Polymerization of 1,3-Pentadiene to cis-1,4 Stereoisomers

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By polymerizing the trans isomer of 1,3-pentadiene two different types of crystalline cis-1,4 polymers have been obtained, one with an isotactic, the other with a syndiotactic structure. The isotactic polymer was obtained by homogeneous systems from an aluminum alkyl chloride and a cobalt compound, the syndiotactic one by homogeneous systems from an aluminum trialkyl and a titanium alkoxide. Some features of the polymerization by Ti and Co catalysts are examined. IR and x-ray spectra, and some physical properties of the crystalline cis-1,4 polymers are presented. The mode of coordination of the monomer to the catalyst, and possible mechanisms for the stereospecific polymerization of pentadiene to cis-1,4 stereoisomers are discussed.

The polymers of 1,3-pentadiene, whatever their structure, exhibit two sites of isomerism per monomeric unit. The number of stereoisomers foreseeable for polypentadiene is therefore higher than for polybutadiene or polyisoprene, these two exhibiting only one site of isomerism per monomeric unit. Thus, although polybutadiene or polyisoprene can each have only one stereoisomer with trans-1,4 or cis-1,4 structure, in the case of pentadiene, owing to the presence of an asymmetric carbon atom in each 1,4 unit, three different trans-1,4 or cis-1,4 polymers are possible—namely, isotactic, syndiotactic, or atactic polymers. Of all the possible stereoregular polymers of 1,3-pentadiene only three types have been obtained and characterized up to now—namely, the trans-1,4 isotactic (5), the cis-1,4 isotactic (6, 7), and cis-1,4 syndiotactic (8) polymers. Polymers, which are predominantly cis-1,4 or trans-1,4, but which are amorphous because of insufficient order in the configurations of the asymmetric carbon atoms are also known (5, 7).

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The cis-1,4 stereoisomers of polypentadiene are interesting as potential elastomers. This paper will report briefly their synthesis, examine their properties, and discuss the mechanism of their formation.

Polymerization

The cis-1,4 syndiotactic polypentadiene has been obtained by soluble catalysts prepared from an aluminum alkyl chloride and a cobalt compound. Only the trans isomer of pentadiene has been polymerized by these catalysts. However, mixtures of the cis and trans isomers can be used, the cis isomer remaining seemingly unaltered. The presence of the cis isomer was found to have no appreciable influence on the stereospecificity when its percentage in the mixture of the two isomers is lower than about 30%. For higher percentages a decrease in the stereoregularity of the syndiotactic polymer obtained was observed.

The soluble catalysts from an aluminum alkyl chloride and a cobalt compound are well known since they have long been used, even on an industrial scale, for polymerizing butadiene to cis-1,4 polymer. The features of pentadiene polymerization by these catalysts are more or less similar to those of butadiene polymerization. Since the latter has been widely investigated and has already been the object of various papers (See e.g. 3, 4), we shall limit ourselves here to underlining the more significant differences that we have observed between the polymerization of butadiene and pentadiene.

It is known that the cobalt catalysts for polymerizing butadiene can be prepared from $Al(C_2H_5)_2Cl$, from $Al_2(C_2H_5)_3Cl_3$, or from $Al(C_2H_5)Cl_2$. From the polymerization of pentadiene, on the contrary, somewhat different results are obtained depending on the particular aluminum compound employed. Catalysts prepared from $Al(C_2H_5)_2Cl$ yield polymers which are predominantly cis-1,4 and exhibit a crystallinity of syndiotactic type. The reproducibility of the results, however, was rather low; the cis-1,4 content of the crude polymers obtained in different runs varied from about 50 to about 80%. These systems are probably rather sensitive to impurities present in the solvent and monomer. On the other hand, catalysts prepared from $Al(C_2H_5)Cl_2$ or $Al_2(C_2H_5)_3Cl_3$ give rise to a cationic polymerization, with formation of amorphous polymers having a low molecular weight and a high 1,2 unit content. The different behavior of pentadiene is caused by its higher sensitivity to the cationic initiation. If, however, a Lewis base, such as thiophene, is added to the catalysts prepared from $Al(C_2H_5)Cl_2$, catalysts are obtained which no longer exhibit cationic activity and which yield, from pentadiene, polymers having a cis-1,4 syndiotactic structure. These catalysts prepared from $Al(C_2H_5)Cl_2$ complexed with a Lewis base were found to be the most reliable for preparing the cis-1,4 syndiotactic polypentadiene, the reproducibility of the results being fairly good. The two systems we have used most in our work are those prepared from $Al(C_2H_5)Cl_2$ complexed with pyridine or thiophene. In these systems the thiophene/aluminum molar ratio can be varied from about 0.5 to about 5 or even more, while the pyridine/aluminum ratio can be varied within a narrower range, from about 0.5 to about 0.9. This is related to the different basicity

of the two electron donors. For ratios lower than those indicated, a cationic polymerization occurs, while for higher ratios no polymerization occurs at all.

