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

I. *Cis*-1,4 isotactic poly (1,3-pentadiene)

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SUMMARY:

The polymerization of 1,3-pentadiene by soluble aluminum alkyl-titanium alkoxide catalysts is reported. Both the *cis* and *trans* isomers of 1,3-pentadiene are polymerized by these catalysts to polymers prevalently constituted of *cis*-1,4 units. By fractionating the crude products obtained from the *trans* isomer, amorphous and crystalline fractions were isolated; the latter were found to have a *cis*-1,4 isotactic structure on X-ray examination. By fractionating the crude products obtained from the *cis* isomer, polymers having only a very weak crystallinity could be isolated. A characterization of the crystalline *cis*-1,4 isotactic polypentadiene by X-ray and IR examination is also reported.

ZUSAMMENFASSUNG:

Die Polymerisation des 1,3-Pentadiens mit löslichen Aluminium-alkyl/Titan-alkoxyd-Katalysatoren wird beschrieben. Sowohl das *cis*- als auch das *trans*-Isomere des 1,3-Pentadiens können mit diesen Katalysatoren polymerisiert werden, wobei Polymere entstehen, die vorwiegend aus 1,4-*cis*-Einheiten aufgebaut sind. Durch Fraktionieren der aus dem *trans*-Isomeren erhaltenen Rohprodukte wurden amorphe und kristalline Fraktionen isoliert; den letzteren wurde auf Grund von Röntgenbeugungsmessungen 1,4-*cis*-isotaktische Struktur zugeschrieben. Durch Fraktionieren der aus dem *cis*-Isomeren erhaltenen Rohprodukte wurden Polymere mit nur sehr geringem Kristallinitätsgrad isoliert. Es wird eine auf Röntgen- und IR-Messungen basierende Charakterisierung des isotaktischen 1,4-*cis*-Polypentadiens gegeben.

Introduction

The polymerization of butadiene and other conjugated diolefins by catalysts obtained from aluminum alkyls and titanium halides has long been studied [1]. However, little is known about the polymerization of these monomers by catalysts based on titanium compounds other than halides, for instance alcoholates or acetylacetonates.

It is known from the fundamental work of ZIEGLER [2], and from subsequent work [3] that catalysts belonging to this class are able to polymerize ethylene to linear high polymers. It is also known that they are homogeneous [3b] and cannot polymerize α-olefins [4].

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In our laboratory we have long been dealing with the polymerization of 1,3-butadiene, isoprene, and 1,3-pentadiene by catalysts of the above mentioned class. From butadiene such catalysts give crystalline polymers having 1,2 syndiotactic structure; from isoprene, amorphous polymers prevalently constituted of 3,4 units (obtained for the first time by these catalysts[5]), and from pentadiene crystalline *cis*-1,4 polymers are obtained which were found to be different by IR and X-ray examination from the *cis*-1,4 syndiotactic polypentadiene obtained previously[6,7].

The preparation and characterization of these polymers has been described so far only in patents[5b,8] and in a preliminary communication[7].

It is the purpose of this and a subsequent paper to report the detailed results of our work on the polymerization of butadiene, isoprene, and pentadiene by the aluminum alkyl-titanium alkoxide catalyst systems. This first paper is concerned with the polymerization of 1,3-pentadiene and with the characterization of the resulting polymers. The following one will be concerned with the polymerization of butadiene and isoprene and will include a discussion on some aspects of the stereospecificity of the catalysts.

The catalytic system

At room temperature and in a hydrocarbon solvent the reaction between $Al(C_2H_5)_3$ and a titanium tetraalkoxide occurs with the evolution of gas and heat, while simultaneously the solution assumes a dark colour. The solution so obtained has catalytic activity. The gas evolved is essentially ethane. The titanium trialkoxides react in an analogous way, giving similar dark solutions. Gas (essentially ethane) is evolved, also in this case.

The evolution of ethane indicates that a step of the catalyst forming reaction consists of an alkylation of the transition metal compound with formation of titanium-carbon bonds, which, at least in part, are rapidly broken. The formation of ethane, instead of an equimolar mixture of ethane and ethylene, as one would expect from a disproportionation of ethyl radicals, could be attributed to one of the following cause: a) hydrogen abstraction from the solvent occurs; b) the ethylene produced in the disproportionation of the ethyl radicals is polymerized, so that only ethane is evolved. In this respect it has to be noted that the titanium catalysts considered here are in fact able to polymerize ethylene.

