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POLYMERIZATION OF 1,3-PENTADIENE BY COBALT CATALYSTS. SYNTHESIS OF 1,2 AND *CIS*-1,4 SYNDIOTACTIC POLYPENTADIENES

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Abstract—A report is given on the polymerization of 1,3-pentadiene by cobalt catalysts prepared from AlEt_2Cl , $\text{Al}_2\text{Et}_3\text{Cl}_3$ or alkyl aluminum compounds containing AlOAl bonds.

Depending on the aluminum compound used for preparing the catalyst and on the polymerization solvent (benzene, *n*-heptane, *cis*-2-butene), different polymers are obtained, i.e., crystalline polymers with a *cis*-1,4 syndiotactic structure, amorphous polymers composed of *cis*-1,4 and 1,2 units, and weakly crystalline polymers with a 1,2 syndiotactic structure.

Characterization of the polymers is reported. The results are discussed in the light of the current theories on the mechanism of catalysis of stereospecific polymerization.

IN RECENT years some work has been performed in our laboratory on the polymerization of 1,3-pentadiene by homogeneous catalysts obtained from a cobalt compound and an alkyl-aluminium chloride.

Depending on the particular organoaluminum compound used for preparing the catalyst (AlEt_2Cl , AlEtCl_2 , $\text{Al}_2\text{Et}_3\text{Cl}_3$, or chloro-alkyl-aluminum compounds containing Al—O—Al bonds) and on the polymerization solvent (benzene, *n*-heptane, *cis*-2-butene) different pentadiene polymers were obtained, namely:

- (a) crystalline polymers having a *cis*-1,4 syndiotactic structure;
- (b) weakly crystalline 1,2 polymers having some degree of stereoregularity of syndiotactic type;
- (c) amorphous polymers, mainly constituted of *cis*-1,4 and 1,2 units.

Preliminary accounts concerning our work on the polymerization of 1,3-pentadiene by various cobalt catalysts and the characterization of the resulting polymers have already been published.⁽¹⁻⁴⁾

We now report a detailed description of the preparation of the polymers, as well as additional data concerning their microstructure.

EXPERIMENTAL

Materials

Benzene, *n*-heptane and *cis*-2-butene, used as the polymerization solvents, were at least 99 per cent pure. Benzene and *n*-heptane were dried by boiling on sodium; then they were distilled and stored on

molecular sieves under nitrogen. *Cis*-2-butene (Phillips Petroleum Company, pure grade) was stored on molecular sieves under nitrogen and distilled into the polymerization vessel immediately before use.

AlEt_2Cl was prepared by mixing stoichiometric amounts of AlEt_3 and of freshly sublimed AlCl_3 , and then distilling the product in vacuum (b.p._{1.2mm} 90°). AlEtCl_2 was prepared in a similar way, and then crystallized.

Chloro-ethyl-aluminum compounds containing Al—O—Al bonds were prepared by reacting AlEt_2Cl with (a) H_2O ⁽⁵⁾ or (b) $\text{Et}_3\text{Sn—O—SnEt}_3$.⁽⁹⁾

(a) 1000 g of benzene, containing 374 mg (20.75 mmoles) of dissolved H_2O were dropped, during 3 hr, into a flask containing 5 ml (41.5 mmoles) of AlEt_2Cl vigorously stirred. After all the benzene had been added, the solution was heated at about 40° for 0.5 hr; then benzene was removed, the remaining solution was transferred into a small flask and benzene distilled completely at about 40° in high vacuum (0.1 mm Hg).

The residue is a dense liquid, which was used for the preparation of the catalysts.

(b) 8.87 g (20.75 mmoles) of $(\text{Et}_3\text{Sn})_2\text{O}$ dissolved in 50 ml of benzene were added slowly to 5 ml (41.10 mmoles) of AlEt_2Cl with stirring. After the addition was complete, the solution was heated at about 40° for 0.5 hr, then benzene and Et_4Sn formed in the reaction were removed under vacuum (20 mm Hg). The distillation of all volatile products was completed at about 40° in high vacuum (0.1 mm Hg). The residue is a dense liquid whose properties (elemental analysis, i.r. and NMR examinations) are similar to those of the product prepared as under (a).

Cobalt diacetylacetonate, $\text{Co}(\text{acac})_2$, was generally used as the cobalt compound in the runs carried out in benzene or *cis*-2-butene. When *n*-heptane was used as the solvent, cobalt triacetylacetonate, $\text{Co}(\text{acac})_3$, was preferably used because of its higher solubility in aliphatic solvents. Both $\text{Co}(\text{acac})_2$ and $\text{Co}(\text{acac})_3$ were prepared as reported in the literature.⁽⁶⁾

Trans-1,3-pentadiene was obtained from a commercial product (Phillips Petroleum Company, 90 per cent) by formation of the sulphone and subsequent decomposition.⁽⁷⁾ The purity of the monomer obtained, determined by gas-chromatography, was found to be 99–99.5 per cent (the main impurity is the *cis* isomer). *Cis*-1,3-pentadiene was a Fluka product (99 per cent pure).

Polymerization

The polymerizations were performed in glass cylindrical reactors, having a central neck and a side arm which was connected with a vacuum-nitrogen apparatus in order to remove the air from the reactor and to introduce nitrogen.