Another observed difference between the polymerization of butadiene and pentadiene concerns the influence of the solvent on the type of polymer obtained. In polymerizing pentadiene, cis-1,4 polymers have been obtained only in aromatic solvents, while in aliphatic solvents, at least with catalysts prepared from $Al(C_2H_5)_2Cl$, polypentadienes having a 1,2 syndiotactic structure have been obtained (9). (The catalyst systems prepared from $Al(C_2H_5)Cl_2$ complexes with pyridine or thiophene are practically insoluble in aliphatic solvents and yield only small amounts of low molecular weight polymer, probably of cationic origin.)

However, it is known that in the case of butadiene, polymers predominantly cis-1,4 can be obtained both in aromatic and in aliphatic solvents, although the polymers obtained in the latter solvents have a somewhat lower cis-1,4 unit content.

Table I reports the results of typical polymerization runs of pentadiene by cobalt catalysts prepared from $Al(C_2H_5)Cl_2$ complexed with thiophene or pyridine. The crude polymerization products obtained by these systems have a cis-1,4 content of about 75–80%. Fractions having a higher cis-1,4 content (about 85%) could be isolated by dissolving the crude polymers in benzene and reprecipitating with methylethyl ketone (MEK). This solvent dissolves only the low molecular weight polymers, which, in this case, have also a low cis-1,4 unit content.

Table I. Polymerization of 1,3-Pentadiene
Acetonate and Al(C_2H_5)Cl_2 Complexed

Run	$Co(acac)_2{}^c$ moles $\times 10^5$	Solvent (benzene) ml.	$Monomer^d$ grams	Polymerization	
				temp., ° C.	time, hrs.
1	5.1	350	28	20	24
2	1.5	50	10.5	20	6
3	0.34	15	3.1	20	12
4	0.68	30	5	0	20
5	0.5	30	3	20	8
6	0.15	15	3.5	0	48
7	0.5	30	3	0	12

[a] Runs 1–6; Al/Thiophene molar ratio:1.
[b] Runs 7 and 8; Al/Pyridine molar ratio:0.53.
[c] Al/Co molar ratio: ~500. Catalyst prepared by introducing first the Co compound and the Lewis base, then the $Al(C_2H_5)C$ ∂ and finally, after a few minutes, the monomer.

Shortly after the cis-1,4 syndiotactic polypentadiene was obtained and characterized, it was observed that the homogeneous systems prepared from an aluminum trialkyl and a titanium tetralkoxide can polymerize pentadiene to polymers predominantly cis-1,4. Both the cis and trans isomers of pentadiene are polymerized by these systems. However, while the crude polymers obtained from the cis isomer were found to be amorphous by x-ray examination, those obtained from the trans isomer were found to be crystalline. The type of crystallinity of these polymers appeared different from that of the polymers

obtained by the cobalt catalysts. On the basis of x-ray analysis, a cis-1,4 isotactic structure was attributed to these new crystalline polypentadienes (6, 7).

Some data concerning the polymerization of pentadiene by the $Al(C_2H_5)_3$-$Ti(O-n-C_4H_9)_4$ system are reported in Table II.

The crude polymerization products obtained from the trans isomer have a cis-1,4 unit content of about 75%. Fractionation of the crude products by dissolving them in benzene and reprecipitating with MEK has permitted isolation of fractions (insoluble in MEK) having a cis-1,4 unit content of about 85%.

The crude polymerization products obtained from the cis isomer have also a high cis-1,4 unit content (about 75%), but as mentioned above, they appear amorphous on x-ray examination. However, by fractionating them, fractions could be isolated exhibiting a very low degree of crystallinity of isotactic type.

