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SOME REMARKS ON THE MECHANISM OF THE STEREOSPECIFIC IONIC COORDINATE POLYMERIZATION OF HYDROCARBON MONOMERS

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INTRODUCTION

Since 1954, *i.e.* since the discovery of some of the most important stereospecific polymerization processes of α-olefins and of diolefins, the field of stereospecific polymerization has been extended considerably. The reason for this great development depends both on the discovery of new classes of stereoregular polymers and of tacticities—also concerning non-hydrocarbon polymers—and on the discovery of new stereospecific catalytic systems. Since then numberless papers have been published on this subject. Moreover, extensive research projects have been developed in laboratories of universities and important industries, owing to the practical interest inherent in many of the stereoregular polymers.

In this paper I shall report the most recent results obtained in my Institute on the polymerization of hydrocarbon monomers, particularly diolefins and cyclic olefins, and I shall try to summarize the contribution given by our School to this field of stereospecific polymerization.

CLASSIFICATION OF THE CATALYTIC SYSTEMS

Polymerization processes are usually grouped according to the reaction mechanism:

(*i*) *radical processes*, in which the end group of the growing polymeric chain is a free radical; the process is generally initiated by substances or energy sources capable of yielding or producing free radicals;

(*ii*) *ionic processes*, when the bond between the terminal atom of the growing chain and the catalyst is of ionic-type or is strongly polarized. These processes are cationic when the end of the growing chain presents a positive charge, though partial; whereas they are anionic when the charge is negative.

Processes are considered as coordinate when the catalyst consists of an electron-deficient complex presenting at least one coordinating atom capable of associating the monomer.

As to the insertion of the coordinated monomer into the growing chain, the coordinating catalysts could generally act, at least in principle, according to one of the mechanisms quoted in (*i*) and (*ii*). However, the most important coordinate processes act through an ionic mechanism; therefore, they have been called "ionic coordinate". A sharp distinction between merely ionic and coordinate ionic processes can hardly be made: in fact many processes usually described as merely ionic (*i.e.* those in which alkyl lithium is used as catalyst) also involve a precomplexation of the monomer to the catalyst. In fact, it is known that, in the catalyst systems mentioned above, lithium acts as a coordinating atom, and alkyl lithium solutions contain associated molecules (polymeric molecules containing even 6 molecules of alkyl lithium have been observed)[1].

We consider as ionic coordinate only those catalysts consisting of a complex in which the coordinating atom is a metal (*e.g.* a transition metal) having a marked tendency to form complexes and to coordinate the monomer molecules.

In the case of non-hydrocarbon monomers, *e.g.* of monomers containing atoms with free electron pairs, such as oxygen or nitrogen, coordination may interest these atoms besides the double bond. Thus, coordinate complexes can be obtained that are more stable than those obtained if coordination involves only the π-electrons of the unsaturated bond.

STEREOSPECIFICITY OF THE CATALYSTS

Polymerizations initiated by radicals are seldom stereospecific: this is due to the fact that, in general, the particular type of presentation is less influenced by steric limitations (such as those occurring in the complexation of the monomer with the transition metal of a catalytic complex). In some cases, however, syndiotactic stereoregular polymers are formed. This, in particular, occurs when very low temperatures are employed and during polymerization of some monomers containing hetero atoms (acrylates, methacrylates, vinyl chloride, acrylic nitrile)[2]. However, this is probably connected with thermodynamic factors[3] (higher free energy variation in the formation of syndiotactic polymer in comparison with other stereoisomers†).

A very particular case of stereoregular radical polymerization is the polymerization of monomers included in some crystals having channels of particular size. For instance, *trans*-1,3-pentadiene included in perhydrotriphenylene can be polymerized by the action of high energy radiations to *trans*-1,4-isotactic polypentadiene[5]. In this case, the included molecules are arranged one after the other in the *trans* conformation and have not a sufficient mobility to make another type of arrangement possible. This shows that stereospecific polymerizations are possible when the presentation of the monomeric units with respect to the growing chain ends are determined independently of the polymerization mechanism. However, very few cases are known of stereospecific radical polymerizations. Consequently, we shall deal in more detail with coordinated ionic polymerizations.

POLYMERIZATION OF α-OLEFINS

Since the discovery of isotactic poly-α-olefins[6] a great amount of experimental research has been carried out in order to clarify the polymerization mechanism.

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† However, the formation of syndiotactic polymers is not general. In some cases, slightly crystalline isotactic polymers can also form[4], probably because in these cases the highest variation of free energy occurs for formation of isotactic polymers.

As we observed in our first work, the formation of isotactic polymers of α-olefins requires the presence of heterogeneous catalysts containing a crystalline solid phase. Moreover, it was our opinion that highly stereospecific catalysts might be obtained only by the use of transition metal halides having, like violet $TiCl_3$ and VCl_3, a layer lattice[7, 8]. In fact, catalysts obtained from $TiCl_4$ and organometallic compounds which are less stereospecific[9], consist of a solid phase containing Ti halides in a valency below 4, and in which crystals of β-$TiCl_3$ having no layer lattice are present[10]. Recent work carried out in our Institute[11] leads us to attribute a considerable importance to the lattice energy of the different crystalline modifications of $TiCl_3$.

According to the hypothesis formulated in a lecture of mine[12] in Rome in 1958, the active complexes probably form in correspondence with surface regions of the lattice, where the six coordination sites of the transition metal atom are not completely occupied. An epitactic adsorption of alkyl metals in solution can possibly occur on these sites.

The Cl atoms present on the surface of the $TiCl_3$ lattice can be replaced by alkyl groups by double exchange reaction between $TiCl_3$ and alkyl aluminium. The complexes thus formed can present an asymmetric structure.

The asymmetry of the active centre could be the cause of the stereospecific course of the polymerization. In fact, investigations performed on the asymmetric synthesis of optically active polymers from monomers that do not contain asymmetric carbon atoms, demonstrated that an optically active catalyst can allow the asymmetric synthesis[13, 14]. The same phenomenon probably occurs with regard to each active centre of a stereospecific catalyst, which should contain an equal number of centres having opposite steric configuration.

With regard to the polymerization kinetics, recent work done at our Institute[15] has demonstrated that the rate of growth of each polymer chain by systems prepared from a transition metal halide and an organometallic compound, varies considerably depending on the nature of the transition metal, but is independent of the organometallic compound (*Figure 1*). This demonstrates that the kinetically determining step of the propagating process is an interaction between the transition metal and the olefin. Unpublished data from our laboratory show that the kinetically determining step is the complexation of the monomer molecule with the transition metal of the catalytic complex.