Little is known about the nature of the catalyst. It seems, however, reasonable to assume that it is a complex containing aluminum and titanium, the latter in a lower valence state. The hypothesis that in the

catalyst forming reaction an aluminum-titanium complex is produced, rather than a simple low valence titanium compound, seems confirmed by the following: the titanium trialkoxides are crystalline solids, sparingly soluble in hydrocarbon solvents; if they were formed in the reaction between $Al(C_2H_5)_3$ and a titanium tetraalkoxide, the formation of a precipitate should be observed, especially at low Al/Ti ratio. No precipitate was noted, however, at any Al/Ti ratio.

No information is yet available concerning the valence state of the titanium in the catalytic complex. An experimental fact reported in a previous communication[9] seems to indicate that at least 1 alkoxy group remains bonded to titanium present in the catalytic complex. In fact, it has been observed that catalysts prepared from $Al(C_2H_5)_3$ and an optically active titanium tetraalkoxide (tetramenthoxide or tetraisoamilate) give a cis-1,4 isotactic polypentadiene which shows a remarkable optical activity. This result is hardly explicable if one assumes that in the reaction between $Al(C_2H_5)_3$ and the titanium tetraalkoxide all the alkoxy groups are removed from titanium[*].

The catalysts obtained from aluminum trialkyls and titanium alkoxides appear to be homogeneous. In fact, they leave no residue on filtration (G 4 filter) and their solutions appear clear. However, it cannot be completely excluded that we are dealing with colloidal dispersions rather than with solutions.

Polymerization of 1,3-pentadiene

The aluminum trialkyl-titanium alkoxide catalyst systems polymerize both the cis and trans isomer of 1,3-pentadiene. The polymers obtained from the trans isomer show a prevalently cis-1,4 addition, as will be discussed in detail in the following section, and appear crystalline on X-ray examination. The polymers obtained from the cis isomer also show a prevalently cis-1,4 addition; however, when examined before fractionation, they appear amorphous on X-ray examination and only after fractionation it was possible to isolate a fraction which shows a very slight crystallinity.

The crystallinity present in the polymers obtained from the trans isomer as well as the very weak crystallinity detected in some fractions of the polymers obtained from the cis isomer is attributable to the presence of chain sections having a cis-1,4 isotactic structure[7].

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[*] Unpublished results have demonstrated that the optical activity of the polymer does not arise from such species as $Al(C_2H_5)_2OR^*$ or $Al(C_2H_5)(OR^*)_2$ originating from the reaction between $Al(C_2H_5)_3$ and the optically active titanium alkoxide, $Ti(OR^*)_4$.

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Table 1. Influence of Al/Ti ratio on the polymerization of 1,3-pentadiene by the
$Al(C_2H_5)_3-Ti(O-n-C_4H_9)_4$ catalyst[a]

$Al(C_2H_5)_3$ (moles)	Al/Ti (molar ratio)	Crude polymer				
		Yield (g.)	I.R. Analysis (%)[b]			$[\eta]^{c)}$ (100 ml./g.)
			cis	trans	3,4	
$4.2 \cdot 10^{-3}$	3	0,3	61	29	10	–
$5.6 \cdot 10^{-3}$	4	2.0	66	22	12	2.92
$9.8 \cdot 10^{-3}$	7	4.6	68	20	12	2.74
$1.4 \cdot 10^{-2}$	10	4.6	55	34	11	1.69
$2.1 \cdot 10^{-2}$	15	4.9	54	35	11	1.25
$4.2 \cdot 10^{-2}$	30	1.0	54	35	11	0.77

a) Polymerization conditions: 100 ml. benzene; 15 g. monomer (98.5% *trans* isomer, 1.5% *cis* isomer); 0 °C., 26 hrs. Time of aging of catalyst: 2–3 min. at 18 °C.
b) For the meaning of *cis*- and *trans*-%, c.f. note on p. 7.
c) Determined in toluene at 30 °C.

