Russian Chemical Reviews **76** (7) 617 – 637 (2007) © 2007 Russian Academy of Sciences and Turpion Ltd

DOI 10.1070/RC2007v076n07ABEH003694

Advances in the development of new catalysts for ethylene and α-olefin polymerisation

S S Ivanchev

Contents

I.	Introduction	617
II.	Catalyst systems based on late transition metal α-diimine and bis(imino)pyridine complexes	619
III.	Phenoxy-imine catalysts for olefin polymerisation	627
IV.	Conclusion	633

Abstract. The role of catalyst systems in the perfection of polymerisation processes and the improvement of the performance characteristics of polyethylene and other polyolefins is considered. The scope of application of post-metallocene catalysts based on transition metal α-diimine, bis(imino)pyridine and phenoxy imine complexes designed in the last decade is analysed. The structures of complexes depending on the type of ligands are described systematically. The development of research into these catalyst systems is discussed, the optimal structures as regards the activity and selectivity are mentioned, and the mechanism of their action and the prospects for industrial use are demonstrated. The bibliography includes 207 references.

I. Introduction

In the early 21st century, the annual production of polymers exceeded hundred million tons (*'World Polymer Products'* issued by the Chemical Marketing Association, Inc., on September 2005) due to the universal use of these materials in industry and other fields of human activity. Among various classes of polymers, there are leaders in both the amount of production and the width of consumption. For example, the percentage of polyolefins in the total annual production of plastic materials (180 – 190 million tons) is higher than 50% (105 mil. tons, including ~64 mil tons of polyethylene and ~41 mil tons of polypropylene). Consequently, polyethylene (PE) and polypropylene (PP) are the most widely used polymer materials, whose production increases annually by 3% – 7%.

Polyolefins attract great attention of both manufacturers and consumers because these materials are produced from inexpensive and readily available sources and are characterised by an attractive combination of their properties and the ease of processing. The advantages of polyolefins are also their hydrocarbon composition and, consequently, the ease of utilisation by recycling or burning. Polyolefins have wide and various applications due to rather high melting points [up to 135 °C for polyethylene, ~160 °C for propylene and ~200 °C for poly(4-methylpentene)] combined with a low weight, transparency, corrosion resistance, rigidity, shock resistance and ability to be modified.

The history of the development of research into polymerisation processes of ethylene, propylene and other α-olefins and the development and commercialisation of polyolefin production processes dates back approximately 70 years. After the first successful technological solutions on procedures for ethylene polymerisation under high pressure, ICI Plc (UK) began commercial production of PE in the late 1930s. More recently, in addition to the autoclave process, a procedure for ethylene polymerisation in tubular reactors was developed and commercialised.[1] These processes hold industrial importance to the present day.

The Nobel Laureates K Ziegler and G Natta laid the scientific foundation for catalytic ethylene and propylene polymerisation at moderate pressure and temperature.[2–7] These scientists have designed catalysts based on titanium chloride and alkylaluminium compounds, which are commonly known as Ziegler – Natta catalysts. The application of these catalysts and their analogues on the industrial scale took great efforts and years because of difficulties in elucidating the mechanism of action of catalysts, choosing the optimal structures of components of catalyst systems and finding conditions for the preparation of polymers with required properties and performance characteristics.

Montagna and Floyd[8] suggested a graphical interpretation of the evolution of catalytic olefin polymerisation as an S-shaped step curve (Fig. 1). This curve reflects the relationship between the level of technological solutions and the molecular architecture (structure) control of polymers, on the one hand, and the structural features of polymerisation catalysts and the time of their design, on the other hand. This plot was published in the recent handbook[9] of polyolefins for characterisation of the steps of perfection of olefin polymerisation processes.

An analysis of the plot presented in Fig. 1 shows that the progress in the control of the polymer structure is always associated with advances in the design of new high-performance and highly selective commercial catalysts.

In the first step of investigations of olefin polymerisation corresponding to the first step in the curve presented in Fig. 1, high-pressure ethylene polymerisation was performed in autoclave reactors. The technology of ethylene polymerisation (1500 atm, 200 °C) by the radical mechanism developed in

S S Ivanchev St Petersburg Department of G K Boreskov Institute of Catalysis, Siberian Branch of the Russian Academy of Sciences, prosp. Dobrolyubova 14, 197198 St Petersburg, Russian Federation.
Fax (7-812) 323 05 57, tel. (7-812) 323 09 85,
e-mail: ivanchev@SM2270.spb.edu

Received 22 January 2007
Uspekhi Khimii **76** (7) 669 – 690 (2007); translated by T N Safonova

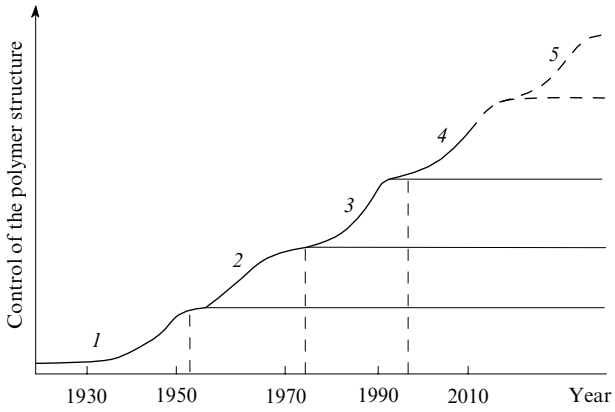


Figure 1. Evolution of olefin polymerisation catalysts.
(*1*) Low-density PE (non-catalytic radical process); (*2*) high-density PE and PP (Ziegler–Natta catalysts); (*3*) gas-phase polymerisation (supported catalysts); (*4*) preparation of homo-and copolymers with different microstructures (single-site catalysts and metallocenes); (*5*) copolymerisation of olefins with polar monomers, functionalised polymers and block copolymers (post-metallocene catalysts).

the late 1930s allowed the preparation of polyethylene with a specific structure. Macromolecules of this polymer contain both long-chain and short-chain branches (Fig. 2 *a*). The process equipment was improved to increase the performance and the degree of control over the structure of high-molecular-weight products with the use of a wider range of initiators (in addition to oxygen, peroxides with different structures). This led to an improvement of the properties and an extension of the assortment of PEs.

The second step in the PE production started in 1950s, when the Standard Oil Company (USA) began the commercial production of PE at moderate pressure ($\sim$40 atm) and temperature of $\sim$100 °C in the presence of an alumina-supported molybdenum oxide catalyst.[10] A new class of complex organometallic catalysts discovered by Ziegler and co-workers[2] in 1953 made a revolution in this technology, resulting in an increase in the efficiency of ethylene polymerisation under moderate pressure. Natta and co-workers[4–6] developed a procedure for stereospecific propylene polymerisation.

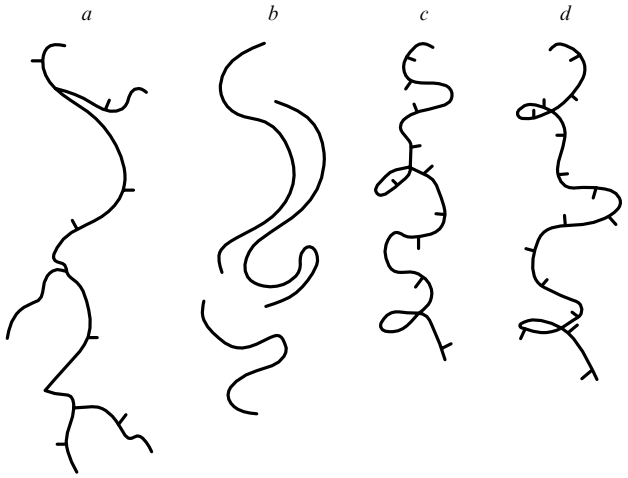


Figure 2. Structures of different types of polyethylene:
(*a*) Long-chain branches combined with short-chain branches; (*b*) unbranched polymer; (*c*) short-chain branches, whose regularity depends on MW; (*d*) short-chain branches (or the insertion of a comonomer) with a regular distribution in the chain.

There are three factors responsible for the unique technological and industrial advances in the improvement of properties and extension of the scope of application of polyolefins:

— strategy of the control over promising technologies to form materials with improved performance characteristics and an extension of the fields of their rational use;

— permanent perfection of the production processes and the improvement of the structure and properties of polymers, the design of new types of polyolefins;

— dynamism of the development of convenient technologies and the efficiency of introduction of modern technological solutions, which is a prerequisite for the design of materials with new properties and new possibilities of their application.

As mentioned above, the design of new-generation catalysts for olefin polymerisation, in-depth investigations of the mechanism of their action and the determination of conditions for their optimal use were and remain the driving force of the progress in studies in this field. Discoveries of higher-performance catalyst systems always led to the perfection of polyolefin production and new advances in the control of the molecular structures of polymers.

For example, the modification of Ziegler–Natta catalysts by electron-donor additives resulted in an increase in the activity and selectivity of the catalysts by two orders of magnitude.[11] The use of such catalysts allowed the simplification of the flow scheme for the polyethylene production (the polymer washing step is excluded) and the improvement of the efficiency of copolymerisation of ethylene with higher α-olefins. As a result, linear low-density polyethylene (LLDPE) was prepared.[11–23] This polymer consists of linear molecules with short-chain branches (see Fig. 2 *c*), and this is the difference from PE prepared earlier, which has a linear structure without branches and is characterised by a high density (see Fig. 2 *b*).

The design of catalyst systems supported on inorganic adsorbents (SiO_2, Al_2O_3 or $MgCl_2$) and, more recently, on polymer supports was an important breakthrough in the perfection of olefin polymerisation catalysts. This gives rise to a new version of the flow scheme, *viz*., gas-phase polymerisation. The Union Carbide Corporation (USA) was the first to employ this scheme in industry. Later on, this process was used also by other companies [British Petroleum, BASF (Germany), *etc*.]. Studies of the characteristic features of the behaviour of supported catalyst systems, primarily of $MgCl_2$-supported catalysts, which were independently performed by the Mitsui Chemical (Japan) and Montedison (Italy) Companies resulted in the design of catalysts allowing the control over the properties and polymer morphology. It appeared that these systems are able to replicate (reproduce the shape) the starting catalyst particles by the resulting polymer particles. This allowed the synthesis of granular polymers directly in a polymerisation reactor.[11,23–28]

A new step in the perfection of olefin polymerisation catalysts (1980s) was associated with investigations of so-called 'metallocene' catalysts based on coordination organometallic compounds. In these complexes, one or two cyclopentadienyl rings (including substituted rings) form a π bond with the central Group IVB, VB or VIB transition metal atom.[11,20,29–39] A new type of organoaluminium compounds, *viz*., poly(methylalumoxane) ($[-Al(Me)O-]_n$, MAO), was used for activation.[40]

In the 25-year metallocene epoch, about 700 patents were granted and more than 10 reviews and monographs devoted to this problem were published (see, for example, Refs 20, 29–31 and 33–39). The following aspects were considered: the evolution of the design of new structures of metallocene complexes, the mechanism of action of catalyst systems based on these complexes with the use of cocatalysts of different nature and the possibility of application of these complexes in

olefin polymerisation and copolymerisation. A detailed analysis of problems associated with the mechanism of olefin polymerisation in the presence of metallocene catalysts and the related publications are beyond the scope of the present review. Let us only note the most important aspects due to which this type of catalysts attracts great interest of researchers.

Metallocene catalyst systems are characterised by a number of important features:

— high activity † in ethylene polymerisation (up to 40 tons of PE per gram of transition metal for 1 h);

— the single-site character of the catalysis process;

— the similarity of the constants of copolymerisation of ethylene and higher α-olefins, which provides the uniform incorporation of α-olefins into the polymer chain regardless of the molecular mass of the copolymer (see Fig. 2 *d*);

— high performance in polymerisation and copolymerisation of a wide range of monomers;

— lower oxophilicity compared to Ziegler – Natta catalysts allowing polymerisation of monomers containing functional groups remote from double bonds.

Judging by numerous predictions, metallocene catalyst systems would replace Ziegler – Natta catalysts in the polyolefin production. However, their introduction occurred much more slowly than expected due primarily to a high price of the components of these catalysts and problems associated with processing of polyolefins.[41, 42]

To summarise the aforesaid, it can be stated that, in spite of great progress in studies of olefin polymerisation catalysts, a number of problems associated with the technology of these processes remain to be solved. For example, copolymers of ethylene and other olefins with various available comonomers containing polar groups cannot be prepared because of the oxophilic character of the components of metallocene catalyst systems. A search for ways for increasing the performance and selectivity of catalysts and controlling the morphology of the resulting polyolefins as well as the improvement of methods for stereochemical control of the growing chain are still important.

Many research teams were engaged in solving these problems. This gave rise to the subsequent step in the history of evolution of olefin polymerisation processes associated with the design of a radically new generation of catalysts. This step is represented by dashed line *5* at the top of Fig. 1 and corresponds to more perfect catalyst systems characterised by high performance and selectivity, a wider range of conditions (temperature and pressure), the possibility to control the catalytic properties by varying the oxophilicity of the ligand and the ability to control the polymerisation process. These catalysts should solve the problem of copolymerisation of ethylene with polar monomers and should be characterised by high efficiency, accessibility and the safe storage and use. In addition, the use of these catalysts provides the possibility of improving the structural characteristics of polyolefins, thus ensuring better recycling and performance characteristics of polymer materials.

First publications on new catalyst systems meeting the above-mentioned requirements date back only 10 years. Nevertheless, numerous papers, patents and reviews have been published during these years.[43 – 52] A new class of high-performance non-metallocene catalyst systems is referred to as 'post-metallocene catalysts'.‡

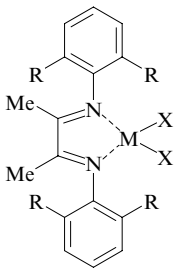
Most of the studies of olefin polymerisation catalysts published in the last decade are related to systems based on late transition metal complexes with nitrogen-containing ligands ('the nitrogen skeleton'). These are primarily nickel and palladium diimine complexes as well as iron and cobalt-bis(imino)pyridine complexes (see, for example, Refs 44, 45, 48, 49 and 51). A new type of post-metallocene catalysts based on phenoxy imine complexes of titanium, zirconium, hafnium and some other transition metals has attracted attention more recently.[47, 50, 52]

In Russia, investigations of post-metallocene catalyst systems started somewhat later. In this connection, the publication of a Russian review devoted to an analysis of the progress in this field will apparently attract interest of researchers concerned with catalytic olefin polymerisation.

II. Catalyst systems based on late transition metal α-diimine and bis(imino)pyridine complexes

1. α-Diimine complexes as catalysts for olefin polymerisation

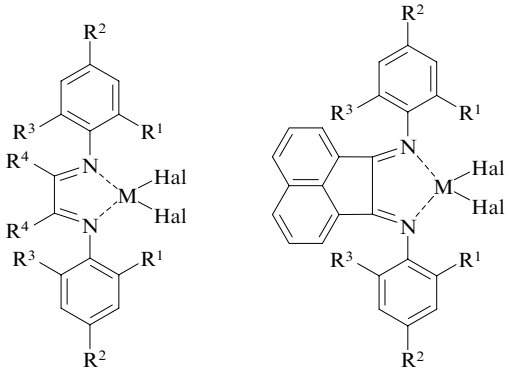
In 1995, the US research team headed by Brookhart obtained first successful results in the design and application of post-metallocene catalyst systems.[53 – 56] The authors demonstrated that ethylene, propylene and hex-1-ene polymerisation can be performed in the presence of nickel or palladium complexes (**1** and **2**, respectively) with bis(arylimine) ligands.



1, **2**

M = Ni (**1**), Pd (**2**); R = Me, Pr^i; X = Cl, Br, Me.

The results of investigations of these systems obtained in the first five years were summarised in the review.[45] α-Diimine fragments most often contain aryl substituents at the nitrogen atoms and are involved in an aliphatic or complex polyaromatic system (for example, the acenaphthylene system). The general structures of nickel and palladium α-diimine complexes can be represented as follows:



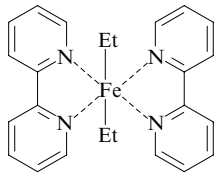
M = Ni, Pd; Hal = Cl, Br; R^1, R^2, R^3 = H, Alk, Ar; R^4 = H, Alk.

A sophisticated analysis of the published data on the synthesis and studies of late transition metal complexes with ligands containing the nitrogen skeleton demonstrated that studies by Brookhart were preceded by earlier investigations in

† Hereinafter, the activities of catalysts are given in units of (amount of a polymer) [mole (or gramme) of a catalyst]$^{-1}$ h^{-1}.