Such complexation of the monomer on the asymmetric catalytic centre can, for steric reasons, give rise preferentially to one of the two possible diastereoisomeric complexes.

Recent works by Corradini have demonstrated that the coordinate complexes of α-olefins on transition metal compounds can be separated into optical antipodes and that the presence of an asymmetry in the complex can favour one particular configuration of the coordinated molecule[16].

In order to obtain a thorough knowledge of the overall polymerization mechanism, investigations must not only concern the growth reaction, but also the chain termination reaction. In previous papers[17] the main termination processes and their kinetics with respect to that of the growth rate were shown. It was found that one of the important chain termination processes is the alkyl exchange between the growing chain and the organometallic compound introduced in the preparation of the catalyst.

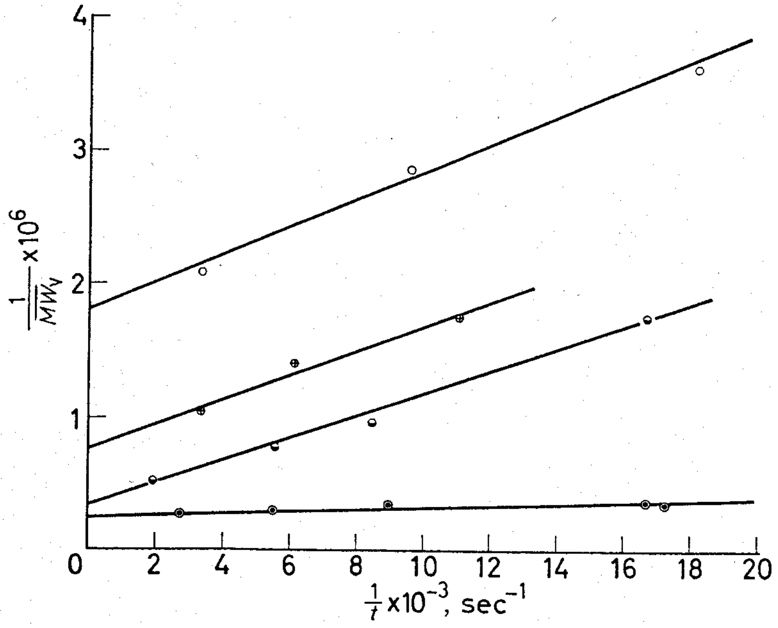


Figure 1. Comparison among the propagation rates of different catalyst systems in the polymerization of butene-1 to isotactic polymer[16], reciprocal of the viscosimetric average molecular weight *vs.* the reciprocal of the polymerization time.
Experimental conditions: T 0°C; toluene 180 cm^3; butene-1 60 g; organometallic compound $6{\cdot}8 \times 10^{-3}$ mols; transition metal halide variable amount.
Catalyst systems:

○ $TiCl_3$ ARA-$Be(C_2H_5)_2$	◒ $TiCl_3$ ARA-$Al(C_2H_5)_2I$
⊕ $TiCl_3$ HRA-$Be(C_2H_5)_2$	⊙ VCl_3—$Al(C_2H_5)_3$

A particular activity in such an exchange is shown by some non-associated organometallic compounds of metals having a sufficient electropositivity (*e.g.*, $Zn(C_2H_5)_2$, $Cd(C_2H_5)_2$)[18] to allow at least a partial polarization of the metal–carbon bond, which is probably analogous to that of the bond between the metal and the terminal carbon atom of the growing chain. *Table 1* shows data concerning the variation in molecular weight of polypropylene obtained

Table 1. Viscosimetric molecular weight of isotactic polypropylenes obtained at various temperatures by the α-$TiCl_3$–$Al(C_2H_5)_3$ system, in the presence of constant amounts of $Zn(C_2H_5)_2$.
Polymerization conditions: α-$TiCl_3$ 0·2 g; $Al(C_2H_5)_3$ 0·5 ml; $Zn(C_2H_5)_2$ 0·35 ml; n-heptane 250 ml; polymerization time 1 h; C_3H_6 0·48 mol/l.

Temperature (°C)	*Viscosimetric M.W.*	
	without $Zn(C_2H_5)_2$	with $Zn(C_2H_5)_2$
70	430,000	150,000
56	380,000	100,000
42	350,000	75,000
42	not det.	68,000
33	370,000	45,000
33	390,000	30,000

by the α-$TiCl_3$–$Al(C_2H_5)_2$ system in the presence of different amounts of $Zn(C_2H_5)_2$.

It was a controversial issue as to whether the catalytically active complex is necessarily bimetallic, as is suggested by the fact that catalytic complexes are formed by reactions of the organometallic compounds of aluminium (or of Be, Li and so on) and Ti (or V, Cr) halides, and whether the growing chain end is directly bound to the transition metal or rather to Al.

A proof of the fact that the growing chain may be bonded to a transition metal atom has been achieved by us[19] since 1957 by preparing, for the polymerization of ethylene, a catalyst from bis cyclopentadienyltitanium diphenyl, which by itself is not catalytically active, and $TiCl_4$. Similar results have been obtained by other authors[20] who prepared a catalyst for ethylene and α-olefin polymerization from $TiCl_3CH_3$, which also is not by itself catalytically active, and $TiCl_3$. These catalyst systems, however, are less active and also less stereospecific than those prepared from transition metal salts and organo aluminium compounds.

Recent work carried out in our Institute[21] on the behaviour of the different catalytic systems, shows that the overall catalytic activity depends on both the alkylating power of the organometallic compound and on its capability to form complexes.

In any case there is no parallelism between catalytic activity of the system and alkylating power of the organometallic compound. These results can be better interpreted by the hypothesis that the catalytic complexes in the systems under examination are bi-metallic. This hypothesis also serves to explain the influence of the organometallic compounds on the stereospecificity of the systems[22, 23]. Schindler[24] came to the same conclusion by studying exchange phenomena between deuterium and hydrogen of the last monomeric unit of the polymer chain.

In the recent literature, two hypotheses have been proposed in order to explain the isotactic stereospecificity. According to Cram[25], the structure of the terminal group determines, by a certain probability factor, the configuration of the new monomeric unit. According to other authors[26], it is the asymmetric structure of the catalyst that determines, depending on a probability factor, the chain structure. In the case of isotactic polymers, at least, stereospecificity was attributed by us to an intrinsic asymmetry of the catalyst[27]. This seems supported by the results obtained in the asymmetric synthesis of high polymers by catalysts complexed with an optically active compound.