Aged catalysts were prepared by introducing the reagents in the following order: solvent, cobalt compound, aluminum alkyl and then, after the desired time, the monomer. When unaged catalysts were used, the reagents were added as follows: solvent, aluminum alkyl, monomer, cobalt compound.

Since the amount of cobalt compound used in each run was very small, a solution in benzene or *n*-heptane was prepared and the desired amount of solution was transferred with a syringe in the reaction vessel. The polymerization temperature was generally 18°.

The polymerizations were terminated by adding a small amount of CH_3OH . The reaction mixture was then poured into a large amount of methanol containing aqueous HCl. The precipitated polymers were thoroughly washed with methanol and dried in vacuum at room temperature. They were usually purified by dissolving them in benzene and washing the solutions with aqueous HCl in order to remove all the mineral parts; the polymers were then reprecipitated with methanol.

Polymer fractionation

In some cases, the polymerization products were fractionated in order to remove the low molecular weight polymers from the crystalline fractions. This was done by dissolving the crude polymers in benzene at room temperature (2–3 per cent by weight) followed by reprecipitation with a large amount of methyl-ethyl-ketone (MEK).

After a further dissolution and reprecipitation, the insoluble fraction was thoroughly washed with MEK, then coagulated with CH_3OH , and finally dried in vacuum at room temperature.

Physical examination of the polymers

Intrinsic viscosities were determined in toluene at 30°, using a Desreux-Bischoff Viscometer. A NMR examination was performed with a Varian HA 100 spectrometer using solutions of polymers in C_6D_6 . Infra-red examination was performed with a Perkin Elmer 137 spectrometer, using CS_2 solutions of the polymers or (for routine analysis) using films obtained by evaporating at room temperature CS_2 solutions of the polymers on a NaCl plate. In the case of *cis*-1,4 stereoregular polymers, annealing of the films for some hours at about 35° is necessary in order to make the crystallinity bands evident.

By combining i.r. and NMR data it is possible to obtain, with good accuracy, an analysis for the 1,2, *cis*-1,4 and *trans*-1,4 units of the polymers.⁽⁸⁾ In the i.r. spectrum both 1,2* and *trans*-1,4 units show an intense band at 965 cm^{-1} with absorptivities of comparable value (absorptivity value used: $15.2 \times 10^4\text{ moles}^{-1}\text{ cm}^2$). The *cis*-1,4 units show a band at 750 cm^{-1} (absorptivity value: $5.0 \times 10^4\text{ moles}^{-1}\text{ cm}^2$). The above absorptivities are actually valid for the polymers in solution but can also be used, without great loss of accuracy, for the analysis of non-annealed films. From i.r. spectra, it is possible therefore to have the ratio of 1,2 plus *trans*-1,4 units to *cis*-1,4 units. From NMR spectra, it is possible to have a value for the ratio of all 1,4 units to 1,2 units. The analysis is based on the different chemical shift of the signals for the methyls of the 1,4 and 1,2 units respectively (0.95 ppm for 1,4 units, 1.65 ppm for 1,2 units). A NMR examination also gives an approximate estimation of the amount of cyclization of the polymers by determining the ratio of saturated to unsaturated protons.

RESULTS

Only the *trans* isomer of 1,3-pentadiene polymerizes with the catalysts prepared from a soluble cobalt compound and an alkylaluminum chloride. From the *cis* isomer, no solid polymer was obtained even after some days at room temperature.

(1) Polymerization in benzene

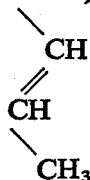
(a) *Catalysts from AlEt₂Cl*. Some data concerning the polymerization by catalysts from AlEt₂Cl and Co(acac)₂ or Co(acac)₃ are reported in Table 1. Benzene dried over molecular sieves or wet benzene were used as the solvent. The results can be summarized as follows.

(i) When using dried benzene, the microstructure of the polymers depends upon the Al/Co molar ratio. At low ratio (less than about 50†) polymers are obtained characterized by an intense i.r. band at about 965 cm^{-1} (*trans* double bonds) which are mostly constituted (NMR examination) by 1,2 units.

The polymers obtained at higher Al/Co ratio are predominantly composed of 1,4 units (55 per cent on the average), the remainder being mostly 1,2. By fractionating these products (dissolution in benzene and precipitation with MEK), fractions were obtained having practically the same composition as the starting product.

(ii) When using non-dried benzene, no solid polymer was obtained at Al/Co molar ratio lower than about 50. At higher Al/Co ratio and for values of the H₂O/AlEt₂Cl molar ratio between about 0.1 : 1 and 0.5 : 1, crude polymerization products were obtained composed of about 90 per cent *cis*-1,4 units and exhibiting at room temperature crystallinity attributable to *cis*-1,4 syndiotactic sequences. At higher values of the H₂O/AlEt₂Cl ratio, syndiotactic *cis*-1,4 polymers are still obtained but the amount of product gradually decreases. At lower values, polymers having a lower *cis*-1,4 content were obtained.

* Since only the *trans* isomer of pentadiene polymerizes, the double bond of the side groups of the 1,2 units ($-\text{CH}_2-\text{CH}-$) has a *trans* configuration.



† This value varies however depending on whether Co(acac)₂ or Co(acac)₃ is used. The ageing of the catalyst also has some effect, as seen, e.g., from runs 3-5, Table 1.