‡ The term 'post-metallocene catalysts' has been used for the first time in the review by Britovsek *et al.*[44]

this field. For example, Yamamoto *et al*. reported [57] the results of tests of catalysts based on cobalt and iron alkyl complexes with bipyridine ligands (for example, compound **3**), in polymerisation of acrylic acid derivatives, as early as in 1970. It is evident that these catalysts are similar to late transition metal α-diimine complexes.



3

Later on, it was demonstrated [57] that bipyridine complexes **3** are characterised by relatively weak coordination of the iron atom by bipyridine ligands. This facilitates side processes, such as β-hydride migration and reductive elimination. The termination of the polymer chain growth leads to fast deactivation of the catalyst [58] and, consequently, to a decrease in its activity. Because of these drawbacks, researchers have lost interest in this type of complexes.

It should be emphasised that the newly synthesised catalysts based on late transition metal complexes containing ligands with the nitrogen skeleton were covered by numerous patents. In the period from 1994 to 2001, 742 patents were issued (cited from the monograph,[51] p. 59), which is comparable only with the number of patents on the design of metallocene systems.

To perform olefin polymerisation, it is necessary to transform α-diimine complexes into the active form. Methylalumoxane or perfluoroaryl boron compounds (the latter are more suitable for complexes with the central palladium atom) are commonly used as activators (or cocatalysts). Somewhat later, it was demonstrated that simple alkyl derivatives of aluminium can also be used for these purposes.[59, 60]

Depending on the structure of the ligand and the reaction conditions, nickel and palladium α-diimine complexes can exhibit high activity in ethylene polymerisation to give PE with molecular weight (MW) varying in a wide range. For example, the performance of up to 11 (kg PE) $mmol^{-1}\ h^{-1}\ bar^{-1}$ was observed for some nickel derivatives,[53] PE with MW of up to 1 million was obtained at low temperatures. On the whole, nickel α-diimine complexes provide higher activity of catalysts in ethylene polymerisation and form polymers with higher MW compared to analogous palladium complexes.

Studies of the PE structures showed that new catalyst systems allow the preparation of polymers with short-chain (methyl, ethyl, butyl or longer) branches.

Based on low-temperature NMR spectroscopic data, the branch migration mechanism for ethylene polymerisation in the presence of nickel or palladium α-diimine complexes was suggested (Scheme 1).[45, 61, 62] The reactions of the complexes with cocatalysts and coordination with ethylene afford the inactive (latent) cationic form **A** and the polymer chain begins to grow. The formation of the growing linear chain can alternate with β-elimination of a hydride ion and the formation of alkenyl hydride complex **B**, whose transformation gives rise to methyl branching in the growing chain. The formation of the whole macrochain is a result of a combination or alternation of the chain growth and β-elimination of a hydride ion in the alkenyl hydride complex, resulting in the next branching.

According to this mechanism, catalyst systems based on Ni and Pd α-diimine complexes afford polymers with methyl branches. Several successive β-hydride transfer reactions give rise to short-chain ethyl, propyl or other (longer) α-alkyl branches. These catalysts are very promising because they allow the preparation of short-chain branched polyethylenes without the use of comonomers.

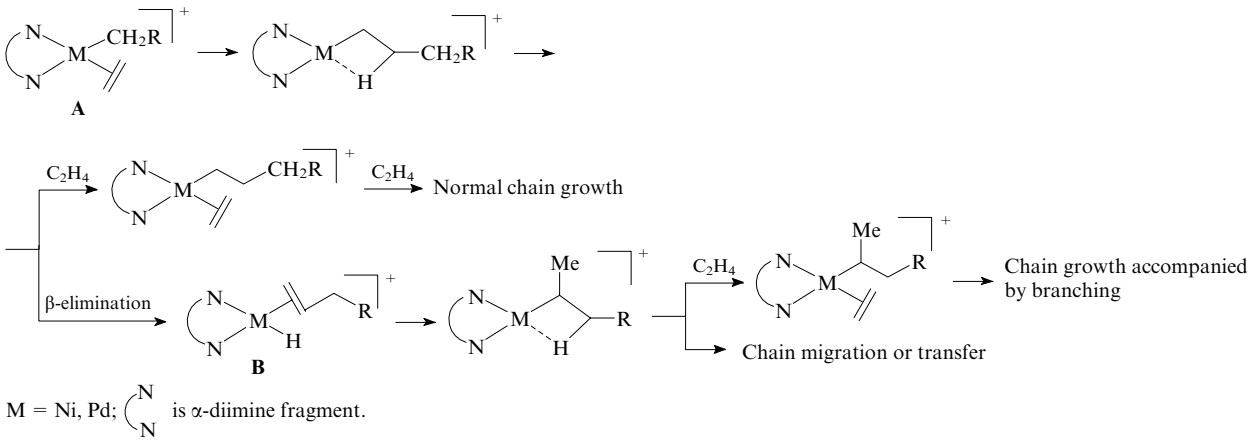
For palladium systems, the barrier to ethylene insertion by the migration mechanism was estimated [53, 63] at 17–18 kcal mol^{-1} (the lowest barrier is observed for the bulkiest imine ligands), whereas this barrier for nickel systems is substantially lower (13–14 kcal mol^{-1}). Therefore, the energy difference of 4–5 kcal mol^{-1} is consistent with higher activity of nickel complexes observed in experiments.

In the presence of palladium catalysts, the branching of PE is independent of the monomer pressure in the polymerisation process. However, the ethylene pressure influences the polymer morphology. At moderate pressures, polymerisation affords viscous amorphous oils; at high pressures, amorphous rubber-like solids, plastomers (Fig. 3).

In the case of nickel complexes, the degree of branching of PE is always lower than that obtained with the use of palladium analogues, and this degree decreases with increasing ethylene pressure. The sensitivity of the degree of branching of the product to the pressure is a result of a competition between two processes, *viz*., trapping of ethylene by the active complex and the chain transfer. High pressures are favourable for trapping of ethylene, resulting in a lower degree of branching.

Polymerisation on diimine catalysts giving high-molecular-mass polymers is characterised by a much higher chain growth rate compared to the chain transfer rate. An increase in steric crowding of the axial regions in the square plane of the complex is the key factor responsible for a decrease in the chain transfer rate.[45] The crystallographic data show that the benzene rings in square-planar palladium α-diimine complexes are located approximately perpendicular to the plane of the square, and the *ortho* substituents are located above and below this plane.

Scheme 1



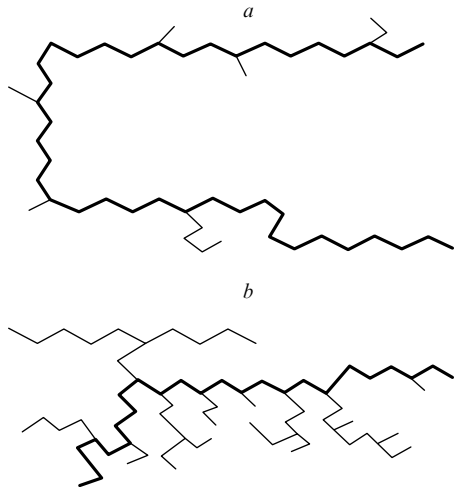


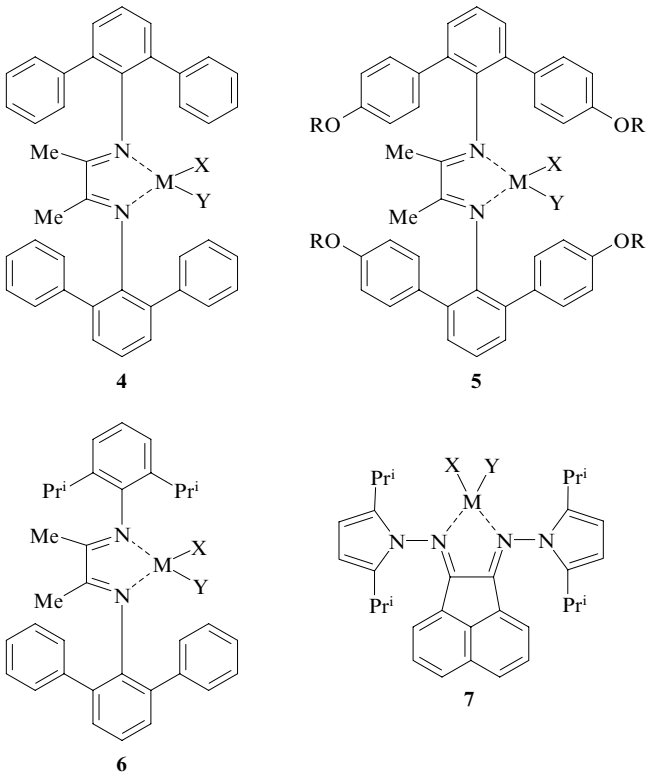
Figure 3. Branched structures formed upon ethylene polymerisation: plastomers (*a*) and hyperbranched low-molecular-weight compounds (oils) (*b*).

Important investigations aimed at optimising the structures of diimine catalyst systems involve variations of the nature of substituents in the ligand and the elucidation of their influence on the characteristics of the resulting polymers. For example, the detailed theoretical investigation of nickel complexes with various diimine ligands was carried out.[64] An increase in the bulkiness of substituents at the nitrogen atom was demonstrated to play a dual role. First, these groups block the access to the transition metal atom in the axial direction. This destabilises the inactive (latent) state of the catalyst and the chain termination transition state, in which both axial positions are occupied. Second, the aryl rings in nickel complexes, unlike those in palladium analogues, are located in one plane with the diimine fragment, which is favourable for stabilisation of the transition state of ethylene insertion compared to the latent state of the catalyst. An increase in the bulkiness of substituents either at the carbon atoms or in the *ortho* positions of the aryl groups at the nitrogen atoms of diimine results in a more rigid fixation of the plane of the aromatic ring perpendicular to the metal–ligand coordination plane. In this case, *ortho* substituents more efficiently block the axial directions.[65]

In particular, the 2,3-bis(2,6-dimethylphenyl)butanediimine nickel dichloride complex (**1**, R = Me, X = Cl) is one of the most active catalysts in this class.[66] Ethylene polymerisation on this catalyst activated by MAO affords PE characterised by the number average MW (M_n) in the range of $(1.7-6)\times10^5$ and a rather narrow molecular weight distribution (MWD) of 2.0–3.5. The degree of branching increases, whereas MW decreases as the temperature of the process is increased. The polymer branching is virtually independent of the Al : Ni molar ratio and the concentration of the catalyst.

Therefore, the main structural feature of ligands in late transition metal α-diimine [as well as bis(imino)pyridine, see below] complexes and catalysts based on these complexes is that the active cationic centre is sterically shielded by bulky *ortho*-substituted aryl groups at the nitrogen atom, resulting in suppression of side processes of chain termination (elimination of the hydrogen atom from the β position and the associative substitution of olefins) during polymerisation. The ability to provide efficient stabilisation of organometallic complexes that are formed in the reactions with monomers is another important property of these ligands. The electronic structure of ligands is rather flexible because it is determined primarily by the nature of substituents in *N*-aryl groups. These characteristic features were observed in many experimental[45,48,49,51,53–58,67–70] and theoretical[60,64,65,71,72] investigations.

Therefore, the activity of α-diimine catalysts based on nickel and palladium complexes in olefin polymerisation was substantially increased by changing the structure of the ligand, to be more precise, by introducing bulky aryl substituents at the *ortho* positions of the phenyl rings at the nitrogen atoms of the imine fragments.[51] Recently, new Ni and Pd complexes with the use of various types of ligand variation were synthesised.[73–75] For example, complexes having symmetric (**4** and **5**) or non-symmetric (**6**) structures and complexes with heteroaromatic substituents (**7**) were prepared.



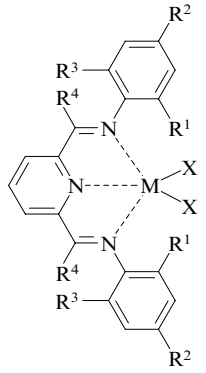
4 **5** **6** **7**

M = Ni, Pd; X, Y = Hal, Me; R = Alk.

The activity of catalyst systems based on compounds **4**–**7** in ethylene polymerisation and MW of polymerisation products appeared to be similar to the corresponding characteristics for complexes, which have been studied earlier by Brookhart. The highest performance was observed for the catalyst based on compound **5**. These systems are characterised by the dependence of the degree of branching of PE and, consequently, of its glass-transition temperature (T_g) on the structure of ligands. For example, complexes **4**, **5** and **7** allow the synthesis of virtually linear PE. In addition, polymerisation in the presence of complex **6** containing unsymmetrical ligands affords PE characterised by a lower degree of branching compared to a polymer prepared with the use of structurally similar Brookhart's complexes. Polymerisation in the presence of catalyst systems based on complexes **7** with peripheral heterocyclic substituents affords polymers with lower MW. It should be noted that an analogous situation is observed for complexes containing other heteroaromatic substituents (for example, indoles, *etc.*) instead of the pyrrole rings.

2. Bis(imino)pyridine complexes as olefin polymerisation catalysts

Several years after the discovery of α-diimine catalysts for olefin polymerisation, Brookhart and co-workers [45, 76, 77] in USA and the research group headed by Gibson [48, 78–84] in UK simultaneously and independently published data on the design and examination of iron and cobalt 2,6-bis(arylimino-alkyl)pyridine [hereinafter, referred to as bis(imino)pyridine] complexes.

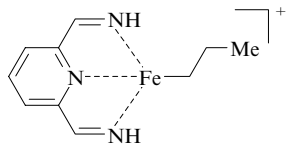


M = Fe, Co; X = Cl, Br; R^1, R^2, R^3 = H, Alk, Ar; R^4 = H, Alk.

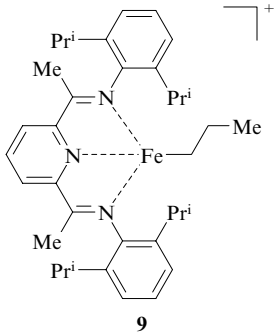
Iron complexes with $R^1 = R^3$ = Me, Pr^i or Bu^t, R^2 = H, R^4 = Me and X = Cl, Br or NO_3 were the first representatives of this type of compounds.[77] A short time later, other researchers were also engaged in the synthesis of complexes with *N*-tridentate ligands (see, for example, Ref. 85).

The characteristic structural feature of these complexes is that the metal atom in them has the coordination number 5 and a pseudosquare-pyramidal coordination geometry with the phenyl rings being virtually perpendicular to the plane of the square. High-molecular-weight polyethylene (M_w up to 7×10^5) was prepared on these catalysts in high yield upon activation by modified methylalumoxane (MMAO) in the presence of ethylene in toluene. As opposed to Ni(II) and Pd(II) diimine catalysts, linear (without branches) PE is formed under analogous conditions even in the presence of bulky ligands in the complexes and at low ethylene pressure. The molecular weight of the polymer varies in a wide range depending on the type of the ligand, the nature of the central metal atom and the concentration of the cocatalyst. As in the above-considered diimine complexes, the bulkiness of the aryl fragments at the imine nitrogen atoms in the ligands in Fe and Co bis(imino)pyridine catalysts plays an important role. Thus, an increase in the bulkiness of the *ortho* substituents also leads to an increase in the activity of the catalyst system.

The mechanism of ethylene polymerisation with the use of catalysts based on Fe(II) bis(imino)pyridine complexes was analysed in detail [86] using quantum chemical calculations by the density functional theory (DFT) method and in combination with the molecular mechanics method. The calculations were carried out for the active state of the catalysts, *viz*., for the model (**8**) and real (**9**) cationic complexes.



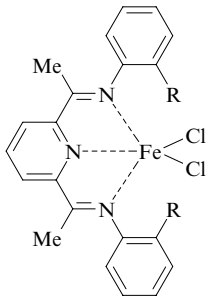
8



9

The trapping of ethylene by the cationic metal alkyl complex was demonstrated [86] to be the rate-determining step of both the chain growth and termination. The mechanism of chain termination involves the β-hydride transfer of the growing chain to the monomer in the active centre as the major process (see Scheme 1). As in the case of α-diimine ligands, the presence of bulky aryl groups containing substituents in the *ortho* positions at the imine nitrogen atom (for example, 2,6-$Pr^i_2C_6H_3$) is desirable for the highest performance. In the presence of complexes with such substituents, the chain termination is suppressed and the rate of monomer insertion into the growing chain increases.

The group headed by Brookhart found [45] that bis(aryl-iminoethyl)pyridine complexes **10**–**12** containing only one *ortho* substituent in each benzene ring are superactive catalysts for ethylene oligomerisation.



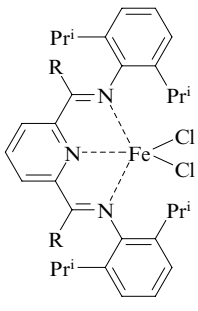
10–**12**

R = Me (**10**), Et (**11**), Pr^i (**12**).

