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On the Epimerization of endo-Dicyclopentadiene during Terpolymerization with Ethylene and Propylene

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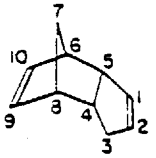
ABSTRACT

The isomerization of endo-DCP (I) to exo-DCP (II) during the synthesis of EPDM with several Ziegler-Natta catalysts has been investigated by means of IR spectroscopy and by reference to EPDM containing different levels of true exo-DCP. The I → II epimerization was absent for all the catalysts examined. Only with the systems VCl_4-Et_2AlCl was a trace of isomerization observed, and then only at the limit of sensitivity of the analytical method. No isomerization was detected via gas-chromatographic analysis in monomeric DCP recovered from the polymerization mixture. Ziegler-Natta catalysts having acidic character can homopolymerize I, but epimerization was observed only with the system $VOCl_3$-$Et_3Al_2Cl_3$. The results obtained have been interpreted in terms of a terpolymerization mechanism having a prevalent coordinated character. The polyfunctionality of Ziegler-Natta catalysts is sometimes responsible of the secondary isomerization process.

INTRODUCTION

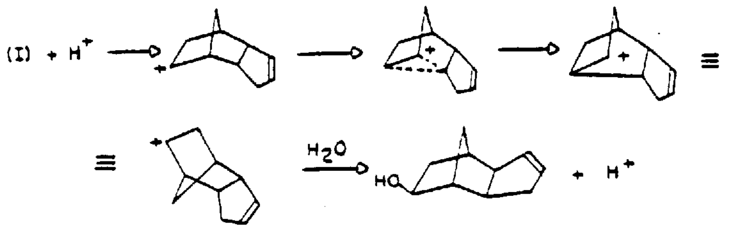
Some years ago De Kock and Veermans [1] reported that during the synthesis of EPDM (ethylene-propylene-unconjugated diene terpolymers) containing dicyclopentadiene [tricyclo-$(5.2.1.0^{4,5})$-deca-1,9-diene: DCP], the endo configuration (I) of the third monomer in the EPDM chains would transform into the exo structure (II):

I



II

Although the termonomer used has the endo structure exclusively (derived preferably, in view of the steric control, from the Diels-Alder dimerization of cyclopentadiene, according to the cis addition rule [2] of Alder), the epimerization of the bridgehead carbon atoms in position 4,5 or 6,8 could not be excluded a priori during the terpolymerization process. In fact, electrophilic agents were found able to convert I into 9,10-derivatives of exo-DCP according to a cationic mechanism [3, 28]:



which may describe the Wagner-Meerwein rearrangement [4].

The De Kock's conclusion [1] was reached on the basis of IR analyses carried out on EPDM prepared with I and by making reference to some model compounds derived from the endo and exo series. However, the range of the IR spectrum examined was quite restricted, from 13.0 to 15.0 μ, and some complications, due to the absorption of the methylenic sequences present in EPDM, were not taken into account.

Recently we had the opportunity to examine the IR spectra of EPDM containing true II [5], and by comparing them with the spectra of EPDM based on I, we have reached the conclusion that, generally, no I – II isomerization takes place. In this paper we report the evidence supporting our conclusion.

EXPERIMENTAL

Materials

endo-DCP (Fluka) was purified by distillation under vacuum: VPC purity was higher than 99.5%, the main impurity being 1,2-dihydrodicyclopentadiene.

exo-DCP was prepared according to Ref. 6: the steric purity was 98%, the remainder being the endo isomer.

9,10-Dihydro-endo-DCP and 9,10-dihydro-exo-DCP were obtained according to Ref. 7. After distillation the products were 99.5% pure (VPC).

The solvents for the polymerization experiments and analyses (toluene, n-heptane, tetrachloroethylene, CCl_4, $CHCl_3$, CS_2) were purified as previously reported [8] and stored under dry nitrogen.

Et_2AlCl, $Et_3Al_2Cl_3$, $EtAlCl_2$, $Al(i\text{-}C_4H_9)_3$, $Al(n\text{-}C_8H_{17})_3$ (Texas Alkyls), VCl_4, $VOCl_3$ (Stauffer), $TiCl_4$ (C. Erba), $VO(O\text{-}n\text{-}C_4H_9)_3$, and $VOCl(OEt)_2$ (Dynamit Nobel) were pure grade reagent and used without a preliminary treatment.

$VAcac_3$ (Acac = acetylacetonate) was prepared according to Ref. 9.

Ethylene and propylene were Phillips products (polymerization grade) and were passed through an AlR_3 solution before use.

Polymerization

The apparatus and the procedure adopted to synthetize EPDM were reported elsewhere [10]. The catalyst was prepared in situ and the third monomer added to the feed, in part (50%) at the beginning of the operation and the remainder as intermittent additions (every minute) during the terpolymerization.

Attempts to isomerize endo-DCP in the presence of cationic or Ziegler-Natta catalysts were carried out in three-necked flasks, equipped with a magnetic stirrer, heated under dry nitrogen, and placed in a thermostatic bath. The reagents were added by means of glass syringes in the following order: solvent, monomer, catalyst. The end of the reaction was obtained by adding an excess of methanol containing NH_3. Samples of the mixture of the reactants were withdrawn and subjected to VPC analysis for testing the isomerization reactions. Poly-DCP was purified through dissolution in $CHCl_3$ and precipitation from methanol.

Analyses

Some analyses of the EPDM's produced (intrinsic viscosity, α-olefine content, crystallinity) were carried out as previously reported [10]. The unsaturations were determined by absorption of ICl (BDH), according to Ref. 11). In some cases they were confirmed by NMR analysis, measuring the areas of signals at 5.50 ppm (olefinic protons of cyclopentene ring), 1.2 ppm (methylenic and methynic protons), and 0.8 ppm (methylic protons), referred to HMDS.

