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Metal-complex catalysis of the polymerisation of α-olefins

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ABSTRACT. The progress in the development and application of metal-complex catalysis in the polymerisation of α-olefins during the last ten years is reviewed and evaluated. The methods of modifying previously known catalytic systems are characterised and the experimental results of studies on novel types of catalysts, including Ti–Mg, metallocene, lanthanide, and ylide systems are reported. Some views about further improvement of the activity and stereospecificity of metal-complex catalysts in relation to the chemistry of polyolefins are stated.

The bibliography includes 242 references.

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I. Introduction

An event which caused a revolution in chemistry in this century was the discovery by K Ziegler and G Natta of the metal-complex catalysis of the polymerisation of olefins. This discovery was not only of outstanding scientific importance but also gave rise to a fundamentally new and simple method of obtaining one of the most important industrial polymers — polyethylene — and to the synthesis of previously unknown crystalline stereoregular polyolefins such as polypropylene and several others. It is perhaps difficult these days to find an area of chemistry that has not experienced in its theoretical and practical aspects the influence of metal-complex catalysis to a greater or lesser extent. Metal-complex catalysis has had a considerable effect on the devlopment and refinement of the priority areas of theoretical and applied chemistry such as the polymerisation of dienes and the production of stereoregular rubbers, the activation of alkanes, highly effective and selective processes for the hydrogenation of unsaturated compounds, hydroformylation, and many others.

It has gained firmly established positions in the present-day chemical industry both in the production of large-tonnage products which govern the industrial potential of a country and in the preparation of products of so-called fine chemistry. Note the final role is also played by metal-complex catalysis in the development of certain biotechnological processes, the significance of which has grown in recent years.

However, the most important area of application of metal-complex catalysis (MCC) in industry still remains the polymerisation of unsaturated hydrocarbons — α-olefins, dienes, acetylenes, and, for the time being to a lesser extent, allenes.

A metal-complex catalytic system used for the polymerisation of α-olefins consists of three main components: 1) a transition metal; 2) a ligand (or several different ligands) bound to the transition metal); and 3) an electron-donor and/or electron-acceptor compound which has a direct effect on the activity and selectivity of the whole system, including the stereoselectivity (in the polymerisation of C_3 olefins or higher). Moreover, if a heterogeneous metal-complex catalyst is used, it contains a polymeric or other type of support as a matrix, the nature of which also affects the stability, selectivity, and activity of the whole catalytic system.

A virtually unlimited number of catalytic systems can be produced by varying the types of components as mentioned above. And in fact, since the discovery and application of Ziegler–Natta metal-complex catalysts, many hundreds if not thousands of catalytic systems for the polymerisation of ethylene, the stereospecific polymerisation of α-olefins (C_3–C_6), dienes, and acetylenic and allenic hydrocarbons have been proposed and in the majority of cases patented. However, until recently only certain compounds of transition metals such as Ti, V, and Cr have found practical application. Many fundamental studies and practical developments have been devoted to metal-complex systems based on them.

There is now no doubt that a necessary condition for catalysis to take place is the coordination of substrate (this is the monomer in polymerisation reactions) with a transition metal compound. The resulting organometallic intermediates participate in the polymerisation process, govern its mechanism, and have a considerable effect on the reaction kinetics and structure of the polymer formed.

However, up to the present time the nature of the active sites and the means of regulating their action have remained in many respects uncertain.

The composition of the intermediates depends on the nature of the transition metal in the catalytic complex, the type of ligand environment, and the donor-acceptor interactions that occur in the reaction sphere. All of these factors cause complications in making a reliable determination of the structure and mechanism of the active sites, which at the present time is made even more difficult because of the widespread use of metal-complex systems immobilised on a polymeric (or other) matrix, since in this case the actual structure of the active site may be considerably modified.

In the development of a metal-complex catalyst it is necessary to aim for a suitable combination of effectiveness, stability, and stereoselectivity. Many groups of researchers are working on a solution to these problems.

This is usually achieved through modification of classical Ziegler–Natta catalytic systems or through the development of new types of catalytic systems.

There is a whole series of theoretical and experimental publications and reviews in the Soviet and foreign literature on this topic.[1–22] Despite this, the problems of MCC in the polymerisation are still a long way from a complete solution and they leave open a sufficiently wide field for scientific research and advances. This has been the reason for writing the present review.

II. Modification of classical Ziegler–Natta catalytic systems

Bearing in mind the undoubtedly provisional nature of the classification that we have adopted, we shall classify catalytic systems made up by compounds of Ti, V, Cr, and certain other transition metals in combination with Al alkyl derivatives as classical Ziegler–Natta systems. The greatest number of studies are devoted to Ti-containing catalytic systems, which were discovered and first studied by Ziegler and Natta et al.[2]

In the polymerisation of ethylene and other α-olefins with catalysts containing Ti compounds, the high activity of the Ti–C bond is of considerable importance. This activity is related to its low energy and the possibility of selective excitation by insertion of a polymerising monomer.[23,24]

In a number of fundamental studies by Soviet research workers who had studied the properties of the Ti–C bond in quite considerable detail, a theory concerning the "lability" of this bond was advanced. The concept of "lability" denotes that the energy profile of the titanium-carbon bond (and in the final analysis its energy) is highly sensitive towards the ligand environment of the metal and towards association and dissociation, protonation and complexation.[8]

Some experimental results indicate the possibility of activation of the Ti–C bond, and hence an increase in activity of the whole catalytic system in the polymerisation of olefins. Thus, it was shown[24–32] that the activation of the metal-carbon bond (through to its homolytic decomposition) occurs on treatment of organic bases, Lewis acids, proton-donating compounds, and also microquantities of water.

The form of the titanium-containing components used in metal-complex systems has a considerable effect on the activity and stereoregularity of polymerisation (in the case of propylene polymerisation).[33–43] Thus, by using microspherical $TiCl_3$ it is possible to achieve a 98% (or higher) degree of isotacticity of the resulting polypropylene.[44–47] It is also significant that microspherical $TiCl_3$ makes it possible directly to obtain granulated polypropylene, which cannot be produced using traditional Ziegler–Natta catalytic systems, and hence an energy-consuming stage—granulation of the polymer—can be eliminated in the production of polypropylene. The structure (sphere) of the catalyst is replicated, as it were, in the polymer.[37]

Improvement of the classical catalytic system $TiCl_3 + AlR_3$ has mainly proceeded in the direction of the introducing certain activating additives, amongst which organomagnesium compounds are of the greatest interest.[48–51] Catalysts modified with these additives constituted the prototype of novel Ti–Mg metal-complex systems that will be examined below.

Table 1[52] contains the experimental results that characterise the activity of modified catalysts for the polymerisation of ethylene. For comparison we can indicate that on typical Ziegler–Natta systems the yield of polyethylene per unit of catalyst is lower by a factor of about 1.5–2.

Table 1. Activity of Ti–Al ethylene polymerisation catalysts modified with organomagnesium compounds.