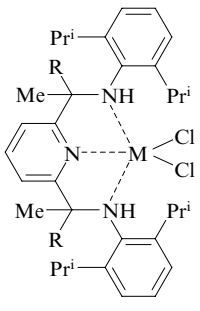
It should be noted that this fact is consistent with the results of our investigation [68] of ethylene oligomerisation with the use of substituted diimine complexes.

In the study,[83] the dependence of the kinetic activity of bis(imino)pyridine complexes in ethylene polymerisation on their structure (primarily, on the size of substituents in the *ortho* position of the arylimine fragment) was found and the molecular characteristics of PE were determined. These characteristics are also not contradictory to the above-considered data.

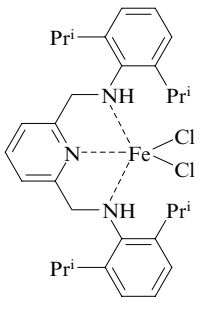
Ethylene polymerisation in the presence of iron complexes with various tridentate nitrogen-containing ligands, such as 2,6-bis(aryliminoalkyl)pyridine (**13**, **14**), 2-arylaminoalkyl-6-aryliminoalkylpyridine (**15**, **16**) and 2,6-bis(arylaminomethyl-pyridine) (**17**), and cobalt complex **18** combined with the cocatalyst MAO was investigated.[84] Compounds containing bis(imine) fragments were demonstrated to have higher catalytic activity than bis(amine) and aminoimine derivatives; complexes with ketimine ligands are more active than complexes with aldimine ligands. Cobalt complex **18** is less active than its iron analogue **15**.



13, **14**



15, **16**, **18**



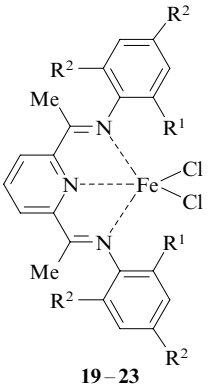
17

M = Fe: R = H (**13**, **15**), Me (**14**, **16**); M = Co, R = H (**18**).

It was noted that lower activity of amine complexes compared to bis(imino)pyridine analogues is possibly attributed to a relatively weak bond between amine and the iron atom, whose cleavage results in dissociation of the amine fragment. In addition, insufficiently strong conjugation of the ligand environment and the spatial orientation of the aminoaryl substituent, which hinders access of the monomer to the catalyst active site and, correspondingly, the growth of the polymer chain, can also play a particular role.

On the whole, ethylene polymerisation catalysts based on transition metal bis(imino)pyridine complexes are attractive because they are synthetically accessible and inexpensive,[87] allow the synthesis of products with both narrow and wide MWD and can be activated by various alkyl derivatives of aluminium.[59,60] The main drawbacks are relatively low thermal stability, which is manifested in a considerable decrease in the catalytic activity of the system as the temperature rises (by a factor of two and nine as the temperature rises to 50 and 70 °C, respectively, compared to the activity at the optimal temperature of 35–40 °C). In addition, an increase in the polymerisation temperature leads to a sharp decrease in MW of polyethylenes prepared with the use of these catalysts. Attempts to eliminate this drawback were made in several studies.

Our research team made a considerable contribution to the solution of this problem.[88,89] For example, we demonstrated that the temperature range, where catalysts based on complexes **19**–**22** containing cycloalkyl substituents in the *ortho* position of the arylimine group exhibit high performance, can be shifted to higher temperatures.



19–**23**

R^2 = Me, R^1 = cyclo-C_nH_{2n-1} [n = 5 (**19**), 6 (**20**), 8 (**21**), 12 (**22**)];
$R^1 = R^2 = Pr^i$ (**23**).

Ethylene polymerisation was performed in toluene using the catalyst : activator (MAO) ratio of 1 : 1500 at ethylene pressure of 0.3 MPa; the reaction time was 1 h.[89] The curves of the temperature dependence of the activity of catalyst systems based on iron bis(imino)pyridine complexes with cycloalkyl substituents **19**–**22** and reference complex **23** containing isopropyl substituents at positions 2, 4 and 6 of the arylimine groups are presented in Fig. 4. It can be seen that the activity of catalyst **23** sharply decreases at temperatures higher than 50 °C, whereas the optimal temperatures for cycloalkyl-substituted complexes are higher, this effect being more pronounced as the number of the methylene groups in the ring is increased. The experimental results were confirmed by quantum chemical calculations for the complexes in question.[88,89]

A generalised analysis of the influence of the structure of transition metal complexes with α-diimine and bis(imino)-pyridine ligands on the activity of catalyst systems based on these ligand was performed in the Polymer Research Laboratory of the BASF Company (see the monograph,[51] pp. 59–98). The authors confirmed that the key feature of the ligand

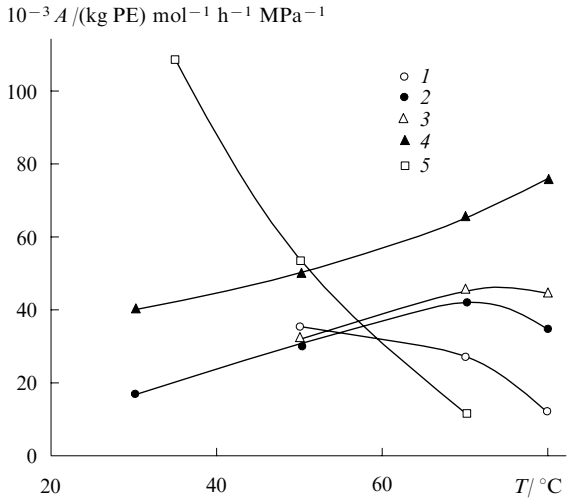
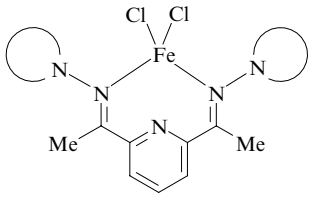


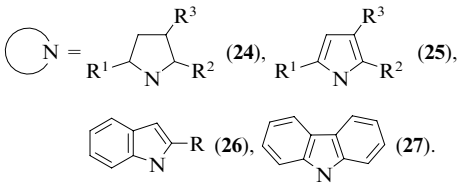
Figure 4. Plot of the activity of complexes **19**–**23** (curves *1*–*5*, respectively) *vs.* the temperature of ethylene polymerisation.[89]

structure of these catalysts is that the active cationic centre is sterically shielded to an extent sufficient to suppress undesirable chain termination processes (primarily, β-hydride elimination and associative substitution of olefins in active complexes). Steric shielding can be provided, for example, by bulky *ortho*-substituted aryl groups bound to the peripheral donor centres (imine nitrogen atoms).

The results of studies of nontraditional substituents at the imine nitrogen atoms of α-diimine and bis(imino)pyridine ligands, for example, of nitrogen-containing heteroaromatic groups, made a substantial contribution to knowledge about the influence of the structure of complexes on their activity. Earlier, when considering the catalytic activity of α-diimine systems containing *N*-pyrrole rings, we have demonstrated that the degree of branching of PE in polymerisation can be changed (decreased or completely suppressed). An similar effect was observed also in the presence of symmetrical (**24**–**27**) or unsymmetrical (**28**) iron bis(imino)pyridine complexes with peripheral *N*-heterocyclic substituents.[51]

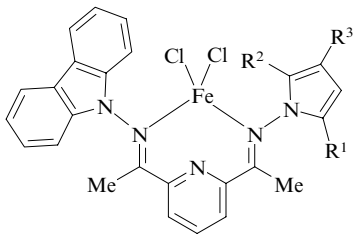


24–**27**



(**24**), (**25**),

(**26**), (**27**).



28

A comparison of the polymerisation activity of systems based on complexes **24**–**28** in ethylene polymerisation with that of the most active classical Brookhart–Gibson catalysts showed that the activity of the former catalyst systems is rather high, but MW of PE prepared with their use is substantially lower. The molecular mass was increased by increasing the bulkiness of the peripheral *N*-azolyl substituents in the catalyst, but this led to a decrease in activity. However, the most substantial difference is that the reaction mechanism changes. Polymerisation with the use of complexes **24**–**28** affords branched polymeric or oligomeric products, whereas polymerisation with the use of Brookhart–Gibson complexes studied earlier gives linear products.

The above-considered data show that there is a fine equilibrium between the following two processes that occur during ethylene polymerisation catalysed by transition metal bis(imino)pyridine complexes: the monomer insertion resulting in the formation of linear PE and β-hydride elimination with the repeated addition of the isomerised chain giving rise to branched structures. This equilibrium substantially depends on the steric and electronic effects of peripheral substituents in catalytic complexes, whose nature (for example, the introduction of the *N*-azolyl fragment instead of the *N*-phenyl group) determines the mechanism of polymer formation. The chain growth can give rise to either linear or branched structures with the use of both α-diimine and bis(imino)pyridine complexes.

When analysing new complexes containing ligands with the nitrogen skeleton, the recently synthesised oligomeric nickel α-diimine complexes[90] and iron bis(imino)pyridine complexes[91] deserve note. Unfortunately, the results of examination of these complexes in ethylene polymerisation were not reported in the study cited.[90] However, in the presence of polyfunctional oligomeric bis(imino)pyridine complexes **29** and **30** (these complexes were synthesised by our group[91]) activated by MAO, polyethylenes with high MW were obtained at high temperatures (70–90 °C), *i.e.*, the temperature range of high performance of the catalyst system was extended.

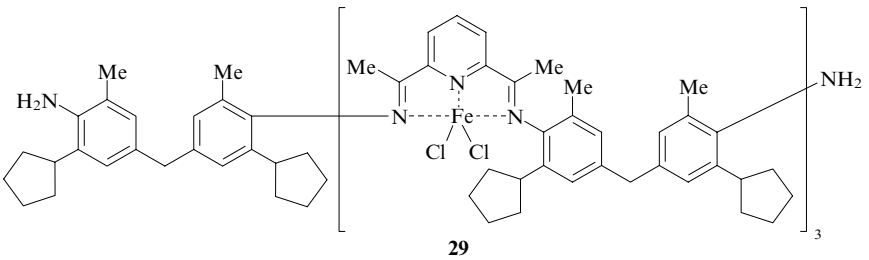
Bis(imino)pyridine complexes not only with the central divalent iron atom but also with other transition metals, such as cobalt, nickel, vanadium, copper, zinc, chromium and manganese, were synthesised. The results of research into the activity of catalyst systems based on various metals were considered.[92–96] Divalent iron complexes exhibited the highest activity in ethylene polymerisation, whereas Fe(III) complexes proved to have low activity. Divalent cobalt complexes, which were synthesised virtually simultaneously with the iron analogues, are generally substantially less active than the latter. However, Co(II) complexes in the presence of MAO show higher activity in polymerisation of vinyl ethers than the corresponding iron complexes.[97] Divalent cobalt complexes containing electron-accepting substituents exhibit high activity also in selective dimerisation and oligomerisation of α-olefins.[98]

Vanadium bis(imino)pyridine complexes were documented.[99] Detailed studies of the influence of the structure of complexes on the properties of the reaction products demonstrated[100, 101] that olefin polymerisation in the presence of vanadium systems gives mainly oligomeric products.

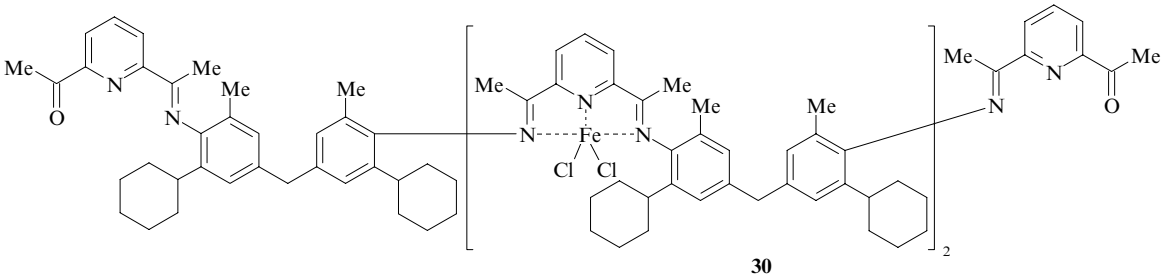
Chromium complexes analogous to iron bis(imino)pyridine complexes have received little study as olefin polymerisation catalysts. As a rule, these complexes exhibit lower activity than the above-considered iron, cobalt and vanadium complexes and often form low-molecular-weight products.[101, 102]

The differences in the behaviour of iron and cobalt 2,6-bis(imino)pyridine complexes activated by modified methylalumoxane in ethylene polymerisation under homogeneous conditions were noted in the recent publication by Kissin *et al.*[103] Cobalt complexes form virtually single-site catalysts with MMAO, whereas iron complexes give multisite (polyfunctional) catalysts, whose character depends on the Al : Fe ratio, the ethylene pressure, the temperature and the nature of substituents in the ligands.

In recent years, great attention has been given to the mechanism of action of Fe(II) 2,6-bis(imino)pyridine complexes in ethylene polymerisation, including the determination of key intermediates. For example, based on the results of ^{1}H and ^{13}C NMR spectroscopic studies of the structures of intermediates formed in homogeneous systems in the reactions of the complexes with an activator, it was concluded[104] that individual Fe(II) complexes rather than cationic intermediates are active components of the catalyst system. In more recent studies,[105–108] this conclusion was reviewed and it was hypothesised that neutral complexes in these systems are precursors of active sites for ethylene polymerisation. The schemes of the transformations of these complexes into active sites were proposed. The influence of activators, *viz.*, various alkyl derivatives of aluminium, on both the activity of the Fe(II) 2,6-bis(imino)pyridine complex and the characteristics of the resulting polyethylene (MW, MWD and the molecular structure) was analysed.[108] In this study, data on the number of active sites and the rate constants of chain growth in ethylene polymerisation were obtained.

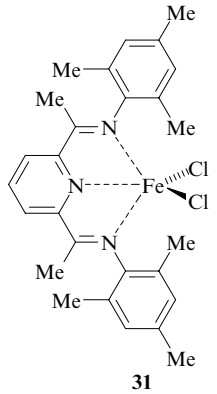


29



30

New views of the mechanism of influence of alkylaluminium cocatalysts AlR_3 (R = Et, Bu^i or n-C_6H_{13}) on the activity of iron bis(imino)pyridine complex **31** were reported in the recent publication.[109]



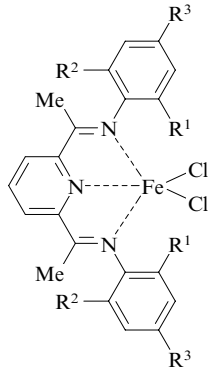
31

It was found that the activity of catalyst systems and the structure, MW and MWD of PE depend on the polymerisation temperature and the Al : Fe molar ratio. The analysis of *in situ* UV-Vis spectra suggested the formation of two types of catalytic species, *viz*., LFeRCl and $LFeR_2$ (L is 2,6-bis-[1-(2,4,6-trimethylphenylimino)ethyl]pyridine), the predominant formation of wich being determined by the Al : Fe molar ratio. The $LFeR_2$ compound has lower activity and favours the formation of low-molecular-mass branched polyethylenes.

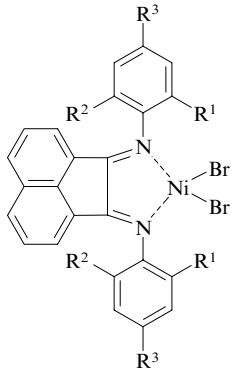
It should be noted that catalysts with the nitrogen skeleton, in particular, α-diimine complexes, can be involved in two-component catalyst systems for olefin polymerisation (the method of reactor mixing). These mixtures (provided that the components are compatible and the catalytic activity is not decreased) are synthesised with the aim of changing the structure and molecular characteristics of PE. Reactor mixtures of PE were prepared by combining two catalyst systems, which provide the modification of polymers in the course of the synthesis, with the possibility of controlling their MW and achieving wider MWD.[110]

The reactor mixtures of PE have been prepared earlier with the use of two-component systems based on Ziegler – Natta catalysts and late transition metal complexes, as well as of metallocene and α-diimine systems.[111, 112]

For these purposes, our research group used two-component heterobimetallic catalyst systems consisting of α-diimine and bis(imino)pyridine complexes.[113] The kinetic features of ethylene polymerisation on methylalumoxane-activated catalysts involving 2,6-bis(imino)pyridyl complexes of iron dichloride **14** and **20** and 1,2-bis(imino)acenaphthyl complexes



14, **20**



32, **33**

R^1 = cyclo-C_6H_{11}, R^2 = R^3 = Me (**20**, **32**);
R^1 = R^2 = Pr^i, R^3 = H (**14**, **33**).

of nickel dibromide **32** and **33** were studied at different ratios of the components in the temperature range of 50 – 70 °C.