Furthermore, recent investigations by P. Pino on the polymerization of racemic α-olefins are in agreement with the last hypothesis. In fact, the formation of macromolecules containing a considerable excess of (R) or of (S) monomeric units from a racemic monomer, is more accurately explained by admitting an asymmetric structure of the catalyst[28].

Further support is given by recent results obtained in our Institute[15, 29] according to which it is possible to obtain, by some catalysts, stereoblock polymers consisting of isotactic and syndiotactic sequences respectively. If the configuration of a monomeric unit were dependent only on the configuration of the terminal group of the growing chain, the formation of stereoblock polymers of the type mentioned above could not be explained.

POLYMERIZATION OF DIOLEFINS

What has been stated for the isotactic stereospecific polymerization of α-olefins—that it requires the presence of a solid catalyst—does not necessarily hold for the polymerization of monomers containing, in addition to the vinyl double bond, other conjugated unsaturated groups (double bonds or aromatic nuclei) or heteroatoms, which are not too far from the vinyl group and contain electron pairs that can be coordinated by a metal atom of the catalyst. In those cases, in fact, stereospecific polymerization can also take place by soluble catalysts, not only for formation of isotactic and syndiotactic polymers, but also of polymers having a stereoregularity of a geometric type. In this short review we shall first examine the case, in which we have been most concerned, of the hydrocarbon diolefin polymers.

Recent results in the field of the polymerization of conjugated diolefins further prove the hypothesis that growth of polymeric chains occurs (*a*) by coordination of the monomer to the transition metal and, subsequently, (*b*) by insertion of the coordinated monomer on the π-allylic bond between the transition metal and the last polymerized unit. The hypothesis that the diolefin monomer first coordinates to the transition metal is now generally accepted. On the other hand, it is not universally accepted that the monomer is incorporated into the π-allylic bond between the transition metal and the last polymerized unit.

However, recent studies on the polymerization of butadiene by π-allylic compounds of transition metals, in the absence of organo aluminium compounds, soundly support this hypothesis. In our Institute, butadiene was polymerized to crystalline *trans*-1,4-polymer by π-allyl-Ni-I and to predominantly *cis*-1,4-(85–90 per cent) polymer by π-allyl-Ni-Cl in benzene[30] (*Table 2*). G. Wilke obtained a polybutadiene with a high *cis*-1,4 content by $(\pi\text{-allyl})_2$Co-I and 1,2-polybutadiene by triallyl chromium[31]. It can be proved that, in these cases, the chain grows by incorporation of the monomer on the π-allylic bond between the transition metal and the last polymerized unit.

In our opinion, the conventional catalysts from aluminium alkyls and transition metal compounds act through an analogous mechanism in the polymerization of diolefins. These catalysts probably consist of bimetallic complexes and some of them have proved to be ionic. Polymer growth, also by these catalysts, probably occurs on the π-allylic bond existing between the transition metal and the last polymerized unit.

The hypothesis that the polymer grows on the π-allylic bond between the transition metal and the growing chain, explains what had been long since observed, *i.e.* that the catalysts based on metals of the 8th group (*e.g.* Co, Ni) are active in the polymerization of conjugated diolefins, but not in the polymerization of mono-olefinic monomers. The latter yield polymers that would be bonded to the transition metal by σ-type bonds. On the other hand, it is known that σ-type Co—C, Ni—C bonds, contrary to the π-allylic bonds, are not stable at room temperature. This seems the reason why the Co or Ni catalysts polymerize diolefins and not α-olefins. The instability of a σ-type Co—C or Ni—C bond also explains why, for example, ethylene or other mono-olefins act as molecular weight regulators in the preparation of *cis*-1,4-polybutadiene by the systems $Al(C_2H_5)_2Cl$—Co compound or

$Al(C_2H_5)_2Cl$—Ni compound. In fact, the insertion of ethylene on the bond between the transition metal and the last polymerized unit, causes the formation of a simple σ-type bond and consequently, due to the instability of such a bond, the separation of the polymer chain.

Table 2. Polymerization of butadiene by π-allyl-nickel-halides in various solvents[a]

π-allyl-Ni-X (moles 10^{-4})	*Solvent*	*Volume of solvent* (ml)	*Butadiene* (g)	*Polymer*[b]				
				g	$\overline{M}_n$	*IR Analysis*		
						trans double bonds (%)	*cis* double bonds (%)	vinyl groups (%)
X = I								
3·06	Benzene	15	3·5	1·20	3925	97·0		3
7·70	Ethanol	25	3·2	0·35		96·0		4·0
3·06	THF	35	9·0	3·25	3710	95·5		4·5
2·14	Dioxane	30	5·0	1·00	3940	97·0		3
3·06	Pentane	60	12·0	0·4		93·0		7
4·60	Ethylether	40	6·5	0·4	1435	94·5		5·5
X = Br								
4·0	Benzene	30	9·0	0·15	872	88·5		11·5
5·5	Ethanol	32	6·5	0·20	1230	96·0		4·0
4·3	Ethanol	15	5·0	0·15	1272	97·0		3·0
2·9	THF	15	3·5	0·10	1197	96·0		4·0
5·5	Dioxane	20	3·0	0·37	1680	97·5		2·5
8·4	Anisole	30	10·0	0·20		93·5		6·5
3·7	Cyclohexanol	15	2·0	0·30	1545	98·0		2·0
X = Cl								
8·0	Benzene	20	4·0	0·2		7·0	89·0	4·0
18·5	Benzene	15	10·0	0·8		14·4	82	4·0
9·5	THF	15	6·5	trace		70		30

[a] Polymerization time and temperature: 80 h at 18°C.
[b] Only the solid polymers have been considered.

The above interpretation of the chain growth phenomenon is not accepted by some authors on the basis that various catalyst systems capable of polymerizing butadiene do not contain transition metal–carbon bonds. For instance, it is known that in the reaction between $Al(C_2H_5)_2Cl$ and $CoCl_2$ or any other soluble Co compound, a complex containing Co^{I} is formed, which does not contain Co—C bonds[32]. The same holds for the systems $Al(C_2H_5)_2Cl$-Nickel compound, $Al(C_2H_5)_2Cl$-$Ti(OR)_4$, *etc.*

We assume that, in these cases, a π-allylic bond is formed by reaction between the diolefin monomer and the catalytic complex containing the low-valence transition metal. Obviously, this corresponds to an increase in the formal valence of the transition metal. Reactions of this type are already known in organometallic chemistry. For instance, it is known that $RuCl_3$ reacts with butadiene to give the complex $Ru(IV)Cl_2C_{12}H_{18}$ containing two π-allylic bonds[33]. G. Wilke has shown[34] that Ni(O) can form π-allylic bonds by reaction with butadiene. Also, it has long been known[35] that Na—C or Li—C bonds form in the reaction between metallic Na or Li with butadiene. Therefore, the catalytic activity does not necessarily depend on the existence of a preformed transition metal–carbon bond, since this bond can form by the action of the monomer on the reaction product between aluminium alkyl and transition metal compound.