Mixtures of the cis and trans isomers yield polymers which are also predominantly cis-1,4 but which are less crystalline than those obtained from the pure trans isomer, the crystallinity being lower for those products obtained from a mixture richer in the cis isomer.

In polymerization runs performed with pure cis isomer and terminated with CH_3OH after a 10–15% conversion, it was found that the unreacted monomer, recovered under vacuum from the polymerization medium, was a mixture of the cis and trans isomers, the latter predominating. Therefore, isomerization of the cis isomer occurs during the polymerization. It is possible

by Catalysts Prepared from Cobalt Diacetyl
with Thiophene[a] or Pyridine[b]

	Crude Polymer			MEK Insoluble Fraction[c]		
yield, grams	IR Analysis %			IR Analysis %		$[\eta]$ dl. g^{-1}
	cis-1,4	trans-1,4		cis-1,4	trans-1,4	
23	77	23		84	16	2.8
8	72	28		85	15	...
2.3	73	27		83	17	2.9
4	81	19		86	14	2.3
2.6	77	23		83	17	1.9
3.2	71	29		85	15	...
1.7	76	25		86	14	...

[a] Trans isomer, 99.5% pure.
[c] Crystalline by x-ray examination (polymer annealed 4 hrs. at 35° C.)·$[\eta]$ was determined in toluene at 30° C.

that only the trans isomer formed by isomerization polymerizes. In this case, the absence or the very low degree of crystallinity observed in the polymers from the cis isomer could depend on the influence of the unaltered cis isomer on the polymerization of the trans isomer formed through isomerization. Disturbing influences of this type, caused by nonpolymerizable unsaturated compounds, upon the stereospecificity of a polymerization by coordination catalysts have been already observed. (It has been reported, for example, that in the polymerization of butadiene by the $Al(C_2H_5)_3$-vanadium triacetyl-

Table II. Polymerization of 1,3-Pentadiene by

Run	Titanium Compound moles $\times 10^3$	Al/Ti molar ratio	Polymerization		Crude Polymer			
			temp., °C.	time, hrs.	yield, grams	cis-1,4	trans-1,4	3,4
						IR Analysis (%)		
1	1.6	5	0	35	6	80	14	6
2	1.4	5	−15	45	6.5	79	15	6
3	2.1	7	0	14	5	73	17	10
4	1.5	6	0	24	5.5	74	14	12
5	1.4	7	0	24	5.8	78	12	10
6	1.4	5	0	60	1.5	75	15	10
7	2.3	7	−15	30	1.2	76	15	9

[a] Polymerization conditions: solvent (benzene or toluene), 100 ml.: monomer, 15 grams [runs 6 and 7, cis isomer (99.9%): other runs, trans isomer (99%)]—Al(C₂H₅)₃ was 96% pure.

acetonate system, the impurities present in the monomer strongly influence the stereospecificity of the polymerization (11).)

It could be, however, that the cis isomer is also able to polymerize slightly, given trans-1,4 or 1,2 units which disturb the formation of cis-1,4 sequences.

That the polymers obtained from the cis isomer are actually formed through isomerization of the monomer is confirmed by the results of polymerizations performed with optically active systems. It has been reported that by polymerizing the trans isomer with the $Al(C_2H_5)_3$-titanium tetramenthoxide system, optically active cis-1,4 polypentadienes are obtained (10). The cis isomer, utilizing the same system, yields polymers which are also optically active (Table III). The optical activity of these polymers is of the same sign as that of the polymers obtained from the trans isomer. This is in accordance with the fact that the cis-1,4 sequences actually originate from the trans isomer formed through isomerization. In effect, if the cis isomer were able to give cis-1,4 polymers without isomerization, one would expect these to have an optical activity of opposite sign to that of polymers from the trans isomer.

Table III. Optical Activity of the cis-1,4 Isotactic Polypentadiene Obtained by the Aluminum Triethyl-Titanium Tetramenthoxide[a] Catalyst System

Monomer	Cis-1,4 Content of the Polymer	$\alpha_D^{18 b}$	$[\alpha]_D^{18}$	$\dfrac{[\eta]}{dl./gram^c}$
trans isomer[d]	79	−0.25	−21.6	6.5
trans isomer	75	−0.21	−19	4.1
trans isomer	72	−0.17	−16.3	...
cis isomer[e]	75.2	−0.205	−18	4.7
cis isomer	72.5	−0.104	−17.5	4.2

[a] (−)Ti(OC₁₀H₁₉)₄ : $[\alpha]_D^{18}$ − 98.3 (c = 5.54 grams/100 ml., benzene); optical purity 98–99%.
[b] Determined in n-hexane solution (l = 4 dm).
[c] Determined in toluene at 30° C.
[d] 99.1% pure.
[e] 99.8% pure.