Components of the catalytic system			Output g PE (g Ti)$^{-1}$	[η], dl g^{-1}
Ti	Al	Mg		
$TiCl_4$	$(C_2H_5)_3Al_2Cl_3$	$(C_6H_5)_2Mg$	18 420	13.8
	$(C_2H_5)_2Al_2Cl_4$	$(C_6H_5)_2Mg$	19 300	13.0
	$(C_2H_5)_3Al$	$(C_6H_5)_2Mg$	31 600	11.2
	$(C_4H_9)_3Al$	$(C_6H_5)_2Mg$	21 140	12.3
	$(C_2H_5)_x(C_4H_9)_yAl$	$(C_6H_5)_2Mg$	18 380	14.2
	$(C_2H_5)_2AlCl$	**$(t\text{-}C_4H_9)Mg$**	18 375	18.6
	$(C_2H_5)_2AlCl$	**$(n\text{-}C_3H_7)_2Mg$**	32 700	16.2
	$(C_2H_5)_2AlCl$	**$(n\text{-}C_4H_9)(OC_3H_7)Mg$**	24 500	17.2
	$(C_2H_5)_2AlCl$	$C_{12}H_{25}MgBr$	34 160	19.9
$Ti(OC_4H_9)_4$	$(C_2H_5)_2AlCl$	$(C_6H_5)_2Mg$	20 120	22.6
$Ti(OC_4H_9)_3Cl$	$(C_2H_5)_2AlCl$	$(C_6H_5)_2Mg$	21 000	20.8
$Ti(OC_4H_9)_2Cl_2$	$(C_2H_5)_2AlCl$	$(C_6H_5)_2Mg$	22 400	24.1
$Ti(OC_4H_9)Cl_3$	$(C_2H_5)_2AlCl$	$(C_6H_5)_2Mg$	20 800	23.8

It had already been established in the earliest studies on the polymerisation of ethylene on Ziegler–Natta catalysts that the molecular weight of polyethylene can be controlled by adding hydrogen, which terminates the chain.[53–56] However, it was shown recently that in certain cases hydrogen can at the same time increase the activity of the catalyst.[55] At the present time the mechanism of this phenomenon is the subject of study and so far there is no unequivocal view about the activating role of hydrogen.

The activating effect of hydrogen on metal-complex catalysis was observed not only in the polymerisation of ethylene but also that of propylene and other α-olefins.[57–59]

Microspherical $TiCl_3$ has also been successfully used for the copolymerisation of propylene and styrene.[60] The best results were achieved when the catalytic system $(RC_5H_4)_2TiMe_2$ (R = H, Me_3) + $TiCl_3$ was used. It is possible to obtain statistical copolymers of styrene and propylene by using this catalyst. When it is used, highly isotactic polymers based on propylene (isotacticity >99%), n-butene (isotacticity >98%), and polystyrene (isotacticity >99%) are obtained. For the polymerisation of ethylene highly crystalline polyethylene was formed, containing virtually no ethyl branches in the macromolecule.[44,45]

Block copolymers of propylene and ethylene were synthesised using microspherical $TiCl_3$.[61,62] In order to improve the morphology of the copolymer of ethylene and propylene obtained using $\delta\text{-}TiCl_3/Al(C_2H_5)_3$, it is recommended to carry out a preliminary activation of this catalyst with small quantities of α-olefins (C_4–C_{12}) or ethylene.[63] Certain attempts were made to define the role of this process.[56,64–66] However, this phenomenon requires a more detailed investigation.

As has been mentioned above, donor-acceptor interactions which occur when electron-donating or electron-withdrawing compounds are added to the reaction sphere have a significant effect on the

activity of Ziegler–Natta catalysts. A large number of examples attesting to this effect have been reported in the literature.[67–73]

The recently published results of Seppälä and Härkönen,[74] who studied the polymerisation of propylene on Ziegler–Natta catalysts incorporating organosilicon donor components, have attracted attention. The following silicon compounds were used as donor additives: $RSi(OCH_3)_3$, $R^1R^2Si(OCH_3)_2$, $RSi(OC_2H_5)_3$, $R^1R^2Si.(OC_2H_5)_2$, $RSi(CH_3)_3$, $R_2^1R^2SiH$, $(n\text{-}C_3H_7O)_3SiCH_3$, $(CH_3)_2Si.[OC(CH_3)=CH_2]_2$.

It was established that the donor components in essence selectively deactivate the atactic active sites, thus increasing the yield of high-molecular weight isotactic polypropylene. The study contains data that characterise the relationship beween the effect of the above donors and their structure.

Interesting results were recently published by Soga et al.,[75] who proposed the use of spherical $TiCl_3$ in combination with Cp_2TiMe_2 without involving organoaluminium compounds in the catalytic complex for the preparation of isotactic polyolefins from propylene, 1-butene, and 4-methyl-1-pentene.

One of the most important methods of modifying Ziegler–Natta catalytic systems is their heterogenisation or, in other words, the immobilisation of the active sites on a support. Inorganic compounds as well as polymers themselves—polyethylene, polypropylene, etc.—can be used as the supports. Immobilised metal-complex systems have considerably greater stability compared to conventional systems and also prove to be more efficient in carrying out polymerisation under industrial conditions.[1,19,76–90]

Amongst the first to start work in this area were Kabanov et al.,[91–92] who developed the so-called gel-immobilised catalytic systems (GCS). In order to obtain such catalysts, functional monomers are initially grafted on to the polymers, for example, a functional monomer such as vinylpyridine or some other is introduced on to butadiene-styrene rubber by copolymerisation (normal or block), and then transition metal compounds [$TiCl_4$, VCl_4, Cp_2TiCl_2, $Ti(OPr)_4$, etc.] are added to the solvent-swollen rubber (gel), fixing on to the functional groups. After removal of the solvent the gel-immobilised catalyst (GC) can be kept in air, not losing its potential activity over a long period. When a GC is introduced into a solvent in which the polymerisation of ethylene or another α-olefin is being carried out it swells and the active sites become accessible for interaction with the monomer and the usual co-catalysts—AlR_2Cl, AlR_3, etc. It should be noted that in those cases where the rate of polymerisation exceeds the rate of diffusion processes related to removal of polymer from the gel, it is possible to destroy the whole system. Therefore, the use of GCS proves to be most effective in processes involving oligomerisation of olefins.

The functionalisation of polyolefins for the successive fixing of transition metal compounds on to them via suitable functional groups has been carried out.[26] Thus, Ti-containing catalysts for the polymerisation of propylene that were immobilised on polypropylene via acrylate groups were obtained, having high stability and making it possible to prepare isotactic polypropylene (96–97%).

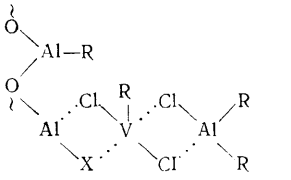
Recently the heterogenisation of homogeneous metal-complex catalytic systems was carried out by means of chelation with macroligands.[93] In order to do this, the functionalisation of the surface of PE was initially carried out. The functionalised support was then transformed through polymer-like reactions into chelating macroligands which formed a heterogenised catalyst with transition metal compounds. The transition metal compounds used were $TiCl_4$, $Ti(OC_4H_9)_4$, VCl_4, $Ni(OCOCH_3)_2$, $CoCl_2$, and $Co(OCOCH_3)_2$.

The bifunctional immobilised catalyst containing Ni and Ti (or V) compounds that is used for the single-stage preparation of linear low-density polyethylene (LLDPE) deserves particular attention. Its action is based on the effective dimerising ability of the Ni-active sites. Ti or V compounds traditionally used in Ziegler–Natta catalysts constitute the second active site in this catalyst.[93]

There is no doubt that the idea of obtaining LLDPE from ethylene in a single stage is attractive, but it is necessary to bear in mind the complexity of controlling simultaneously the different active sites that are functioning.