Although, at present, it seeems established that the incorporation of the monomer takes place on the π-allylic bond between the transition metal and the last polymerized unit, the causes determining the type of stereospecificity of the different catalysts in the polymerization of conjugated diolefins are still uncertain. Experimental data accumulated so far, however, allow us to single out at least some of the factors influencing the stereospecificity. One of them is the mode of coordination of the monomer to the transition metal of the catalyst. There can be little doubt that in the polymerization of diolefins by the homogeneous systems from aluminium alkyl halides and Co or Ni compounds, the monomer is coordinated by these metals by both the double bonds, in the *cis* conformation, before being incorporated as *cis*-1,4 unit.

Homogeneous catalysts from $Al(C_2H_5)_2Cl$ and V compounds (*e.g.* vanadium triacetylacetonate, or $VCl_3 \cdot 3$ THF) give *trans*-1,4 polybutadiene[36]; it is likely that butadiene coordinates to the vanadium of these systems with only one double bond, before being incorporated as *trans*-1,4 unit. The *trans* configuration of the double bond in the monomeric unit might result from the fact that butadiene monomer, at room temperature, is practically all in the *trans* conformation[37]. *Trans*-1,4 polymers of conjugated diolefins (butadiene, isoprene, 2,3-dimethylbutadiene, pentadiene-1,3) can be obtained by heterogeneous catalysts (*Table 3*) prepared from alkyl aluminiums and *e.g.* crystalline $TiCl_3$ or VCl_3[38]. In these cases, stereospecificity is certainly influenced by absorption phenomena of the monomer, with both the double bonds on the surface of the crystalline substrate. It is interesting that, while the homogeneous systems containing V and THF yield crystalline *trans*-1,4-polymers only from butadiene, the heterogeneous systems from crystalline VCl_3 give crystalline *trans*-1,4-polymers also from 1,3-pentadiene and from other butadiene homologues.

Table 3. Polymerization of conjugated diolefins by catalyst systems from vanadium compounds

Catalyst system	*Monomer*	*Polymer structure*	
		IR	X-ray
$Al(C_2H_5)_3$–VCl_3 (heterogeneous)	Butadiene	*trans*-1,4 99–100%	Crystalline
	Isoprene	*trans*-1,4 99–100%	Crystalline
	Pentadiene-1,3[a]	*trans*-1,4 99–100%	Crystalline (isotactic)
$Al(C_2H_5)_2Cl$–$VCl_3 \cdot 3$THF (homogeneous)	Butadiene	*trans*-1,4 99–100%	Crystalline
	Isoprene	*trans*-1,4 99–100%	Crystalline
	Pentadiene-1,3[b]	*trans*-1,4 + 1,2 ($\sim$ 60%)	Amorphous

[a] Both the *cis* and the *trans* isomer can be used.
[b] Only the *trans* isomer polymerizes.

In the case of homogeneous catalysts, a coordination of butadiene by only one vinyl group can lead to 1,2 instead of *trans*-1,4 polymers. Halogen-containing homogeneous catalysts usually give 1,4 polymers, while catalysts containing alkoxy groups or other organic groups yield 1,2 polymers[39].

We have observed that, in some cases, the polymerization solvent influences the stereospecificity. An interesting case concerns the polymerization of 1,3-pentadiene by systems from alkyl aluminium chlorides and cobalt compounds[40]. These systems, in benzene, yield syndiotactic *cis*-1,4-pentadiene polymers, while, in n-heptane, syndiotactic 1,2 polymers are obtained (*Table 4*). An examination of the $Al(C_2H_5)_2Cl$–$CoCl_2$ system in benzene showed that benzene coordinates to the cobalt of the catalytic system. In fact, from the reaction product between $Al(C_2H_5)_2Cl$ and $CoCl_2$, it is possible to isolate the $[(arene)_2Co]^+$ cation, as salt with anions like BPh_4^-, PF_6[41]. The coordination of arene to Co causes a steric arrangement, which is probably different from that existing around Co of the catalytic complexes prepared in an aliphatic solvent. It seems plausible that the different coordination originated by arene around Co is the reason for the different stereospecificity observed in the polymerization of pentadiene by Co catalysts, in benzene and in n-heptane respectively. The *cis*-1,4-polymer is obtained because pentadiene coordinates to Co by both the double bonds, in the *cis* conformation. This coordination, however, certainly occurs in two steps: first, the coordination of the vinyl group and, secondly, that of the other double bond. Owing to the type of coordination existing around Co in aromatic solvents, it seems likely that the succession of these two steps is very rapid. In an aliphatic solvent, the monomer would also coordinate to Co first with the vinyl group only. Subsequently, it might also coordinate with the other double bond, thus yielding *cis*-1,4 units (which are actually present, though in a small percentage, in the product prepared in n-heptane). On the other hand, the monomer might be incorporated in the polymer as 1,2 units. This last step in heptane is kinetically predominant with respect to the formation of *cis*-1,4 units. To conclude, in the case examined above, it seems probable that the influence of solvent on structure depends on the fact that, when varying the solvent, the type of coordination around the transition metal also varies.

Table 4. Polymerization of pentadiene-1,3 (*trans* isomer) by homogeneous systems from alkyl aluminium halides–Cobalt compounds in various solvents[a]

Catalyst system	*Solvent*	*Type of polymer* IR	X-ray
$Al(C_2H_5)_2Cl \cdot Co(acac)_3$[b]	Benzene	*cis*-1,4 85%	Crystalline; syndiotactic
$Al(C_2H_5)_2Cl$–$CoCl_2 \cdot 2py$	Toluene	*cis*-1,4 85%	Crystalline; syndiotactic
$Al(C_2H_5)_2Cl$–$Co(acac)_3$	Pentane	1,2 98%	Crystalline under stretching; syndiotactic
$Al(C_2H_5)_2Cl$–$Co(acac)_3$	n-Heptane	1,2 98%	Crystalline under stretching; syndiotactic

[a] Polymerization at room temperature.
[b] $Co(acac)_3$ = cobalt triacetylacetonate.