These components were confirmed to be compatible in one reactor, and it was demonstrated that they can be efficiently used (at high rates) to synthesise polyethylene with different MW and short-chain branches. A mixture of complexes **14** and **32** proved to be an optimal combination of the components of a binary catalyst system, which retains high activity and gives rise to branched polyethylenes with satisfactory molecular characteristics.

3. Compolymerisation of ethylene with polar monomers in the presence of catalysts based on α-diimine and bis(imino)pyridine complexes

The structures and low oxophilicity of late transition metal complexes containing ligands with the nitrogen skeleton hold promise for their use as catalysts for copolymerisation of ethylene with polar monomers.

For example, catalyst systems based on palladium α-diimine complexes were successfully used by Brookhart and coworkers [53, 54, 56] for copolymerisation of ethylene and propylene with monomers containing functional groups. Methyl acrylate, *tert*-butyl acrylate, methyl vinyl ketone and fluorooctyl acrylate served as polar comonomers; the process was carried out in the presence of the [LPdMeCl] – $NaBAr_4$ systems (L is the α-diimine ligand) using the catalyst in an amount of 0.1 mmol per mole of the monomer in CH_2Cl_2 at 25 – 35 °C for 18 – 37 h. High-molecular-mass random polymers, which are amorphous highly branched structures with approximately 100 branches per 1000 carbon atoms, were synthesised. These polymers are characterised be the predominant arrangement of the ester groups at branches or at the ends of the chain (Fig. 5). The glass-transition temperature of these products varies from −67 to −77 °C. The maximum degree of introduction of the comonomer was 12.1%, 0.7%, 1.3% and 5.6% for methyl acrylate, *tert*-butyl acrylate, methyl vinyl ketone and fluorooctyl acrylate, respectively.

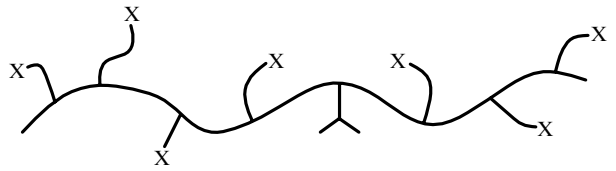


Figure 5. Structure of copolymers of ethylene with acrylates prepared with the use of Pd-(α-diimine) catalysts (X are acrylate groups).

The introduction of functional groups of amines and nitriles into the polymer chain of polyolefins was reported.[114] The efficiency of binding of the metal centre of the catalyst to the fragments of the $CH_2{=}CH(CH_2)_nX$ monomers (X = CN, NH_2 or NMe_2), *viz*., the *N*-containing polar group and the π-system of the double bond, was compared [115] by the density functional theory method. The energies of stabilisation of π- and *N*-complexes of monomers with Ni(II)- and Pd(II)-based catalysts containing diimine and salicylaldiminate ligands were calculated, and the energy diagrams of their decomposition were constructed. It appeared that π coordination of a monomer to metal is more favourable for systems with the central palladium atom, which provides the further growth of the polymer chain. In the presence of nickel catalysts, stronger metal – nitrogen bonds are formed and the latter hinder efficient copolymerisation, which accounts for the lack of success in ethylene copolymerisation with the use of this type of systems.

Chien *et al.*[116] successfully performed copolymerisation of ethylene with a series of polar monomers, such as hex-5-en-1-ol, undec-10-enoic acid, methyl vinyl ketone, vinyl acetate and ε-caprolactam. The authors modified the catalyst system by activating bis(imino)acenaphthene nickel(II) dihalide with a mixture of methylalumoxane (or diethylaluminium chloride) and dibutylmagnesium.

In the review,[117] the optimal structures of nickel and palladium diimine complexes were proposed for copolymerisation of ethylene with polar monomers and the mechanism of formation of copolymers with polar functional groups was analysed based on the results obtained by the research teams headed by Brookhart and Chien. As a result of the electron distribution in the complexes, these palladium catalysts are polar compounds due to which they readily form highly branched PE, and provide the introduction of polar (in particular, acrylate) fragments into the ends of branches in copolymerisation reactions (see Fig. 5).

It should be noted that the possibility of polymerisation of methyl methacrylate in *o*-xylene at 90 °C in the presence of divalent iron complexes with tetradentate nitrogen-containing ligands, for example, with [*N,N′*-diphenyl-*N,N′*-di(quinolin-2-ylmethyl)]-1,2-ethylenediamine (using ethyl 2-bromoisobutyrate as the initiator) was demonstrated for the first time in the recent publication by Seppälä and co-workers.[118] In this case, iron complexes catalyse the so-called atom transfer radical polymerisation (ATRP).

4. Supported catalyst systems based on α-diimine and bis(imino)pyridine complexes

As mentioned above, catalyst systems based on α-diimine and bis(imino)pyridine complexes are characterised by relatively low thermal stability and, as a consequence, rapidly lose activity during high-temperature polymerisation. The use of catalysts adsorbed on the surface of inorganic supports is a way to overcome this drawback.[119] Experiments with supported catalyst systems demonstrated that they not only have high thermal stability but also allow the synthesis of polymers with substantially higher MW, improve their morphology and density and prevent adsorption of polymers on the walls of the reactor.

Patents [120, 121] on the preparation of supported α-diimine and bis(imino)pyridine complexes were issued shortly after the discovery of post-metallocene catalysts. These supported catalyst systems were studied in detail.[122, 123] A comparison of the efficiency of ethylene polymerisation in the presence of the MAO-activated 2,6-bis[1-(2,6-diisopropylphenylimino)ethyl]-pyridine complex of iron dihalide under homogeneous conditions and in the presence of the SiO_2-supported complex showed [123] that the activity of the supported system is 5 times lower. However, the polymer formed on the supported catalyst has higher MW and better morphology.

Our research group [124] studied the kinetic features of ethylene polymerisation in the suspension and gas-phase modes in the presence of SiO_2-supported 2,6-bis(arylimino)-pyridine complexes of iron chloride and 1,2-bis(arylimino)acenaphthyl complexes of nickel bromide containing cycloalkyl substituents in the *ortho* positions of the aryl groups. We prepared supported catalysts under the conditions described in the patents.[120, 121] It was found that supported catalyst systems based on iron bis(imino)pyridine complexes **19**–**22** allow a decrease in the amount of the required activator (the optimal Al : Fe ratio is 110). The kinetic characteristics of polymerisation were steady in time (during > 1 h), whereas a sharp decrease in the polymerisation rate during the process was observed for the analogous homogeneous catalyst. For supported systems, the pattern of the dependence of the catalytic activity on the bulkiness of the cycloalkyl substituent in the *ortho* position of the aryl ring also changes. In the latter case, complex **20** with the cyclohexyl group showed the highest performance, whereas the activity of the corresponding homogeneous analogues increases with increasing bulkiness of the substituent in the series cyclopentyl (**19**) < cyclohexyl (**20**) < cyclooctyl (**21**).

In the presence of substituted 1,2-bis(imino)acenaphthyl complexes of nickel bromide (for example, compound **32**), polymerisation proceeds without the additional (except for the step of catalyst deposition) introduction of a cocatalyst. The kinetic profile of the process is generally similar to that observed with the use of bis(imino)pyridine systems.

In the very recent study by Zakharov and co-workers,[125] the characteristic features of ethylene polymerisation in the presence of the 2,6-[$(2,6\text{-}Me_2C_6H_3N{=}CMe)_2C_5H_3N$]$FeCl_2$ (**34**) complex activated by various alkyl derivatives of aluminium, such as MAO, $AlMe_3$, $AlBu^i_3$ and $Al(n\text{-}C_8H_{17})_3$, were investigated. The catalytic behaviour of these systems under homogeneous conditions was compared with that of the systems supported on SiO_2, Al_2O_3 or $MgCl_2$. The supported catalysts showed high activity, retained stability up to 70–80 °C and gave higher-molecular-mass products. The polymers synthesised with the use of both homogeneous and supported systems were characterised by rather wide MWD. The authors also compared the number of active sites and determined the rate constants for chain growth in the presence of both types of catalysts. It should be noted that these constants for the homogeneous and heterogeneous systems were of the same order in the beginning of the process. However, in the presence of the supported catalysts, these constants remained virtually unchanged with time, whereas they were decreased by a factor of three already within 5 min of polymerisation in the presence of the homogeneous catalysts. The absolute values of the effective rate constants for chain growth [125] for the homogeneous systems (2.6×10^4 litre $mol^{-1}\ s^{-1}$) are rather similar to those for the supported systems [$(1.2-2.4) \times 10^4$ litre $mol^{-1}\ s^{-1}$], whereas the numbers of the active sites are substantially different. In the case of the supported systems (0.028–0.032 mol per mole of Fe), this number is lower than that for the homogeneous systems (0.41 mol per mole of Fe). Unfortunately, this fact remained unexplained.

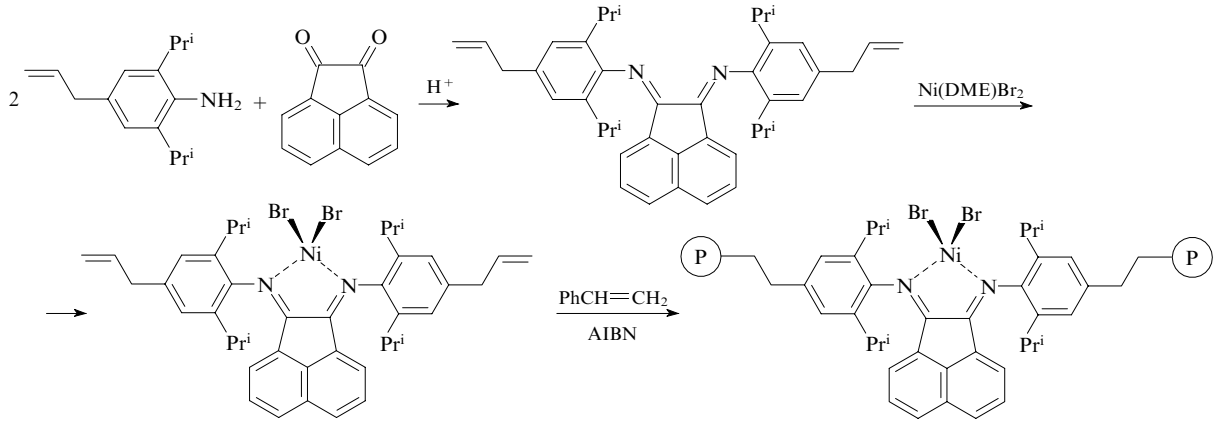
The interaction of the bis(imino)pyridine complex of divalent iron with oxide supports was studied by diffuse reflectance IR spectroscopy.[126] This study showed that the complex was strongly fixed possibly as a result of interactions of the ligand with several hydroxyl groups on the oxide surface, the geometric arrangement of these groups favours a multisite (according to the nomenclature used by the authors) contact. In aluminium oxide, both hydroxyl groups and Lewis acid sites are located on the surface, which provides stronger binding of the nitrogen-containing ligand to the support.

In the case of formation of supported catalysts on the surface of $MgCl_2$, the $LFeCl_2$ complex [L is the bis(imino)-pyridine ligand] interacts only with Lewis acid sites of activated magnesium chloride.[127] Consequently, when choosing the conditions for deposition of the catalyst system, it is necessary to take into account the character of its interaction with the support. A characteristic feature of the behaviour of nickel α-diimine complexes immobilised on $MgCl_2$ is that the particle shape of the dispersed catalyst system is replicated by the polymer formed on this system.[128]

The scope of action and the elucidation of the optimal conditions for the preparation of SiO_2-supported two-component catalyst systems based on α-diimine and bis(imino)-pyridine complexes were described in our study.[129]

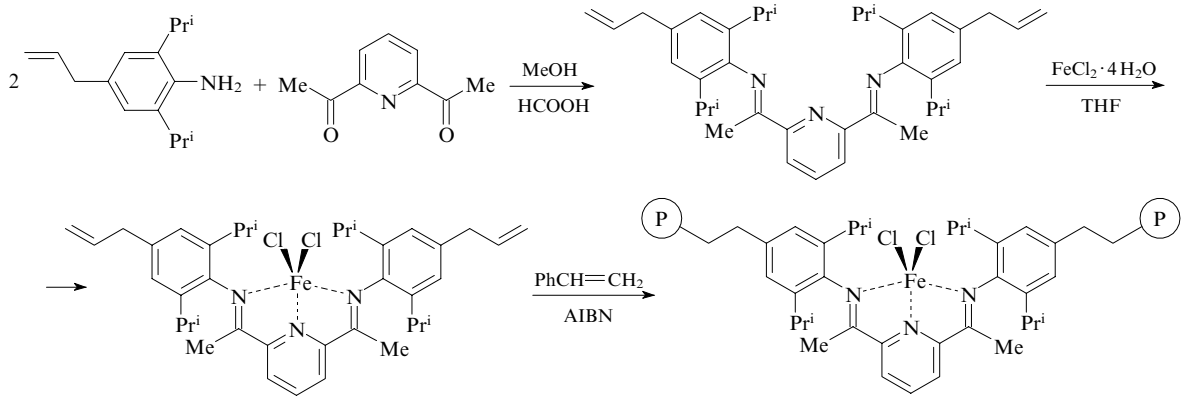
Recently, an original procedure for immobilisation of nickel α-diimine complex **35** (Scheme 2) and iron bis(imino)-pyridine complex **36** (Scheme 3) on a polymeric support (polystyrene) has been published.[130] These catalysts were

Scheme 2



DME is dimethoxyethane, AIBN is azobis(isobutyronitrile), (P) is polystyrene.

Scheme 3



called polymerised catalysts. Copolymerisation of an excess of styrene with comonomer complexes in toluene afforded copolymers with low molecular weight (MW ~ 10 000) involving the catalytic complex.

Procedures for the synthesis of the corresponding ligands and complexes containing alkenyl groups, capable of polymerisation, were reported.[131–134] A procedure was developed for the preparation of an SiO_2-supported polymerised catalyst as spherical particles with a core–shell structure.[130]

The resulting polymerised systems were examined as ethylene polymerisation catalysts in the suspension mode using activation by MMAO. These catalysts showed high activity and gave good results as regards the replication ability in the formation of polymer particles, which confirms the prospects of this field of investigation.

III. Phenoxy-imine catalysts for olefin polymerisation

1. General views

A new generation of post-metallocene catalysts for olefin polymerisation based on transition metal phenoxy-imine § complexes was discovered by the research group from the Mitsui Chemical, Inc., Company (Japan) in the framework of the Project 'Ligand-Oriented Catalyst Design' started in the mid-1990s.

§ The term phenoxy-imine complexes is generally referred to complexes containing salicylaldiminate ligands and their analogues.

First patents [135, 136] and articles (see, for example, Ref. 137) on phenoxy-imine catalyst systems, which were issued less than 10 years ago, marked the beginning of a large series of publications on this problem in different journals.

As the authors noted, the concept of the above-mentioned project was based on the analysis of advances in the design of high-performance single-site olefin polymerisation catalysts and was aimed at searching for systems satisfying the following main criteria:

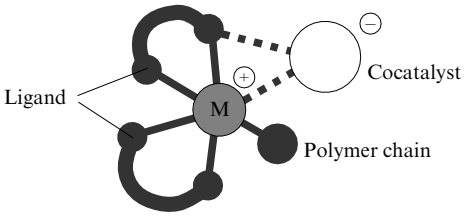
— catalyst systems should provide an efficient insertion of structurally different olefins, including sterically hindered olefins, as well as polar monomers, into the polymer chain;

— stability of catalysts under standard conditions of the polymerisation process;

— the possibility to control the chain transfer reaction, the achievement of the uniform distribution of the comonomer and stereochemical control of the product;

— extension of the range of the produced polymers by performing copolymerisation with the previously unused monomers.

An important principle of this concept was that olefin polymerisation is accompanied by extensive electron exchange between transition metal and ligands. In this case, it is necessary that the ligands should contain heteroatoms (as a rule, oxygen and/or nitrogen atoms), coordinate metal atoms in a bidentate fashion and have an unsymmetrical structure with mobile electrons (the so-called electron-flexible structure). The ability of transition metals to coordinate olefins and to be introduced into the polymer chain combined with such oriented ligands would provide high activity of the system in



M is metal.