TABLE 1. POLYMERIZATION OF *trans*-1,3-PENTADIENE IN BENZENE BY CATALYSTS FROM COBALT ACETYLACETONATE AND DIETHYLALUMINUM CHLORIDE*

Run No.	Co acetyl acetate (moles.10 ⁵)†	Al/Co molar ratio	Catalyst ageing (min)	Polymerization time (hr)	Conversion (%)	[η] (dl.g ⁻¹)	i.r. analysis <i>trans</i> %‡ <i>cis</i> %	
1	1.6	600	10	20	39	1.69	40	60
2	1.6	600	0	20	78	1.37	55	45
3	1.6	300	0	15	95	1.35	70	30
4	1.6	300	2	15	75	1.45	50	50
5	1.6	300	20	15	50	1.60	35	65
6	1.6	10	0	15	70	2.70	80	20
7	2.5	30	2	15	89	2.72	84	16
8	2.5	3300	2	15	72	1.49	42	58
9	3.1	17	30	20	85	1.81	72	28
10	3.1	625	30	20	65	1.10	35	65
11	3.8	660	2	20	74	1.05	51	49
12	3.8	660	2	20	90	1.04	42	58
13	3.8	660	2	20	83	1.03	24	76
14	3.8	660	30	20	68	1.10	14	86

* Polymerization temperature = about 18°. Pentadiene = 2 ml, benzene = 10 ml. Benzene dried on molecular sieves was used in runs 1–11 (H₂O content about 25 ppm; i.e. about 1.2×10^{-5} moles in each experiment). Benzene containing larger amounts of water was used in the other runs; run 12 $3 \cdot 10^{-5}$, run 13 6.6×10^{-5} , run 14 $2.4 \cdot 10^{-5}$ moles.

† Co(acac)₂ in runs 1–6; Co(acac)₃ in runs 7–14.

‡ According to NMR analysis, the units characterized by *trans* double bond are mostly 1,2. *Trans*-1,4 units have been found to vary approximately from 3 to 6 per cent (with respect to the total units) in runs 1–10, from 0.5 to 1 in runs 11–14.

In the presence of the amount of H₂O indicated above, AlEt₂Cl shows some cationic activity, which gives rise to non-*cis*-1,4 low molecular weight polymers,* thus lowering the total *cis*-1,4 content of the crude polymerization product. It is therefore useful, when operating in the presence of H₂O, to add thiophene to the catalyst solution (thiophene/AlEt₂Cl molar ratio 0.5 to about 5) in order to avoid cationic activity.

It is to be noted that benzene dried with sodium or molecular sieves, which gives polymers having a *cis*-1,4 content of about 55 per cent, also contains a certain amount of H₂O (about 25 ppm, under our experimental conditions). We do not know whether benzene having a lower H₂O content would give polymers having a *cis*-1,4 content lower than about 55 per cent.

(b) *Catalysts from chloro-ethyl-aluminum compounds containing Al—O—Al bonds.* Chloro-ethyl-aluminum compounds containing Al—O—Al bonds can be prepared by reacting a dialkylaluminum chloride with (a) H₂O⁽⁵⁾ or (b) an alkyldistannoxane, (R₃Sn)₂O.⁽⁹⁾

* According to NMR analysis the cationic polymers obtained by the reaction product between AlEt₂Cl and H₂O have approximately the following composition: *trans*-1,4 units about 65 per cent; 1,2 units about 35 per cent. The same composition was found for the cationic polymers obtained from AlEtCl₂ or Al₂Et₃Cl. All these polymers, however, are highly cyclized, as indicated by the low value of the unsaturation. The microstructure reported for these cationic polymers in a previous paper⁽²⁾ (that is, mainly 1,2) was based only on i.r. analysis and must be considered incorrect.

The first product in these reactions is presumably *bis*(chloro-alkyl-aluminum) oxide, $[\text{Cl}(\text{R})\text{Al}]_2\text{O}$, which, however, cannot be isolated because it rapidly disproportionates, due to exchange reactions of the groups bonded to Al, as exemplified by the following equation:



The final product of the reaction between AlEt_2Cl and H_2O or $(\text{Et}_3\text{Sn})_2\text{O}$ respectively is therefore an equilibrium mixture containing $[\text{Cl}(\text{Et})\text{Al}]_2\text{O}$ and its homologues, as well as small amounts of AlEt_2Cl . We shall refer to this equilibrium mixture by the conventional name of chloroethylaloxanes.

The results of some polymerization runs carried out in benzene by cobalt catalysts from chloroethylaloxanes are reported in Table 2. The resulting polymers have a

TABLE 2. POLYMERIZATION OF *trans*-1,3-PENTADIENE IN BENZENE BY CATALYSTS FROM COBALT DIACETYLACETONATE AND CHLOROETHYLALOXANES*

Run No.	Al/Co molar ratio	Thiophene/Al molar ratio	Catalyst ageing (min)	Polymerization time (hr)	Conversion %	$[\eta]$ (dl.g ⁻¹)	i.r. analysis <i>trans</i> %† <i>cis</i> %	
1	600	2	10	20	86	1.15	8	92
2	600	2	0	20	82	1.40	7	93
3	600	0	0	20	85	0.82	18	82
4	600	2	0	20	82	2.03	11	89
5	85	9	0	20	57	1.99	12	88
6	85	9	10	60	22	1.44	21	79
7	600	13	0	60	0	—	—	—
8	40	3	0	20	0	—	—	—
9‡	1000	2	0	4.5	55	1.67	65	35
10‡	1000	2	0	4.5	94	1.67	11	89
11‡	1000	2	0	4.5	66	1.75	9	91
12‡	1000	2	0	4.5	57	1.77	8	92
13‡	1000	2	0	4.5	43	1.60	11	89

* Polymerization temperature = 18°. Benzene (dried on molecular sieves) = 10 ml. $\text{Co}(\text{acac})_2 = 1.6 \times 10^{-6}$ moles, pentadiene = 2 ml. All the polymers obtained are crystalline at room temperature (i.r. and X-ray spectra) and exhibit the crystallinity typical of *cis*-1,4 syndiotactic structure.