The IR spectra were performed on a Perkin-Elmer spectrophotometer (Model 225), using films obtained by evaporation of CS_2 solutions of EPDM. DCP homopolymers were examined by means of both KBr disk and solution (CCl_4) technique. The optical densities at 12.7, 13.5, 13.9, and 14.5 μ were read with respect to a base line drawn, respectively, between 12.5 and 13.0 μ, 13.4 and 13.7 μ, 12.9 and 15.1 μ, and 14.2 and 14.9 μ.

The model compounds were examined with IR spectroscopy as pure liquids.

VPC analyses were carried out with a C.Erba instrument (Fractovap Model GT) having a ionizing flame detector and a Carbowax 20 M column. Conditions: column 3 m, diameter 4 × 2 mm, $T_{col} = 90°C$, $T_{evap} = 155°C$, carrier N_2. Under these conditions, 0.2% of exo-DCP, in the presence of endo-DCP, can be detected.

NMR measurements were carried out with a Varian spectrometer (Model HA-100) from CCl_4 or $CDCl_3$ solutions of the polymers.

RESULTS AND DISCUSSION

Spectroscopic Observations

Figures 1 and 2 show the IR spectra of two EPDM's containing, respectively, I and II and having the same content of third monomer (13 wt%). In order to facilitate the examination of Figs. 1 and 2, we report in Figs. 3 and 4 the significant part of the IR spectra of 9,10-dihydro-endo-DCP and 9,10-dihydro-exo-DCP which simulate the structures of I and II when they are inserted in the EPDM chains.

For the sake of clarify, the spectra herein reported will be discussed, with other data, in the following paragraphs.

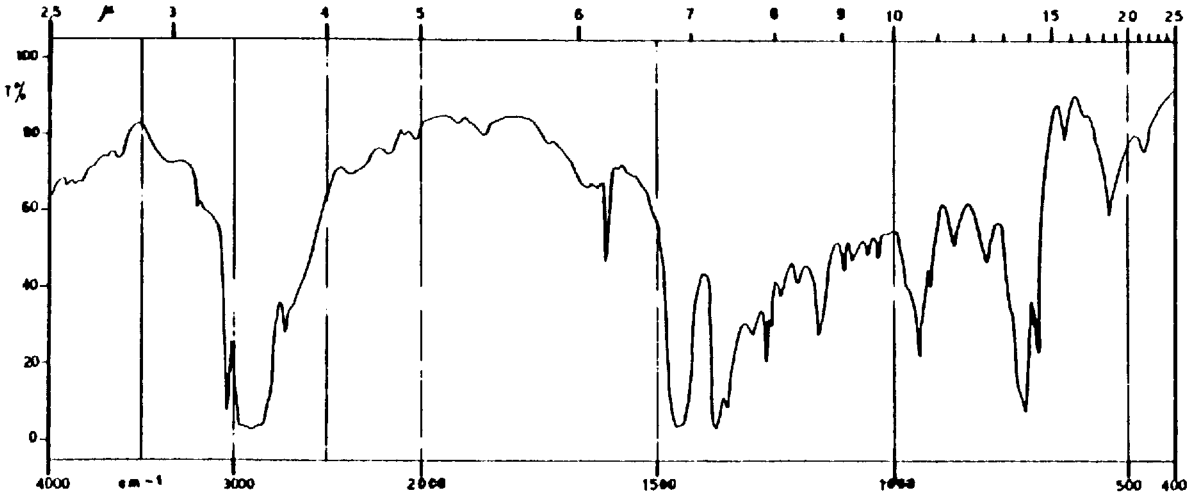


FIG. 1. IR spectrum of EPDM containing 13.0 wt% endo-DCP.

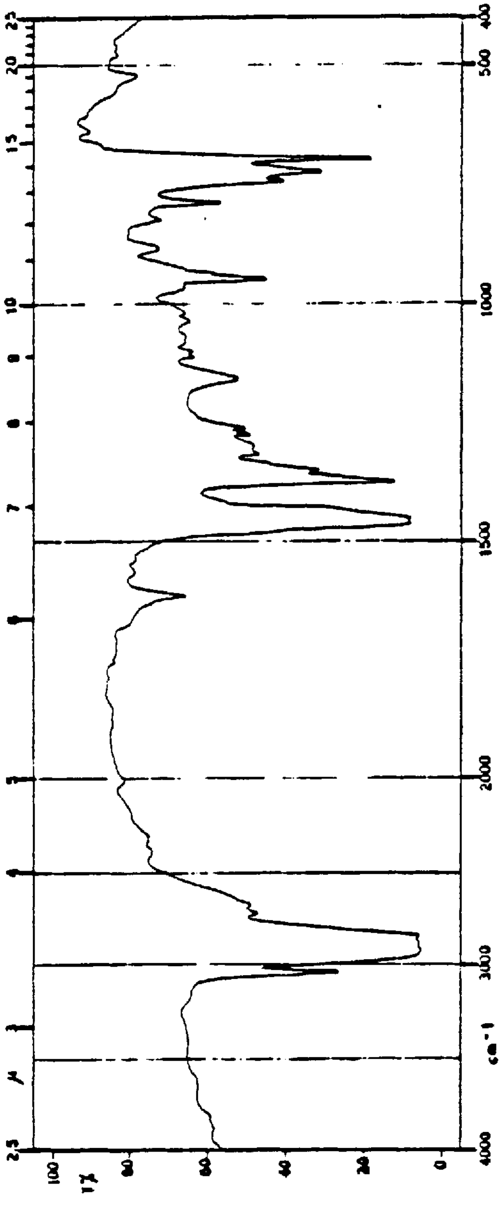


FIG. 2. IR spectrum of EPDM containing 13.0 wt% exo-DCP.