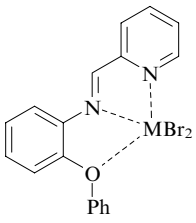
Figure 6. Schematic representation of catalysts discovered based on ligand-oriented catalyst design.[52]

polymerisation. Figure 6 schematically shows a catalyst system based on ligand-oriented catalyst design.[52]

It was demonstrated that polydentate electron-flexible unsymmetrical ligands, which are capable of chelating and forming five- or six-membered rings, satisfy the above-mentioned conditions. These are primarily ligands containing phenoxy, pyridine and/or conjugated imine fragments. These ligands are characterised by stability under the reaction conditions, have required electron-donating properties for the efficient olefin insertion and stabilisation of the transition state and contain accessible coordination sites necessary for polymerisation.

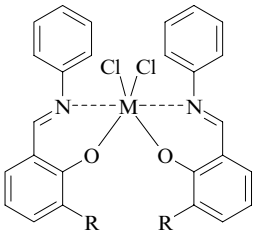
However, in my opinion, the authors of this concept, when designing a new class of high-performance phenoxy-imine catalysts, did not give proper attention to studies of the Shell Company on the development of SHOP (Shell Higher Olefin Process) catalysts and improvement of nickel catalyst systems for ethylene oligomerisation and polymerisation.[138–143]

Initially, the research group headed by Fujita [135–137] synthesised catalytic complexes with unsymmetrical electron-flexible ligands based on *N*-(*o*-phenoxyphenyl)pyridylaldimine (**37**, **38**) and salicylaldiminate (**39**–**41**) derivatives.



37, **38**

M = Co (**37**), Ni (**38**).



39–**41**

R = Bu^t, M = Zr (**39**);
R = H: M = Ti (**40**), Hf (**41**).

Studies of the catalytic activity of cobalt complex (**37**) and nickel complex (**38**) in MAO-mediated ethylene polymerisation in toluene showed that the former complex is inactive and the latter complex has lower activity than Ni catalysts with α-diimine ligands. Zirconium complex **39** in toluene at 25 °C exhibited activity of 519 (t PE) mol^{-1} h^{-1} (the molecular mass of the polymer was ~10^4), which is 20 times higher than the activity of the metallocene catalyst Cp_2ZrCl_2 (Cp = η-C_5H_5). In addition, this zirconium complex is characterised by rather high stability in a wide temperature range (the activity gradually decreases as the temperature is raised).

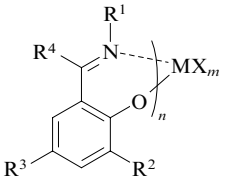
Over a rather short period of time, this research group synthesised a large number of structurally different phenoxy-imine complexes containing substituents of different nature both at the imine nitrogen atom and the phenoxy group,[144, 145] including those with perfluorinated fragments.[146–149] Conceptually similar derivatives based on nitrogen-containing heterocycles, *viz*., indolyl-imine [150] and pyrrolyl-imine [151] complexes, were also synthesised.

Shortly thereafter, the results of investigations in this field were summarised and systematised, which showed considerable progress in the design of this new class of post-metallocene catalysts.[52, 149, 152, 153] For example, the classification of different catalysts, which were developed based on the ligand-oriented catalyst design concept, was proposed in the review.[52] Table 1 summarises the general structures of phenoxy-imine and analogous chelate complexes. It should be noted that not only complexes, in which metal atoms are coordinated by heteroatoms (oxygen and nitrogen), but also titanium phenoxy-cyclopentadienyl complexes with similar properties are referred to this class.[160, 161]

Many complexes listed in Table 1 proved to be high-performance catalysts for the synthesis of a number of special polymers and copolymers. For example, particular phenoxy-cyclopentadienyl complexes of Group IV transition metals showed high activity in copolymerisation of ethylene with sterically hindered monomers. In the presence of titanium bis(pyrrolyl-imine) complexes, living copolymerisation of ethylene with norbornene giving rise to high-molecular-weight copolymers and block copolymers can be performed at room temperature. The titanium indolyl-imine complex allows living polymerisation of ethylene and propylene and their living block copolymerisation at room temperature.

Among the above-mentioned structures, phenoxy-imine catalysts (or FI catalysts according to the nomenclature by Fujita [137]) are most promising due to high catalytic activity, the possibility of varying substituents in the ligand and the simplicity of the synthesis. These catalysts are considered in more detail below.

The general structure of FI complexes consists of two bidentate unsymmetrical phenoxy-imine ligands coordinated to transition metal.



M = Ti, Zr, Hf, V, Cr, *etc*.; R^1, R^2, R^3 and R^4 = Alk, Ar and other groups; X = Hal.

As can be seen in Fig 7, the complexes with $n = m = 2$ can exist in five isomeric forms having an octagonal coordination

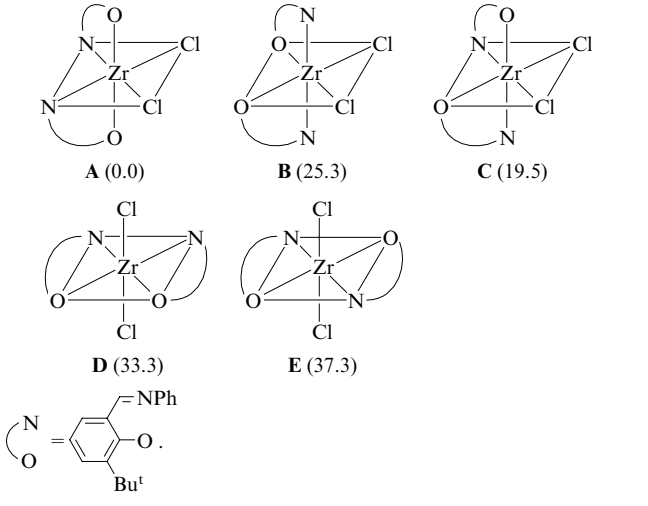
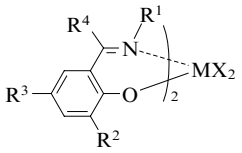
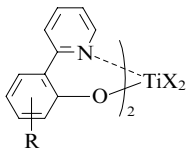
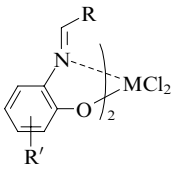
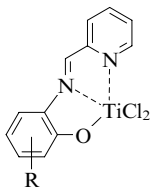
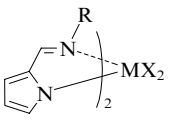
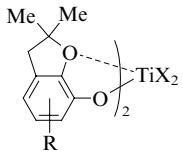
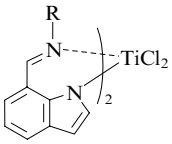
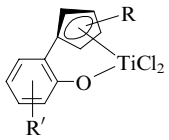
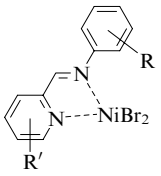
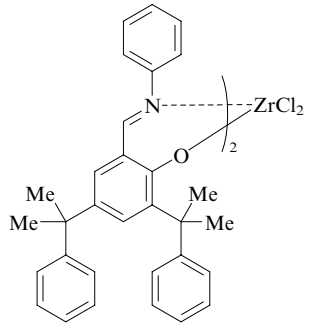


Figure 7. Possible isomeric forms of the octagonal coordination of FI catalysts [the energies of their formation (kJ mol^{-1}) for complex **39** are given in parentheses].[52]

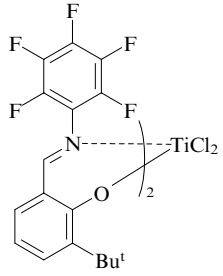
Table 1. Ligand-oriented olefin polymerisation catalysts.

Complex	Structure	Ref.	Complex	Structure	Ref.
Bis(phenoxy-imine)	 M = Ti, Zr, Hf, V, Cr, *etc.*	135 – 137, 144, 145	Bis(phenoxy-pyridine)		158
	 M = Ti, Zr	135 – 137, 154	Phenoxyimino-pyridine		149
Bis(pyrrolyl-imine)	 M = Ti, Zr, Hf	151, 155, 156	Bis(phenoxy-ether)		149, 159
Bis(indolyl-imine)		150, 157	Phenoxy-cyclopentadienyl		160, 161
Phenylimino-pyridine		149			

(depending on the arrangement of the ligand). According to the ^{1}H NMR spectroscopic data,[52] FI catalysts with the central Ti, Zr or Hf atom exist in solution as mixtures of isomers. Quantum chemical calculation (the density functional theory) of the corresponding energies of the formation of isomers showed that isomers **A** and **B** are most often present in solution (see Fig. 7). It should be noted that for some FI complexes the formation of only one isomer is favourable. For example, Zr complex **42** exists predominantly as isomer **B**, whereas Ti complex **43** containing the perfluoroaryl fragment at the imine nitrogen atom exists exclusively as isomer **A**.



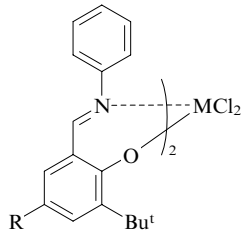
42



43

The coexistence of different isomeric forms of FI catalysts can be responsible for deviation from the single-site character of the catalyst system formed on their basis.

The structural characteristics and stereochemistry of FI complexes have been extensively studied, including by X-ray diffraction. The geometric parameters of four FI complexes **39** and **44** – **46**, in which the natures of metal and the substituent in the phenoxy group were varied, were determined.[52, 162]



39, **44** – **46**

M = Zr: R = H (**39**), Me (**44**); M = Ti: R = H (**45**), Me (**46**).

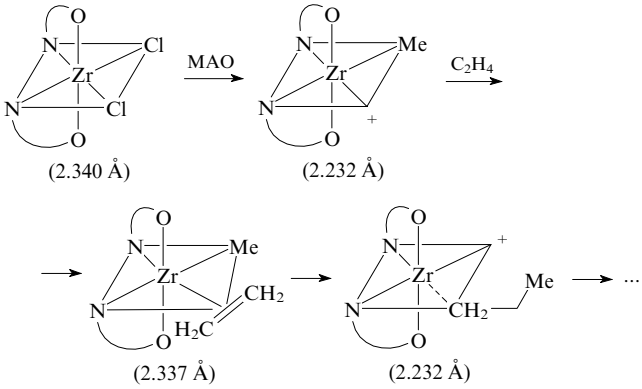
The X-ray diffraction study demonstrated [52] that these complexes in the solid state contain the metal centre (Zr or Ti) in a nearly octahedral coordination environment characterised by the space group C_2 with the O, N and Cl atoms being in *trans*, *cis* and *cis* positions, respectively. The bond lengths and bond angles in complexes **39** and **44** and in their homologues **45** and **46** determined by different research groups [52, 162] are given in Table 2. It can be seen that these results are in good agreement with each other. Small differences in the bond angles are attributed to the presence of the methyl substituent in complexes **45** and **46**.

Table 2. Geometric parameters of FI complexes **39** and **44**–**46**.

Complex	Bond lengths /Å			Bond angles /deg			Ref.
	M–O	M–N	M–Cl	OMO	NMN	ClMCl	
39	1.985(2)	2.355(2)	2.423(5)	165.5(1)	74.0(1)	100.3(8)	52
44	1.980(3)	2.351(4)	2.428(8)	157.9(9)	84.3(3)	94.6(1)	52
45	1.852(4)	2.236(4)	2.305(2)	171.6(2)	76.4(2)	103.1(1)	162
46	1.844(3)	2.212(5)	2.306(2)	164.0(3)	86.0(3)	94.08(1)	162

The results of quantum chemical calculations [52] (the density functional theory) for the structures of the precursors of the ethylene-coordinated methyl cationic catalyst, which is generated in the reaction of highly active Zr complex **39** with MAO (the calculated Zr–N bond lengths are given in parentheses), are presented in Scheme 4. The cationic complex has a distorted octahedral coordination, the Zr–N bonds and the polymerisation site being located in one plane. The interaction with a monomer leads to an increase in the length of this bond from 2.232 to 2.337 Å, whereas the Zr–O bond lengths remains unchanged. The change in the Zr–N bond length is indicative of a flexible exchange between the metal atom and the ligands, and the *cis* arrangement of the active site combined with the nature of the ligands is, apparently, responsible for high activity of this FI system [519 (t PE) mol^{-1} h^{-1}].

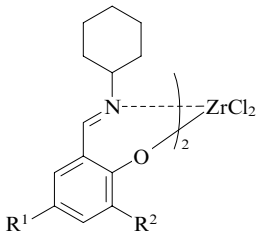
Scheme 4



New FI catalyst systems synthesised by Fujita and coworkers [163, 164] were studied as ethylene polymerisation catalysts. The authors analysed the dependence of the catalytic activity on the nature of transition metal and the nature and size of substituents at the imine nitrogen atom and in the *ortho* and *para* positions of the phenoxy group. For example, after the replacement of Zr by Ti, Hf, V or Cr in complex **39** combined with the cocatalyst MAO, the catalytic activity was 3, 26, 4 and 1 (t PE) mol^{-1} h^{-1}, respectively.

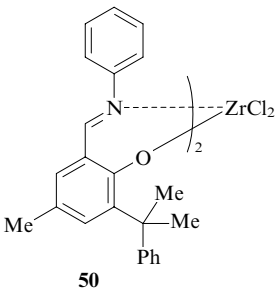
The first conclusions about the influence of the bulky substituents in the *ortho* position of the phenoxy group and the small substituent at the imine carbon atom were made in the publications.[163, 164] The steric hindrance caused by the bulky substituent adjacent to the oxygen atom of the phenoxy group protects the latter from the electrophilic attack of a Lewis acid, which is present in the polymerisation system, and facilitates the efficient separation of the cationic active species and the anionic species of the cocatalyst. Small substituents in the imine fragment leave sufficient space for the approach of the monomer to the active site of the growing chain. Hence, the presence of the aldimine fragment in the complex provides high activity of the catalyst, whereas ketimine-type FI systems (for example, those containing the substituted RC=N fragment, where R = Me, Et or Ph) are substantially less active.[165]

Complexes **47**–**50** are ethylene polymerisation catalysts of exceptionally high efficiency.



47–**49**

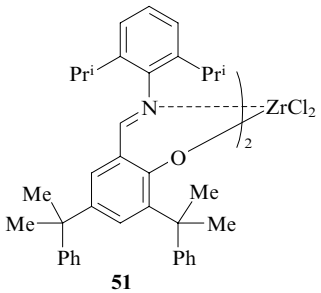
R^1 = H, R^2 = Ph_2MeC (**47**),
R^1 = Me: R^2 = $PhMe_2C$ (**48**),
2-adamantyl (**49**).



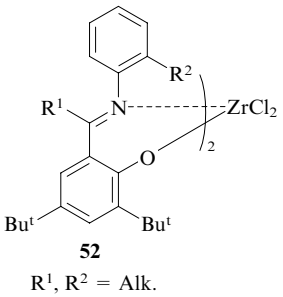
50

For example, MAO-activated FI system **47** exhibits the surprisingly high activity [6552 (kg PE) $mmol^{-1}$ h^{-1}, 25 °C, MW of the polymer was $\sim 1 \times 10^4$] and is characterised by the record turnover frequency of 64 900 s^{-1} atm^{-1}.[52] The activities of bis[*N*-(3-cumyl-5-methylsalicylidene)phenylaminato]$ZrCl_2$ (**50**) and bis[*N*-(3-cumyl-5-methylsalicylidene)cyclohexylaminato]$ZrCl_2$ (**48**) are as high as 2 (t PE) mol^{-1} h^{-1} and are increased as the concentration of the catalyst is slightly decreased. For bis[*N*-(3-(2-adamantyl)-5-methylsalicylidene)-cyclohexylaminato]$ZrCl_2$ (**49**), the yield of the polymer is 0.7 t min^{-1} (Refs 144 and 145). It was noted [166, 167] that FI complex **42** shows the unusual behaviour, which is manifested in that MWD of the product varies with the temperature. At 0 and 25 °C, the monomodal curve is observed, whereas the curve at 75 °C is bimodal, which was attributed to a change in the ratio between the coordination isomers in the FI system.

Zirconium complexes (for example, **51**), in which the phenyl group at the imine nitrogen atom contains substituents in both *ortho* positions, were also reported.[168] The use of these systems generally results in a decrease in the activity of catalysts. Catalysts **52** are exceptions to the general rule.



51



52

R^1, R^2 = Alk.

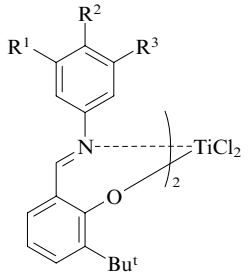
In spite of the facts that ketimine complexes are less active than aldimine complexes [165] and that the presence of an *ortho* substituent in the aniline fragment does not lead to an increase in the activity of the system, complexes **52** showed high catalytic activity, and high MW of the resulting polyethylene were achieved.[169]

Our research group revealed the relationship between the structure of such catalysts and their activity in ethylene polymerisation using the density functional theory method.[170] The influence of the structure of complexes on the energy effects of the formation of catalytically active species, the formation of π complexes of the catalysts with ethylene, the chain growth and chain transfer and deactivation of the system was analysed for five titanium and zirconium phenoxy-imine complexes. The results of investigation provided an explanation for the different behaviour of Ti and Zr complexes and the dependence of the activity of the catalyst system on the ligand structure.