The fact that the polymers obtained from the cis isomer are optically active also proves that these polymers, notwithstanding that they are amorphous by x-ray, are not atactic. In fact if they were atactic in the proper meaning of the word—that is if the configurations of the asymmetric carbon

the Al(C₂H₅)₃-Ti(O-n-C₄H₉)₄ Catalyst System [a]

MEK Insoluble Fraction[b]

IR Analysis (%)			X-ray
cis-1,4	trans-1,4	3,4	Examination[c]
85	10	5	crystalline
87	9	4	crystalline
82	12	6	crystalline
86	9	5	crystalline
84	8	8	crystalline
79	13	8	amorphous
84	10	6	crystalline traces

[b] 30-40% of the crude polymer $-[\eta]$: 5-7 dl. gram^{-1} (determined in toluene at 30° C.).
[c] The polymers were annealed 4 hrs. at 35° C. before examination.

atoms were randomly distributed—no optical activity should be noted when they are produced by an optically active system. The presence of an optical activity proves that these polymers possess a certain stereoregularity of isotactic type. The fact that they are amorphous indicates that they are constituted of cis-1,4 isotactic sequences which are not sufficiently long to give rise to crystallinity detectable by x-ray.

Characterization and Structure of the cis-1,4 Polypentadienes

IR spectra of the cis-1,4 isotactic or syndiotactic polymers, in the molten state or in solution, and of the amorphous polymers are practically identical. All are characterized by an intense band at 751.8 cm.$^{-1}$ (cis double bonds). In the spectra of the solid isotactic or syndiotactic polymers, however, new bands appear which are typical of the crystallinity of the polymers (Figure 1 and 2). The positions of the most intense of these bands are as follows: (1) isotactic polymers: 746.2; 843.8; 925.9; 1005 cm.$^{-1}$; (2) syndiotactic polymers: 757.5; 854.7; 925.9; 1000; 1136 cm.$^{-1}$ It is interesting to observe that the band of the
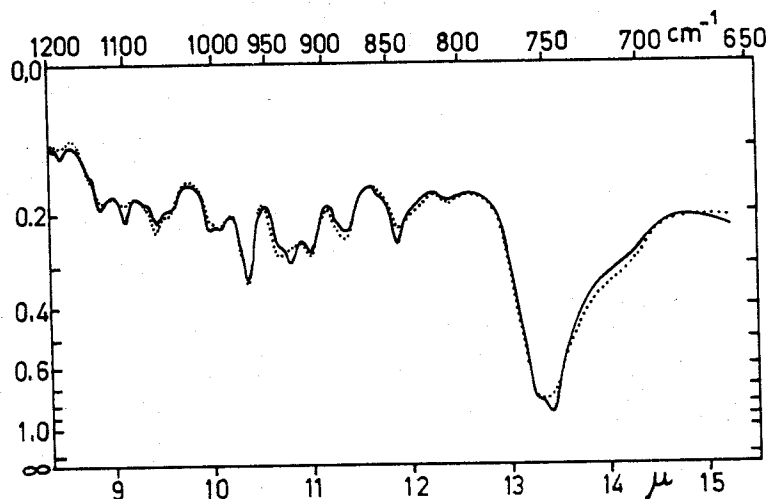