Attention has been drawn in the literature to the nature of the active sites of supported vanadium catalysts for the polymerisation of ethylene. For immobilisation of the components of the catalyst, supports that contained hydroxyl functional groups (and adsorbed water)—$SiO_2.Al_2O_3.H_2O$, kaolin, chalk, pyrite—and also supports with reactive alkyl groups—polyalkylalumoxanes $R_2Al(OAlR)_m-(OAlX)_m-OAlR_2.kEt_2O$, where X = Cl, OMg, iso-Bu, $OR(OC_6H_5)_2$; $n + m \geqslant 20$; $k = 0.1$—were chosen.[94–96] The higher valency vanadium compounds used were $VOCl_3$, VCl_4, $VO(OEt)_3$, and ethyl and isobutyl derivatives of aluminium were used as the organoaluminium component.

Si–O–V and V–O–Al bonds were fixed on the surface of the support. $Al(iso\text{-}Bu)_3$ served as the co-catalyst. It was shown experimentally that in catalytic complexes of supported systems chemical bonding of vanadium to the surface of the support occurs, lowering the mobility of the vanadium atom and reducing the probability of octahedrally coordinated vanadium being formed. The highest catalytic activity in the polymerisation of ethylene occurs in vanadium-alumoxane systems in which the active site is not bound chemically to the support. The structure of the active sites of vanadium alumoxane catalysts can be represented schematically as follows:



X = R, OR, Cl, OMgR, OP $(OC_6H_5)_2$.

The vanadium catalysts immobilised on alumoxanes are more stable than those immobilised on oxide supports. Their output is also higher by a factor of 4–6.

In one study[97] several new approaches to stereoregulation processes in the polymerisation of propylene on solid complex catalysts based on α- and δ-$TiCl_3$ (or VCl_3) + AlR_3 (or AlR_2Cl) were examined. The mechanism of polymerisation was shown to be multicentred. The active sites of the catalyst differed according to both reactivity and stereoregulating ability.[98]

It is significant that an isotactic fraction of PP that has virtually uniform stereoregularity is not of uniform molecular weight. This fact suggests that the two types of active site in the catalyst are not interrelated in terms of activity and stereospecificity. It is necessary to take into account this factor when interpreting the experimental data on the stereospecific polymerisation of propylene and other α-olefins.

Soviet research workers[99] studied the mechanism of the formation and structure of the active sites formed when organometallic catalysts are fixed to the surface of a support. This is of considerable importance for achieving controlled polymerisation of ethylene and other α-olefins on heterogenised catalysts, since the

process of fixation of the active sites on the surface of the support and the subsequent polymerisation are accompanied by a number of quite complex side reactions that have an effect on the activity of the whole catalytic system and the kinetic mechanisms of polymerisation. The fixation of metal complexes of $TiCl_4$ and $AlEt_2Cl$ or $AlEt_3$ to the surface of Aerosil was selected as a model.

It was established that in the polymerisation of ethylene and propylene on this catalytic system, different types of active site can occur depending on the conditions under which it is formed. Thus, when a titanium compound that is already fixed is treated with organoaluminium compounds (the "direct" method), titanium occurs on the surface of the support as a separate $TiCl_4$ complex, and a $TiCl_3$ phase is not formed, as was previously supposed.[82]

The use of the "reverse" method for fixing the catalyst, in which $AlEt_3$ is fixed first, results in the formation of a $TiCl_3$ phase on the surface of the support. When $AlEt_3$ interacts with the OH groups of Aerosil, alkyls of the type $Si-O-AlEt_2$ are formed on the surface, having good reducing ability. According to polarographic data, after interaction of such groups with $TiCl_4$ a system containing a maximum quantity of Ti^{3+} (95%) and containing virtually no Ti^{4+} or Ti^{2+} is formed.

If $AlEt_2Cl$ is used instead of $AlEt_3$, the active sites formed on the surface in the "reverse" method of producing fixed metal complexes are quite different in nature. In this case reaction with OH groups results in the formation of $Si-O-Al$ compounds of lower reactivity, and after adsorption of $TiCl_4$ a surface complex is formed in which titanium remains almost completely in the tetravalent state. Such sites are highly active in the polymerisation of propylene, as a result of which irregular low-molecular weight polypropylene is formed.

According to IR spectroscopy data the polypropylene formed on sites of this type contains a large number of irregular additions and is similar to the polypropylene obtained on classical cation catalysts (BF_3, $AlBr_3$). The atactic fraction of polypropylene is virtually no different from the traditional form.

Thus from the experimental data examined above it can be concluded that there is a possibility of the directed formation of different active sites in the polymerisation of α-olefins on heterogenised Ziegler–Natta catalytic systems.

In two studies by D'yachovskii et al.[100,101] it was found that when catalytic systems based on $Ti(OR)_4$, $TiCl_3$, and $VO(OR)_4$ fixed on graphite were used, it was possible to obtain highly isotactic PP. The theory was advanced that the graphic acts as a unique macroligand that permits the formation of active sites with a high stereoregulating capacity.[101,102] The graphite support was also successfully used in the polymerisation of 1-butene on Ziegler–Natta catalytic systems.[103]

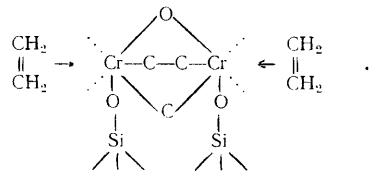
There is no doubt that the role of a graphite support, which has unusual properties that other layered supports may also possibly have, deserves detailed study. This opens up new possibilities for the development of unconventional heterogenised metal-complex polymerisation systems.

X-Ray diffraction studies were carried out[103] on the polymerisation of 1-butene on Ziegler–Natta systems fixed on graphite and they helped to identify the properties of the graphite support with a number of transition metal compounds ($TiCl_4$, $SnCl_4$, $FeCl_3$, etc.) fixed on it. The X-ray diffraction studies demonstrated that these complexes penetrate inside the quasi-monocrystalline graphite. However, the distance between the carbon layers in the graphite when it is treated with heptane, $AlEt_2Cl$, $TiCl_4$ + $AlEt_2Cl$ does not alter, namely, the formation of layered graphite compounds does not occur with these products.

As a result of the polymerisation of ethylene and 1-butene in the presence of the catalytic system $TiCl_4$ + $AlEt_2Cl$ fixed on a quasi-monocrystal of graphite, the crystal expands and increases its width by a factor of 3–5 depending on the polymerisation conditions. This suggests that the polymerisation of olefins occurs both on the outer surface and inside the crystal. Thus, the hypothetical concept which regards graphite as a macroligand requires experimental confirmation.

At the same time as Ziegler–Natta catalytic systems, chromium oxide catalysts comprising Cr compounds deposited on Al_2O_3 (Phillips catalysts) were proposed and even found industrial application for the polymerisation of ethylene.[2,104,105] In due course the characteristics of the polymerisation of ethylene and other olefins on these catalysts were studied in detail by Topchiev et al.[106] and the chemical interaction between transition metal and support was demonstrated experimentally. The interest in chromium oxide catalysts has now diminished somewhat because of the development of new highly effective and stereoselective catalytic systems. Nevertheless, several studies have appeared in the literature in recent years[107–111] devoted to chromium catalysts for the polymerisation of ethylene.