Some data concerning the polymerization of pentadiene by systems obtained from aluminum alkyls and some titanium alkoxides are summarized in Table 1. The optimum Al/Ti molar ratio, both with regard to polymer yield and *cis*-1,4 content, was found to be about 6. When increasing the Al/Ti ratio a decrease in the molecular weight was observed (Table 1), probably because of a transfer between the growing polymer chains and the aluminum alkyl or some species derived from it. A phenomenon of this type has also been observed and studied in detail in the case of α-olefin polymerization by $Al(C_2H_5)_3$-$TiCl_3$ (violet modifications) catalysts[10].

No significant difference has been observed between catalysts prepared from different titanium alkoxides (Table 2). Dialkylaluminum hydrides have been used instead of aluminum trialkyls with similar results.

Some influence on the *cis*-1,4 content is exerted by the polymerization temperature, the polymers obtained at lower temperature showing a higher *cis*-1,4 content.

In order to isolate the more stereoregular macromolecules, the crude polymerization products were fractionated by repeatedly dissolving them in benzene and reprecipitation with methyl ethyl ketone (MEK). Two fractions were so obtained, one soluble in MEK, amorphous by X-ray and having lower molecular weight, the other insoluble and crystalline by X-ray (in the products obtained from the *cis* isomer, as already mentioned, the crystallinity of this fraction is extremely low).

Table 2. Polymerization of 1,3-pentadiene by catalysts obtained from aluminum alkyls and titanium alkoxides[a]

Run	Aluminum alkyl	Titanium compound	(moles ·10³)	Al/Ti (molar ratio)	Monomer[b] (g.)	Polymerization temp (°C.)	time (hrs.)	Yield (g.)	Crude polymer IR analysis[d] (%) cis	trans	3,4	MEK insoluble fraction[c] IR analysis[d] (%) cis	trans	3,4	X-ray examination
1	Al(C₂H₅)₃	Ti(O–n–C₄H₉)₄	4.2	3	5	0	26	0.2	66	25	9	—	—	—	—
2	Al(i–C₄H₉)₃	Ti(O–i–C₃H₇)₄	12	4	5.5	0	40	5.1	67	24	9	82	11	7	crystalline
3	Al(C₂H₅)₂H	Ti(O–n–C₃H₇)₄	4.4	4	6	10	15	3.9	58	30	12	74	19	7	crystalline
4	Al(C₂H₅)₃	Ti(O–n–C₄H₉)₄	6	5	14	0	30	1.0	70	20	10	85	10	5	crystalline
5	Al(CH₂–CH–(CH₂)₂–CH₃)₃ –CH₃	Ti(O–n–C₄H₉)₄	7	5	15	–15	45	6.9	78	16	6	87	9	4	crystalline
6	Al(C₂H₅)₃	Ti(O–n–C₄H₉)₄	8	5	16	0	35	6	80	14	6	85	10	5	crystalline
7	Al(CH₃–CH–(CH₂)₂–CH₃)₃ –CH₃	Ti(O–n–C₄H₉)₃	6.4	5	18	0	70	2.2	77	17	6	81	13	6	crystalline
8	Al(C₂H₅)₃	Ti(O–n–C₄H₉)₄	16	6	15	–15	70	2	71	21	8	85	12	4	crystalline
9	Al(C₂H₅)₃	Ti(O–n–C₄H₉)₄	16	7	13	20	5	6.2	64	27	9	81	14	5	crystalline
10	Al(C₂H₅)₃	Ti(O–n–C₄H₉)₃	12	7	20	0	70	3.3	60	30	10	78	15	7	crystalline
11	Al(C₂H₅)₃	Ti(O–i–C₅H₁₁)₄	15	7	12	0	14	5	70	23	7	81	13	6	crystalline
12	Al(C₂H₅)₃	Ti(O–n–C₄H₉)₄	20	7	10	0	40	4.6	54	30	16	60	25	15	amorphous
13	Al(C₂H₅)₃	Ti(O–n–C₄H₉)₄	14	10	14.5	0	26	4.6	55	34	11	71	17	12	crystalline
14	Al(C₂H₅)₃	Ti(O–n–C₄H₉)₄	7	5	17.5	0	60	1.5	75	15	10	79	13	8	amorphous
15	Al(C₂H₅)₃	Ti(O–n–C₄H₉)₄	16	7	11.2	–15	30	1.2	76	15	9	84	10	6	trace of crystall.