Figure 1. IR spectrum of a sample of cis-1,4 isotactic polypentadiene; continuous line—crystalline polymer; dotted line—molten polymer.
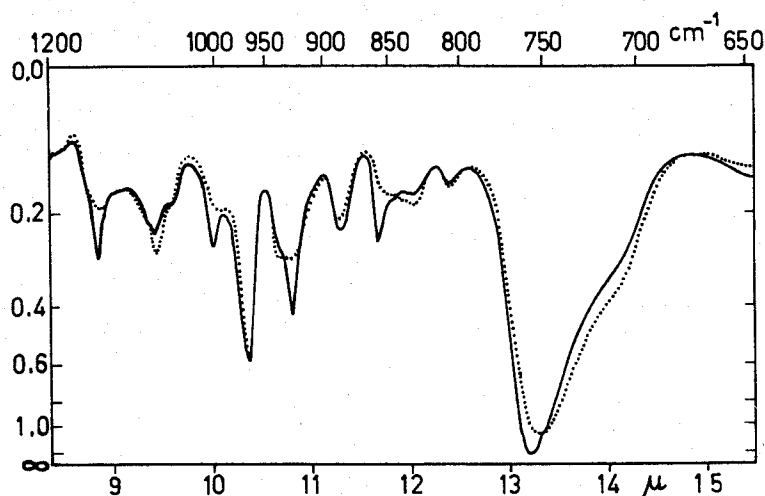
*Figure 2. IR spectrum of a sample of cis-1,4 syndiotac-
tic polypentadiene; continuous line—crystalline
polymer; dotted line—molten polymer.*

cis double bonds, which is at 751.8 cm.$^{-1}$ in the spectra of the molten or dis-
solved cis-1,4 stereoregular polymers (and also in that of the amorphous
polymers), shifts to 746.2 cm.$^{-1}$ in the spectrum of the isotactic, and to 757.5
cm.$^{-1}$ in the spectrum of the syndiotactic polymers in the solid state. This
difference in the positions of the bands of the cis double bonds in the IR spectra
of the two polymers in the solid state is the best criterion for distinguishing
between the isotactic and the syndiotactic cis-1,4 polypentadiene.

The x-ray spectra, registered by a Geiger counter, of the isotactic and
syndiotactic cis-1,4 polypentadienes are reported in Figure 3. One can see from
these spectra that the degree of crystallinity is not high, and this can be easily
accounted for if we consider that the polymers do not have a very high cis-1,4
content. Evidently they consist of macromolecules containing cis-1,4 stereo-
regular sequences sufficiently long to give rise to crystallinity and interspersed
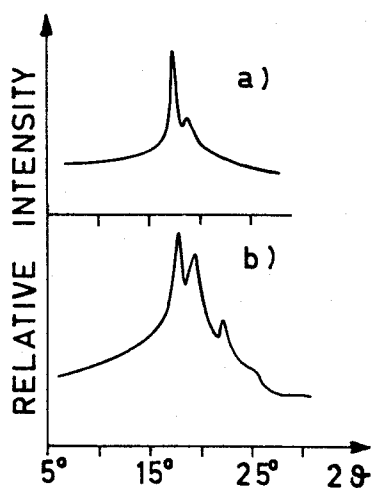with units of other types.

*Figure 3. X-ray spectra
(CuKα), registered by a
Geiger counter, of (a) iso-
tactic and (b) syndiotactic
cis-1,4 polypentadiene*

Some properties of the polymers are reported in Table IV. The identity periods observed for the two polymers are rather close—i.e., 8.1 and 8.45 A. Conformational analysis of the chain of the cis-1,4 polypentadiene led us to attribute the syndiotactic structure to the polymer having an identity period of 8.45 A. and the isotactic structure to that having an identity period of 8.1 A. The correctness of this attribution is confirmed by the observed distribution of the diffracted intensity on the first and second layers in the fiber spectra (6, 8). The chain conformations of the two cis-1,4 polypentadienes in the crystalline state are reported in Figure 4. It is interesting that the chain conformation of cis-1,4 syndiotactic polypentadiene is identical with that of cis-1,4 polybutadiene and cis-1,4 polyisoprene (12) (except, obviously, for the absence of the methyl groups in polybutadiene and the different positions of these groups in polyisoprene and polypentadiene).

Table IV. Some Physical Properties of the Stereoregular cis-1,4 Polypentadienes

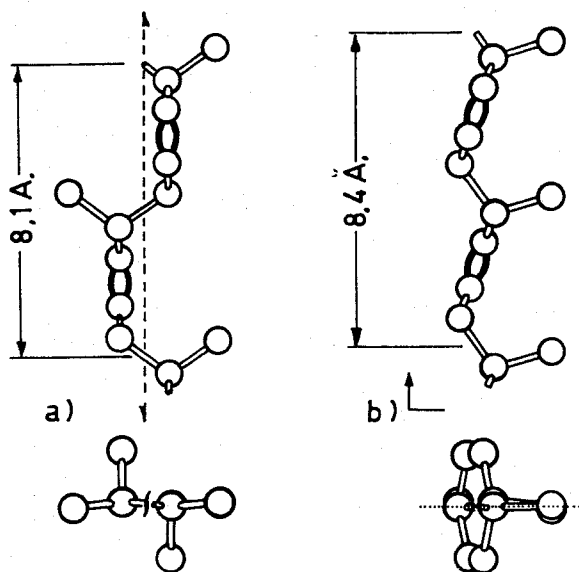| Polymer	Melting Temp., °C.	Identity Period A.	Density Grams/Ml.
Isotactic	43–47	8.1	0.924
Syndiotactic	50–53	8.4	0.915