In the recent study,[171] an attempt was made to systematise the results of research into the influence of substituents in phenoxy-imine complexes on their catalytic activity in ethylene polymerisation by analysing FI systems, in which the substituents either at the imine nitrogen atom or in the phenoxy group were varied. An investigation of ten structurally different FI complexes demonstrated that the substituents at the imine nitrogen atom influence not only the activity of the catalyst system but also the temperature range of the efficient catalyst functioning. Sterically hindered substituents in the *ortho* position of the phenoxy group should have the optimal volume; otherwise, the activity of the catalyst system decreases.

In the presence of particular FI catalysts in polymerisation systems, polymerisation can proceed according to the living polymerisation mechanism. Initially, this mechanism was established for structures containing perfluorinated aryl groups at the imine nitrogen atom.[146–148] For example, living polymerisation of not only ethylene but also of propylene was successfully performed in the presence of complex **43**. In the latter case, syndiotactic polypropylene (SPP) with narrow MWD ($M_w : M_n = 1.11$) was obtained.

Polyethylene was synthesised by living polymerisation with the use of complexes **53**–**56** combined with MAO [the activity was 43.3 (kg PE) $mmol^{-1}\ h^{-1}$, $M_n = 1.36 \times 10^6$].[147]



53–**56**

$R^1 = R^3 = H$, $R^2 = F$ (**53**); $R^1 = R^3 = F$, $R^2 = H$ (**54**);
$R^1 = R^2 = R^3 = F$ (**55**); $R^1 = R^3 = CF_3$, $R^2 = H$ (**56**).

Quantum chemical molecular orbital calculations demonstrated that the characteristic features of the mechanism of living polymerisation with the use of these systems are associated with the electron-accepting effect of the fluorine atoms, resulting in an increase in the electrophilicity of the metal centre and a decrease in the activation energy for ethylene insertion.

The possibility of living ethylene and propylene polymerisation was demonstrated by Bulychev and co-workers[172] using dinuclear fluorine-containing titanium bis(salicylidene)-imine complexes. According to the results of calculations (the density functional theory), fluorine-substituted phenyl groups at the imine nitrogen atom provide the living polymerisation mechanism. In the course of polymerisation, the fluorine atom in the active state of the catalyst interacts with the hydrogen atom in the β position of the polymer chain thus preventing β hydride transfer.

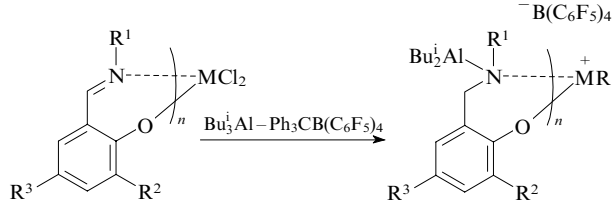
Living ethylene and propylene polymerisation is successfully used for the preparation of a number of unique block copolymers (both diblock and multiblock copolymers).

We were the first to perform living ethylene polymerisation with the use of non-fluorinated titanium FI systems. For example, it was demonstrated[162,173] that ethylene polymerisation on the MAO-activated bis[*N*-(3-(*tert*-butyl)-5-methylsalicylidene)anilinato]$TiCl_2$ complex (**46**) affords the polymer, whose molecular mass linearly increases with time. After termination of feeding of ethylene and subsequent introduction of hex-1-ene into the polymerisation system, polyethylene–block–poly(hex-1-ene) was obtained. This confirms that polymerisation proceeds accoridng to the living polymerisation mechanism. The detailed analysis of living olefin polymerisation in the presence of various catalyst systems, including phenoxy-imine complexes, was performed in the recent review.[174]

2. Influence of activators on catalytic activity and selectivity of FI complexes

The influence of the nature of the cocatalyst on the activity and selectivity of Ziegler–Natta catalysts, as well as of metallocene systems, in olefin polymerisation was considered in-depth in numerous monographs and reviews (see, for example, Refs 8, 12, 16, 17, 22, 36 and 40). Taking into account that FI ligands contain heteroatoms, it could be expected that these complexes would be activated with a larger number of structurally different cocatalysts compared to metallocenes.

Earlier, the successful use of MAO or its modified derivatives as activators of FI complexes has been documented. In addition, the $Bu^i_3Al-Ph_3CB(C_6F_5)_4$ systems can serve this purpose.[144,175–179] It was found that the mechanism of activation of FI catalysts by this system is based on the formation of amino-ligated complex **57** catalysing polymerisation.



57

M = Ti, Zr, Hf, *etc.*; R^1, R^2, R^3 = Alk or Ar.

The use of FI complexes combined with the $Bu^i_3Al-Ph_3CB(C_6F_5)_4$ system in olefin polymerisation results in a decrease in the activity compared to that observed in the presence of MAO; neverthelss, the activity remains at a satisfactory level, MW of the polymers being substantially increased.

Taking into account the specific mechanism of activation, the structure of FI complexes substantially influences the efficiency and selectivity of this type of catalyst systems. For example, polymerisation with the use of FI complex **39** activated with $Bu^i_3Al-Ph_3CB(C_6F_5)_4$ at 50 °C affords polyethylene with MW $\sim 5 \times 10^6$, and the activity of the catalyst was 11 (kg PE) $mmol^{-1}\ h^{-1}$, while the same system combined with MAO exhibited activity of 519 (kg PE) $mmol^{-1}\ h^{-1}$, and MW of the resulting polyethylene was as low as $\sim 1 \times 10^4$. It should be emphasised that the application of the $Bu^i_3Al-Ph_3CB(C_6F_5)_4$ system as the activator proved to be very useful.

Magnesium chloride-supported organic derivatives of aluminium, for example, $R'_nAl(OR)_{3-n}/MgCl_2$ (R and R′ = Et or Bu^i), were proposed as promising cocatalysts for FI systems. These activating systems simultaneously serve as supports for FI complexes. Earlier attempts[180,181] to use these systems

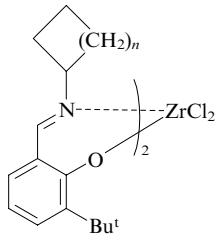
combined with metallocene catalysts have failed. Recently, it has been demonstrated [182–184] that the efficiency of the use of specially treated $MgCl_2$ as the cocatalyst for olefin polymerisation is determined by the presence of heteroatoms in FI systems.

The latest advances in research into the FI complex–$R'_nAl(OR)_{3-n}/MgCl_2$ catalyst systems were considered in the publication.[185] For example, the activity of catalyst **49** in ethylene polymerisation in the presence of $R'_nAl(OR)_{3-n}/MgCl_2$ amounts up to 1819 (kg PE) $mmol^{-1}\ h^{-1}$ (50 °C, 0.9 MPa).[185] The use of vanadium-based FI systems in the presence of this type of activators makes it possible to perform polymerisation with high efficiency at high temperatures (75 °C). Modified $MgCl_2$ serves as the active cocatalyst for living olefin polymerisation with the use of fluorinated FI ligands.[186]

Substantial advantages of activators based on modified $MgCl_2$ are that the polymer morphology is improved (replication of spherical, including ultradisperse, particles of the supported catalyst) and the polymer has a high bulk density and is not deposited on the walls of the reactor.[185] The characteristic features of immobilisation of complexes on modified $MgCl_2$ and the coordination mode of ligands in supported catalyst systems were reported.[187, 188]

3. Use of FI catalyst systems for the preparation of non-traditional polyolefins

The use of FI catalysts can allow the preparation of polymers with a nonconventional topology. For example, MAO-mediated complexes **58** and **59** catalyse the formation of low-molecular-mass polyethylenes with terminal vinyl groups (the percentage of vinyl groups at one of the ends of the polymer chain is no lower than 90%).[189] High reactivity of the terminal groups is combined with rather high melting points of these polymers (> 120 °C). Polymerisation in the presence of complex **58** affords a product with the weighted-average molecular weight (M_w) of 2100 and the ratio $M_w : M_n = 1.52$; in the case of compound **59**, $M_w = 3800$ and $M_w : M_n = 1.82$.



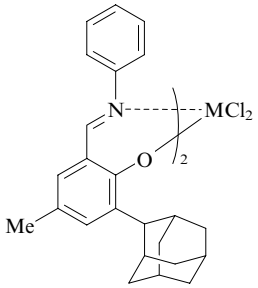
58–61

n = 1 (**58**), 2 (**59**), 3 (**60**), 4 (**61**).

The steric factors rather than the electronic nature of substituents play the key role in the formation of the terminal vinyl groups of the polymers when polymerisation is catalysed by complexes containing lower cycloalkyl (cyclobutyl or cyclopentyl) substituents in the imine fragment. Recently,[190] the structures of zirconium bis(phenoxy)imine complexes **58–61** containing various cycloalkyl groups at the imine nitrogen atom were studied by X-ray diffraction. It was noted that the substituents greatly influence the kinetic behaviour of these complexes in ethylene polymerisation (MAO as the cocatalyst, 25 °C). Complexes **58–61** were demonstrated to have identical coordination geometry irrespective of the number of CH_2 groups in the ring. Nevertheless, the cyclic substituent strongly influences the steric environment of the potential active sites of polymerisation and, consequently, the catalytic activity of complexes **58–61** depends on the bulkiness of the cycloalkyl substituent. Both low- and high-molecular-weight polyethylenes containing unsaturated vinyl groups at the ends of the polymer chain can be prepared with the use of these phenoxy-imine complexes due to the fact that the β-hydride transfer to monomers prevails over the transfer to the metal centre. This character of the transfer process was confirmed by quantum chemical calculations and experiments on the effect of the ethylene pressure on the polymerisation process. Thus, the influence of substituents in phenoxy-imine complexes on the mechanism of elementary steps of chain transfer in olefin polymerisation was demonstrated for the first time in the study.[190]

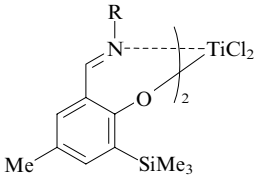
Polymers containing terminal vinyl groups can find use as macromers for the preparation of copolymers with long-chain branches. Various modifying additives as well as graft and block copolymers can be synthesised by functionalisation of vinyl fragments in theses polymers.

Propylene polymerisation catalysed by FI complexes **62** and **63** afforded highly isotactic polypropylene.[179] Isotactic polypropylene (IPP) with $M_w = 172\,000$ and the ratio $M_w : M_n = 2.1$ was synthesised with the use of zirconium complex **62** combined with the $Bu^i_3Al-Ph_3CB(C_6F_5)_4$ system. This polymer is characterised by a high percentage of *mm* triads¶ (98%) and the relatively high melting point (164 °C). The catalyst based on analogous hafnium complex **63** facilitates the formation of IPP with $M_w = 364\,000$, $M_w : M_n = 3.5$, [*mm*] = 98% and $T_m = 165$ °C.



62, 63

M = Zr (**62**), Hf (**63**).



64, 65

R = Ph (**64**), C_6F_5 (**65**).

Syndiotactic polypropylene was synthesised on MAO-activated titanium FI complexes **64** and **65**.[191, 192] Polymerisation with the use of complex **64** containing the phenyl substituent at the imine nitrogen atom at 1 °C afforded SPP containing 91% of *rr* triads with $T_m = 140$ °C. The replacement of this substituent by the perfluorinated phenyl group (complex **65**) resulted in the formation of SPP with [*rr*] = 94% and $T_m = 156$ °C. Polymerisation in the presence of $Bu^i_nAl(OR)_{3-n}/MgCl_2$-activated catalyst **65** at 25 °C gave SPP with [*rr*] = 97%, $T_m = 155$ °C and $M_w = 32\,000$. The characteristic features of the formation of SPP were discussed.[192–196]

It is generally very difficult to synthesise stereo- and regioregular higher α-olefins because of the difficulties in performing stereocontrol of the process (exclusion of 'regio errors'). Another problem is associated with a decrease in the activity of the catalyst because of steric hindrance to the approach of the monomer to the active site. These difficulties were successfully overcome with the use of $Bu^i_3Al-Ph_3CB(C_6F_5)_4$-activated titanium phenoxy-imine complex **40** as a catalyst for hex-1-ene polymerisation.[176] In this case, atactic (non-regioregular) polyhexene with $M_w = 720\,000$, $M_w : M_n = 1.68$ and the regio error of ~50% was obtained at

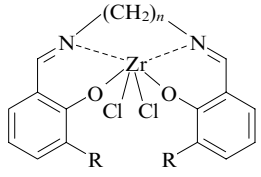
¶ Isotactic diads (*m*-diads) are characterised by an identical arrangement of the methyl groups with respect to the plane of the carbon chain of the macromolecules, as opposed to syndiotactic (*r*) diads, in which the methyl groups of propylene are located on the opposite sides of this plane.[39]

25 °C. Under analogous conditions, polyoctene, poly(4-methylpentene) and other higher polyolefins were prepared. The catalytic activity decreases in the following series of monomers: 4-methylpentene > dodec-1-ene > oct-1-ene > hex-1-ene.

Recently, the advances in the synthesis of isotactic polypropylene have been demonstrated with the use of titanium phenoxy-aldimine and -ketimine complexes containing *ortho*-phenoxyhalide substituents.[197]

4. Non-standard phenoxy-imine and structurally similar complexes

Group IV metal complexes with tetradentate ligands containing hydrocarbon-bridged phenoxy-imine fragments are of particular interest as high-performance olefin polymerisation catalysts.[198]



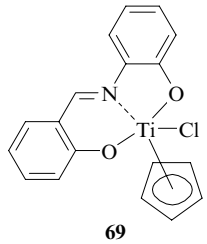
66–68

m = 1, R = H, n = 2 (**66**);
m = 0; R is 2-adamantyl, n = 2–6 (**67**); R = CH_2Ph, n = 4 or 6 (**68**).

The rigidly organised structure of these complexes is responsible for their high thermal stability and provides stereospecificity in polymerisation reactions. For example, the activity of SiO_2-supported compound **66** in the presence of MAO is 3.53 (kg PE) $mmol^{-1}\ h^{-1}$, which is 30 times higher than the activity of an analogous catalyst under homogeneous conditions.[198]

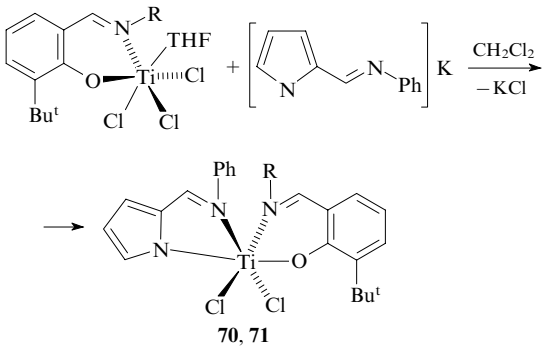
The catalytic activity of tetradentate bis(phenoxy-imine) complexes **67** and **68** was studied.[199–201] These catalysts are characterised by high stability and can function at high temperatures [for example, in the course of solution ethylene polymerisation at 150 °C, the activity of compound **67** was 143 (kg PE) $mmol^{-1}\ h^{-1}$]. It should be noted that the activity of such catalyst systems increases with the number of CH_2 groups in the bridge between the imine nitrogen atoms.[200]

Tridentate titanium complexes containing simultaneously the phenoxy-imine and cyclopentadienyl ligands were synthesised;[202] however, their activity in ethylene polymerisation appeared to be low. For example, the activity of compound **69** was 15.6 (g PE) $mmol^{-1}\ h^{-1}$, the molecular weight of the resulting polymer being 1 630 000.



69

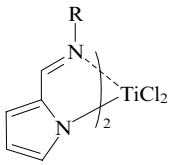
In 2005, hybrid titanium (phenoxy-imino-pyrrolyl-imine) complexes **70** and **71** were described.[203] These complexes showed high activity in MAO-mediated ethylene polymerisation. The complexes were prepared by the reaction of the titanium mono(salicylaldiminate) complex with the metallated pyrrolylaldiminate ligand.



70, **71**

R = Ph (**70**), C_6F_5 (**71**).

Bis(pyrrolyl-imine) complexes of Group IV metals, which are structurally similar to FI systems and were synthesised by Fujita and co-workers,[204,205] are of great interest in both theoretical and commercial aspects.



R = Et, n-C_6H_{13}, cyclo-C_6H_{11}, Ph.

Such complexes with the central titanium atom proved to be better ethylene polymerisation catalysts than zirconium complexes. As in the case of phenoxy-imine ligands, methylalumoxane is a more efficient cocatalyst for these compounds than the $Bu^i_3Al-Ph_3CB(C_6F_5)_4$ system, with MW of the resulting polymers being of the same order of magnitude.