† NMR examination shows that the units characterized by *trans* double bond are almost completely 1,2 (*trans*-1,4 units are less than 1 per cent of the total units).

‡ In runs 9–13, mixtures of AlEt_2Cl and chloroethylaloxanes were used. Al as AlEt_2Cl is 100, 75, 50, 25, 0 per cent respectively, with respect to the total amount of Al.

cis-1,4 content of about 90 per cent and are crystalline at room temperature, with a syndiotactic structure. The results obtained by catalysts from chloroethylaloxanes appear practically identical with those obtained by catalysts from AlEt_2Cl in the presence of H_2O , which supports the view that the influence of H_2O , (see runs 12–14 of Table 1), is essentially that of producing *in situ* the aloxanes.

The *cis*-1,4 content of the polymerization product obtained by chloroethylaloxanes catalysts is generally higher when a small amount of thiophene is added to the catalyst solution (thiophene/Al molar ratio about 2). A similar phenomenon, as already mentioned, was observed in polymerizations carried out in wet benzene with catalysts from AlEt_2Cl .

In a series of runs (Table 2, runs 9–13) catalysts prepared from mixtures of AlEt_2Cl and chloroethylaloxanes were used. The polymers obtained have a *cis*-1,4 content higher than 80 per cent if at least 15 per cent of the total Al is present as aloxanes. This is consistent with the results obtained by the catalysts from AlEt_2Cl in the presence of H_2O , which indicate that about 8 moles of H_2O per hundred moles of AlEt_2Cl are sufficient to yield polymers having 80 per cent or more *cis*-1,4 units.

No difference was observed using chloroethylaloxanes prepared from H_2O or from $(\text{Et}_3\text{Sn})_2\text{O}$, provided that thiophene is added to the catalyst solution.

(c) *Catalysts from $\text{Al}_2\text{Et}_3\text{Cl}_3$ or AlEtCl_2 .* Catalysts from $\text{Al}_2\text{Et}_3\text{Cl}_3$ yield crude polymerization products constituted of 65–70 per cent *cis*-1,4 units. Fractionation of these products by repeating dissolutions in benzene and reprecipitations with MEK yields two distinct fractions: (a) low molecular weight polymers, soluble in MEK, characterized by *trans* double bonds in the i.r. spectrum (b) polymers of higher molecular weight, insoluble in MEK, which contain 85–90 per cent *cis*-1,4 units and appear crystalline (i.r. and X-ray examinations) at room temperature, with a *cis*-1,4 syndiotactic structure (Table 3).

Polymerization products having a higher *cis*-1,4 content (85–90 per cent) have been obtained by adding thiophene to the $\text{Al}_2\text{Et}_3\text{Cl}_3$ — $\text{Co}(\text{acac})_2$ catalyst system (thiophene/ $\text{Al}_2\text{Et}_3\text{Cl}_3$ molar ratio from 0.5 to about 2). Thiophene evidently inhibits the cationic activity of $\text{Al}_2\text{Et}_3\text{Cl}_3$, which is responsible for the low molecular weight polymers obtained along with the crystalline *cis*-1,4 polymers, in the absence of thiophene.

The catalyst system AlEtCl_2 — $\text{Co}(\text{acac})_2$ yields by itself low molecular weight polymers, originating from the cationic activity of AlEtCl_2 . By adding thiophene to the catalyst system, however, polymerization products are obtained which have a *cis*-1,4 content of about 85 per cent, and which are crystalline at room temperature, with a syndiotactic structure. Fractionating the crude polymerization products by dissolution in benzene and reprecipitation with MEK gives a fraction, insoluble in MEK, containing about 90 per cent *cis*-1,4 units.

TABLE 3. POLYMERIZATION OF *trans*-1,3-PENTADIENE IN BENZENE BY CATALYSTS FROM COBALT DIACETYLACETONATE AND AlEtCl_2 OR $\text{Al}_2\text{Et}_3\text{Cl}_3$ *

Run No.	Al/Co molar ratio	Thiophene/Al molar ratio	Catalyst ageing (min)	Polymerization time (hr)	Conversion (%)	$[\eta]$ (dl.g ⁻¹)	i.r. analysis <i>trans</i> %† <i>cis</i> %	
1	1200	1	2	15	82	1.70	15	85
2	1200	2	2	15	82	1.72	17	83
3	1200	0	0	20	70	—	100	0
4	1200	2	0	20	95	1.71	15	85
5	1200	0	0	20	95	—	33	67

* Polymerization temperature = about 18°. Pentadiene = 2 ml, Benzene (dried on molecular sieves) = 10 ml, $\text{Co}(\text{acac})_2 = 1.6 \times 10^{-6}$ moles. AlEtCl_2 was used in runs 1, 2, 3; $\text{Al}_2\text{Et}_3\text{Cl}_3$ was used in runs 4 and 5. Fractionation of the product of run 5, by dissolving in benzene and reprecipitating with MEK, gave a MEK insoluble fraction (about 60 per cent of the total polymer) having the composition: 89 per cent *cis*, 11 per cent *trans*. Fractionation of the products of runs 1, 2 and 4 gives a fraction only slightly richer in *cis*-1,4 units than the starting product.