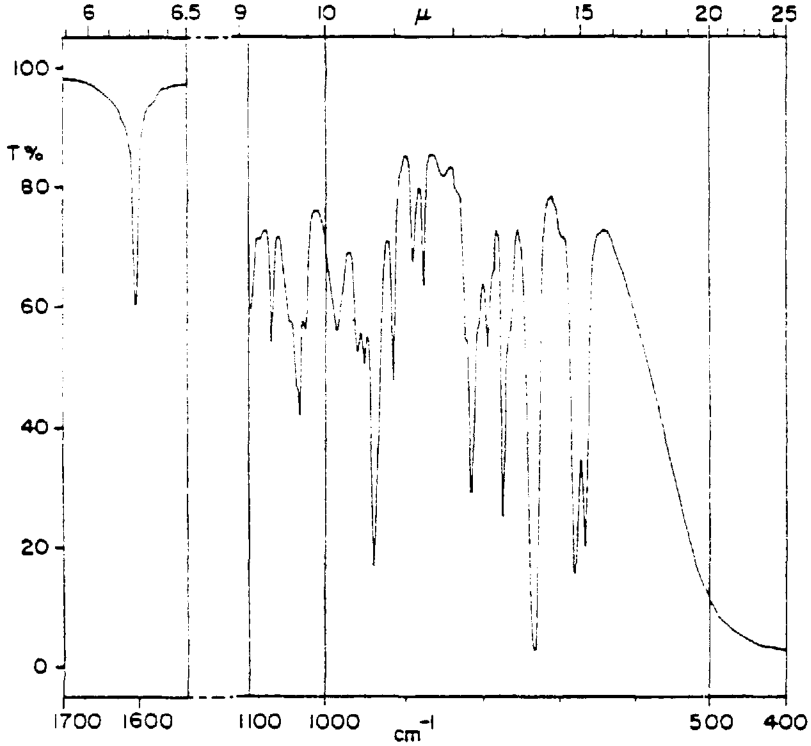


FIG. 3. Significant part of the IR spectrum of 9,10-dihydro-endo-DCP.

There are two bands, at about 13.5 and 14.5 μ, which are present both in the endo and exo series of DCP derivatives. Both were attributed [12] to the out-of-plane deformation of a H of a cis double bond. However, their intensities are opposite, i.e., compounds in the endo series have the stronger absorption at about 13.5 μ and the weaker one at about 14.5 μ, whereas compounds in the exo series have the stronger absorption at about 14.5 μ and the weaker one at about 13.5 μ. The same results were found by De Kock [1] on investigating several model compounds. From those IR spectra and from Fig. 4 it is possible to calculate approximately the ratio of the optical densities at 13.5 and 14.5 μ for the exo series as $R = D_{14.5}/D_{13.5} = 1.0-2.1$ (in one case R = 8.5). On the other hand, for the endo series R = 0.33-0.49 (cf. Ref. 1 and Fig. 3).

In the case of our terpolymer containing II, it is possible to

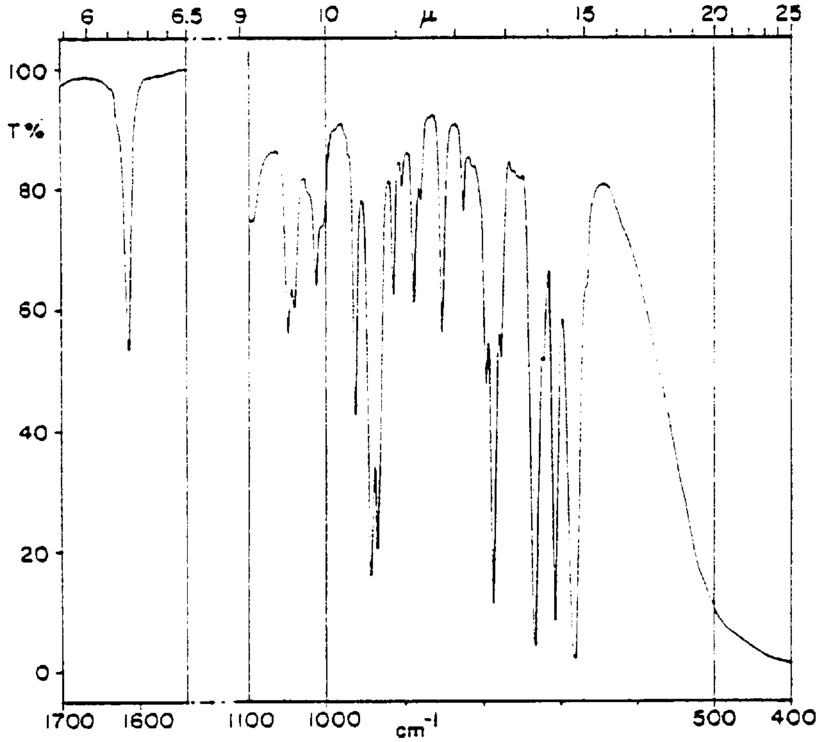


FIG. 4. Significant part of the IR spectrum of 9,10-dihydro-exo-DCP.

evaluate (Fig. 2) R = 1.3, which is in agreement with the model compounds results.

There are also two bands at 6.19 and 6.23 μ (attributed [1] to the stretching of the cis double bond present in the cyclopentene ring) which are characteristic, respectively, of the exo and endo series. However, their intensities are rather weak and useless for our purposes.