Thus, in a recently published study by Rebentorf[112] the number of active sites in samples of a Phillips catalyst—0.5% Cr^{6+} and 0.074% Cr^{6+} (on silica gel)—was determined. It was shown that the number of active sites increases with a decrease in Cr content in the catalytic system. Rebentorf, in the same way as the Soviet scientists, assumes that in this case there is chemical reaction between Cr and the support:[112]



Gan et al.[108–110] examine a new type of chromium catalyst for the polymerisation of olefins, consisting of specially prepared chromium acetate combined with $AlEt_2Cl$. This catalyst exhibits a very high activity in the polymerisation of ethylene, amounting to 1180 g PE (g Cr)$^{-1}$ h^{-1}.

III. Novel types of catalytic systems

1. Titano-magnesium catalytic systems

In considering the different methods for modifying "classical" Ziegler–Natta catalytic systems we have already drawn attention to the activating effect of organomagnesium compounds. These studies have served as the basis for the development of a new generation of highly active Ti–Mg catalysts. At the present time heterogeneous titano-magnesium catalysts represent the most widely used metal-complex systems for the production of polyethylene and other polyolefins, in particular, isotactic polypropylene. Essentially these catalytic systems are supported, since $MgCl_2$ should legitimately be regarded as a support. Experimental data characterising the activity and stereospecificity of certain titanomagnesium catalysts used in the polymerisation of propylene are presented in Table 2.[113] It should be noted that in all cases the fairly high stereospecificity of such catalysts is due to the addition of electron-donating compounds (ethers and esters, phosphorus- and silicon-containing compounds, etc.).

Ti–Mg catalysts (in their various forms) have served as a subject of research for scientists of different countries.[1,114–123] A considerable contribution has also been made to the development and practical application of Ti–Mg catalysts by Soviet scientists (the school of Yu E Ermarkov and V A Zakharov in the Institute of Catalysis, Siberian Branch of the USSR Academy of Sciences).[82,120,124–128]

Table 2. Some results on the polymerisation of propylene on titanium–magnesium catalysts.[113]

Solid catalyst	Co-catalyst	Activity, g PP (g Ti)$^{-1}$	Index of isotacticity
$TiCl_3$	$(MeC_5H_4)_2TiMe_2$	27	98
	$(MeC_5H_4)_2TiCH_2(Me)AlMe_2$	37	93
$TiCl_4/MgCl_2$	$(MeC_5H_4)_2TiMe_2$	160	90
	$Cp_2TiCH_2(Me)AlMe_2$	940	87
$TiCl_4$/EB*/$MgCl_2$	Cp_2TiMe_2	970	95
	$Cp_2TiCH_2(Me)AlMe_2$	3250	93
$TiCl_4$/n-BP**/$Mg(OEt)_2$	Cp_2TiMe_2	60	97
	$Cp_2TiCH_2(Me)AlMe_2$	2400	97
$TiCl_4$/n-BP/$MgCl_2$	Cp_2TiMe_2	90	96
	$Cp_2TiCH_2(Me)AlMe_2$	3700	95
	$AlEt_3$	4000	76

Polymerisation conditions: $P_{C_3H_6}$ = 1 atm, T = 40 °C, τ = 2 h, heptane solvent (100 ml).

* EB = ethyl benzoate. **n-BP = n-butyl phthalate.

Attention is drawn in the literature to the fact that the properties of Ti–Mg catalysts depend to a significant extent on the structure of the support and the method of fixing transition metal compounds to it. Magnesium chloride is the most suitable support for obtaining a highly active propylene polymerisation catalyst because of the similarity between the structures of $TiCl_3$ and $MgCl_2$.[129–134] Thus, an active catalyst was obtained by grinding together a mixture of anhydrous $MgCl_2$ and the complex $TiCl_4.C_6H_5-COO-C_2H_5$. The ester is an electron donor and it is needed to achieve a high degree of stereoregularity. On a catalyst prepared in this manner the yield of PP reached 9 to 17 kg (g M)$^{-1}$ h^{-1} with a degree of isotacticity of 94–95%.[135]

Polish research workers[135] showed that the presence of a given quantity of ethanol in the reaction medium during preparation of the catalyst increases the efficiency of a Ti–Mg catalyst (modified none the less with ester). During the experiment the presence of ethanol assisted the formation of the spherical type of catalyst grain. However, the specific output of the catalyst was not sufficiently high ~6 kg PP (g Ti)$^{-1}$ h^{-1}.[135]

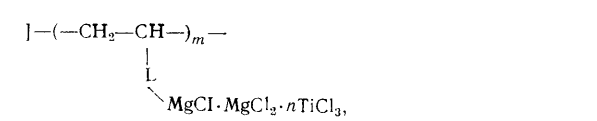
A detailed study was made on the copolymerisation of ethylene with α-olefins on Ti–Mg and similar supported catalytic systems. The subject of the study was the suspension copolymerisation of ethylene with propylene, 1-butene, and 1-hexene on supported Ti–Mg (TMC) and V–Mg (VMC) catalysts.[111] In the copolymerisation on TMC and VMC the catalysts can be arranged in the following order of copolymerising ability: V–Mg > $TiCl_3$ > Ti–Mg. It was established in a separate series of experiments that there is a virtually constant value of the copolymerisation constant over the temperature range 40 to 80 °C.

As has already been mentioned above, the structure of the electron-donating component has a significant effect on the activity and stereospecificity of Ti–Mg catalysts.[136–145] In this respect consideration should be given to a recently published study,[146] in which a new highly active supported catalyst for the polymerisation of propylene based on $TiCl_4$ and $MgAlk_2$ compounds and sterically hindered aromatic esters is described, the esters used being ethyl 2,6-dimethylbenzoate, ethyl 2,4,6-trimethylbenzoate, or isopropyl benzoate. The support is deposited from a solution of $MgAlk_2$ with SiR_4 and then activated by treatment with $TiCl_4$ and dibutyl phthalate in chlorobenzene. A Ti–Mg catalyst prepared in this manner gives high yields of isotactic PP [16–17 kg PP (g Ti)$^{-1}$ h^{-1}] (70 °C, 10 atm).

There are reports in the patent literature[147–152] on many methods for preparing Ti–Mg catalysts which we naturally do not have the opportunity of examining within the scope of this review. A number of studies[31,122,140,142,153–175] are devoted to establishing the nature of the active sites of Ti–Mg catalysts.

The desire to increase the number of isospecific sites in a Ti–Mg catalyst has compelled research workers to seek the most effective electron-donating components which cause an increase in the number of these same active sites. Amongst the electron-donating components studied, special consideration should be given phthalate esters.[142–144] In a study of the copolymerisation of ethylene and 1-hexene, 1-decene, and 4-methyl-1-pentene on a Ti–Mg catalyst, Ivanchev et al.[176,177] and also other research workers[56,63–65,178] showed that the α-olefin molecules act as modifiers of the growth sites, increasing the rate of growth of the polymer chain by a factor of 6–9. This interaction during the suspension polymerisation process is satisfactorily represented by a scheme involving equimolar equilibrium complexation with a constant that is close to unity.