† NMR examination shows that the *trans* units are almost completely 1,2 in runs 1, 2 and 4 (*trans*-1,4 units are less than 1 per cent of the total units). The polymerization in run 3 is cationic and the unsaturated units are approximately 65 per cent *trans*-1,4 and 35 per cent 1,2.

Besides thiophene, pyridine (py) can also be used to inhibit the cationic activity of AlEt_2Cl_2 . The py/ AlEt_2Cl_2 molar ratio, however, must be between 0.5 : 1 and 1 : 1. At higher ratios any catalytic activity disappears, while at lower ratios cationic activity is still present.

Other Lewis bases, such as THF, $\text{P}(\text{Ph})_3$, did not give satisfactory results, under the conditions examined, as they caused the disappearance of any catalytic activity. Presumably, with these bases, the Al/base ratio must be kept within very narrow limits in order to have only disappearance of cationic activity and formation of *cis*-1,4 polymers.

(2) Polymerization in *n*-heptane

(a) *Catalysts from AlEt_2Cl* . The $\text{AlEt}_2\text{Cl}-\text{Co}(\text{acac})_3$ system exhibits in *n*-heptane a different behaviour than in benzene. While the polymers obtained in benzene are about 55 per cent *cis*, the ones obtained in *n*-heptane are predominantly 1,2. The percentage of 1,2 units is slightly dependent on the polymerization temperature and can be as high as about 90 per cent* (Table 4). A characterization of the 1,2 polymers

TABLE 4. POLYMERIZATION OF *trans*-1,3-PENTADIENE IN *n*-HEPTANE BY CATALYSTS FROM COBALT TRIACETYLACETONATE AND DIETHYLALUMINUM CHLORIDE*

Run No.	$\text{Co}(\text{acac})_3$ (moles.10 ⁶)	Al/Co molar ratio	Catalyst ageing (min)	Polymerization time (hr)	Conversion %	$[\eta]$ (dl.g ⁻¹)	i.r. analysis	
							<i>trans</i> %†	<i>cis</i> %
1‡	1.6	600	10	20	78	3.87	94	6
2‡	1.6	600	0	20	86	2.90	95	5
3	1.6	600	0	20	75	3.76	93	7
4	1.6	600	8	20	57	5.44	95	5
5	1.6	3000	2	40	95	3.60	92	8
6	1.6	90	2	40	88	3.90	92	8
7	1.6	260	0	20	80	—	90	10
8	1.6	260	0	20	80	—	70	30

* Polymerization temperature = about 18°. Pentadiene = 2 ml. Heptane = 10 ml. Heptane dried on molecular sieves was used in runs 1–6 (H_2O content about 25 ppm; i.e. about 1.2×10^{-5} moles in each experiment). Wet heptane (H_2O content about 5.10^{-5} moles in each experiment) was used in runs 7 and 8. In run 8 the catalyst was prepared by introducing in *n*-heptane first AlEt_2Cl , then, after 30 min, the cobalt compound and the monomer.

† According to NMR analysis the *trans* double bonds correspond mostly to 1,2 units; *trans*-1,4 units are for each run, about 3–5 per cent with respect to the total units.

‡ In runs 1 and 2 thiophene was added. Thiophene/Al molar ratio 2 : 1.

has already been reported⁽⁴⁾ and it has also been indicated that they are amorphous at room temperature, but appear crystalline (although weakly) at low temperature or even at room temperature under stretching. From the observed identity period (about 5.1 Å), it has been deduced that the crystallinity is due to stereoregular 1,2 syndiotactic sequences. The weak tendency of this polymer to crystallize is presumably attributable to a low stereoregularity.

* In a previous communication⁽⁴⁾ a higher 1,2 unit content (up to 98 per cent) was reported for the polymers obtained in *n*-heptane by the $\text{AlEt}_2\text{Cl}-\text{Co}(\text{acac})_3$ system. The present value, based on i.r. and NMR analyses, must be considered more correct than that previously reported, based only on i.r. analysis.

The presence of H₂O in the polymerization solvent causes a decrease of the 1,2 units and an increase of the *cis*-1,4 units of the polymers (runs 7 and 8). The effect of H₂O is particularly evident if catalysts are prepared by introducing first AlEt₂Cl into *n*-heptane saturated with H₂O and after some time, e.g. 30 min, the cobalt compound and the monomer; in this case polypentadienes have been obtained containing 60–70 per cent 1,2 units, the remaining being mostly *cis*-1,4.

