume that the coordination occurs through the vinyl group, as 1,2 and 3,4 polymers are obtained respectively.

One might think that in the case of pentadiene the *cis*-1,4 addition arises from the fact that the monomer coordinates in the *cis* conformation, both double bonds being used. This hypothesis, however, can readily be rejected in the case of the *cis* isomer (which, we may recall, also gives *cis*-1,4 polypentadiene). In fact, for this isomer the *cis* conformation is sterically hindered. We must assume, therefore, that it coordinates to the transition metal only through the vinyl group prior to its incorporation in the polymer as a *cis*-1,4 unit. In the case of the *trans* isomer, the *cis* conformation is permissible, but other considerations lead to the conclusion that also in the case of this isomer the coordination occurs through

the vinyl group only, as for the other isomer. In fact, if the steric situation around the transition metal were such as to permit a coordination of the *trans* isomer of pentadiene in its *cis* conformation, one should expect isoprene or butadiene to coordinate in the same way, yielding *cis*-1,4 units in the polymer. We must conclude that the *cis* and *trans* isomers of pentadiene coordinate to the transition metal through their vinyl group prior to their incorporation as *cis*-1,4 units; therefore, the different type of structure of polypentadiene with respect to polybutadiene or polyisoprene does not arise from a different type of coordination.

In the case of polyisoprene and polypentadiene the different type of addition of the monomeric units seems explicable taking into account the different charge distribution which exists in the two monomers, as a consequence of the different position of the methyl group. In fact, it seems reasonable to assume that the new metal-carbon bond will be formed preferentially at C<sub>3</sub> of coordinated isoprene (Fig. 4) and at C<sub>1</sub> of coordinated pentadiene (Fig. 5).

This situation would lead to 3,4 units in the case of isoprene, while in the case of pentadiene two intermediate stages can arise, one (I) leading to 1,2 units, the other (II) to *cis*-1,4 units. The fact that in polypentadiene 1,2 units are very few in comparison to *cis*-1,4 units means that the intermediate stage II is much more favoured. This might depend on the fact that the density of positive charge at C<sub>4</sub> is higher than at C<sub>2</sub> due to the presence of methyl group in position 4.

Butadiene appears to behave similar to isoprene as also in this case it seems plausible that the new metal-carbon bond will be formed preferentially at the secondary carbon atom of the coordinated monomer\*). The formation of butadiene 1,2 units would occur therefore according to the same scheme outlined in Fig. 4 for isoprene.

#### *Formation of cis-1,4 isotactic polypentadiene*

It is particularly interesting that *cis*-1,4 isotactic polypentadiene is obtained by a homogeneous catalyst (in the sense explained in <sup>1)</sup>).

So far, isotactic hydrocarbon polymers in which the substituent bonded to the asymmetric carbon atom is a saturated group have been obtained only by heterogeneous catalysts. This is the case, *e.g.*, for isotactic polymers of  $\alpha$ -olefins.

\*) With regard to this, *c.f.* the work by K. ZIEGLER and coworkers on the mechanism of polymerization of butadiene by butyl or phenyl lithium in diethyl ether (Liebigs Ann. Chem. 567 (1950) 43).

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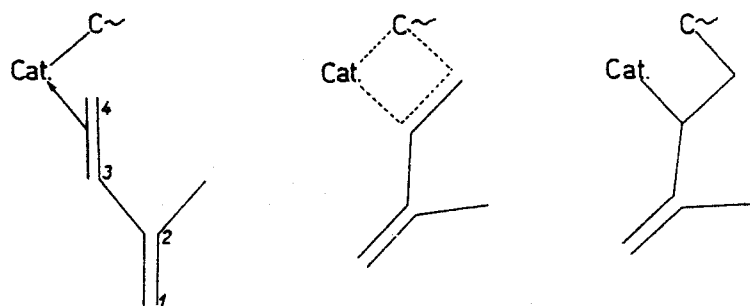