Interesting results were obtained by Krentsel' et al.[8] in a study of the polymerisation of ethylene on Ti–Mg catalysts that were immobilised on polymeric supports. The structure of the catalyst used in this study can be represented by the following general scheme:



where L is a functional group such as allyl alcohol, acrylic acid, and others. The steady-state rate of ethylene polymerisation at 70 °C and 2 atm reached 85 mol C_2H_4 (mol Ti)$^{-1}$ s^{-1}.

This type of Ti–Mg catalyst for the polymerisation of ethylene is characterised by a low Mg content which is comparable to the concentration of Ti, which, in the opinion of Krentsel' et al.,[8] makes it possible to control the molecular weight properties of polyethylene.

In general, control of the molecular weight and molecular weight distribution of polyethylene formed by the polymerisation of ethylene on Ti–Mg catalysts is a complex task. In this respect the studies which demonstrated the possibility of controlling the molecular weight distribution in the polymerisation of ethylene on Ti–Mg catalysts by the introduction of various halogenated compounds such as butyl chloride, chlorobenzene, and others are of undoubted interest.[179,180] From the experimental data obtained it

could be assumed that termination of the chain occurred as a result of the addition of a strongly polarised RX molecule or contact ion pair R^+X^-. In all of the experiments there was a narrowing of the molecular weight distribution. However, for the time being it is not possible to provide a reliable explanation for this phenomenon. The mechanism of interaction between RX and an active site is so far unclear and requires further study.

It may be assumed that there is a certain critical size of the catalyst macroparticles, depending on which the process occurs in the kinetic or diffusion region. In turn this critical size depends on the activity of the catalyst sample used, being determined by the concentration of active sites and the rate constant of growth.

From an analysis of the experimental data on the polymerisation of ethylene and other α-olefins on supported Ti–Mg catalytic systems, these catalysts can be considered to be amongst those with the greatest future potential.

2. New homogeneous metallocene catalytic systems

The most prominent event in metal-complex catalysis of the polymerisation of α-olefins since the discovery of this reaction by Ziegler and Natta was the creation by Kaminsky et al. (FRG)[181,182] of new homogeneous catalytic systems based on metallocene-alumoxane complexes. Such catalysts, having very high activity in the polymerisation of ethylene (tens of tons of polymer per gram of metal) can be used to effect stereocontrol of polymers in a homogeneous reaction medium.[183] The considerable scientific and practical interest shown at the present time in all countries in such metal-complex systems is due to this factor.

Catalysts of this type are formed by reaction of a metallocene of a transition metal such as Zr, Hf, and others, for example, bis-(cyclopentadienyl)dimethyl(or dichloro)zirconium with alumoxanes

$$-\left(-\underset{\displaystyle R}{\underset{|}{Al}}-O-\right)_n-,$$

where R = CH_3, C_2H_5, etc., n = 10–20.

During the last few years a large number of studies devoted to the polymerisation of olefins on such homogeneous complexes, in particular on zirconocene complexes with alumoxanes have been published.[178,184–202] Experimental data characterising the relative activity of such homogeneous catalysts in the polymerisation of ethylene[189] are given in Table 3.

It was calculated for the zirconium catalyst that at a polymerisation temperature of −20 °C about 70% of all zirconium atoms participate in polymerisation.

Experimental data on the polymerisation of ethylene on different Zr-containing catalytic systems[189] are given in Table 4.

Homogeneous zirconocene catalysts proved to be active not only in the polymerisation of ethylene but also in the copolymerisation of ethylene with hexene. The latter process is of considerable practical importance and is used to obtain linear low-density polyethylene (LLDPE). This polyethylene differs from low density polyethylene obtained by high-pressure radical polymerisation in its lower degree of chain branching and improved mechanical properties.

Interesting results were obtained when organozirconium compounds complexed with oligomeric alumoxanes were used as ethylene polymerisation catalysts. These catalysts are distinguished by their stability and can be used to obtain PE with a narrow molecular weight distribution. Isotactic polypropylene with a novel steroblock microstructure was obtained by using soluble bis(cyclopentadienyl)bis(phenyl)titanium/methylalumoxane catalysts.[6]

Three reports[183,192,196] indicate the unusual effects observed in the polymerisation of propylene carried out on homogeneous catalysts containing bulky or chiral ligands. Thus, Ewen[6] showed that when sterically hindered ethylenebis(1-indenyl)titanium dichloride (a mixture of the meso form and racemate) was used as a catalyst for the polymerisation of propylene, there is the formation of 63% isotactic and 37% atactic polypropylene. If chiral ethylenebis-(4,5,6,7-tetrahydro-1-indenyl)zirconium dichloride is used together with methylalumoxane $[AlMe-O-]_n$ as the co-catalyst, highly isotactic polypropylene is obtained.[183]

Table 3. Comparative activity of homogeneous ethylene polymerisation catalysts.[189]

System	Effective rate of polymerisation, litre mol^{-1} s^{-1}	Mole fraction of transition metal participating in the reaction
Cp_2ZrMe_2–MAO *	109 000	1
Cp_2TiCl_2–MAO	800	0.7
$TiCl_3 \cdot AlEt_2Cl$	2.7	0.005

* MAO = methylalumoxane.

Table 4. Polymerisation of C_2H_4 on different Zr systems.

Compound	Type of alumoxane	Activity, kg PE mol^{-1} h^{-1} bar^{-1}	T, °C
Cp_2ZrCl_2	Methylalumoxane	820	20
	"	242 000	80
$(Cp_2ZrCl)_2O$	"	203 000	80
Cp_2ZrMe_2	"	152 000	80
$Cp_2ZrCl(OBu)$	"	73 000	80
Cp_2ZrCl_2	Ethylalumoxane	2 100	60
Cp_2ZrMe_2	Tetraisobutylalumoxane	15 900	70

It is worth noting two studies[197,198] which are concerned with the preparation of high-molecular weight atactic polypropylene on homogeneous cene catalysts. Thus, by using bis(cyclopentadienyl)zirconium dichloride it is possible to obtain almost exclusively atactic polypropylene with molecular weights of up to 600 000. This type of polypropylene is characterised by a set of mechanical properties which is unusual for this polymer and may prove important for its use in producing seals, road and roof covers, and in a number of composite materials.

Chiral ethylenebis(4,5,6,7-tetrahydro-1-indenyl)zirconium dichloride cannot only be used to obtain isotactic polypropylene but also has polymerising activity which is 2–3 times higher than a catalyst on which only atactic polypropylene is formed. While the rates of polymerisation of ethylene and propylene on bis(cyclopentadienyl)zirconium compounds are 25 : 1, when this chiral catalyst is

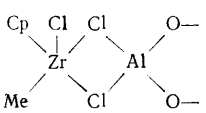
used this ratio is equal to 10:1.[187,188] These experimental results once again confirm the significant role played by steric factors during the polymerisation of α-olefins on homogeneous metal-complex systems.