Figure 4. Chain conformation of the isotactic, (a), and the syndiotactic, (b), cis-1,4 polypentadienes in the crystalline state

Mechanism of Formation

The possibility of obtaining, from the same monomer, different stereoregular polymers having an isotactic or a syndiotactic structure is, perhaps, the most challenging feature of the stereospecific polymerization.

We wish to discuss, in the following, the factors which could determine, in the polymerization of pentadiene by Ti or Co catalysts, the formation of cis-1,4 isotactic or syndiotactic sequences, respectively.

Mode of Coordination of the Monomer. It is now generally admitted that in the case of Ziegler catalysts, incorporation of the monomer into the growing polymer chain is preceded by coordination of the monomer to the transition metal of the catalyst. Some information concerning the mode of coordination of the monomer to Ti can be derived from the following experimental findings: (1) butadiene and isoprene are polymerized by titanium catalysts to 1,2 and 3,4 polymers, respectively (13); (2) both the cis and the trans isomers of pentadiene are polymerized, cis-1,4 polymers being obtained from each isomer.

The above findings suggest the hypothesis that in the case of Ti catalysts, the monomer coordinates to the active center by the vinyl group only. This hypothesis seems quite reasonable in the case of butadiene and isoprene since 1,2 and 3,4 polymers, respectively are formed from these monomers. The situation could seem different in the case of pentadiene which yields cis-1,4 polymers. On could suppose that in this case the formation of cis-1,4 units is caused by the fact that pentadiene coordinates to Ti by the two double bonds in the cis conformation before it is incorporated into the growing chain.

Let us examine separately the case of the cis and trans isomers of pentadiene. For the trans isomer the cis conformation is permissible so that one cannot assume *a priori* that this isomer won't coordinate to Ti by the two double bonds. This hypothesis, however, can be easily rejected by the following considerations. If the steric situation around Ti during the polymerization were to permit the coordination of the trans isomer of pentadiene by the two double bonds, in the cis conformation, butadiene or isoprene should also coordinate the same way. In this case, however, cis-1,4 units should be obtained both from butadiene and isoprene, and not 1,2 and 3,4, respectively, as observed. It seems reasonable to conclude, therefore, that the trans isomer of pentadiene coordinates to Ti by the vinyl group only, as butadiene or isoprene, before it is incorporated as a cis-1,4 unit.

The same conclusions can be reached for the cis isomer. As already mentioned, isomerization of this isomer occurs in the polymerization medium. If we admit that only the trans isomer formed through isomerization polymerizes, we fall under the case examined above. If we admit also that the cis isomer can polymerize to cis-1,4 units, we must assume that also in this case the coordination occurs only through the vinyl group and not through the two double bonds, in the cis conformation. The cis isomer, in fact, cannot assume the cis conformation for steric reasons. On the other hand, coordination by the internal double bond, both for the cis and trans isomers, appears less probable (for steric reasons) than the coordination by the vinyl group.

The case of the Co catalysts appears different. Some information concerning the mode of coordination of pentadiene to these systems can be derived from the following points:

(1) The Co catalysts polymerize only the trans isomer of pentadiene.

(2) They give polymers which are prevalently cis-1,4 (at least 70%) from all the common hydrocarbon diolefins (butadiene (3, 4), isoprene (14), pentadiene (8), 1,3-dimethyl-butadiene (14)).

(3) When they are used in aromatic solvent (and in the case of pentadiene polymerization they must be used in aromatic solvent in order to obtain cis-1,4

polymer), two molecules of arene are coordinated by Co. Furthermore, evidence exists that the coordination of the diolefin occurs through displacement of the arene.