The stereospecific polymerization of pentadiene to *cis*-1,4 polymer has been particularly studied by us in the last years. Using different catalysts, two different crystalline *cis*-1,4 polymers were obtained: one with an isotactic[42] and the other with a syndiotactic structure[43]. The catalysts used were homogeneous in both cases: the isotactic polymer was obtained by the $Al(C_2H_5)_3$–$Ti(OR)_4$ system and the syndiotactic one, as already stated, by systems prepared from aluminium alkyl halides and Co compounds. The examination of the polymerization mechanism led us to the hypothesis that in this case Ti and Co catalysts exhibit a different stereospecificity essentially because the former contain only one site of coordination for the monomer and the latter, two[41].

In the latter case, the alternate coordination of the monomer to one and to the other site, would produce enantiomorphous situations for the successive monomeric units and hence syndiotactic sequences would form.

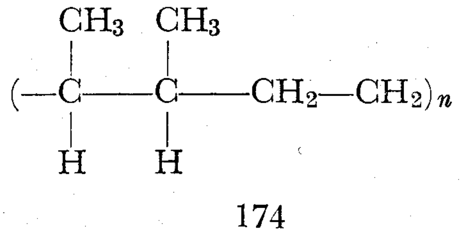
In some cases, stereospecificity is influenced by steric factors due to the presence in the monomer of substituents favouring one type of addition. For instance, it is known that the typical catalysts for the stereospecific polymerization of α-olefins to isotactic polymers [$Al(C_2H_5)_3$-$TiCl_3$; $Al(C_2H_5)_3$-VCl_3] generally yield, in the polymerization of conjugated diolefins, *trans*-1,4 polymers[38]. On the contrary, in the case of 4-methyl-1,3-pentadiene, these catalysts yield 1,2-isotactic polymers[44]. This is due to the presence of the methyl group in the position 4, which favours the formation of 1,2 rather than 1,4 units. Therefore, 4-methyl-1,3-pentadiene behaves under this respect as an α-olefin monomer. It is interesting that this monomer which, by heterogeneous catalysts from α-$TiCl_3$ or VCl_3, yields 1,2-isotactic polymers, by homogeneous catalysts yields 1,2-polymers that are amorphous probably because of a low order in the configuration of the asymmetric carbon atoms of the chains.

STEREOSPECIFIC POLYMERIZATION OF HYDROCARBONS HAVING AN INTERNAL DOUBLE BOND

Linear Aliphatic Internal Olefins

Aliphatic olefins with an internal double bond hardly homopolymerize by anionic catalysts. They yield irregular low polymers only in the presence of the traditional cationic catalysts (*e.g.* $AlCl_3$). However, we found[45] that they can be polymerized with ethylene by coordinate organometallic catalysts containing vanadium as transition metal. The copolymerization rate of the internal olefins is far lower than that of ethylene and decreases when the bulkiness of the substituents is increased. Thus, *e.g.* pentene-2 copolymerizes with ethylene more slowly than butene-2.

In some cases, when the excess of the internal olefin in the monomer mixture is very high (molar fraction of internal olefin $\geqslant 0{\cdot}95$), it is possible to isolate alternating copolymers, *i.e.* copolymers in which the two different monomeric units are arranged in an alternating succession. For instance, with butene-2, which is the least hindered aliphatic internal olefin, a copolymer is obtained having the structure of 1,2-dimethyl-butamer:



$$\left(-\overset{CH_3}{\underset{H}{\overset{|}{\underset{|}{C}}}}-\!\!-\overset{CH_3}{\underset{H}{\overset{|}{\underset{|}{C}}}}-\!\!-CH_2-CH_2\right)_n$$

A different behaviour was observed in the copolymerization of the *trans* and, respectively, the *cis* isomer of butene-2. The first yielded amorphous alternating copolymers both by homogeneous and heterogeneous catalysts[46]. On the other hand, *cis*-butene-2 gives amorphous alternating copolymers by homogeneous systems and stereoregular crystalline alternating copolymers by heterogeneous systems. The latter copolymers were found by X-ray analysis to have an erythro di-isotactic structure.

We attributed this different behaviour[47] to the fact that only *cis*-butene-2 presents, with respect to the plane passing through the 4 carbon atoms, two equal and superimposable faces, while the *trans* isomer has two enantiomorphous faces (*Figure 2*). This agrees with the finding recently reported by Corradini and Pajaro[16], who prepared and determined by X-rays the structure of complexes of a transition metal of the 8th group (Pt) with the two isomers of butene-2. While the complex containing the *trans* isomer consists of a separable mixture of two enantiomorphous structures, the complex containing the *cis* isomer consists of a unique species.

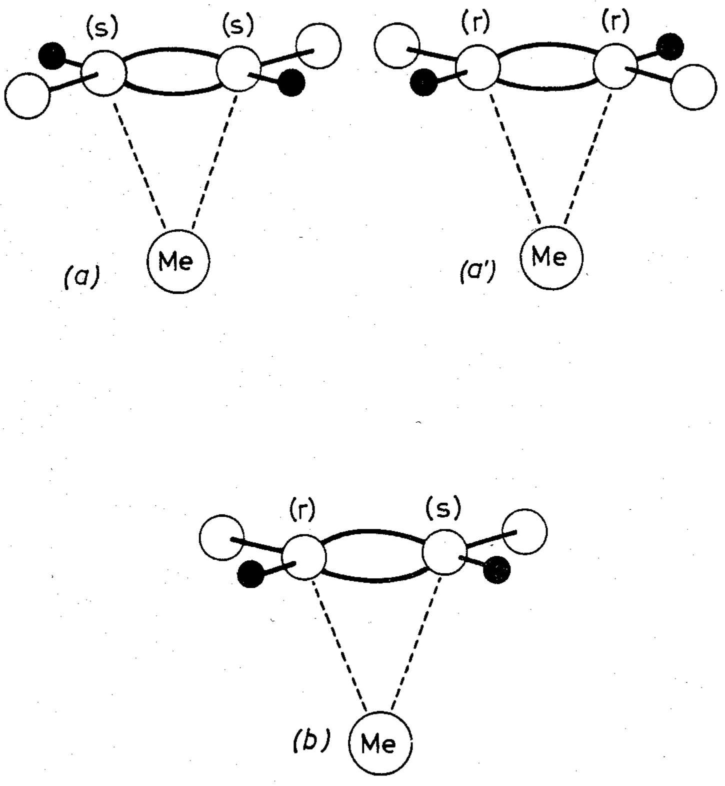


Figure 2—*Trans*-but-2-ene (*a*, *a'*) may be co-ordinated to a transition metal in two enantiomorphous ways, whereas *cis*-but-2-ene (*b*) may be co-ordinated in one configurational way only

Cyclo-olefins

The polymerization of cyclo-olefins is far less simple than that of linear olefins, since it can give rise to polymers having a different chemical structure, depending on whether polyaddition occurs by opening of the double bond or of a single bond of the cycle (*Figure 3*). In the former case, saturated cyclic monomeric units are obtained, that contain asymmetric carbon atoms, while in the latter, the monomeric units produced are linear and unsaturated. In the case of unsubstituted cyclic olefins, polymers formed by ring cleavage exhibit stereoisomerism of the geometrical type only. On the other hand, the substituted ones give polymers which exhibit stereoisomerism of both types. We are going to examine the two cases separately.

