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Mixed and hybrid multisite catalysts for ethylene polymerization

I V Sedov, P E Matkovskiy

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Abstract. Multisite catalytic systems for ethylene polymerization based on transition metal complexes are considered. The relationship between the composition and properties of catalytic systems is analyzed. Specific features of the synergistic effect shown by the catalyst components depending on the method of catalyst preparation are demonstrated. The key kinetic models of ethylene polymerization in the presence of multisite catalysts are discussed. The bibliography includes 138 references.

I. Introduction

Polymers based on ethylene and propylene are produced on large scale: in 2007 alone, 65 million tons of polyethylene (PE) and 50 million tons of polypropylene were produced worldwide.[1] These polymers are used in many branches of industry. The world market of polymers based on ethylene and propylene is increasing every year owning to the increase in both production volumes and product range.

Currenty, a great number of techniques are available for controlling the true density (from 0.88 to 0.98 g cm^{-3}), grain size distribution, strain – strength, rheological, and other properties of polyolefins.[2] The most effectively and rapidly developing area of research on the methods of tailoring polymer properties deals with design of new polymerization catalysts, as well as with modification of classical homogeneous and heterogeneous Ziegler – Natta catalysts,[3] chromium oxide catalysts,[4] metallocene [1] and post-metallocene catalysts,[5] including catalysts based on Group VIII transition metal complexes.[6] Requirements on new catalysts are becoming increasingly strict. New catalysts should exhibit high activity, productivity, stereospecificity (in polymerization of propylene and higher olefins) and regioselectivity (in copolymerization processes), as well as enable the synthesis of polymers with tailored characteristics.

In most cases, the PE properties are controlled by changing the molecular weight (MW), molecular weight distribution (MWD) and polymer chain branching. The MWD character ($M_w : M_n$) dictates the rheological properties of PE. For example, the narrow MWD ($M_w : M_n \approx 2$) of polymers produced in the presence of multisite (metallocene and many post-metallocene) catalysts is responsible for considerable difficulties in their further processing.[2]

Polyethylenes with bimodal MWD, in which the low-molecular-weight fraction is a linear crystalline polymer with a lamellar structure and the high-molecular-weight fraction is characterized by a high branching level (and therefore, resistant to the development of defects and cracks), are suitable for the production of various pipes, including those operating at high pressure.[7]

The molecular weight of a polymer can be easily controlled by adding hydrogen to the gas phase in the course of polymerization [8] or introducing chain-transfer agents into the catalytic system.[9] However, these methods are inefficient for controlling the MWD of polymers obtained with the use of metallocene catalysts. The following methods are used for broadening the MWD:[10]

— mechanical mixing of products synthesized in the presence of different catalysts (or) under different conditions is a rather energy-consuming method, which affects the cost of the end product; in addition, highly viscous (high-molecular-weight) polymers are hard to mix with each other so that it is in principle impossible to obtain ideal homogeneous blends by the mechanical method;

— the use of a cascade of reactors in the process flow chart scheme, polymerization conditions in each of the reactors being different; this method is also costly because of the necessity of using metal-consuming equipment and the long duration of the process;

— the change in polymerization parameters, such as temperature, comonomer concentration and hydrogen pressure, in the course of the process (nonstationary polymer-

I V Sedov, P E Matkovskiy Institute of Problems of Chemical Physics, Russian Academy of Sciences, prosp. Akad. Semenova 1, 142432 Chernogolovka, Moscow Region, Russian Federation.
Fax: (7-496) 522 35 07,
tel. (7-496) 522 10 65, e-mail: isedov@icp.ac.ru (I V Sedov),
tel. (7-496) 522 18 46, e-mail: pem@icp.ac.ru (P E Matkovskiy)

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ization); industrial implementation of such processes is a challenging technological problem;[11]

— 'reactor blending' is a less laborious and energy-consuming method, as compared with the above methods, which implies using a mixture of single-site catalysts or their combination with conventional titanium–magnesium catalysts in the course of polymerization in order to obtain polymers with good rheological properties.[12,13]

An efficient technique that enables the control over the MW and MWD of polyethylene produced with the use of complex organometallic catalysts implies adding a reversible chain transfer agent (a main group metal organometallic compound). Reactions of this type are referred to as 'coordinative chain transfer polymerization'.[9] Under the conditions of fast exchange (the reversible chain transfer rate is much higher than the chain propagation rate) of alkyl groups between active sites of polymerization and the chain transfer agent, the MW characteristics are statistically averaged and the M_w and M_n values change depending on the nature and concentration of the chain transfer agent.[14] Under these conditions, 'quasi-living' ethylene polymerization is also possible[15] resulting in polymers with a narrow MWD ($M_w : M_n \approx 1$) close to the Poisson distribution.[16] In this case, polymerization involves chain growth on the chain transfer agent catalyzed by transition metal and lanthanide compounds. If the chain transfer agent is added to mixed catalytic systems containing two types of active site precursors, there can be observed the averaging of MW characteristics of polymers obtained under the action of both types of active sites and the change in MWD curves (from bimodal to unimodal) owing to growing chain shuttling between the two active sites.[17,18] Adding the chain transfer agent to a system containing a mixture of two catalysts one of which is responsible for the high and the other, for the low degree of incorporation of an α-olefin comonomer in the growing PE chain leads to formation of alternating block copolymers of ethylene with higher α-olefins.[17]

Polymers with new properties can be obtained by using an approach in which olefin macromonomers are first synthesized and then introduced into the copolymerization process catalyzed by another catalyst that enables living polymerization.[19] Such macromonomers can be prepared in situ[9] in the presence of catalysts that catalyze chain growth on main group metal atoms in metal alkyls (AlR_3, ZnR_2).