With the same concentrations of monomers (pressure and polymerisation temperature) the factors which affect the activity of these catalysts are the degree of oligomerisation of the alumoxane and the concentrations of the catalytic components. The activity of the catalysts increases significantly as the concentration of zirconium decreases and the concentration of aluminium increases.[107]

The presence of methylalumoxane oligomer residues in very active homogeneous coordination catalysts for the polymerisation of α-olefins is unusual. The answer to this question will serve as a key for the preparation in future of new highly active catalytic systems.[184]

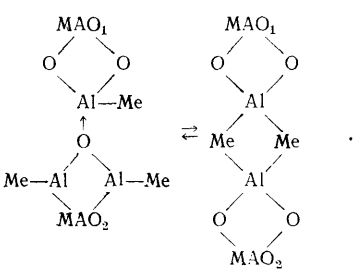
In a number of studies[199,200] particular attention is given to the role of alumoxanes in homogeneous metallocene catalytic systems. At one of the symposia on the relationship between the mechanism of heterogeneous and homogeneous catalysis, it was suggested for the polymerisation of α-olefins that alumoxanes can legitimately be regarded as a kind of support on which the active sites responsible for growth of the polymer chain are immobilised in a particular way.[81]

In an EPR study of the reactions that occur between a metallocene and methylalumoxane (MAO) it was found[84] that as a result of complexation and alkylation there was the formation of a compound with bridging bonds



Thus the proposal made previously about the similarity between alumoxane and a support is to a certain extent borne out. It is thought that when the metallocene reacts with MAO electron-deficient bridging complexes are formed and the bridging ligands are replaced by alkyls (from MAO) followed by elimination of the non-bridging groups as alkanes.

Consideration has been given to the probable establishment of an associative-dissociative equilibrium of MAO in which acid-base electron-deficient bridged complexes participate.

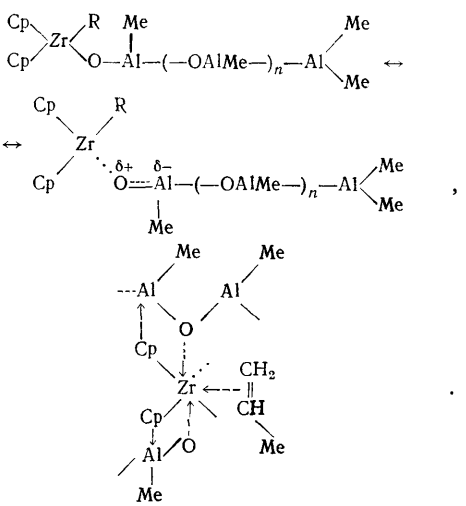


The catalytic sites deactivate each other in proportion to the concentration of Zr.[195]

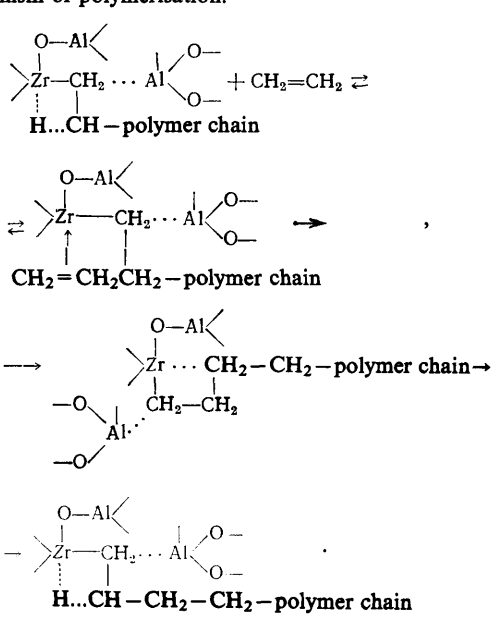
The theory advanced in this study[195] is confirmed experimentally in the observed relationship between the activity of the catalytic system and the content of Zr in it.

Despite the considerable number of theoretical and experimental studies, the most important of which were considered above, up to now there has been an absence of sufficiently reliable data on the structure and reaction mechanism of the active sites in homogeneous zirconocene catalytic systems containing alumoxanes. Recently fresh attempts were made to establish the details of the mechanism of polymerisation using carbonyl groups labelled on the carbon atom which are formed by treatment of the catalytic system with ^{14}CO.[185] However, because of a number of experiment difficulties which occurred, it was not possible to obtain sufficiently accurate results. Also, the use of CH_3OT as a label proved unacceptable.[185]

Nevertheless, proposals which do not contradict the experimental data have been made about the mechanism of complexation of a zirconocene compound with MAO, based on the electronic structure of the reacting components of catalytic system and monomer.[184,186] The essence of the proposed mechanism is as follows. On treatment with MAO polarisation of the π-electrons of the double bond in propylene occurs. As a result, a partial negative charge δ-arises on the carbon atom furthest from the methyl group. Because of this propylene is inserted into the polarised $Zr^{\delta+}-C^{\delta-}$ bond strictly stereospecifically.



The following scheme has been put forward to depict the possible mechanism of polymerisation:[190,200]



"Bridging" hydrogen is replaced by ethylene, which is initially π-bonded and then inserted into the Zr–C bond. This model

conforms with the hypothesis according to which chain growth is due to the existence of electron-deficient compounds in pentacoordinate bimetallic complexes.

An experimental study of the polymerisation of ethylene on these catalytic systems showed that the ligand environment of Zr has a significant effect on the yield and molecular weight of the resulting PE [201] (Table 5). It transpired that when MAO obtained by hydrolysis of $AlMe_3$ was used, a polymer with a lower value of $\overline{M}_n$ and wider molecular weight distribution is obtained.

Table 5. Effect of Cp substituent on the molecular weights and molecular weight distribution of polyethylene.[201]

Metallocenes	Yield, g PE $(g\ M)^{-1}\ h^{-1}\ atm^{-1}$	$MW \times 10^{-3}$	MW distribution
$(MeC_5H_4)_2ZrCl_2$	467	212	3.8
$(EtC_5H_4)_2ZrCl_2$	306	171	3.8
Cp_2ZrCl_2	252	140	3.5
$C_5Me_5ZrCl_2$	71	63	4.7

Table 6. Results of polymerisation on a TBP complex—MAO.[196]

Catalyst	Activity, g polymer $(g\ M)^{-1}\ h^{-1}$	$\overline{M}_w \times 10^{-4}$	$\overline{M}_w/\overline{M}_n$
Polymerisation of ethylene*			
(TBP)$TiCl_2$	228	360	2.0
(TBP)Ti(OPr-iso)$_2$	188	420	2.5
(TBP)Zr(OPr-iso)$_2$	6	—	—
Cp_2ZrCl_2	266	62	2.0
Polymerisation of propylene**			
(TBP)$TiCl_2$	186.0	800	2.2
(TBP)Ti(OPr-iso)$_2$	87.0	800	2.0
(TBP)Zr(OPr-iso)$_2$	0.2	380	2.4
Cp_2ZrCl_2	17.6	7.6	2.0
Ti(OPr-iso)$_4$	4.8	41.15	6.9

* Ethylene polymerisation conditions: amount of catalyst = 1.1×10^{-6} mol, MAO = 5.17 mmol, toluene = 10 ml, $P_{ethylene}$ = 1 atm, T = 20 °C, τ = 10 s.

** Propylene polymerisation conditions: amount of catalyst = 1.1×10^{-6} mol, MAO = 5.17 mmol, weight of propylene = 30 g, T = 20 °C, τ = 1 h.