a) Polymerization conditions: 100 ml. solvent (runs 3,8–10: toluene; the other runs: benzene) – In runs 4, 6, 7, 10, 14 the catalyst was aged at room temperature for about 20 min.; in the other runs the monomer was added immediately after the catalyst formation.

b) Run 1–11,13: trans isomer (98–99%); run 12: mixture of trans (50%) and cis (50%) isomers; run 14–15: cis isomer (99.9%).

c) 30–35% of the crude polymer; [η] 5–7 (100 ml./g.; in toluene at 30 °C.).

d) For the meaning of cis- and trans-%, c.f. note on p. 7.

This method of fractionation gives satisfactory results because in these products the macromolecules which are less stereoregular and have a lower *cis*-1,4 content, are also of lower molecular weight. Although it is not very accurate this method allows the amorphous polymers (which constitute the major part of the polymerization products, about 65 %) to be removed in a rapid and simple way from the crude products, leaving as residue crystalline fractions sufficiently pure to be characterized.

Characterization of the pentadiene polymers

In the IR spectrum of the polypentadienes obtained by the aluminum alkyl-titanium alkoxide system, the useful bands for the determination of the various types of addition are those at 10.35 μ (internal double bonds of the *trans* type), at 11 μ (vinyl groups), and at 13.3 μ (internal double bonds of the *cis* type). While the band at 11 μ can only be attributed to 3,4[*] units, the attribution of the bands at 10.35 μ and 13.3 μ is not as unambiguous as in the case of polybutadienes. In fact, in the polymers of pentadiene not only the 1,4 units have internal double bonds, but also the 1,2 units have those in the side chain (*cis* or *trans*), which could therefore exhibit adsorptions in the regions of the IR spectrum indicated above. However, according to a recent study[11], the band at 13.3 μ seems attributable only to *cis*-1,4 units since 1,2 pentadiene units having a *cis* double bond in the side chain do not exhibit adsorption at 13.3 μ, but at about 13.75 μ. These findings have been confirmed by our studies on polypentadienes prevalently constituted of 1,2 units[12].

On the other hand, the band at 10.35 μ is common both to *trans* 1,4 and to 1,2 units having a *trans* double bond in the side chain. Hence, the band at 10.35 μ is unsuitable for the quantitative determination of these two types of units. It was observed, however, that from the high resolution IR spectrum it is possible to distinguish between *trans*-1,4 and 1,2 (*trans*) units, as the methyl group of the *trans*-1,4 unit exhibits a band at 7.29 μ, while that of the 1,2 (*trans*) unit exhibits a band at 7.26 μ.

The polypentadienes we have obtained all exhibit an intense band at 13.3 μ, while the band at about 13.75 μ is absent or hardly detectable. In addition, all the polymers show an intense band at 7.29 μ, while the band at 7.26 μ has a very low intensity. These two findings are indicative of a prevalently *cis*-1,4 addition, which is also confirmed by NMR[13] and

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[*] We define as 3,4 units those derived from the polymerization of the internal double bond of 1,3-pentadiene, and 1,2 as those derived from the polymerization of the vinyl group. Other authors who indicate 1,3 pentadiene as 1-methyl-1,3-butadiene define as 1,2 the units we define as 3,4 and *vice versa*.

X-ray examination. In fact, the identity period (about 8.1 Å) measured from the fiber spectra of the crystalline polymers is in agreement only with a cis-1,4 isotactic structure, as for 1,2 isotactic or syndiotactic structures identity periods of about 6.5 Å and 5.15 Å respectively would be expected.