Further investigations[151,206] demonstrated an interesting possibility of living copolymerisation of ethylene with norbornene in the presence of these systems. This process gives copolymers whose composition is similar to that of alternating copolymers. It should be emphasised that these catalysts are inactive in living homopolymerisation of both norbornene and ethylene. It was found[207] that the introduction of substituents into the pyrrolidine ring does not change the activity of the catalyst system.

Pyrrolyl-imine catalysts are very efficient in copolymerisation of ethylene with propylene and α-olefins providing a high degree of comonomer insertion.

A search for and investigation of new structures of phenoxy-imine catalysts and their analogues having unusual and sometimes exotic structures are presently underway. Unfortunately, it is impossible to mention all results obtained by numerous research groups in this important and interesting field of investigation. Nevertheless, the present review hopefully provides insight into the advances and prospects in the design of post-metallocene catalysts for olefin polymerisation.

IV. Conclusion

The fifty-year history of the large-scale production of the most important polymers, *viz*., polyethylene and polypropylene, which are widely used in various fields of human activity, shows a tremendous role of catalysts in the perfection of the polymerisation process. The use of Ziegler–Natta catalysts, catalyst systems for gas-phase polymerisation and transition metal metallocene complexes made a considerable contribution to the perfection of polyolefin production processes and improvement of their performance characteristics.

The chronology of the design and introduction of new catalysts showed that the search for active and selective catalyst systems for olefin polymerisation is a high-priority field in polymer chemistry. In recent years, the design of these catalysts has become more extensive. It took 30 years to change over Ziegler – Natta catalysts to metallocene catalysts, whereas the last decade witnessed the discovery of a new type of catalysts, *viz*., transition metal post-metallocene complexes, which hold considerable promise for commercial olefin polymerisation and copolymerisation.

Over a short period of time, the characteristics of post-metallocene polymerisation catalysts, such as activity, selectivity, sensitivity to the reaction conditions, availability, safety and the range of monomers used in polymerisation, became as good as and even better than those of metallocene complexes. The use of these catalysts becomes preferable also from the economical point of view. Post-metallocene systems are characterised by a wide range of activators and supports ensuring their functioning. A wide range of ligands for these systems and prospects for solving the problems of monitoring (NMR method) and controlling the structures of the resulting polymer systems (molecular weight, branching and block structure) substantially extend the scope of their commercial application. The experimentally established possibility of the synthesis of superhigh-molecular-weight polymers and copolymers by the living polymerisation mechanism, the synthesis of block copolymers of different composition, an increase in the percentage of sterically hindered monomers in copolymers and the formation of low-molecular-weight polymers with unsaturated reactive groups are some of the characteristic features of new post-metallocene systems demonstrating their great potentialities. Great prospects for their use are associated also with high performance of heterogeneous complexes, in which modified $MgCl_2$ serves as the activator and support.

Post-metallocene catalyst systems have been discovered rather recently. Nevertheless, the main aim of investigations of these systems would be expected to be changed, the research into commercial applications of catalysts will be more intensive, interest in the design of new complexes being retained, as well as the mechanism of polymerisation with the use of these catalysts will be refined. The immobilisation of catalyst systems, an increase in the temperature range of their steady activity, the extension of the possibilities to control the structure and performance characteristics of the resulting polymers, simulation of polymerisation processes and tailoring of pilot devices to real industrial conditions will likely receive more attention.

I thank Academician G A Tolstikov and Dr. N I Ivancheva for helpful discussion of some aspects of the present review and Dr S V Myakin for help in preparing this review.

References

1. *Polietilen Vysokogo Davleniya. Nauchno-tekhnicheskie Osnovy Promyshlennogo Sinteza* (Low-Density Polyethylene. Scientific and Technological Foundations of Industrial Synthesis) (Ed. A V Polyakov) (Leningrad: Khimiya, 1988)
2. K Ziegler, H G Gellert, K Zosel, W Lehmkuhl, W Pfohl *Angew. Chem.* **67** 424 (1955)
3. K Ziegler, E Holzkamp, H Breil, H Martin *Angew. Chem.* **67** 541 (1955)
4. G Natta, P Pino, P Corradini, F Danusso, E Mantica, G Mazzanti, G Moraglio *J. Am. Chem. Soc.* **77** 1708 (1955)
5. G Natta, P Corradini, G Allegra *J. Polym. Sci.* **51** 399 (1961)
6. *Stereoregular Polymers and Stereospecific Polymerizations* (Eds G Natta, F Danusso) (Oxford: Pergamon Press, 1967)
7. J Boor Jr *Ziegler – Natta Catalysts and Polymerizations* (New York: Academic Press, 1979)
8. A A Montagna, J C Floyd *Hydrocarbon Process.* **73** (3) 57 (1994)
9. *Handbook on Polyolefins* (2nd Ed.) (Ed. C Vasile) (New York, Basel: Marcel Dekker, 2000) p. 41
10. *Polietilen Nizkogo Davleniya. Nauchno-tekhnicheskie Osnovy Promyshlennogo Sinteza* (High-Density Polyethylene. Scientific and Technological Foundations of Industrial Synthesis) (Ed. A V Polyakov) (Leningrad: Khimiya, 1980)
11. S S Ivanchev *Katal. Prom-sti* (6) 15 (2002)
12. N M Chirkov, P E Matkovskii, F S D'yachkovskii *Polimerizatsiya na Kompleksnykh Metalloorganicheskikh Katalizatorakh* (Polymerisation on Complex Organometallic Catalysts) (Moscow: Khimiya, 1976)
13. J C W Chen *Preparation and Properties of Stereoregular Polymers* (Eds R W Lenz, F Ciardelli) (Dordrecht: Reidel, 1980) p. 113
14. T E Nowlin *Prog. Polym. Sci.* **11** 29 (1985)
15. Yu V Kissin *Transition Metal Catalyzed Polymerizations: Alkenes and Dienes* Pt. B (Ed. R P Quirk) (New York: Harwood Academic Publ., 1985) p. 597
16. A Zambelli, M C Sacchi, P Locatelli *Transition Metal Catalyzed Polymerizations: Alkenes and Dienes* Pt. B (Ed. R P Quirk) (New York: Harwood Academic Publ., 1985) p. 83
17. Yu V Kissin *Isospecific Polymerization of Olefins with Heterogeneous Ziegler – Natta Catalysts* (New York: Springer, 1985)
18. V A Zakharov, Yu I Yermakov *Catal. Rev. Sci. Eng.* **19** 67 (1979)
19. A V Kryzhanovskii, S S Ivanchev *Vysokomol. Soedin., Ser. A* **32** 1383 (1990) [a]
20. B A Krentsel, Yu V Kissin, V Y Kleiner, L L Stotskaya *Polymers and Copolymers of Higher α-Olefins. Chemistry, Technology, Applications* (Munich, Vienna, New York: Hanser Publ., 1997)
21. B A Krentsel', F S D'yachkovskii *Vysokomol. Soedin., Ser. A* **31** 1123 (1989) [a]
22. *Ziegler Catalysts* (Eds G Fink, R.Mülhaupt, H H Brintzinger) (Berlin: Springer, 1995)
23. G Di Drusco, R Rinaldini *Hydrocarbon Process.* **63** (11) 113 (1984)
24. P C Barbe, G Cecckin, L Norish *Adv. Polym. Sci.* **81** 1 (1986)
25. *Chem. Week* **147** (25) 13 (1990)
26. P Galli, G Vecellio *Prog. Polym. Sci.* **26** 1287 (2001)
27. N Kashiwa, T Tsutsui *Macromol. Rapid Commun.* **4** 491 (1983)
28. S-i Kojoh, N Kashiwa *Chem. Rec.* **3** 342 (2004)
29. S S Reddy, S Sivaram *Prog. Polym. Sci.* **20** 309 (1995)
30. J Huang, G L Rempel *Prog. Polym. Sci.* **20** 459 (1995)
31. W Kaminsky *Macromol. Chem. Phys.* **197** 3907 (1996)
32. M Bochman *J. Chem. Soc., Dalton Trans.* 255 (1996)
33. A E Hamielec, J B P Soares *Prog. Polym. Sci.* **21** 651 (1996)
34. O Olabisi, M Atiqullah, W Kaminsky *J. Macromol. Sci., Part C: Polym Rev.* **37** 519 (1997)
35. K Soga, T Shiono *Prog. Polym. Sci.* **22** 1503 (1997)
36. *Metalorganic Catalysts for Synthesis and Polymerization* (Ed. W Kaminsky) (Berlin, Heidelberg: Springer, 1999)
37. H G Alt, A Koppl *Chem. Rev.* **100** 1205 (2000)
38. G G Hlatky *Chem. Rev.* **100** 1347 (2000)
39. N M Bravaya, P M Nedorezova, V I Tsvetkova *Usp. Khim.* **71** 57 (2002) [*Russ. Chem. Rev.* **71** 49 (1002)]
40. E Y-X Chen, T J Marks *Chem. Rev.* **100** 1391 (2000)
41. *GAK* **51** 64 (1998)
42. D Rottman *Chem. Week* **159** (20) 23 (1997)
43. A L McKnight, R M Waymouth *Chem. Rev.* **98** 2587 (1998)
44. G J P Britovsek, V C Gibson, D F Wass *Angew. Chem., Int. Ed.* **38** 428 (1999)
45. S D Ittel, L K Johnson, M Brookhart *Chem. Rev.* **100** 1169 (2000)
46. L Bourget-Merle, M F Lappert, J R Severn *Chem. Rev.* **102** 3031 (2002)
47. H Makio, N Kashiwa, T Fujita *Adv. Synth. Catal.* **344** 477 (2002)
48. V C Gibson, S K Spitzmesser *Chem. Rev.* **103** 283 (2003)
49. R Mulhaupt *Macromol. Chem. Phys.* **204** 289 (2003)
50. Y Suzuki, H Terao, T Fujita *Bull. Chem. Soc. Jpn.* **76** 1493 (2003)

51. *Late Transition Metal Polymerization Catalysis* (Eds B Rieger, L S Baugh, S Kacker, S Striegler) (Weinheim: Wiley, 2003)
52. M Mitani, J Saito, S-i Ishii, Y Nakayama, H Makio, N Matsukawa, S Matsui, J-i Mohri, R Furuyama, H Terao, H Bando, H Tanaka, T Fujita *Chem. Rec.* **4** 137 (2004)
53. L K Johnson, C M Killian, M Brookhart *J. Am. Chem. Soc.* **117** 6414 (1995)
54. L K Johnson, S Mecking, M Brookhart *J. Am. Chem. Soc.* **118** 267 (1996)
55. C M Killian, D J Tempel, L K Johnson, M Brookhart *J. Am. Chem. Soc.* **118** 11664 (1996)
56. S Mecking, L K Johnson, L Wang, M Brookhart. *J. Am. Chem. Soc.* **120** 888 (1998)
57. A Yamamoto, T Shimizu, S Ikeda *Makromol. Chem.* **136** 297 (1970)
58. A Yamamoto *J. Chem. Soc., Dalton Trans.* 1027 (1999)
59. K R Kumar, S Sivaram *Macromol. Chem. Phys.* **201** 1513 (2000)
60. R J Maldanis, J S Wood, A Chandrasekaran, M D Rausch, J C W Chien *J. Organomet. Chem.* **645** 158 (2002)
61. S A Svejda, L K Johnson, M Brookhart *J. Am. Chem. Soc.* **121** 10634 (1999)
62. L C Simon, C P Williams, J B P Soares, R F de Souza *J. Mol. Catal. A: Chem.* **165** 55 (2001)
63. D J Tempel, M Brookhart *Organometallics* **17** 2290 (1998)
64. L Deng, T K Woo, L Cavallo, P M Margl, T Ziegler *J. Am. Chem. Soc.* **119** 6177 (1997)
65. T Schleis, T P Spaniol, J Okuda, J Heinemann, R Mülhaupt *J. Organomet. Chem.* **569** 159 (1998)
66. F Zhu, W Xu, X Liu, S Lin *J. Appl. Polym. Sci.* **84** 1123 (2002)
67. D Pappalardo, M Mazzeo, C Pellecchia *Macromol. Rapid Commun.* **18** 1017 (1997)
68. S S Ivanchev, G A Tolstikov, V K Badaev, N I Ivancheva, I I Oleinik, S Ya Khaikin, I V Oleinik *Vysokomol. Soedin., Ser. A* **44** 1478 (2002) [a]
69. M E Bluhm, C Folli, M Döring *J. Mol. Catal. A: Chem.* **212** 13 (2004)
70. S S Ivanchev, G A Tolstikov, V K Badaev, I I Oleinik, N I Ivancheva, D G Rogozin, I V Oleinik, S V Myakin *Kinet. Katal.* **45** 192 (2004) [b]
71. L Deng, P Margl, T Ziegler *J. Am. Chem. Soc.* **119** 1094 (1997)
72. P Margl, L Deng, T Ziegler *Organometallics* **18** 5701 (1999)
73. M Schmid, R Eberhardt, J Kukral, B Rieger *Z. Naturforsch., B* **57** 1141 (2002)
74. M Schmid, Dissertation, Universität Ulm, Germany, 2001
75. B Lindner, Dissertation, Universität Ulm, Germany, 2001
76. B L Small, M Brookhart, A M A Bennett *J. Am. Chem. Soc.* **120** 4049 (1998)
77. B L Small, M Brookhart *Macromolecules* **32** 2120 (1999)
78. G J P Britovsek, V C Gibson, S J McTavish, G A Solan, A J White, D J Williams, B S Kimberley, P J Maddox *Chem. Commun.* 849 (1998)
79. G J P Britovsek, M Bruce, V C Gibson, B S Kimberley, P J Maddox, S Mastroianni, S J McTavish, C Redshaw, G A Solan, S Strömberg, A J P White, D J Williams *J. Am. Chem. Soc.* **121** 8728 (1999)
80. G J P Britovsek, S Mastroianni, G A Solan, S P D Baugh, C Redshaw, V C Gibson, A J P White, D J Williams, M R J Elsegood *Chem. – Eur. J.* **6** 2221 (2000)
81. G J P Britovsek, V C Gibson, B S Kimberley, S Mastroianni, C Redshaw, G A Solan, A J P White, D J Williams *J. Chem. Soc., Dalton Trans.* 1639 (2001)
82. V C Gibson, M J Humphries, K P Tellmann, D F Wass, A J P White, D J Williams *Chem. Commun.* 2252 (2001)
83. G J P Britovsek, S P D Baugh, O Hoarau, V C Gibson, D F Wass, A J P White, D J Williams *Inorg. Chem. Acta* **345** 279 (2003)
84. G J P Britovsek, V C Gibson, S Mastroianni, D C H Oakes, C Redshaw, G A Solan, A J P White, D J Williams *Eur. J. Inorg. Chem.* 431 (2001)
85. T M Kooistra, Q Knijnenburg, J M M Smits, A D Horton, P H M Budzelaar, A W Gal *Angew. Chem.* **113** 4855 (2001)
86. L Deng, P Margl, T Ziegler *J. Am. Chem. Soc.* **121** 6479 (1999)
87. G Marsh *Mater. Today* **1** 6 (1998)
88. S S Ivanchev, A V Yakimanskii, D G Rogozin *Dokl. Akad. Nauk* **393** 504 (2003) [c]
89. S S Ivanchev, A V Yakimansky, D G Rogozin *Polymer* **45** 6453 (2004)
90. H-K Luo, H Schumann *J. Mol. Catal. A: Chem.* **227** 153 (2005)
91. G A Tolstikov, S S Ivanchev, I I Oleinik, N I Ivancheva, I V Oleinik *Dokl. Akad. Nauk* **404** 1 (2005) [c]
92. B de Bruin, E Bill, E Bothe, T Weyhermüller, K Wieghardt *Inorg. Chem.* **39** 2936 (2000)
93. I Kim, B H Han, Y-S Ha, C-S Ha, D-W Park *Catal. Today* **93** 281 (2004)
94. J-Y Liu, Y Zeng, Y-G Li, L Pan, Y-S Li, N-H Hu *J. Organomet. Chem.* **690** 1233 (2005)
95. F Pelascini, F Peruch, P J Lutz, M Wesolek, J Kress *Eur. Polym. J.* **41** 1288 (2005)
96. I Kim, Y S Ha, C-S Ha *Macromol. Rapid Commun.* **25** 1069 (2004)
97. K P Tellmann, V C Gibson, A J P White, D J Williams *Organometallics* **24** 280 (2005)
98. D Reardon, F Conan, S Gambarotta, G Yap, Q Wang *J. Am. Chem. Soc.* **121** 9318 (1999)
99. R Schmidt, M B Welch, R D Knudsen, S Gottfried, H G Alt *J. Mol. Catal. A: Chem.* **222** 9 (2004)
100. B L Small, M J Carney, D M Holman, C E O'Rourke, J A Halfen *Macromolecules* **37** 4375 (2004)
101. Y Nakayama, K Sogo, H Yasuda, T Shiono *J. Polym. Sci., Part A: Polym. Chem.* **43** 3368 (2005)
102. M J Carney, N J Robertson, J A Halfen, L N Zakharov, A L Rheingold *Organometallics* **23** 6184 (2004)
103. Yu V Kissin, C Qian, G Xie, Y Chen *J. Polym. Sci., Part A: Polym. Chem.* **44** 6159 (2006)
104. E P Talzi, D E Babushkin, N V Semikolenova, V N Zudin, V A Zakharov *Kinet. Katal.* **42** 165 (2001) [b]
105. E P Talsi, D E Babushkin, N V Semikolenova, V N Zudin, V N Panchenko, V A Zakharov *Macromol. Chem. Phys.* **202** 2046 (2001)
106. K P Bryliakov, N V Semikolenova, V N Zudin, V A Zakharov, E P Talsi *Catal. Commun.* **5** 45 (2004)
107. I I Zakharov, V A Zakharov *Macromol. Theory Simul.* **13** 583 (2004)
108. A A Barabanov, G D Bukatov, V A Zakharov, N A Semikolenova, T B Mikenas, L G Echevskaja, M A Matsko *Macromol. Chem. Phys.* **207** 1368 (2006)
109. S Wang, D Liu, R Huang, Yu Zhang, B Mao *J. Mol. Catal. A: Chem.* **245** 122 (2006)
110. L A Utracki *Polymer Alloys and Blends* (Munich: Hanser, 1989)
111. S Mecking *Macromol. Rapid Commun.* **20** 139 (1999)
112. F A Kunrath, R S Mauler, R F de Souza, O I Casagrande Jr *Macromol. Chem. Phys.* **203** 2058 (2002)
113. S S Ivanchev, V K Badaev, N I Ivancheva, E V Sviridova, D G Rogozin, S Ya Khaikin *Vysokomol. Soedin., Ser. B* **46** 1959 (2004) [a]
114. S G Correia, M M Marques, J R Ascenso, A F G Ribeiro, P T Gomes, A R Dias, M Blais, M D Rausch, J C W Chien *J. Polym. Sci., Part A: Polym. Chem.* **37** 2471 (1999)
115. D V Deubel, T Ziegler *Organometallics* **21** 1603 (2002)
116. J C W Chien, S Fernandes, S G Correia, M D Rausch, L C Dickson, M M Marques *Polym. Int.* **51** 729 (2002)
117. L S Boffa, B M Novak *Chem. Rev.* **100** 1479 (2000)
118. K Ibrahim, K Yliheikkilä, A Abu-Surrah, B Löfgren, K Lappalainen, M Leskelä, T Repo, J Seppälä *Eur. Polym. J.* **40** 1095 (2004)
119. *Khimiya Privitykh Poverkhnostnykh Soedinenii* (The Chemistry of Graft Surface Compounds) (Ed. G V Lisichkin) (Moscow: Fizmatlit, 2003) p. 481
120. WO PCT 99/12981A1 (1999)
121. WO PCT 99/62968A1 (1999)
122. V F V Marques, C C Pombo, R A Silva, A Conte *Eur. Polym. J.* **39** 561 (2003)
123. Z Ma, Y Ke, H Wang, C Guo, M Zhang, W-H Sun, Y Hu *J. Appl. Polym. Sci.* **88** 466 (2003)