When the ethylene content of EPDM's is higher than 50 mole %, their IR spectra show a strong absorption at 724 cm^{-1} (13.93 μ) to be ascribed [13] to the rocking motion of the methylenic sequencies ($-(CH_2)_n-$, where $n > 5$ [14]).

In the case of EPDM based on I the stronger band at 13.9 μ partially overlaps the band at about 13.5 μ. However, the absorption at 13.5 μ is still evident through the presence of a shoulder, but it is impossible to calculate, even in an approximate way, the intensity of the band at 13.5 μ.

A similar situation occurs in the spectra reported by De Kock, but the complication arising with respect to the model compounds spectra was not discussed [1]. This is an important point; in fact, De Kock concludes that there is a I – II isomerization during the terpolymerization since only the band at 14.5 μ is clearly evident in his spectra, assuming (in contrast with the experimental evidencies shown by the model compounds) that the absorption at 14.5 μ is exclusively characteristic of the exo-compounds.

It is worth noting the similarity of our Fig. 1 with the spectra previously reported [1]. This similarity can be described on a quantitative basis by the ratio $R' = D_{14.5}/D_{13.9}$. In fact, from Fig. 1 R' = 0.32 is obtained and R' = 0.43 can be calculated from Ref. 1. The discrepancy may be attributed to differences in the composition of the EPDM's investigated (unfortunately, De Kock did not report the composition of the polymer studied).

In order to confirm this preliminary conclusion, we have examined two series of EPDM's having the same composition and containing I or II in different amounts. The results are reported in Table 1, and it is possible to deduce therefrom that the ratio R' is useful to distinguish between EPDM's containing I or II. In fact, in the case of II the value of R' is about 5 times higher than the value of R' calculated for EPDM based on I (Fig. 5). Obviously the comparison has to be made between EPDM's having similar composition since the bands used (13.9 and 14.5 μ) are related to ethylene and third monomer contents. However, when the amount of DCP is higher than 5 wt% and the content of ethylene is not rigorously constant, $R' > 0.5$ for EPDM containing II and $R' < 0.5$ in the case of I.

The comparison of Fig. 1 with Fig. 2 shows that the band at 12.76 μ (784 cm^{-1}) is characteristic of the exo series. In fact it is always present in the IR spectra of the model compound of II (Fig. 4) and also of pure II [6]. Furthermore, it was observed [15] in a low MW homopolymer of II. Up to now, its origin is unknown.

On the contrary, the absorption at 12.7 μ is practically absent in the IR spectra of EPDM based on I, of pure I, and other derivatives of I (Fig. 3).

Therefore this band can be utilized to detect the presence of II in the EPDM chains. In fact (Table 2), by employing as third monomer mixtures of I and II having different contents of stereoisomers, it is possible to observe the absorption at 12.7 μ in the corresponding EPDM.

TABLE 1. Spectroscopic Properties of EPDM[a] Containing endo or exo-DCP

Sample No.[b]	Termonomer Type	Termonomer wt%	$D_{14.5}/D_{13.9}$	$D_{12.7}/D_{14.5}$
1	endo-DCP	3.3	0.086	0
2	exo-DCP	3.7	0.36	0.08
3	endo-DCP	6.9	0.20	0
4	exo-DCP	6.8	1.08	0.17
5	endo-DCP	13.0	0.35	0
6	exo-DCP	13.0	1.20	0.24

[a] Prepared by using the catalyst $VAcac_3$-$AlEt_2Cl$ at 0°C.
[b] Average content of ethylene, 50 wt%.

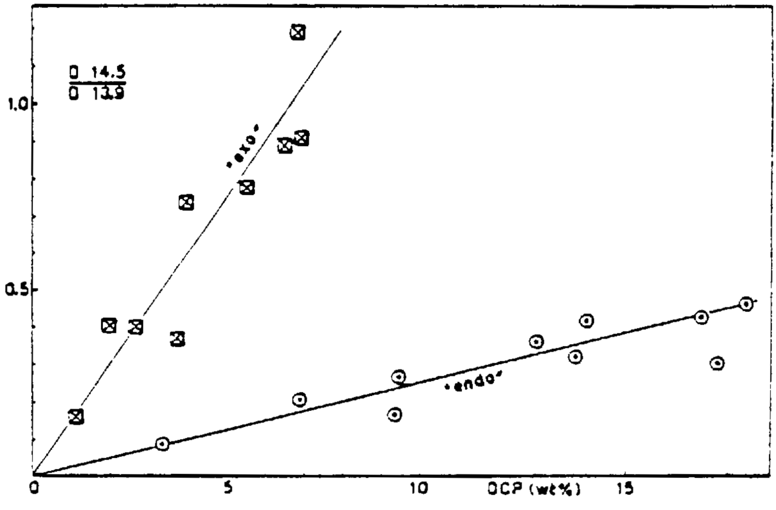


FIG. 5. Relationship between $D_{14.5}/D_{13.9}$ and the DCP content of EPDM containing endo or exo-DCP.

TABLE 2. Properties of EPDM Containing Different Amounts of endo and exo-DCP

Sample No.	exo-DCP in the feed (%)	Total DCP in the polymer[a] (wt%)	C_2H_4 (wt%)	$[\eta]$[b] (dl/g)	Band at 12.7 μ	$D_{14.5}/D_{13.9}$	$D_{12.7}/D_{14.5}$	exo-DCP in the polymer[c] (%)
1	100	13.0	60	2.54	Present	1.20	0.29	100
2	37.5	13.4	52	1.52	Present	0.91	0.14	47
3	5	13.8	54	1.16	Present	0.42	0.09	30
4	2.5	14.9	63	2.25	Present	0.33	0.04	12
5	1.5	15.7	54	0.97	Absent	0.35	0	0

[a] Determined by ICl absorption.
[b] From toluene solutions at 30°C.
[c] Extimated through the ratio $D_{12.7}/D_{14.5}$ assuming a direct proportionality.