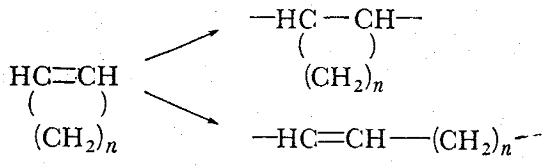


Figure 3. Polymerization of cyclo-olefins

(*i*) *Polymerization by opening of the double bond*—This polymerization presents some analogies with the polymerization of linear aliphatic internal olefins. In the case of cyclo-olefins containing more than 4 carbon atoms in the ring, no homopolymerization of this type takes place in the presence of co-ordinate anionic catalysts, due to the steric hindrance originated from the bulkiness of the ring. On the other hand, the copolymerization of cyclo-olefins with ethylene is possible by these catalysts[48]. In this case, as in that of linear internal aliphatic olefins, it is possible to obtain alternating copolymers, by operating with high concentrations of cyclo-olefins with respect to ethylene. The copolymerization rate is relatively high when the cyclo-olefins have an odd number of carbon atoms (cyclopentene, cycloheptene) and is relatively low when their number is even (cyclohexene and cyclo-octene)[47]. Moreover, the former generally yielded crystalline alternating copolymers; the latter, in general, yield hardly any alternating copolymers, which are always amorphous. In the case of cyclopentene[48] and cycloheptene[49], crystalline alternating copolymers have been obtained by catalysts from vanadium salts. Both heterogeneous and homogeneous catalysts were found to be stereospecific. The stereoregularity of the ethylene–cyclo-olefin alternating copolymers always appeared of the erythro-di-isotactic type, independently of the type of catalyst (homogeneous, heterogeneous).

The copolymerization of cyclo-olefins is of interest because it represents a particular case in which the stereospecificity is determined by factors depending on the structure of the monomer molecule rather than on the catalyst. The lower reactivity of the even-membered cyclo-olefins was attributed by us[47] to the symmetric conformation of the molecule presenting two identical faces, both characterized by the shielding of the double bond by methylenic groups, which hinders the co-ordination and probably also incorporation of the monomer in the polymer. On the contrary, in the case of odd-membered cyclo-olefins, the two faces are different, and one of them is preferred for the co-ordination. This allows a constant mode of presentation of the monomer to the catalyst which is one of the factors determining the stereospecificity (*Figures 4* and *5*). A more detailed examination of the phenomenon is reported in a published paper[47].

The fact that all the stereoregular alternating copolymers prepared so far have an erythro-di-isotactic structure proves that, in ionic polymerization, the double bond usually opens in the *cis* position (*Figure 6*). This agrees with what is observed in the polymerization of ethylene[50] and propylene[51, 52] by co-ordinate anionic catalysts, and with what is shown by the IR spectra of the polymers obtained from deuterated monomers[53].

An interesting behaviour is shown by the polymerization of cyclo-olefins having less than five carbon atoms in the ring. They can homopolymerize in a stereospecific manner, by opening of the double bond, to polymers having the poly-cyclobutylenamer structure[54]. So far it has not been possible

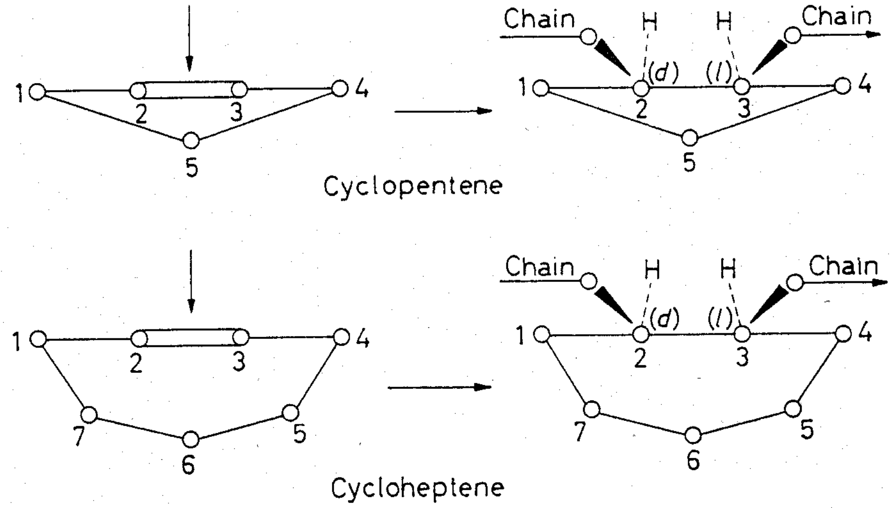


Figure 4. Schematic drawing of the *cis* opening of the double bond in odd-membered cyclo-olefins (projection on a plane perpendicular to the plane of the C—C double bond)