The coordination of the arene to Co can be proved by the following: when the reaction between $Al(C_2H_5)_2Cl$ and a cobalt compound is performed in benzene saturated with hexamethylbenzene (the latter, being a solid melting at $166°$ C. cannot be used by itself as solvent) the cation $\{Co[(C_6CH_3)_6]_2\}^-$ can be isolated from the reaction products (14). This cation, as already known (1, 15), has sandwich structure and is stable in H_2O, from which it can be precipitated by anions such as $B(C_6H_5)_4^-$, PF_6, etc. From solutions of the catalyst in pure benzene, the cation $[Co(C_6H_6)_2]^+$ could not be isolated, owing to its instability in H_2O (it decomposes giving equivalent amounts of metallic Co and $CoCl_2$). It is obvious, however, that a cation of this type exists in the catalyst solution in benzene. The much higher stability of the cation containing $C_6(CH_3)_6$ is caused by the fact that $C_6(CH_3)_6$ is a much stronger electron donor than C_6H_6. The fact that coordination of the diolefin occurs by displacing the arene is shown by following: the rate of polymerization of butadiene by the $Al(C_2H_5)_2Cl$ cobalt compound system depends on the type of solvent, and more precisely, is lower in those solvents having a higher basicity. In fact, the rate of polymerization decreases in the order: benzene > toluene > xylene > 1,3,5-trimethylbenzene (14). Furthermore, adding hexamethylbenzene to a benzene solution of the catalyst slows down the rate of, and high concentration completely stops, polymerization. All these facts are interpretable assuming that during the polymerization there is a competitive coordination of the diolefin and arene to Co. When the arene is $C_6(CH_3)_6$, the polymerization does not occur because the diolefin cannot displace this arene.

All the findings reported under 1,2, and 3 suggest the hypothesis that, in the case of Co catalysts, the monomer coordinates to the active center in the cis conformation before it is incorporated into the growing chain. This hypothesis easily explains why the cis isomer of pentadiene is not polymerized, the cis conformation being prohibited for this isomer. It also explains why all the common conjugated hydrocarbon diolefins yield predominantly cis-1,4 polymers by these catalysts. In fact, if all the different diolefins coordinate to Co predominantly in the cis conformation (by the two double bonds), predominantly cis-1,4 polymers will be obtained in every case.

The fact that coordination of the diolefin occurs by displacing the arene also favors the hypothesis that the diolefin coordinates in the cis conformation by the two double bonds. Displacement reactions of this type are well known in organometallic chemistry (See e.g. (2)) and, in the cases already clarified, it has been shown that diolefin coordinates in the cis conformation by the two double bonds. This is not surprising if we consider that the diolefin, coordinated in this way to a transition metal, has a quasi-aromatic character owing to the complete delocalization of the π-electrons.

The conclusions we can draw from the above facts concerning the mode of coordination of pentadiene to Ti and Co, respectively are as follows: coordination to Ti most probably occurs by the vinyl group only, while coordination to Co occurs by the two double bonds, with the monomer in the cis conformation. Furthermore, we have seen that the Co catalysts contain two sites of

coordination per Co, which, in the absence of monomer, are occupied by two molecules of arene.

Models for the Stereospecific Polymerization. The different modes of coordination of pentadiene to Ti and Co catalysts, respectively suggest two possible schemes for polymerizing this monomer to cis-1,4 isotactic or syndiotactic polymer.

A scheme for forming cis-1,4 syndiotactic sequences is presented in Figure 5. In this figure, (a) represents the last polymerized unit, bonded to the transition metal and a molecule of pentadiene coordinated to it by the two double bonds; (b) represents the transition state; (c) represents the transition metal with the monomer which was coordinated in (a) already incorporated and a new monomer coordinated. It is easily seen that (c) represents a situation which is the enantiomorph of that represented in (a). Therefore, the monomer which is coordinated in (c) will give, after incorporation into the growing chain, a unit having the opposite configuration of the preceding one. Hence, by this mechanism, cis-1,4 syndiotactic sequences will be formed.
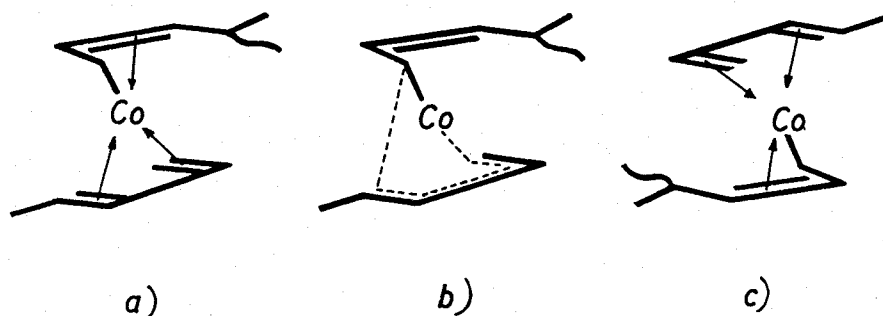

a)   b)   c)