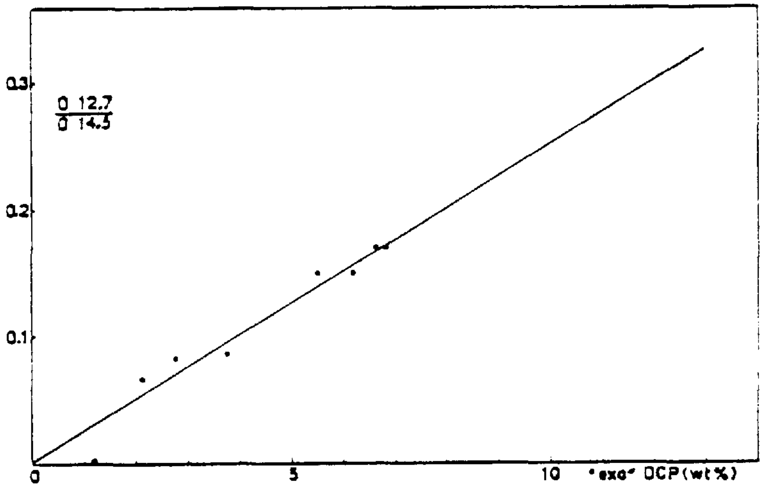


FIG. 6. Dependence of the ratio $D_{12.7}/D_{14.5}$ on the content of exo-DCP present in EPDM.

The minimum level of II detectable in EPDM through the intensity of the absorption at 12.7 μ has been evaluated from Fig. 6 which illustrates the dependence of the ratio $D_{12.7}/D_{14.5}$ on the content of II in different samples of EPDM. This minimum level is less than 2 wt% and corresponds, in the series of samples reported in Table 2, to about 10% of II with respect to the overall content of DCP.

When the content of ethylene is nearly constant in different samples of EPDM having different amounts of II, the ratio $D_{14.5}/D_{13.9}$ is roughly proportional (Table 2) to the content of II in the feed. However, the ratio $D_{12.7}/D_{14.5}$ does not depend on the content of ethylene and is more regularly proportional to the low concentrations of II in the feed.

The use of NMR measurements was found very useful in determining endo or exo configuration, both in low molecular weight products [6] and in polymers [15].

Relatively high concentrations of the epimeric forms are unfortunately required to obtain clear NMR spectra, and this is not the case for low amounts of third monomer present in EPDM. Our attempts, carried out on EPDM containing less than 8 wt% of II, were unsuccessful.

Terpolymerization Experiments

Our results, reported in the previous section, were obtained from EPDM's prepared with the catalyst system $VAcac_3$-$AlEt_2Cl$. Unfortunately there is no indication in the paper of De Kock [1] about the preparation of the EPDM investigated except that Ziegler catalyst are cited incidentally for polymerization reactions of this type. Therefore we had to examine the most typical catalyst systems utilized in the synthesis of ethylene-propylene rubbers [16, 17] in order to check the existence of the I – II rearrangement during the terpolymerization process.

Table 3 contains the catalysts utilized to synthetize EPDM by employing I. Figure 7 shows the significant part of the IR spectra recorded from the terpolymers obtained which, generally, contain more than 10 wt% of DCP. According to Fig. 7 there is, generally, no evidence of absorption at 12.7 μ due to II. Only the sample prepared with the catalyst VCl_4-$AlEt_2Cl$ shows a very weak band at 12.7 μ whose intensity, on the basis of Fig. 6, could indicate the presence of 1-2 wt% of exo-DCP in the sample. However, apart some differences between the spectra of Fig. 7, which can be attributed to the different composition of the EPDM's investigated (owing to the fact that we adopt a constant ethylene/propylene molar ratio in the feed), the spectra of Fig. 7 are similar to the one of Fig. 1 and quite different from the one of Fig. 2.

Terpolymerization Mechanism

Despite the enormous amount of work on the Ziegler-Natta catalyst systems, there is not, up to now, a unique view concerning the mechanism of this peculiar polymerization. Several authors consider the mechanism to be anionic-coordinate [18], in particular when it is referred to ethylene-propylene copolymerization [17]. Apart from some important details concerning the single steps of the mechanism, the more recent views favor monometallic active sites on the transition metal atom, activated by the organometallic component [19]. According to these studies [20] it is necessary to distinguish between "isospecific," "syndiospecific," and "aspecific" mechanisms in the homopolymerization of α-olefins, and it is not correct to speak of them in terms of conventional mechanisms (ionic or radicallike), even though, in the past, a number of results were interpreted in terms of anionic-coordinate mechanism [21].