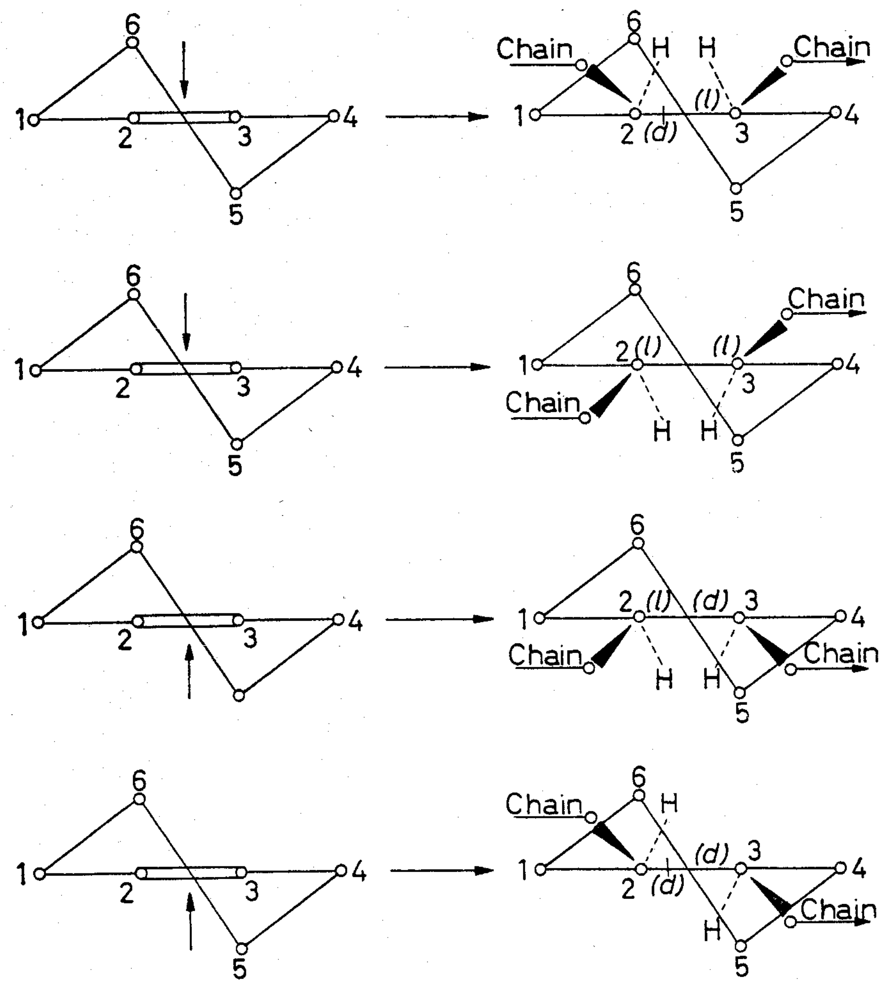


Figure 5. Schematic drawing of the possible openings of the double bonds in cyclohexene (projection on a plane perpendicular to the plane of the C—C double bond)

to obtain alternating ethylene-cyclobutene copolymers. In fact, the copolymerization of these two monomers, in the presence of anionic coordinate catalysts, always yielded copolymers with random distribution[47]. The higher reactivity of the small cycles must be attributed to the far higher ring tension as well as to the lower steric hindrance with respect to the larger rings.

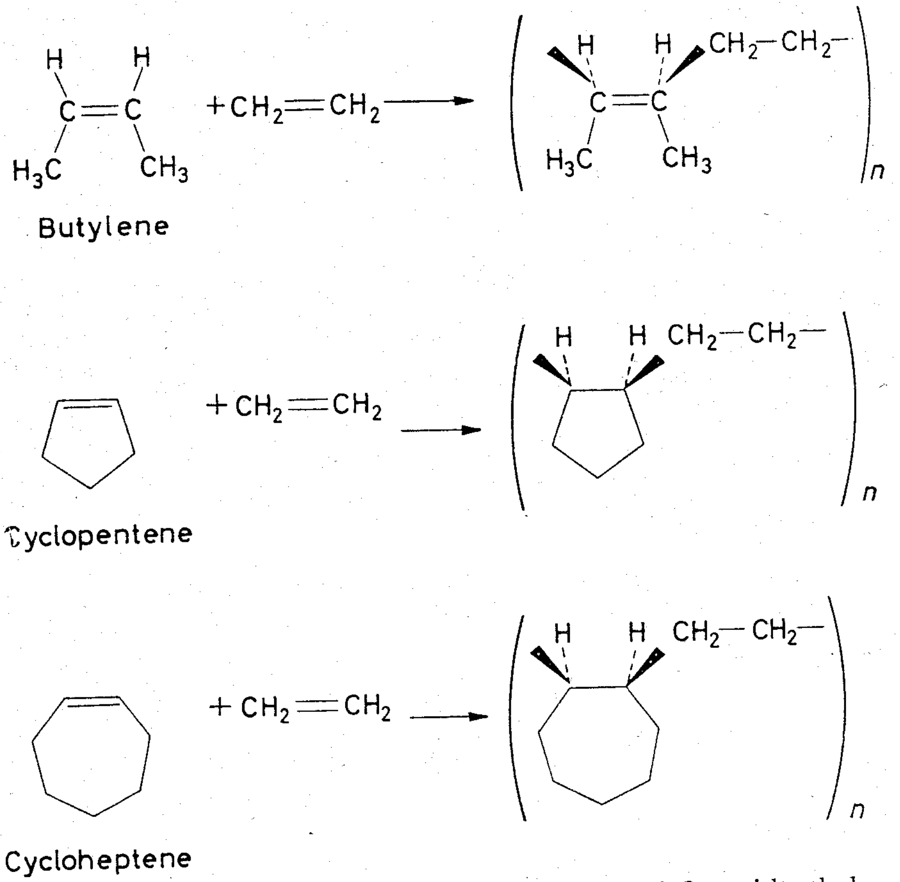


Figure 6. Examples of alternating copolmerization of internal olefins with ethylene involving *cis* addition to the internal double bond.

Cyclobutene polymers having polycyclobutylenamer structure have been obtained by catalysts, both homogeneous and heterogeneous, prepared from vanadium salts and organo-aluminium compounds. In both cases, the polymers are crystalline. The X-ray and IR spectra of the polymers obtained by the two types of catalysts are different. Although the structure of these polymers cannot be determined as yet, we think that, in analogy with what occurs in the polymerization of propylene, the two types of polymer should have a di-isotactic and di-syndiotactic structure respectively[55].

The crystalline di-isotactic polymer of cyclobutene is also obtained by the catalytic system consisting of rhodium trichloride and water[56] and by π-allyl-nickel-bromide in ethanol[30a]. It is known that these catalysts do not polymerize α-olefins but they polymerize butadiene to 1,4-polybutadiene[57]. The fact that they homopolymerize cyclobutene suggests that the metal–carbon bond is more stable than the single bond connecting the catalyst to a saturated chain. This behaviour seems analogous to that of the allylic bond, which is stable also in the presence of alcohols and of water. This behaviour might be attributed to the delocalization of

π electrons, which could be favoured by the high strain in four-membered rings which stabilizes the coordination of the monomer to the transition metal.

Also, 3-methylcylobutene can be homopolymerized by vanadium catalysts; however, it yields amorphous polymers even by heterogeneous catalysts[58]. This can be most likely attributed to the lack of stereoregularity on the carbon atoms bearing the methyl groups.