Fig. 4

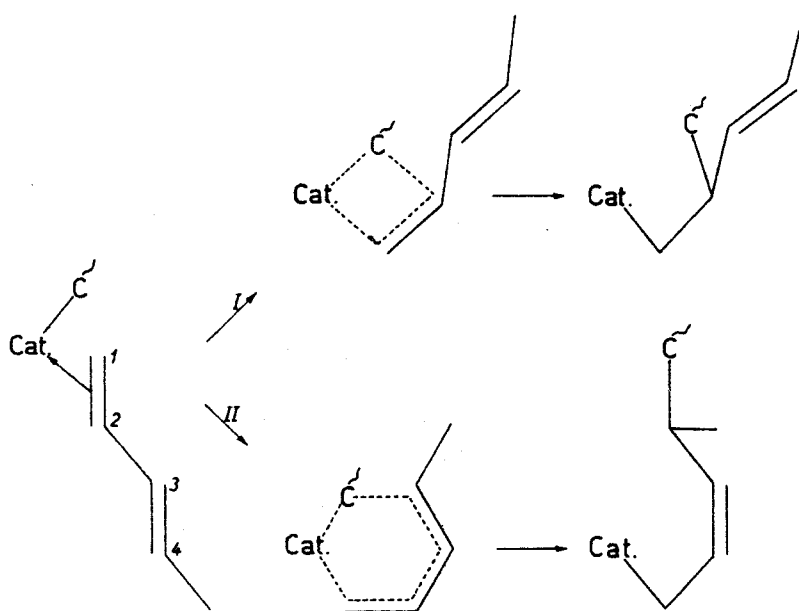


Fig. 5

The nature of the mechanism of pentadiene polymerization to *cis*-1,4 isotactic polymer is not yet clear. However, we wish to present here a scheme of polymerization, which could explain the formation of *cis*-1,4 isotactic polypentadiene by a homogeneous catalyst, taking into account the experimental results from this work. Obviously this scheme is not to be considered as a complete interpretation of the mechanism of polymerization, but only as a model.

The bond between the transition metal of the catalyst and the last monomeric unit of the growing chain is of the allylic type and can be represented in our case as in Fig. 6.

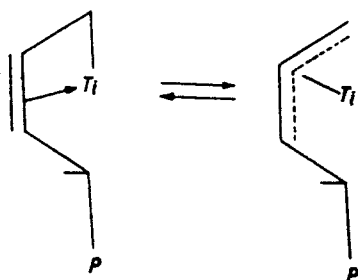


Fig. 6

The last polymerized unit and the coordinated monomer can be represented as in Fig. 7\*).

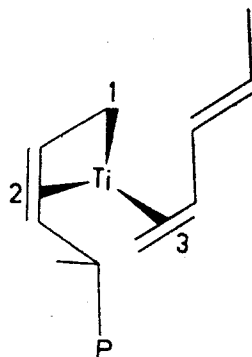


Fig. 7

In this figure the transition metal is in the plane of the paper, while the ends of the bonds are on a plane above that of the paper. Bond 1 is the metal-polymer bond; bonds 2 and 3 are dative bonds from the double bonds of the polymerized and coordinated monomer respectively to the catalytic center.

The incorporation of the coordinated monomer into the polymer chain is schematically outlined in Fig. 8a-c.

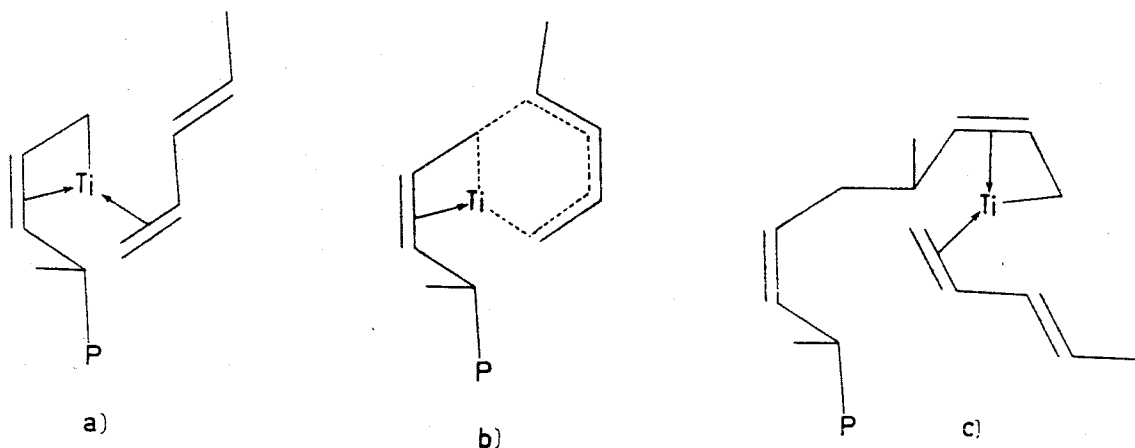


Fig. 8

Fig. 8a represents the same situation as Fig. 7, Fig. 8b represents the transition state, and Fig. 8c the final stage, with the monomer unit already incorporated and a new incoming monomer coordinated to the