In the field of the ethylene-propylene copolymerization few contributions have so far been published concerning mechanistic aspects of the process, after the foundamental work of Carrick [22],

TABLE 3. Properties of EPDM Prepared with endo-DCP and Different Catalyst Systems

Sample No.	Catalyst system[a]	$[\eta]$[e] (dl/g)	DCP[g] (wt%)	C_2H_4 (wt%)	Band at 12.7 μ	$D_{14.6}/D_{13.9}$
1	$VAcac_3 + AlEt_2Cl$ (1/8)	1.09	13.0	41	Absent	0.35
2	$VCl_4 + AlEt_2Cl$ (1/6)	0.75	14.0	63	Present[f]	0.42
3	$VOCl_3 + Al_2Et_3Cl_3$ (1/10)[b]	0.82	16.8 (17.7)	53	Absent	0.30
4	$VCl_4 + Al(n\text{-}C_8H_{17})_3$ (1/25)	3.33	9.4	41	Absent	0.25
5	$VOCl_3 + AlEtCl_2$ (1/10)[b,c]	1.12	9.3 (9.1)	57	Absent	0.16
6	$VOCl_3 + Al(i\text{-}C_4H_9)_3$ (1/3)[b]	n.d.	16.5	n.d.	Absent	0.42
7	$VO(O\text{-}n\text{-}C_4H_9)_3 + AlEtCl_2$ (1/10)	0.49	13.9 (14.6)	57	Absent	0.31
8	$VOCl(OEt)_2 + AlEt_2Cl$ (1/5)	1.58	18.3	68	Absent	0.45
9	$TiCl_4 + Al(n\text{-}C_8H_{17})_3$ (1/3)[d]	n.d.	7.3	n.d.	Absent	0.39

[a] Experimental conditions: solvent = toluene; T = 0°C; endo-DCP = 0.147 mole/liter; $(C_3H_6)/(C_2H_4)$ = 2.0 in the gaseous stream; the V/Al molar ratio is given in parentheses.

[b] T = 20°C.

[c] Solvent = tetrachloroethylene; the sample shows polyethylene crystallinity (5%).

[d] $(C_3H_6)/(C_2H_4) = 6.0$.

[e] From toluene solutions at 30°C.

[f] $D_{12.7}/D_{14.6} = 0.025$.

[g] Determined by ICl absorption; NMR data in parentheses.

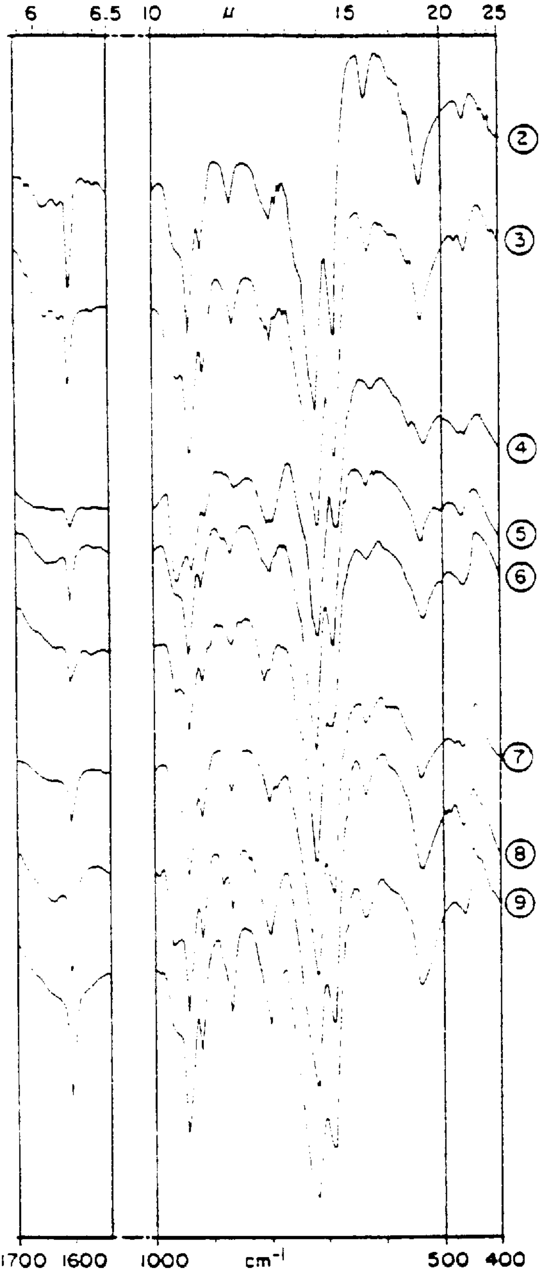


FIG. 7. Significant part of the IR spectra of EPDM prepared with different catalysts (the numbers refer to the samples of Table 3).

Natta [23], and Zambelli [20]. Very recently it has been shown that Ziegler-Natta systems used in the ethylene-propylene copolymerization, sometimes, contain more than one type of active centers and the determination of the reactivity ratios requires particular caution [25]. This means that much work is necessary before a conclusive mechanistic picture can be arrived at, even though the values of the reactivity ratios obtained for several catalyst systems were found to be in agreement with an anionic mechanism [26]. A more detailed discussion on the mechanistic aspects of EPDM synthesis will be published elsewhere [31].

However, apart the problems under discussion, an explanation of the action of Ziegler-Natta catalysts via a cationic mechanism was proposed occasionally and sometimes limited to a single step of the complex mechanism [24], thus it does not find persuasive support in the experimental material so far collected. As a matter of fact, none of the more recent reviewers of the subject has proposed a cationic mechanism providing the action of the Ziegler-Natta catalyst [19a, 30].

This picture is not consistent with the view of De Kock [1] who invocked an overall cationic terpolymerization mechanism to explain the supposed endo-DCP – exo-DCP isomerization through a Wagner-Meerwein rearrangement.

It seems more reasonable, in agreement with the experimental evidence, to attribute the fundamental process of terpolymerization to a coordinate mechanism, whereas some occasional epimerization, involving the molecule of DCP, should be ascribed to the particular heterogeneity or polyfunctionality of some Ziegler-Natta catalysts which can, sometimes, promote cationic processes when the monomers involved are suitable [29]. Undoubtly this is the case of the I – II isomerization via a Wagner-Meerwein rearrangement, but the degree of acidity of the catalyst is decisive in inducing the cited isomerization [15].