(b) *Catalysts from chloroethylaloxanes.* The catalysts from chloroethylaloxanes yield, in *n*-heptane, polymerization products which are predominantly *cis*-1,4 (up to about 90 per cent) and which exhibit, at room temperature, the crystallinity typical of the *cis*-1,4 syndiotactic polypentadiene (Table 5). As observed when using benzene

TABLE 5. POLYMERIZATION OF *trans*-1,3-PENTADIENE IN *n*-HEPTANE BY CATALYSTS FROM COBALT TRIACETYLACETONATE AND CHLOROETHYLALOXANES*

Run No.	Al/Co molar ratio	Thiophene/Al molar ratio	Catalyst ageing (min)	Polymerization time (hr)	Conversion (%)	[η] (dl.g ⁻¹)	i.r. analysis	
							<i>trans</i> %†	<i>cis</i> %
1	600	2	10	20	86	1.28	6	94
2	600	2	0	20	93	1.33	8	92
3	600	0	10	20	96	1.16	10	90
4	600	0	0	20	90	1.11	12	88
5‡	600	2	0	20	89	1.25	7	93
6	85	9	0	20	78	1.39	14	86
7	85	9	10	63	50	1.56	16	84
8	40	3	0	20	0	—	—	—
9§	1000	2	0	4.5	75	1.50	16	84
10§	1000	2	0	4.5	95	1.63	6	94

* Polymerization temperature=18°. Heptane (dried on molecular sieves) = 10 ml. Co(acac)₃ = 1.6 × 10⁻⁶ moles. Pentadiene = 2 ml. All the polymers obtained are crystalline at room temperature (i.r. and X-ray spectra) and exhibit the crystallinity typical of *cis*-1,4 syndiotactic structure.

† NMR examination shows that the units characterized by *trans* double bond are almost completely 1,2 (*trans*-1,4 units are less than 1 per cent with respect to the total units).

‡ In this run, 4 ml of pentadiene and 8 ml of heptane were used.

§ In runs 9–10, the aluminum compound was prepared by reacting AlEt₂Cl with (Et₃Sn)₂O. In run 10, Al is present completely as chloroethylaloxanes; in run 9, about 75 per cent of the Al is as AlEt₂Cl, 25 per cent as chloroethylaloxanes.

as the solvent, the *cis*-1,4 content of the polymerization products is slightly higher if thiophene is added to the catalyst solution, in order to inhibit cationic activity.

The polymers obtained with the catalyst from chloroethylaloxanes in *n*-heptane practically do not differ from those obtained in benzene by the same system, either with regard to *cis*-1,4 content or the molecular weight.

It is interesting that, while the catalyst system AlEt₂Cl—Co(acac)₃ is influenced by the nature of the hydrocarbon solvent, the catalyst system chloroethylaloxanes—Co(acac)₃ yields practically identical results in *n*-heptane and benzene.

The fact that, when using AlEt₂Cl in *n*-heptane saturated with H₂O, polymers having a low *cis*-1,4 content have been obtained, as seen in the preceding paragraph, seems attributable to the slowness of formation of chloroethylaloxanes from AlEt₂Cl and H₂O in *n*-heptane, under the conditions examined.

(c) *Catalysts from Al₂Et₃Cl₃ or AlEtCl₂*. The Al₂Et₃Cl₃—Co(acac)₃ system yields, in *n*-heptane at room temperature, products composed of approximately equal numbers of *cis*-1,4 and 1,2 units (Table 6). Adding of thiophene to the catalyst solution has a small influence on the composition of the products. By fractionating the crude products, polymers have been obtained having approximately the same microstructure

TABLE 6. POLYMERIZATION OF *trans*-1,3-PENTADIENE IN *n*-HEPTANE, BY CATALYSTS FROM COBALT TRIACETYLACETONATE AND Al₂Et₃Cl₃*

Run No.	Al/Co molar ratio	Thiophene/Al molar ratio	Catalyst ageing (min)	Polymerization time (hr)	Conversion (%)	[η] (dl.g ⁻¹)	i.r. analysis <i>trans</i> %† <i>cis</i> %	
1	1100	2	0	20	95	1.13	42	58
2	1100	0	0	20	95	1.05	51	49

* Polymerization temperature = about 18°. Pentadiene 2 ml. Heptane (dried on molecular sieves) = 10 ml, Co(acac)₃ = 1.6 × 10⁻⁶ moles. Fractionation, by dissolving in benzene and reprecipitating with MEK, did not give a fraction richer in *cis*-1,4 units than the starting product.

† NMR examination shows that the *trans* units are almost completely 1,2.

as the starting products. Either the crude products or the fractions obtained have been found to be amorphous by X-ray or i.r. examination. It thus seems that the macromolecules obtained by the Al₂Et₃Cl₃—Co(acac)₃ system must be considered as copolymers composed of approximately the same amount of *cis*-1,4 and 1,2 units. The AlEtCl₂—Co(acac)₃ system yields low molecular weight products of cationic origin. Adding thiophene causes the precipitation of the catalyst complex, which, in a different phase, shows only a very weak catalytic activity.

(3) Polymerization in *cis*-2-butene

Cis-2-butene has been reported⁽¹⁰⁾ to be an excellent solvent for the polymerization of butadiene to *cis*-1,4 polymer by cobalt catalysts prepared from alkyl aluminum compounds containing Al—O—Al bonds. In a series of runs, we have examined the

TABLE 7. POLYMERIZATION OF *trans*-1,3-PENTADIENE IN *cis*-2-BUTENE BY CATALYSTS FROM COBALT DIACETYLACETONATE*

Run No.	<i>cis</i> -2-butene (ml)	<i>trans</i> -1,3-pentadiene (ml)	Al/Co molar ratio	Thiophene/Al molar ratio	Conversion (%)	[η] (dl.g ⁻¹)	i.r. analysis <i>trans</i> %† <i>cis</i> %	
1	10	2	600	2	79	3.26	5	95
2	10	2	600	0	89	1.39	15	85
3	8	4	600	2	50	3.6	11	89
4	10	2	600	0	79	3.5	92	8

* The aluminum was as chloroethylaloxanes in runs 1–3, as AlEt₂Cl in run 4. *Cis*-2-butene was dried on molecular sieves. Co(acac)₂ = 1.6 × 10⁻⁶ moles. Polymerization temperature = 0°. Polymerization time = 20 hr. The catalyst was not aged.