However, using the bands at 7.26 μ and at about 13.75 μ it is difficult to obtain accurate quantitative determinations of the 1,2 units present among the largely prevalent 1,4 units. This is due to the fact that the adsorption coefficients of the two bands are not precisely known; in addition, the band at 7.26 μ is too close to that at 7.29 μ, for an exact measurement of its intensity. For these reasons the analyses reported in this paper, concerning the cis-1,4 content of the polymers, are to be considered as approximate *).
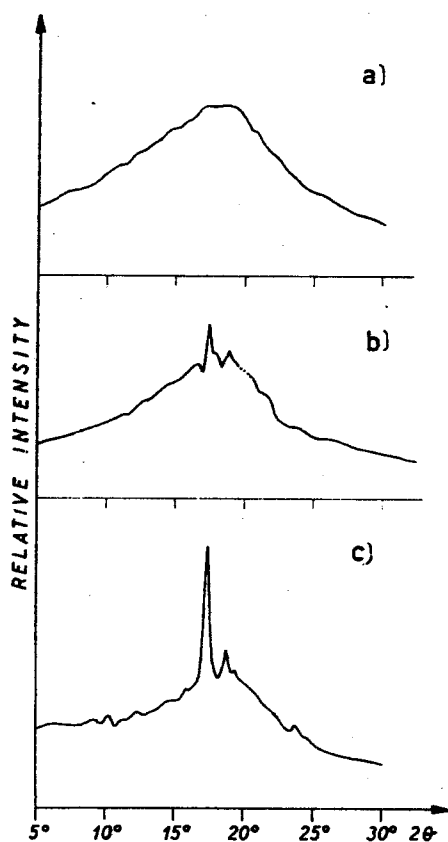

Fig. 1. X-ray powder spectra (CuK$_\alpha$) registered by a GEIGER counter of polypentadienes obtained by the aluminum alkyl-titanium alkoxide systems: a) MEK soluble fraction, obtained from the trans isomer; b) MEK insoluble fraction, obtained from the cis isomer; c) MEK insoluble fraction, obtained from the trans isomer

*) Tables 1 and 2 report only the total percentage of the units characterized by cis or trans internal double bonds (indicated as cis- and trans-% respectively), without distinguishing between 1,4 and 1,2 units, due to the difficulty of obtaining accurate analyses. It is clear, however, from the above that the 1,2 units especially in the crystalline fractions (MEK insoluble) are present only to a limited extent, so that cis-% or trans-% correspond approximately to the percentage of cis-1,4 or trans-1,4 units.

The crystalline polymers (MEK insoluble fraction) obtained from the *trans* isomer have the following average composition: *cis*-1,4 units: 80 to 85 %; 3,4 units: 4—5 %; *trans*-1,4 and 1,2 units: 9—15 %. Considering that the amount of units other than *cis*-1,4 is not negligible we must assume that the macromolecules are composed of chain sections of isotactic *cis*-1,4 units, sufficiently long to give rise to crystallinity, interspersed by units of the other types. The X-ray spectrum of the crystalline fraction obtained from the *trans* isomer is shown in Fig. 1c. It is characterized by two maxima corresponding to molecular distances d = 5.17 Å and 4.71 Å respectively. A comparison between this spectrum and that of *cis*-1,4 syndiotactic polypentadiene, and an examination of the conformations of the chains of the two polymers in the crystals has already been published[7].

A typical analysis of the MEK insoluble fraction of the polymers obtained from the *cis* isomer is as follows: *cis*-1,4 units: $\sim$ 85 %; 3,4 units: 5 %; *trans*-1,4 and 1,2 (*trans*) units: 10 %. In spite of the relatively high *cis*-1,4 unit content (comparable to that observed in the polymers obtained from the *trans* isomer) this fraction shows only a trace of crystallinity, on X-ray examination (Fig. 1b). This fact is apparently due to a very low degree of steric regularity in the *cis*-1,4 isotactic sequences.