In order to confirm this conclusion and our above-mentioned results, we have tested the possibility of using acidic (in the sense of Lewis) catalysts in the terpolymerization process.

Table 3 shows, in addition to some of the most typical Ziegler-Natta catalysts, some particularly acidic systems since both the transition metal compound and the organometallic component are good Lewis acid (see Samples 3 and 5 of Table 3).

Also in these experiments no isomerization was observed; therefore the data of Table 3 show that the presence of isomerized DCP in EPDM is a scarcely probable event which, however, has little extension when strong acidic Ziegler-Natta systems are employed.

In order to collect further informations on the terpolymerization mechanism of DCP, we examined the structure of monomeric DCP recovered from the reaction mixture containing both cationic initiators and Ziegler-Natta catalysts. The aim of these experiments was to check the preliminary epimerization of I to II before entering the polymerization reactions. The results (Table 4) indicate

TABLE 4. Behavior of endo-DCP in the Presence of Typical Ziegler-Natta or Cationic Catalysts

Expt. No.	Catalyst[a]	Solvent		endo-DCP (cm³)	ΔT[b] (°C)	exo-DCP in the recovered fraction (%)[c]	Conversion of endo-DCP[f]
		Type	cm³				
1	$VCl_4 + AlEt_2Cl$ (1/6)	n-Heptane	40	4	4	0	17.6[d]
2	$VCl_4 + AlEt_2Cl$ (1/6)	n-Heptane	100[h]	8	0	0	n.d.
3	$VOCl_3 + Al_2Et_3Cl_3$ (1/10)	n-Heptane	40	4	6	Trace[g]	57.9[e]
4	$VOCl_3 + Al_2Et_3Cl_3$ (1/10)	n-Heptane	100[h]	8	0	0	n.d.
5	$VAcac_3 + AlEt_2Cl$ (1/8)	Toluene	35	4	0	0	0
6	VCl_4	n-Heptane	40	4	0	0	2.3
7	$AlEtCl_2$	n-Heptane	40	4	0	0	3.3[d]
8	$AlEt_2Cl$	n-Heptane	40	4	0	0	0
9	$TiCl_4$	n-Heptane	40	4	0	0	0
10	$TiCl_4$	Toluene	5	5	0	0	0.3

[a] Added to the DCP solution within 3 *min*; T = 0°C; *reaction time* = 30 min; transition metal compound or catalyst = 2 mmoles.

[b] Increase of temperature during the reaction time.

[c] Determined by VPC analyses (*see* Experimental section).

[d] The polymer shows a ratio $R = D_{14.5}/D_{13.5} > 1$ (cf. the text) and a broad singlet in the NMR spectrum at 7.5 τ (referred to TMS) both typical of poly-exo-DCP [15]; [η] = 0.16 dl/g from $CHCl_3$ solution at 30°C in the case of expt. 1.

[e] The polymer shows an absorption at 12.65 μ in the IR spectrum, the ratio $R = D_{14.6}/D_{13.5} > 1$ (cf. the text), and a broad signal at 7.5 τ in the NMR spectrum, all of which are typical of poly-exo-DCP [15]; [η] = 0.46 dl/g from $CHCl_3$ solution at 30°C.

[f] Obtained gravimetrically.

[g] Less than 0.2%.

[h] Saturated with a stream of ethylene and propylene (molar ratio C_3H_6/C_2H_4 = 2.0) according to Ref. 10.

that this fact does not take place under the typical and mild conditions of the EPDM synthesis; therefore, the eventual isomerization of I should be a simultaneous reaction with the polymerization process.

Furthermore, only the more acidic catalysts of Table 4 are able to homopolymerize I. The yields increase when the overall acidity of the systems increases and, generally, the isomerization I → II is observed under the conditions adopted. These results agree with the characteristics of a cationic homopolymerization of DCP [32] and also with some preliminary data reported in the literature.

In fact, recently the homopolymerization of I via the norbornene double bond opening was investigated [15] by using cationic initiators. Low MW polymers containing the monomeric units rearranged in the exo configuration were obtained when a strong cationic initiator ($BF_3.OEt_2$) was used. A mild initiator such as $PdCl_2(PhCN)_2$ was active only at elevated temperatures (170° C), and the resulting polymer contained the repeat units in the endo configuration.

In another recent paper [12] the homopolymerization of dicyclopentadiene, induced by Ziegler-Natta catalyst, was carefully investigated. The more relevant results of this study were the complexity of the recurring units and the drasticity of the conditions adopted to induce the polymerization reaction. Furthermore, the I → II isomerization was not observed when Ziegler-Natta catalyst of the type $TiCl_4$-$Al(i\text{-}C_4H_9)_3$ or VCl_4-$AlEt_3$ was used. Only the cationic initiator $TiCl_4$ (i.e., without organometallic cocatalyst) is able to give a low yield of homopolymer having both endo and exo forms; however, $TiCl_4$ is a weak catalyst, as we confirmed in a previous paper [27].

CONCLUSIONS

Several evidences have been collected against a generalized isomerization of endo-DCP to exo-DCP during the terpolymerization of ethylene, propylene, and endo-DCP.

1) The presence of exo-DCP in EPDM can be ascertained by using the absorption band at 12.76 μ. The minimum level of exo-DCP detectable by IR spectroscopy is between 1 and 2 wt%.

2) The absorption bands near 13.5 and 14.5 μ can give only a rough evaluation of the exo-DCP content in EPDM, in particular at a low level of diene, owing to the perturbing effect of the band at 13.9 μ on the former band.