124. S S Ivanchev, V K Badaev, N I Ivancheva, E V Sviridova, S Ya Khaikin, D G Rogozin, A S Abakunchik *Vysokomol. Soedin., Ser. A* **47** 934 (2005) [a]
125. V A Zakharov, N V Semikolenova, T B Mikenas, A A Barabanov, G D Bukatov, L G Echevskaya, M A Mats'ko *Kinet. Katal.* **47** 303 (2006) [b]
126. N V Semikolenova, V A Zakharov, E A Paukshtis, I G Danilova *Top. Catal.* **32** 77 (2005)
127. T B Mikenas, V A Zakharov, L G Echevskaya, M A Matsko *J. Polym. Sci., Part A: Polym. Chem.* **43** 2128 (2005)
128. J C Chadwick, J R Severn *Kinet. Katal.* **47** 186 (2006) [b]
129. S S Ivanchev, N I Ivancheva, S Ya Khaikin, E V Sviridova, D G Rogozin *Vysokomol. Soedin., Ser. A* **48** 423 (2006) [a]
130. J Zhang, X Wang, G-X Jin *Coord. Chem. Rev.* **250** 95 (2006)
131. H B Zhu, G-X Jin, N H Hu *J. Organomet. Chem.* **655** 167 (2002)
132. C-K Liu, G-X Jin *New J. Chem.* **26** 1485 (2002)
133. D Zhang, G-X Jin *Appl. Catal. A: General* **262** 13 (2004)
134. D Zhang, G-X Jin, L-H Weng, F Wang *Organometallics* **23** 3270 (2004)
135. Eur. P. 0874005; *Chem. Abstr.* **129** 331166 (1998)
136. WO PCT 01/55231A1; *Chem. Abstr.* **135** 137852 (2001)
137. S Matsui, T Fujita *Catal. Today* **66** 63 (2001)
138. W Keim, F H Kowaldt, R Goddard, C Krüger *Angew. Chem., Int. Ed. Engl.* **17** 466 (1978)
139. U Müller, W Keim, C Krüger, P Betz *Angew. Chem., Int. Ed. Engl.* **28** 1011 (1989)
140. K Hirose, W Keim *J. Mol. Catal.* **73** 271 (1992)
141. U Klabunde, S D Itten *J. Mol. Catal.* **41** 123 (1987)
142. C Wang, S Friedrich, T R Younkin, R T Li, R H Grubbs, D A Bansleben, M W Day *Organometallics* **17** 3149 (1998)
143. T R Younkin, T F Connor, J I Henderson, S K Friedrich, R H Grubbs, D A Bansleben *Science* **287** 460 (2000)
144. S Matsui, M Mitani, J Saito, Y Tohi, H Makio, N Matsukawa, Y Tagaki, K Tsuru, M Nitabaru, T Nakano, H Tanaka, N Kashiwa, T Fujita *J. Am. Chem. Soc.* **123** 6847 (2001)
145. N Matsukawa, S Matsui, M Mitani, J Saito, K Tsuru, N Kashiwa, T Fujita *J. Mol. Catal. A: Chem.* **169** 99 (2001)
146. J Saito, M Mitani, J-i Mohri, S-i Ishii, Y Yosida, T Matsugi, S-i Kojoh, N Kashiwa, T Fujita *Chem. Lett.* 576 (2001)
147. S-i Ishii, J Saito, M Mitani, J-i Mohri, N Matsukawa, Y Tohi, S Matsui, N Kashiwa, T Fujita *J. Mol. Catal. A: Chem.* **179** 11 (2002)
148. M Mitani, J-i Mohri, Y Yoshida, J Saito, S-i Ishii, K Tsuru, S Matsui, R Furuyama, T Nakano, H Tanaka, S -i Kojoh, T Matsugi, N Kashiwa, T Fujita *J. Am. Chem. Soc.* **124** 3327 (2002)
149. S-i Ishii, R Furuyama, N Matsukawa, J Saito, M Mitani, H Tanaka, T Fujita *Macromol. Rapid Commun.* **24** 452 (2003)
150. T Matsugi, S Matsui, S-i Kojoh, Y Takagi, Y Inoue, T Fujita, N Kashiwa *Chem. Lett.* 566 (2001)
151. Y Yoshida, J-i Mohri, S-i Ishii, M Mitani, J Saito, S Matsui, H Makio, T Nakano, H Tanaka, M Onda, Y Yamamoto, A Mizuno, T Fujita *J. Am. Chem. Soc.* **126** 12023 (2004)
152. J Saito, M Mitani, J-i Mohri Y Yoshida, S Matsui, S-i Ishii, S-i Kojoh, N Kashiwa, T Fujita *Angew. Chem., Int. Ed.* **40** 2918 (2001)
153. H Makio, T Fujita *Bull. Chem. Soc. Jpn.* **78** 52 (2005)
154. Y Suzuki, N Kashiwa, T Fujita *Chem. Lett.* 358 (2002)
155. S Matsui, T P Spaniol, Y Takagi, Y Yoshida, Y Okuda *J. Chem. Soc., Dalton Trans.* 4529 (2002)
156. S Matsui, Y Yoshida, Y Tagaki, T P Spaniol, J Okuda *J. Organomet. Chem.* **689** 1155 (2004)
157. T Matsugi, S Matsui, S-i Kojoh, Y Takagi, Y Inoue, T Nakano, T Fujita, N Kashiwa *Macromolecules* **35** 4880 (2002)
158. Y Inoue, T Nakano, H Tanaka, N Kashiwa, T Fujita *Chem. Lett.* 1060 (2001)
159. L E Turner, M G Thorn, R D Swartz II, R W Chesnut, P E Fanwick, I P Rothwell *Dalton Trans.* 4580 (2003)
160. Y Zhang, Y Mu, C Lu, G Li, J Xu, Y Zhang, D Zhu, S Feng *Organometallics* **23** 540 (2004)
161. Y Suzuki, Y Inoue, H Tanaka, T Fujita *Macromol. Rapid Commun.* **25** 493 (2004)
162. S S Ivanchev, V A Trunov, V B Rybakov, D V Al'bov, D G Rogozin *Dokl. Akad. Nauk* **404** 57 (2005) [c]
163. S Matsui, M Mitani, J Saito, J Tohi, H Makio, H Tanaka, T Fujita *Chem. Lett.* 1263 (1999)
164. S Matsui, M Mitani, J Saito, N Matsukawa, H Tanaka, T Nakano, T Fujita *Chem. Lett.* 554 (2000)
165. S Reinartz, A F Mason, E B Lobkovsky, G W Coates *Organometallics* **22** 2542 (2003)
166. Y Tohi, H Makio, S Matsui, M Onda, T Fujita *Macromolecules* **36** 523 (2003)
167. Y Tohi, T Nakano, H Makio, S Matsui, T Fujita, T Yamaguchi *Macromol. Chem. Phys.* **205** 1179 (2004)
168. A Pärssinen, T Luhtanen, M Klinga, T Pakkanen, M Leskeli, T Repo *Eur. J. Inorg. Chem.* 2100 (2005)
169. S Chen, X Zhang, H Ma, Y Lu, Z Zhang, H Li, Z Lu, N Cui, Y Hu *J. Organomet. Chem.* **690** 4184 (2005)
170. A V Yakimanskii, S S Ivanchev *Dokl. Akad. N*auk **410** 217 (2006) [c]
171. N I Ivancheva, M Yu Malinskaya, S S Ivanchev, I I Oleinik, A I Kochnev, G A Tolstikov *Kinet. Katal.* **48** (6) (2007) (in the press) [b]
172. S K Gagieva, T A Sukhova, D B Savinov, N M Bravaya, Yu N Belokon', B M Bulychev *Ross. Khim. Vest.* **53** 2763 (2004)
173. S S Ivanchev, V K Badaev, N I Ivancheva, S Ya Khaikin *Dokl. Akad. Nauk* **394** 639 (2004) [c]
174. G J Domski, J M Rose, G W Coates, A D Bolig, M Brookhart *Progr. Polym. Sci.* **32** 30 (2007)
175. J Saito, M Mitani, S Matsui, Y Tohi, H Makio, T Nakano, H Tanaka, N Kashiwa, T Fujita *Macromol. Chem. Phys.* **203** 59 (2002)
176. J Saito, M Mitani, S Matsui, N Kashiwa, T Fujita *Macromol. Rapid Commun.* **21** 1333 (2000)
177. J Saito, M Onda, S Matsui, M Mitani, R Furuyama, H Tanaka, T Fujita *Macromol. Rapid Commun.* **23** 1118 (2003)
178. J Saito, Y Suzuki, T Fujita *Chem. Lett.* 236 (2003)
179. A V Prasad, H Makio, J Saito, M Onda, T Fujita *Chem. Lett.* 250 (2004)
180. K Soga, T Uozumi, M Saito, T Shiono *Macromol. Chem. Phys.* **195** 1503 (1994)
181. Yu V Kissin, T E Nowlin, R I Mink, A J Brandolini *Macromolecules* **33** 4599 (2000)
182. Y Nakayama, H Bando, Y Sonobe, H Kaneko, N Kashiwa, T Fujita *J. Catal.* **215** 171 (2003)
183. Y Nakayama, H Bando, Y Sonobe, T Fujita *J. Mol. Catal. A: Chem.* **213** 141 (2004)
184. Y Nakayama, J Saito, H Bando, T Fujita *Macromol. Chem. Phys.* **206** 1847 (2005)
185. Y Nakayama, J Saito, H Bando, T Fujita *Chem.–Eur. J.* **12** 7546 (2006)
186. Y Nakayama, H Bando, Y Sonobe, T Fujita *Bull. Chem. Soc. Jpn.* **77** 617 (2004)
187. J R Severn, J C Chadwick *Macromol. Chem. Phys.* **205** 1987 (2004)
188. J R Severn, J C Chadwick, V Van Axel Castelli *Macromolecules* **37** 6258 (2004)
189. S -i Ishii, M Mitani, J Saito, S Matsuura, S -i Kojoh, N Kashiwa, T Fujita *Chem. Lett.* 740 (2002)
190. H Terao, S-i Ishii, J Saito, S Matsuura, M Mitani, N Nagai, H Tanaka, T Fujita *Macromolecules* **39** 8584 (2006)
191. R Furuyama, J Saito, S-i Ishii, M Mitani, S Matsui, Y Tohi, H Makio, N Matsukawa, H Tanaka, T Fujita *J. Mol. Catal. A: Chem.* **200** 31 (2003)
192. M Mitani, R Furuyama, J-i Mohri, J Saito, S -i Ishii, H Terao, T Nakano, H Tanaka, T Fujita *J. Am. Chem. Soc.* **125** 4293 (2003)
193. G Milano, L Cavallo, G Guerra *J. Am. Chem. Soc.* **124** 13368 (2002)
194. V Busico, R Cipullo, F Cutillo, N Friederichs, S Ronca, B Wang *J. Am. Chem. Soc.* **125** 12402 (2003)
195. M Lamberti, D Pappalardo, A Zambelli, C Pellecchia *Macromolecules* **35** 658 (2002)
196. G Talarico, V Busico, L Cavallo *J. Am. Chem. Soc.* **125** 7172 (2003)

197. M Mazzeo, M Strianese, M Lamberti, I Santoriello, C Pellecchia *Macromolecules* **39** 7812 (2006)
198. T Repo, M Klinga, P Pietikainen, M Leskeli, A-M Uusitalo, T Pakkanen, K Hakala, P Aaltonen, B Lofgren *Macromolecules* **30** 171 (1997)
199. J P Corden, W Errington, P Moore, M G H Wallbridge *Chem. Commun*. 323 (1999)
200. S-i Ishii, M Mitani, J Saito, S Matsuura, R Furuyama, T Fujita *Science and Technology in Catalysis (Studies in Surface Science and Catalysis)* (Eds M Ango, M Onaka, H Yamashita) (Amsterdam: Elsevier, 2003) Vol. 145, p. 49
201. P D Knight, A J Clarke, B S Kimberley, R A Jackson, P Scott *Chem. Commun*. 352 (2002)
202. J Huang, B Lian, Y Qian, W Zhou, W Chen, G Zheng *Macromolecules* **35** 4871 (2002)
203. D A Pennington, S J Coles, M B Hursthouse, M Bochman, S J Lancaster *Chem. Commun*. 3150 (2005)
204. Y Yoshida, S Matsui, Y Tagaki, M Mitani, M Nitabaru, T Nakano, H Tanaka, T Fujita *Chem. Lett*. 1270 (2000)
205. Y Yoshida, S Matsui, Y Tagaki, M Mitani, T Nakano, H Tanaka, N Kashiwa, T Fujita *Organometallics* **20** 4793 (2001)
206. Y Yoshida, J Saito, M Mitani, Y Takagi, S Matsui, S-i Ishii, T Nakano, N Kashiwa, T Fujita *Chem. Commun*. 1298 (2002)
207. Y Yoshida, S Matsui, T Fujita *J. Organomet. Chem*. **690** 4382 (2005)

[a] — *Polym. Sci. (Engl. Transl.)*
[b] — *Kinet. Catal. (Engl. Transl.)*
[c] — *Dokl. Phys. Chem. (Engl. Transl.)*