Mention has already been made above of the polymerisation of propylene on homogeneous zirconocene-containing catalytic systems containing chiral ligands. Experimental data have recently been published on the preparation of stereoregular polypropylene using catalytic systems with the following structure:[202]

μ-X $(C_5H_2R^1R^2)_2ZrCl_2$, where

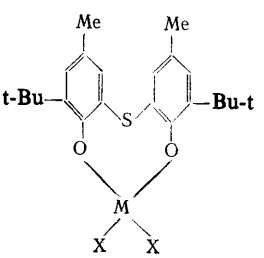
R^1 = t-Bu; R^2 = H; μ-X = $Me_2\overset{|}{C}-\overset{|}{C}Me_2$;

R^1 = t-Bu; R^2 = H; μ-X = Me_2Si ;

R^1 = t-Bu; R^2 = Me; μ-X = Me_2Si ;

R^1 = iso-Pr; R^2 = Me; μ-X = Me_2Si .

There is considerable interest in titanium and zirconium compounds with a bidentate 2,2′-thiobis(6-t-butyl-4-methylphenoxy) ligand (TBP), which in combination with MAO exhibit extremely high activities in the polymerisation of olefins or styrene.[203,204] The catalytic systems



M = Ti, Zr;
X = Cl, OPr-iso;

in combination with MAO not only are highly active but also can be used to obtain polyethylene and stereoregular polypropylene with high molecular weights (Table 6).[196]

Interesting data on the microstructure of polypropylene were obtained when the homogeneous catalytic systems—$C_2H_4Ind_2.ZrCl_2$—MAO [205] and $C_2H_4(4,5,6,7\text{-}H_4Ind)_2ZrCl_2$ [206]—were used as the polymerisation catalyst. The resulting polypropylene contains units from both 1,2- and 1,3-addition.[207–209] It was established that the stereospecific action of the catalytic system decreases with an increase in temperature of polymerisation. The polymer obtained is completely soluble in the reaction medium, in contrast to the ordinary isotactic material. These types of polymers were called "anisotactic" by Rieger and Chien as distinguished from polypropylene obtained at a lower temperature.[209] The polypropylene which was soluble in acetone and ether is waxy, while the polymer isolated from hydrocarbon solutions will be more crystalline. Ishihara et al.[206,210] showed in the case of the polymerisation of styrene that by using zirconium and other similar catalytic systems it is possible to obtain hydrocarbon polymers with a syndiotactic structure. They used heterogeneous systems in combination with MAO, such as $Ti(OBu)_4/MAO/SiO_2$, as catalysts. It was established by Pellechia et al.[211–213] that an effective catalyst for the preparation of syndiotactic polystyrene has a low ratio of MAO to Ti. In other studies[211,212,214] an organozirconium system combined with MAO was used to obtain syndiotactic polystyrene. It should be mentioned that a similar catalytic system was tested in the polymerisation of 1,3-butadiene, isoprene, and 4-methyl-1,3-pentadiene.[215] The first two monomers gave the corresponding 1,4-*cis*-polymers, while the latter gave a 1,2-syndiotactic polymer. Catalytic hydrogenation of syndiotactic poly(1,2-[4-methyl-1,3-pentadiene]) resulted in the formation of crystalline poly(4-methyl-1-pentene) mainly with a syndiotactic microstructure and a softening point of 186 °C.[215]

Brinzinger[216] in an extension of studies on the stereospecific polymerisation of α-olefins with homogeneous metallocene catalysts synthesised and studied a number of chiral metallocenes with different structures and obtained from them active catalysts for the synthesis of isotactic polypropylene. Kaminsky et al.[217] successfully used chiral zirconocene compounds complexed with MAO for the copolymerisation of ethylene and propylene with other α-olefins.

As was mentioned above, MAO plays an important part in the polymerisation of olefins in which it participates. It is appropriate to mention that the addition of MAO to the catalytic system $Ti(OBu)_4/SiO_2$ markedly increases the activity of this system in the preparation of highly syndiotactic polystyrene.[218] However, the mechanism of this effect remains unclear. It is still not understood why the catalytic system consisting of Cp_2MCl_2 (M = Ti, Zr) and MAO, which is well known as an olefin polymerisation catalyst, is ineffective in the preparation of syndiotactic polystyrene, whereas the system $Ti(OPr)_4$–MAO, which is used to obtain syndiotactic polystyrene, also catalyses the polymerisation of olefins[219] but does not assist the copolymerisation of styrene and olefins.[220]

The effect of the nature of organozirconium and organoaluminium compounds on the properties of homogeneous catalytic systems for the polymerisation of α-olefins was also studied in the case of the homo- and co-polymerisation of ethylene with higher α-olefins on different organozirconium compounds.[220–222] The results of the investigation showed that the catalytic systems based on zirconocene combined MAO can be arranged in the following order of activity:

$$(C_5H_4SiMe_3)_2ZrCl_2 > Cp_2ZrCl_2 > (C_5H_4CH_2)_2ZrCl_2 >$$
$$> (C_5H_4Bu\text{-}t)_2ZrCl_2 > Ind_2ZrCl_2.$$

It has been suggested that the increase in catalytic activity of zirconocenes is in agreement with the increase in the electron-deficiency of the Zr atom in this series. This factor facilitates the reaction of the respective zirconocene with electron-donating MAO molecules.[142] However, a study of the reaction between the zirconocene dichloride derivatives $(C_5H_4SiMe_3)_3ZrCl_2$ or $(t\text{-}BuC_5H_4)_2ZrCl_2$ and MAO in an atmosphere of argon and ethylene using IR spectroscopy, and ^1H, ^{13}C, ^{27}Al, and ^{29}Si NMR [222] showed that the difference in the relative electronic effect from the alkyl groups is comparatively small. Taking into account the complexity of the catalytic system as a whole, it is difficult to accept that it is solely the electronic effect of the substituents in the Cp rings of zirconocenes that has a decisive role in the polymerisation process.

By studying the polymerisation of ethylene on the system $(RC_5H_4)_2ZrCl_2$–MAO, Nekhaeva et al.[221] found that a zirconium compound with an isopropyl substituent had a high activity (A_m), which cannot be due solely to the steric or electronic effect of this substituent

Substituents in Cp ring	H	Et	n-Pr	iso-Pr	$(iso\text{-}Pr)_2$
$A_m \times 10^{-6}$, g PE $(mol\ M)^{-1}\ h^{-1}$	20.6	24.7	11.3	34.1	22.4

One of the factors that governs the high activity of the system with the isopropyl substituent would appear to be the development of hydride sites on the zirconium atom, in whose formation the hydrogen atoms of the α-carbon atom of the substituent participate.

Copolymers of ethylene containing from 1 to 10% of vinylcyclohexane, 4-methyl-1-pentene, and 3-methyl-1-butene were obtained on the same catalysts.[178,194]

Quite recently a very interesting report[223] was published on the use of a homogeneous catalytic system to synthesise polypropylenes with different structures depending on the experimental conditions—from stereoregular crystalline structures to amorphous products which were thermoplastic elastomers. This suggests the possibility of producing from the same hydrocarbon monomer various structural modifications which have a different set of mechanical and industrial properties.

The experimental data examined above show that the use of homogeneous metal-complex catalytic systems for the polymerisation of olefins can be used to obtain polyolefins with different structures. There is no doubt that this area will be developed further and will be extended not only to linear but also to branched higher α-olefins. There is a future for them in resolving the main scientific and practical problem—the directed synthesis of polymer structures with a given set of properties.