3) EPDM's containing endo-DCP show values of the ratio $D_{14.5}/D_{13.3}$ about 5 times lower than EPDM's containing exo-DCP, provided the composition of terpolymers is nearly the same.

4) Under typical terpolymerization conditions, also carried out

with Ziegler-Natta catalysts having acidic character, the endo-exo isomerization of DCP has been detected in the resulting EPDM's only for the system VCl_4-Et_2AlCl. However, the extent of the epimerization reaction is very low, near to the sensitivity limit of the analytical method.

5) Only acidic Ziegler-Natta catalysts convert endo-DCP to solid homopolymer via norborne double bond opening; the endo-exo isomerization was usually observed with the systems able to homopolymerize endo-DCP under the conditions adopted.

6) Endo-DCP, unreacted under cationic or coordinated conditions, shows an unchanged structure when examined at the end of the reaction period.

7) The results reported in this paper are consistent with several data of the literature which attribute to the EPDM synthesis a mechanism having a prevalent coordinated character. Under particular conditions, Ziegler-Natta catalysts having enhanced electrophilic character may originate secondary reactions. Among them, the epimerization of DCP via a Wagner-Meerwein rearrangement can take place to a very limited extent in the presence of ethylene and propylene.

REFERENCES

[1] R. J. De Kock and A. Veermans, Makromol. Chem., 95, 179 (1966).

[2] J. Sauer, Angew. Chem., Int. Ed., 6, 18 (1967).

[3] P. D. Bartlett and A. Schneider, J. Amer. Chem. Soc., 68, 6 (1946).

[4] H. Meerwein and K. Emster, Chem. Ber., 53B, 1815 (1920).

[5] Snam Progetti S.p.A., Italian Patent, 857,556 (June 8, 1968).

[6] S. Cesca, M. L. Santostasi, W. Marconi, and N. Palladino, Ann. Chim. (Rome), 55, 704 (1965).

[7] S. Cesca, M. L. Santostasi, W. Marconi, and M. Greco ibid. 55, 682 (1965).

[8] S. Cesca, S. Arrighetti and W. Marconi, Chim. Ind. (Milan) 50, 171 (1968).

[9] S. Cesca, A. Roggero, G. Bertolini and W. Marconi, Ibid., 50, 183 (1968).

[10] S. Cesca, G. Bertolini, G. Santi and P. V. Duranti, J. Polym. Sci., Part A-1, 9, 1575 (1971).

[11] M. E. Tunnicliffe, D. A. Mackillop, and R. Hank, Eur. Polym. J., 1, 259 (1965).

[12] G. Dall'Asta, G. Motroni, R. Manetti, and C. Tosi, Makromol. Chem., 130, 153 (1969).

[13] (a) H. L. McMurry and V. Thornton, Anal. Chem., 24, 318 (1952). (b) J. Van Schooten, E. V. Duck, and R. Berkenbosch, Polymer, 2, 357 (1961).

[14] G. Natta, G. Mazzanti, A. Valvassori, G. Sartori, and D. Morero, Chim. Ind. (Milan), 42, 125 (1960).

[15] T. Corner, R. G. Foster and P. Hepworth, Polymer, 10, 393 (1969).

[16] D. L. Christman and G. I. Keim, Macromolecules, 1, 361 (1968).

[17] G. Natta, A. Valvassori, and G. Sartori, in Polymer Chemistry of Synthetic Elastomers, Part 2, (J. P. Kennedy and E. Tornquist, eds.), Wiley (Interscience), New York, 1969, p. 682.

[18] (a) L. Reich and A. Schindler, Polymerization by Organometallic Compounds, Wiley (Interscience), New York, 1966, p. 294. (b) R. W. Lenz, Organic Chemistry of Synthetic High Polymers, Wiley (Interscience), New York, 1967, p. 620.

[19] (a) J. Boor, Macromol. Rev., 2, 115 (1967). (b) G. Allegra, Makromol. Chem., 145, 235 (1971).

[20] (a) A. Zambelli, M. G. Giongo, and G. Natta, Makromol. Chem., 112, 183 (1968). (b) A. Zambelli, A. Lety, C. Tosi, and I. Pasquon, ibid., 115, 73 (1968).

[21] Ref. 18a, p. 294.

[22] F. J. Karol and W. L. Carrick, J. Amer. Chem. Soc., 83, 2654 (1962).

[23] G. Natta, G. Mazzanti, A. Valvassori, G. Sartori, and A. Barbagallo, J. Polym. Sci., 51, 429 (1961).

[24] (a) J. P. Kennedy and A. W. Langer, Advan. Polym. Sci., 3, 508 (1964). (b) H. Ulzmann, J. Polym. Sci., 32, 457 (1958).

[25] C. Cozewith and G. Ver Strate, Macromolecules, 4, 482 (1971).

[26] G. Natta, G. Crespi, A. Valvassori, and G. Sartori, Rubber Chem. Technol., 36, 1609 (1963).

[27] S. Cesca, A. Priola, and G. Santi, J. Polym. Sci., Part B, 8, 573 (1970).

[28] H. E. Bruson and T. W. Riener, J. Amer. Chem. Soc., 67, 723 (1945); 68, 8 (1946); 70, 2869 (1948).

[29] (a) G. Natta, G. Dall'Asta, G. Mazzanti, U. Giannini, and S. Cesca, Angew. Chem., 71, 205 (1959). (b) G. Natta and G. Mazzanti, Tetrahedron, 8, 86 (1960).

[30] D. F. Hoeg, in The Stereochemistry of Macromolecules, Vol. 1 (A. D. Ketley, ed.), Dekker, New York, 1967, p. 47.

[31] S. Cesca, To Be Published.

[32] A. Priola and S. Cesca, Unpublished Results.

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