(*ii*) *Polymerization by opening of the cycle*—The polymerization of cycloolefins by ring cleavage, as mentioned above, yields polymers having the structure of linear polyalkylenamers.

$$—CH{=}CH—(CH_2)_n—$$

The first homopolymerization of this type was discovered by us in the case of cyclobutene[54]. In this case the type of polymerization is conditioned by the nature of the transition metal. In fact, while the organometallic catalysts based on vanadium salts yield polymers with cyclic monomeric units, analogous catalysts based on titanium or molybdenum salts yield predominantly polymers with linear unsaturated monomeric units[55]. Among the catalyst systems containing metals of the 8th group, prepared in the absence of organometallic compounds and acting in the presence of protic solvents, the substitution of rhodium or nickel by ruthenium salts leads to the polymerization of cyclobutene and of 3-methylcyclobutene to polymers having the structure of 1,4-polybutadiene and 1,4-poly-(1,3)-pentadiene respectively[59]. These polymers exhibit stereoisomerism of the geometric type. The polymerization of cyclobutene can take place stereospecifically and yield polymers having predominantly *cis* or predominantly *trans* double bonds (*Table 5*).

Table 5. Behaviour of different transition metals in the homopolymerization of cyclobutene

Catalyst system	*Monomeric units contained in the polymer*		
	Cyclobutylenamer (%)	*Butadiene* (%) *cis*-1,4	*trans*-1,4
$CrO_2Cl_2/Al(C_2H_5)_2Cl$/toluene	100	0	0
$VCl_4/Al(C_2H_5)_3$/n-heptane	99	0	1
$MoCl_5/Al(C_2H_5)_3$/toluene	30	30	40
$WCl_6/Al(C_2H_5)_3$/toluene	40	30	30
$TiCl_4/Al(C_2H_5)_3$/toluene	5	30	65
π-allyl Ni bromide/C_2H_5OH	100	0	0
$RhCl_3/H_2O$	99	0	1
$RhCl_3/C_2H_5OH$	98	0	2
$RuCl_3/H_2O$	0	50	50
$RuCl_3/C_2H_5OH$	0	0	100

From the chemical point of view, 3-methylcyclobutene shows a similar behaviour to cyclobutene, but differs from the latter in that its polymers are amorphous. This is probably due to the lack of stereoregularity of the tertiary carbon atom to which the methyl group is bound.

The experimental data accumulated so far are insufficient to clarify why polymerization occurs in some cases by ring cleavage while in others occurs with opening of the double bond. The polymerization chemism depends essentially on the nature of the transition metal and proves that, in all the cases examined, polymerization is of the co-ordinate type. Also, the influence of the electropositivity of the transition metal can be qualitatively detected[43]. In fact, among the catalytic systems prepared by reaction between an organometallic compound of aluminium and a transition metal compound, the most electronegative systems (Cr and V) polymerize by opening of the double bond, while the more electropositive ones (Ti, Mo, W) polymerize by ring cleavage. Similarly, among the metals of the 8th group yielding coordinate anionic catalysts without the use of organometallic compounds, the more electronegative ones (Ni and Rh) polymerize cyclobutene by opening of the double bond, while the more electropositive one (Ru) polymerizes by opening of the cycle (*Table 5*).

Cyclopentene can also be polymerized by ring cleavage to linear unsaturated polymers which differ from 1,4-polybutadiene by the presence of three instead of two methylenic groups in every monomeric unit of the polymer chain[60]. It is interesting that polymerization of cyclopentene can yield polymers having a higher degree of chemical and steric regularity than those of the corresponding polymers obtained from cyclobutene (*Figure 7*).

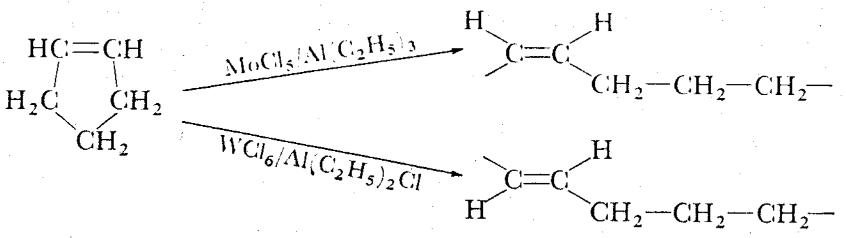


Figure 7. Polymerization of cyclopentene

In fact, polymers can be obtained that are completely free from cyclic units and present essentially all *cis* or all *trans* double bonds. Stereospecificity depends on the transition metal, on the organometallic compound and on the polymerization conditions. The most stereospecific catalyst to obtain *cis*-polypentenamer is prepared from $MoCl_5$ and $Al(C_2H_5)_3$, whereas *trans*-polypentenamer was obtained by the system $WCl_6 + Al(C_2H_5)_2Cl$ or, with far lower yields, by the system $TiCl_4 + Al(C_2H_5)_3$. This type of polymerization takes place by catalysts acting through a coordinate anionic mechanism. In fact, the cationic, the traditional anionic catalysts and the radical initiators experimented with in our Institute, never led to the formation of considerable quantities of polypentenamers, not even atactic ones.

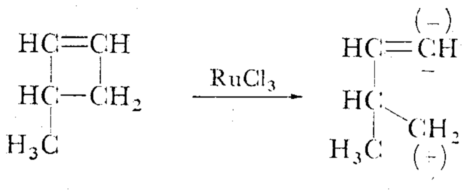


Figure 8. Polymerization of 3-methyl cyclobutene in presence of ruthenium trichloride

Experimental evidences make us believe that ring cleavage takes place exclusively on a single bond adjacent to the double bond. In fact, in the case of polybutenamer, the IR examination revealed the presence of vinyl and methyl end groups, In the case of 3-methyl cyclobutene, the polymerization in the presence of $RuCl_3$ yielded polybutadienes having vinylidenic end groups, as it might be foreseen from the position of the ring cleavage (*Figure 8*).

CONCLUSIONS

Eleven years of research have extended the study of stereospecific polymerization to several classes of monomers, both linear hydrocarbons and cyclic, as well as to many classes of monomers containing different chemical functions. In some cases high polymers have been obtained from those monomers which previously could not be polymerized (or else polymerized to low polymers) by other classes of catalysts. However, the great importance attached to coordinate ionic catalysis (in particular the anionic one) is due to the fact that polymerization can be carried out in a very regular manner both from the chemical and steric standpoints and can be directed, depending on the catalyst used, toward the almost exclusive formation of one of the possible stereoisomers. All this brought a revolutionary contribution in the field of macromolecular chemistry.

Since a great amount of research is being done in university and industry laboratories on the coordinate ionic polymerization, our knowledge of this type of polymerization will possibly increase considerably in the next few years, and will enable us to understand its mechanism more fully.

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