† NMR examination shows that the *trans* units are almost completely 1,2. *Trans*-1,4 units are less than 1 per cent with respect to the total units in runs 1–3 and about 3–4 per cent in run 4.

polymerization of *trans*-1,3-pentadiene in such a solvent, using cobalt catalysts prepared from AlEt_2Cl and chloroethylaloxanes respectively.

The results of the polymerizations in *cis*-2-butene can be summarized as follows (Table 7).

(a) *Catalysts from AlEt_2Cl* . These catalysts yield polymers predominantly composed of 1,2 units (about 90 per cent), which practically do not differ, with regard to the microstructure and molecular weight, from those obtained in *n*-heptane.

(b) *Catalysts from chloroethylaloxanes*. These catalysts yield crystalline polymers having a *cis*-1,4 syndiotactic structure. In the presence of small amounts of thiophene (thiophene/Al molar ratio from 0.5 to about 2), crude polymerization products are obtained containing up to 90 per cent *cis*-1,4 units. With regard to the microstructure (i.r. and NMR examinations) these polymers do not differ from those obtained in benzene or *n*-heptane, but their molecular weight is noticeably higher.

DISCUSSION

Microstructure of the polymers

The most interesting features of the polymerization of *trans*-1,3 pentadiene by cobalt catalysts, as deduced from the above data, can be summarized as follows: (a) the polymers obtained are almost exclusively composed of *cis*-1,4 and 1,2 units, the percentage of *trans*-1,4 units being generally very low. (b) the ratio of *cis*-1,4 to 1,2 units in the polymers depends on the alkyl aluminum compound used for the preparation of the catalyst and on the polymerization solvent; actually it is possible to obtain polymers which are about 90 per cent *cis*-1,4 and polymers which are about 90 per cent 1,2.

A possible rationalization of these facts is the following.

A *cis*-1,4 unit derives presumably from a coordination of the monomer to Co through the two double bonds. Such a type of coordination occurs, however, in two steps; the first occurs only through the vinyl double bond,* the second occurs through the internal double bond, as outlined in Fig. 1 (a and b).

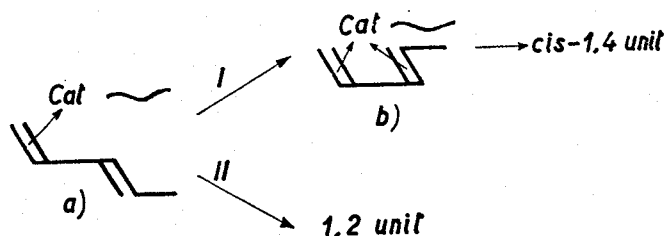


FIG. 1. Possible scheme for formation of 1,2 vs. *cis*-1,4 pentadiene units.

* A coordination of pentadiene through the internal double bond is, at least in principle, also possible. Such a coordination could lead to the formation of 3,4 units, $-\text{CH}(\text{CH}=\text{CH}_2)-\text{CH}(\text{CH}_3)-$, which however have not been found in the polymers (absence of vinyl groups) or also of *cis*-1,4 units, through coordination of the other double bond. We are, however, of the opinion that, for steric reasons, the coordination will first occur through the vinyl group.

It is improbable, in fact, that the coordination through the two double bonds [Fig. 1(b)] can occur in a single step. If this were the case, only the *cisoid* conformer could coordinate to Co. This conformer, however, is present in the monomer in a very low amount, at the polymerization temperature, and, therefore, the coordination (and hence the polymerization) would be extremely slow, contrary to the experimental evidence. It seems appropriate to recall here that it is accepted that the Diels-Alder reaction, which appears analogous to the process of formation of a *cis*-1,4 unit according to the scheme of Fig. 1, also occurs in two steps.⁽¹¹⁾

It is seen from the scheme of Fig. 1 that the coordination of pentadiene through the vinyl group, which can lead to a *cis*-1,4 unit via route I, can also lead to a 1,2 unit via route II. According to this scheme, the relative rate of the two reactions (I and II respectively) determines the structure of the polymer.

Several factors presumably affect the relative rate of reactions I and II, but little is known at present as to their nature. One factor is probably the type of coordination around Co, which could depend on the solvent and on the particular aluminum compound used. Other factors are probably related to the nature of ligands around Co in the catalytic complex, and to their electron donating power.