The MEK soluble fractions of the polymers obtained both from the *cis* and *trans* isomer have a *cis*-1,4 unit content of about 55—60 %. They are characterized by a higher percentage of 1,2 units than the MEK insoluble fractions, and are completely amorphous on X-ray examination (Fig. 1a) as already mentioned.
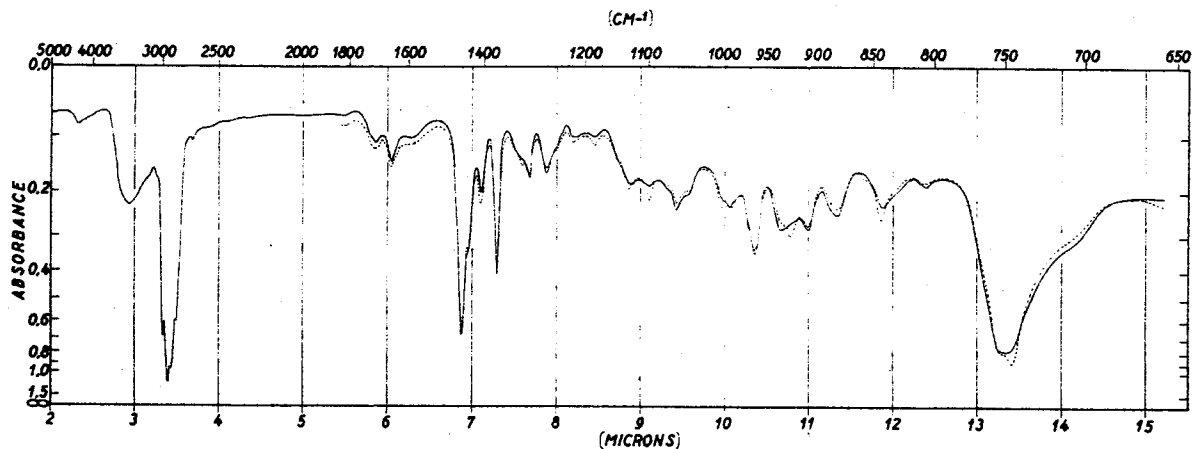

Fig. 2. IR spectrum of *cis*-1,4 isotactic polypentadiene (MEK insoluble fraction obtained from the *trans* isomer). Solid line: molten polymer; broken line: crystalline polymer

A comparison between the IR spectrum of a cis-1,4 isotactic polypenta-
diene in the molten and crystalline state respectively is reported in Fig. 2.
In the spectrum of the crystalline polymer some bands appear, which are
not present in the spectrum of the molten or dissolved polymer. The most
intense of these bands, which are characteristic of the regular confor-
mation of the chains, are at 13.40, 11.85, 10.80, and 9.95 μ.

It has to be noted that the characteristic band of the cis-1,4 units,
which occurs at 13.3 μ in the spectrum of the molten or dissolved polymer,
shifts to 13.4 μ and exhibits a higher intensity in the spectrum of the
crystalline polymer (Fig. 3). The position of this band in the spectrum of
the crystalline polymer is the most reliable parameter for distinguishing
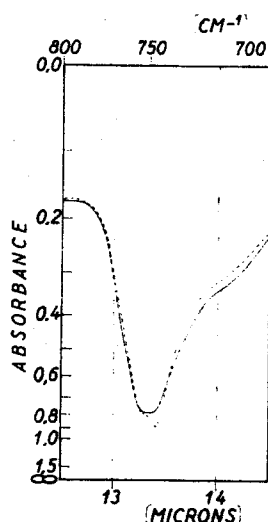the isotactic from the syndiotactic cis-1,4 polymer. In this respect it must

Fig. 3. A detail of the IR spectrum of the cis-1,4 isotactic polypentadiene (solid line:
molten polymer; broken line: crystalline polymer)

be remembered that the IR spectra of the two polymers in the molten or
dissolved state are practically identical and that differences are observed
only in the spectra of the polymers in the crystalline state. The most
noticeable difference, however, is found in the position of the band of the
cis-1,4 units which shifts to 13.4 μ in the isotactic polymer, as already
mentioned, and to 13.2 μ in the syndiotactic one.

Some physical properties of cis-1,4 isotactic polypentadiene are reported
in Table 3; they refer to the purest product obtained by the aluminum
trialkyl-titanium alkoxide system. For comparison the corresponding
properties of the cis-1,4 syndiotactic polymer are also included.