\*) The bonds of Fig. 7 could be part of a tetrahedron or a trigonal pyramid or an octahedron. Only the angles between the bonds vary depending on the type of coordination. The actual coordination of the titanium in the catalyst is unfortunately not yet known. However, the validity of the model presented here is independent of whether this coordination is tetrahedral or trigonal bipyramidal or octahedral.

active center. The final stage creates a situation which is identical to the initial one; this is easily seen by a comparison of Fig. 8a with Fig. 8c.

Therefore, if we assume the same type of addition for all incoming monomer molecules (which is quite reasonable) isotactic sequences should be formed.

### *Experimental*

#### *Products*

For the solvents, aluminum alkyls, and titanium alkoxides, *cf.*<sup>1)</sup> PHILLIPS butadiene ("pure grade" 99%) and isoprene ("polymerization grade", > 99%) were usually used. In some runs isoprene from decomposition of the crystalline sulphone was used. All the monomers were distilled immediately before use.

#### *Polymerization and polymer fractionation*

The polymerizations were carried out by the technique used in the case of pentadiene (see<sup>1)</sup>). The polybutadienes were fractionated by extraction with boiling ether in order to separate the amorphous (soluble in ether) from the crystalline fraction (remaining as residue). This method of fractionation suffers from limitations when cross-linked polymers are present as pointed out in a previous paper<sup>2)</sup>. In this case the residue of ether extraction consists not only of crystalline polymers but also of cross-linked products.

#### *Copolymerization of butadiene with pentadiene*

80 ml. of benzene, 0.3 ml. of  $Ti(O-n-C_4H_9)_4$  and 0.88 ml. of  $Al(C_2H_5)_3$  were used for the preparation of the catalyst. The catalytic solution was aged for 15 min. at 20°C., then a mixture of pentadiene (14 ml.; *trans* isomer: 98.5%; *cis* isomer: 1.5%) and isoprene (6 ml.) was introduced. After 2 days of polymerization at 20°C., the polymer was coagulated by  $CH_3OH$  by the usual technique. 1.3 g. of product were obtained. This was fractionated as follows. The crude polymer was dissolved in benzene and then precipitated by pouring the benzene solution into a large excess of acetone. The precipitated polymer was separated by decantation from the acetone, which was then removed under vacuum to isolate the low molecular weight polymer, soluble in this solvent (fraction I). The acetone insoluble fraction was again dissolved in benzene and reprecipitated by methyl ethyl ketone (MEK). The MEK soluble polymer constitutes fraction II. The MEK insoluble polymer was once again dissolved in benzene and from this solution 2 additional fractions (V, IV) were separated by addition of 2 successive amounts of  $CH_3OH$ . The remaining polymer was precipitated by an excess of  $CH_3OH$  to give fraction III. Each of the 5 fractions was examined by IR and X-ray. The results are summarized in Table 5.

#### *Physical examination of the polymers*

IR analyses of polybutadienes and polyisoprenes were performed by the methods already described<sup>6,7)</sup>. IR analyses of isoprene-pentadiene copolymers were performed as follows. Isoprene content was calculated from the band at 11.25  $\mu$  (vinylidene groups), and pentadiene content from the bands at 13.3  $\mu$  (*cis*-1,4 units), 11  $\mu$  (vinyl groups, from 3,4 units), and 10.35  $\mu$  (*trans*-1,4 and possibly 1,2 units), respectively. The coefficients  $10 \cdot 10^4$ ,  $6 \cdot 10^4$ ,  $12 \cdot 10^4$ ,  $10 \cdot 10^4$  moles<sup>-1</sup>·cm<sup>-1</sup>·ml. were used for the above bands.

Isoprene 1,4 units, which should be characterized by a band at about 12  $\mu$  are present in the copolymers to such a small extent that they can be neglected in the analyses.

For the other physical determinations on the polymers *cf.*<sup>1)</sup>.

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