It is interesting to compare the microstructure of the polymers obtained from butadiene and pentadiene respectively by the cobalt catalysts examined in this paper (Table 8). One observes that the polymers of pentadiene generally have a lower *cis*-1,4 content and a higher 1,2 content than the polymers of butadiene obtained by the same catalyst. The most pronounced difference is between the polymers obtained by $\text{AlEt}_2\text{Cl}-\text{Co}(\text{acac})_3$ in *n*-heptane, which are predominantly *cis*-1,4 for butadiene and

TABLE 8. MICROSTRUCTURE OF THE POLYMERS OBTAINED FROM 1,3-BUTADIENE AND *trans*-1,3-PENTADIENE RESPECTIVELY BY VARIOUS COBALT CATALYSTS*

Al compound used for the catalyst system	Polymerization solvent†	Microstructure of the polymers	
		Polybutadienes	Polypentadienes
AlEt_2Cl	Benzene	98% <i>cis</i> -1,4	55% <i>cis</i> -1,4
	<i>n</i> -heptane	85-98% <i>cis</i> -1,4	90% 1,2
$\text{Al}_2\text{Et}_3\text{Cl}_3$ ‡	Benzene	98% <i>cis</i> -1,4	85% <i>cis</i> -1,4
	<i>n</i> -heptane	90% <i>cis</i> -1,4	60% <i>cis</i> -1,4
AlEtCl_2 ‡	Benzene	98% <i>cis</i> -1,4	85% <i>cis</i> -1,4
	<i>n</i> -heptane§	—	—
Chloroalkylaloxanes ‡	Benzene	99% <i>cis</i> -1,4	90% <i>cis</i> -1,4
	<i>n</i> -heptane	97% <i>cis</i> -1,4	90% <i>cis</i> -1,4

* $\text{Co}(\text{acac})_2$ or $\text{Co}(\text{acac})_3$ as the Co compound. Al/Co molar ratio more than 50.

† Sodium-dried and stored on molecular sieves.

‡ Thiophene was added to inhibit cationic activity.

§ The catalyst is insoluble and very poorly active in *n*-heptane.

|| The remaining units are mostly 1,2.

predominantly 1,2 for pentadiene. In our opinion these facts may well be accounted for by the scheme of Fig. 1, the passage from step a to step b being conceivably more rapid for butadiene than for pentadiene. It is to be noted that even a very small difference in the relative rate of reactions I and II (Fig.1) may cause a pronounced difference in the microstructure of the polymers.

Stereoregularity of the polymers

A possible scheme for the formation of *cis*-1,4 syndiotactic sequences in pentadiene polymers by cobalt catalysts was examined in a previous paper.⁽²⁾ It was based on the assumption that the diolefin coordinates to Co through both the double bonds, before being incorporated into the growing chain as a *cis*-1,4 unit.

Such a scheme is obviously an oversimplification, the catalytic mechanism being a complex phenomenon which cannot be easily represented by a diagram.

With regard to the formation of syndiotactic 1,2 sequences by $\text{AlEt}_2\text{Cl}-\text{Co}(\text{acac})_3$ in *n*-heptane, it is not clear at present how they can be formed.

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Résumé—Ce travail porte sur la polymérisation du 1,3-pentadiène avec des catalyseurs au Cobalt préparés à partir de AlEt_2Cl , $\text{Al}_2\text{Et}_3\text{Cl}_3$ ou de composés alcoylés d'aluminium contenant des liaisons AlOAl .

Selon le composé de l'aluminium utilisé pour préparer le catalyseur et le solvant dans lequel s'effectue la polymérisation (benzène, *n*-heptane, butène-2 *cis*) on a obtenu différents polymères: des polymères cristallins avec une structure syndiotactique *cis* 1,4, des polymères amorphes contenant des motifs 1,2 et *cis* 1,4 et des polymères faiblement cristallisés avec une structure syndiotactique 1,2.

On caractérise ces polymères. On discute les résultats à l'aide des théories courantes sur le mécanisme de catalyse des polymérisations stéréospécifiques.

Sommario—Viene riferito sulla polimerizzazione del pentadiene-1,3 in vari solventi (benzolo, eptano, butene-2 *cis*) mediante catalizzatori al cobalto preparati rispettivamente da AlEt_2Cl , $\text{Al}_2\text{Et}_3\text{Cl}_3$, composti alluminio alchilici contenenti legami AlOAl . Secondo l'alluminio alchile usato per preparare il catalizzatore e secondo il solvente di polimerizzazione possono essere ottenuti polimeri cristallini a struttura 1,4-*cis* sindiotattica, polimeri amorfi a struttura mista 1,4 *cis* e 1,2, polimeri debolmente cristallini a struttura 1,2 sindiotattica. Viene riportata una caratterizzazione dei polimeri ottenuti ed i risultati vengono discussi alla luce delle attuali conoscenze sul meccanismo dei catalizzatori stereospécifici di polimerizzazione.

Zusammenfassung—Es wird berichtet über die Polymerisation von 1,3-Pentadien durch Kobalt-Katalysatoren, hergestellt aus AlEt_2Cl , $\text{Al}_2\text{Et}_3\text{Cl}_3$ oder Alkyl-aluminium Produkten, die AlOAl Bindungen enthalten.

In Abhängigkeit von dem zur Herstellung des Katalysators verwendeten Aluminium-Produkt und von dem Lösungsmittel bei der Polymerisation (Benzol, *n*-Heptan, *cis*-2-Buten) werden verschiedene

Polymere erhalten, und zwar kristalline Polymere mit einer *cis*-1,4-syndiotaktischen Struktur, amorphe Polymere zusammengesetzt aus *cis*-1,4 und 1,2 Einheiten und schwach kristalline Polymere mit einer 1,2 syndiotaktischen Struktur.

Die Charakterisierung der Polymeren wird beschrieben und die Ergebnisse diskutiert im Hinblick auf gegenwärtige Theorien über den Mechanismus der Katalyse der stereospezifischen Polymerisation.