Table 3. Some physical properties of the two stereoregular *cis*-1,4 polypentadienes

	Melting temp. (°C.)	Identity period (Å)	Density (g. ml.$^{-1}$)
Isotactic	43–47	8.1	0.924
Syndiotactic	50–53	8.4 .	0.915

Experimental

Products

Benzene and toluene (RP, ERBA) were dehydrated by boiling over Na-K alloy, then distilled and stored under dry N_2. Titanium tetrabutoxide and tetraisopropoxide were obtained from STAUFFER Chemical Co. (Weston, Mich., USA.) and were distilled under vacuum (0.05 mm.) before use. The titanium tributoxide was prepared by reduction of the tetrabutoxide with potassium[14]. Aluminum triisobutyl was kindly supplied by MONTE-CATINI S.p.A. (Milano, Italy); it was distilled under vacuum and the fraction boiling at 63–65 °C./0.1 mm. was collected. Aluminum triethyl was prepared by the exchange reaction between aluminum triisobutyl and ethylene[15], while the other aluminum trialkyls were prepared from $LiAlH_4$ and the corresponding α-olefins[16]. Aluminum diethyl mono-hydride was supplied by MONTECATINI S.p.A.

The *cis* and *trans* isomers of pentadiene were isolated from a crude product (HOUDRY Process Corp., Philadelphia, Pa, USA.) having the following composition; *trans* isomer 67%; *cis* isomer 25%; cyclopentene 7%; cyclopentadiene and isoprene 1%. The *trans* isomer was obtained by formation of the sulphone and subsequent decomposition[17]; purity 98–99% (1–2% of *cis* isomer). The *cis* isomer was obtained by chromatographic separation from the crude monomer (PERKIN-ELMER Fractovap, preparative column H); purity about 99.5% (0.5% *trans* isomer).

Polymerization

The polymerizations were performed in cylindrical glass vessels, of about 200 ml. capacity, equipped with a central stopcock and a side arm. The catalyst was prepared at room temperature by introducing the aluminum alkyl in the solution of the titanium compound. Sometimes the catalyst was aged before the addition of the monomer. In some runs the catalyst was prepared by introducing the aluminum compound into the solution containing the monomer and the titanium compound. During the polymerization the reaction vessel was kept in a thermostat and shaken occasionally. The polymerizations were stopped by addition of methanol, the polymers coagulated with excess of CH_3OH containing dissolved aqueous HCl, thoroughly washed with pure CH_3OH, then dried under vacuum at room temperature.

Polymer fractionation

The crude polymerization products were fractionated in order to separate the amorphous from the crystalline fractions. The crude polymers were dissolved in benzene at room temperature (2–4% solutions), then reprecipitated into a large amount of MEK. The precipitated polymer was again dissolved in benzene, then once more reprecipitated by MEK. The insoluble fraction, repeatedly washed with MEK by decantation, was finally coagulated with CH_3OH, then dried.

The MEK solutions were collected together and evaporated under vacuum to a small volume at room temperature; the polymer was then coagulated by addition of CH_3OH.

Physical measurements

The IR analyses were performed in CS_2 solutions, following a procedure analogous to that for polybutadienes[18]. For the bands at 10.35, 11, 13.3 μ the coefficients $10 \cdot 10^4$; $12 \cdot 10^4$; $6 \cdot 10^4$ $mol^{-1} \cdot cm^{-1}$ ml. were used. Such coefficients correspond to the average values given in the literature[19].

In the case of the band at 10.35 μ, the above coefficient was checked on the trans-1,4 isotactic polypentadiene, which is constituted of practically 100% trans internal double bonds.

The analyses can also be performed using films from CS_2 solutions on NaCl plates.

The instrument used was a Perkin-Elmer spectrophotometer mod. 221 (NaCl optics) or mod. 125.

X-ray examinations were performed with a Norelco diffractometer, supplied with a Geiger counter. The polymers of pentadiene were usually examined after annealing at ca. 35 °C. for about 10 hrs. It has been noted that the cis-1,4 isotactic polypentadienes obtained by precipitating the dissolved polymer with methanol, or by evaporating the solvent from a solution, are sometimes amorphous on X-ray examination. They become crystalline after annealing at a temperature as close as possible to their melting temperature.

The melting temperatures were determined with the aid of a polarizing microscope and also sometimes dilatometrically.

The intrinsic viscosities were determined in toluene, at 30 °C., using a Desreux-Bischoff viscosimeter.

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