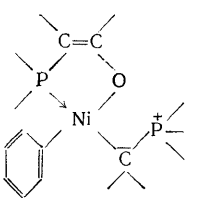
3. Catalysis based on organometallic lanthanide compounds

Fairly recently the first studies were published[223–228] on metal-complex catalytic systems containing organic compounds of metals of the lanthanide group, in particular neodymium. Particular attention was given to this question by Chinese research workers[229] who studied the stereospecific polymerisation of the dienes—butadiene and isoprene. Lanthanide catalytic systems have attracted the attention of research workers because of their high stereospecificity and also by the fact that in using them the possibility of oligomers being formed, which usually occurs when polydienes are being prepared in the presence of other metal-complex systems, is excluded. Thus, the absence of oligomers is of considerable importance in the development of an ecologically clean technology for obtaining stereoregular polyisoprene.[230]

Attention has also been drawn[230–233] to the future potential in using such catalytic systems in the polymerisation of α-olefins.[234] Thus the copolymerisation of α-olefins with methyl acrylate on organometallic ytterbium compounds has been reported by Japanese authors.[235,236] This opens up the possibility of carrying out the copolymerisation of olefins with polar monomers, which had previously been virtually impossible because of the "poisoning" of the active sites of the catalyst by the polar monomers.

4. Ylide polymerisation catalysts

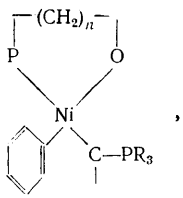
Interesting possibilities for obtaining linear and branched polyethylene are opened up by using recently proposed ylide nickel complexes as catalysts.[156,157,237] It is assumed[238] that in this type of catalyst the following coordinate structural residues occur:



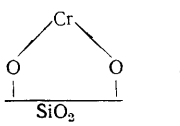
Linear polyethylene has been obtained with the use of this catalyst.

In an alternative method, two successive processes—the oligomerisation of ethylene to oligomeric α-olefins and the subsequent copolymerisation of them with the initial ethylene—can be carried out on the ylide catalyst. In this case LLDPE-type polyethylene is formed.[239] In order to carry out this process, bis(ylido)nickel catalytic systems are used in combination with a heterogeneous chromium catalyst, which function successfully in the absence of aluminium alkyls as co-catalysts.[240] In this residue the nickel complex is immobilised on the chromium catalyst, and a new

active bifunctional catalyst for the polymerisation of ethylene is formed, consisting of two components, one of which causes the oligomerisation reaction and the other causes copolymerisation of the α-olefins (C_6-C_3) formed at the first stage with ethylene:
oligomerisation:

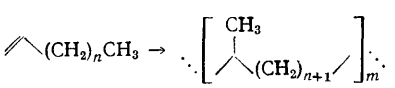


polymerisation:



By controlling the ratio of Ni to Cr and the polymerisation temperature it is possible within certain limits to change the degree of branching of PE and the length of these branches in the desired direction.

Mention should also be made of one nickel catalyst with which a novel type of polymerisation of α-olefins can be carried out. This refers to a homogeneous complex of nickel with a phosphorane ligand — bis(trimethylsilyl)aminobis(trimethylsilylimino) phosphorane.[241] Polymerisation of both linear and branched α-olefins occurs on this catalyst. The structure of the resulting poly(α-olefins) is unusual. It a linear α-olefin participates in polymerisation the polyolefin contains only one methyl branch separated by given segments of the polymer chain:



IV. Emergence of new possibilities for the development of highly effective metal-complex catalytic systems

Above we examined the main areas of metal-complex catalysis of the polymerisation of olefins that have undergone rapid development in recent years. Naturally this review has not covered all of the publications in this area, but from the results that it contains the reader can, in our opinion, form a sufficient idea of the state of this problem.

Nevertheless we thought it necessary in conclusion to draw attention to the future, and from our viewpoint, most fruitful methods of developing metal-complex catalysis in relation to the polymerisation of α-olefins.

Cossee,[242] who attempted to reveal the nature of the active sites of transition metal complexes in the polymerisation of α-olefins, showed how the metal–carbon bond (the alkyl group of α-olefins) is preserved throughout the whole reaction cycle, with the energy losses in the strength of this bond not exceeding 20% and being fully compensated by the formation of a new bond during polymerisation.

The reactions which occur in this manner can legitimately be classed as concerted reactions, which are characterised by a synchronous redistribution of electron density in the bonds, giving rise to low values of the energy of activation.[23,24]

In this respect metal-complex catalysis is similar to enzyme reactions, which also take place via the formation of intermediates and are classed as reactions that occur with a concerted mechanism. A new bond is formed in these reactions at the same time as the destruction of the old one, which helps to stabilise the transition state and accelerates the reaction.

In terms of stereoselectivity and mechanistic action there is also a certain similarity between metal-complex catalysis (in particular the polymerisation of α-olefins) and enzyme catalysis. In both cases the concerted reactions occur under mild conditions, in non-polar solvents, and at high rates. It should be noted here that the high rates that are typical for enzyme reactions have so far not been reached in metal-complex catalysis. It may be assumed that this is due to the fact that the degree of concertedness which occurs in enzyme catalysis has so far been achieved in metal-complex catalysis. It is not excluded that the required degree of concertedness can be achieved through new catalytic systems as well as through the use of reaction equipment which ensures that the reaction occurs only in the kinetic region.

Research and development on catalytic systems containing several transition metals with a different ligand environment should also prove to have future potential.

It is to be expected that new lanthanide metal-complex catalysts will be synthesised for the preparation of copolymers of α-olefins with polar monomers. At the present time only the high-pressure radical copolymerisation of ethylene with vinyl acetate and acrylic monomers is known.

The development of microheterogeneous catalytic systems has future potential. The idea for developing such catalysts is derived from the fact that high-molecular weight compounds in solution that are not cross-linked form threads which comprise macromolecules with a high content of solvent in them. On particles like this that are not cross-linked it is possible to fix in a specific way virtually any transition metal complexes whose active sites are responsible for growth of the polymer chain. Microheterogeneous catalysts are most readily designed in a form that has the greatest resemblance to enzymes. Such microheterogeneous catalysts have already been used with considerable effectiveness in hydrogenation and hydroformylation, for example. However up to the present time there has been no information on the use of such catalysts in polymerisation processes.

Interesting effects can be expected from the use of surfactants in metal-complex catalysis of polymerisation. When present in concentrations above the critical micelle concentration, surfactants are known to have colloidal properties. In a number of cases the rate constants of the reactions that occur with the participation of such micellar solutions of surfactants increase by several orders, which is due to concentration and orientation effects. There is reason to believe that these effects can also be achieved when surfactants are used in the metal-complex catalysis of polymerisation processes. In this case there is the possibility of bringing together the existing methods of ionic coordination polymerisation of olefins and emulsion polymerisation methods. There is the so-called micellar polymerisation catalysis, which in certain cases can be of definite practical interest.

Finally, the use of heterogenised cluster transition metal complexes in the polymerisation of α-olefins is attractive. There is every reason to expect a combination of high effectiveness and the necessary stereospecific action for such catalysts. It is therefore

necessary to bear in mind the possibility of achieving the introduction of microcluster transition metals into zeolites (serving as supports). On the surface the atoms of this type of microcluster have free valence bonds which make these atoms unusually reactive. A systematic investigation of cluster catalysts, including fairly complex physical methods for studying three-dimensional cluster lattices, is required for progress in the use of these catalysts.

It is probable that the trends in extensive scientific research into the improvement of existing methods and the development of fundamentally new methods in the interesting area of metal-complex polymerisation catalysis are not restricted to the examples considered here.

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