Figure 5. Possible scheme for formation of cis-1,4 syndiotactic polypentadiene

A possible scheme for forming cis-1,4 isotactic sequences is represented in Figure 6. In this figure, (a) represents the Ti, with the last polymerized unit bonded to it and a monomer coordinated through the vinyl group. The three bonds of (a) could be part of a tetrahedron, of a trigonal bipyramid, or of an octahedron. Only the angles between the three bonds vary depending on the type of coordination. What the type of coordination around Ti actually is during the polymerization is not yet known. However, the scheme of polymerization discussed here is valid independently of the type of coordination actually existing around Ti. It is clear, that in Figure 6 (a) the transition metal lies on the plane of the paper, while the coordinated monomer and the last polymerized unit are above that plane. Figure 6 (b) represents the transition state, and Figure 6 (c) represents the monomer which was coordinated in (a), already incorporated into the growing chain and a new monomer coordinated to Ti by the vinyl group. It is easily seen that Figure 6 (c) represents a situation which is identical with that represented in Figure 6 (a). Therefore, the monomer coordinated in (c) will give, after incorporation, a monomeric unit having the same configuration as the preceding one. Hence, by this mechanism, cis-1,4 isotactic sequences will be formed.
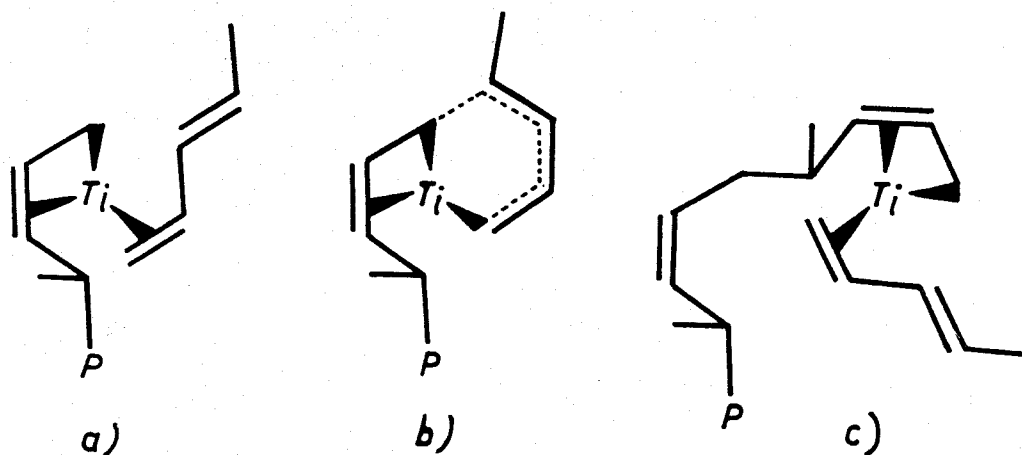
Figure 6. Possible scheme for formation of cis-1,4 isotactic polypentadiene.

Obviously, the schemes of Figures 5 and 6 will not represent a complete interpretation of the phenomena actually occurring during the polymerization, which are presumably rather complex. They are used only as models to try to interpret how the different mode of coordination of the monomer and the existence, in the case of Co catalysts, of two sites of coordination could give rise to a different stereospecificity.

We wish also to point out that the fact that in the above schemes only the transition metal, the last polymerized unit, and the coordinated monomer are represented does not mean that the catalysts prepared from $Al(C_2H_5)_3$ and a titanium alkoxyde or from $Al(C_2H_5)_2Cl$ and a Co compound are pure organometallic compounds of Ti or Co, respectively. These catalysts are presumably complexes containing Al and the transition metal, the latter probably being part of a cation, the Al of an anion. In the above schemes we have represented only the transition metal for the sake of simplicity.

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