The MW distribution of the comonomer units obtained with the use of the conventional Ziegler–Natta catalysts and chromium oxide catalysts is shown in Fig. 1 *a*. With an increase in MW, the number of comonomer units decreases. The same pattern is observed for the systems with mixed two-site catalysts in which the low-molecular-weight fraction forms under the action of a single-site catalyst and the high-molecular-weight fraction forms under the action of the conventional Ziegler–Natta or chromium oxide catalyst. If the single-site catalyst in a mixed system ensures the formation of a higher-molecular-weight fraction, the end product can have an 'inverse' MW distribution of comonomer units; *i.e.*, with an increase in MW, the comonomer content in such polymers increases (Fig. 1 *b*).[20] Polyolefins with the inverse distribution of comonomer units have improved consumer properties and are more easily processed.

By controlling the branching of a polymer chain, one can regulate the true density of polymers and produce

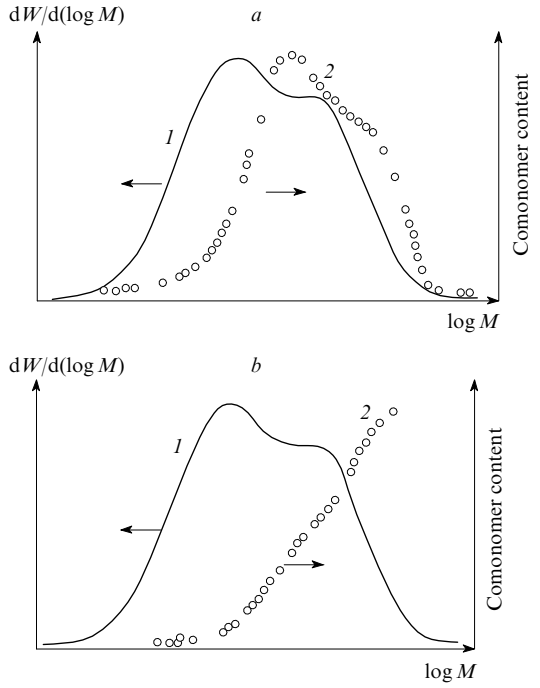


Figure 1. Common (*a*) and 'inverse' (*b*) MW distribution of comonomer units.[20]
(*1*) MWD curve, (*2*) comonomer content; *W* is the weight fraction of macromolecules with the molecular weight *M*.

medium- and low-density PE, including linear low-density PE consisting of long carbon backbones with periodically arranged short-chain branches. Such a microstructure of a polymer chain is mainly obtained by ethylene copolymerization with higher α-olefins (1-butene, 1-hexene, 1-octene *etc.*).[21] Efficient single-site catalysts of ethylene copolymerization with α-olefins are constrained-geometry metallocene complexes, which are successfully used by the Dow Chemical company.[22] The difficulty of synthesizing and isolating olefin comonomers creates additional challenges for producing linear low-density PE. To simplify the process flow chart, it has been suggested to carry out ethylene oligomerization to higher olefins and their subsequent copolymerization with ethylene in one reactor with the use of dual-functional catalysts.[23] Such catalysts are a special case of concurrent tandem catalysts,[24] which allow carrying out so-called cascade reactions ('domino' reactions).† The schemes of action of similar catalysts involve several catalytic cycles, the product of each of them being the reagent in the next cycle.[24]

Selective catalysts of ethylene oligomerization to higher olefins (1-butene, 1-hexene and 1-octene) are best to use for designing tandem catalysts since they provide better possibilities for controlling the structure and composition homogeneity of a copolymer.

Based on the above, it is possible to distinguish two ways of designing multisite catalytic systems of olefin polymerization.[25]

† The end product is synthesized in several stages, each being a separate chemical reaction yielding an intermediate, an individual chemical compound that can be isolated in pure form.

— in a catalytic system, each of the active sites formed by precursors of different nature functions independently of the other sites; the resulting products have the properties of mixtures of polymers obtained under the action of the corresponding individual catalytic systems;

— in a catalytic system, one of the types of active sites catalyzes formation of low-molecular-weight olefins (individual or a statistical mixture), comonomers in the copolymerization reaction with ethylene that occurs on the active site of the other type (this is a special case of so-called concurrent tandem catalysis).[24]

Basic criteria that should be met in both cases are the compatibility of the catalyst components (none of the components suppresses the activity of the other components) and their high activity. If a mixed catalyst is intended for production of polymers with a bimodal MWD or polymers with an inverse MW distribution of comonomer units, the system components are selected in such a way that the polymer fractions formed under the action of each of the components have different MWs and different comonomer contents.

Homogeneous[26] and heterogeneous[27] mixed catalysts of ethylene polymerization have been reviewed in the literature; however, complex analysis of the possibility of heterogenization of known homogeneous systems and their application in gas-phase polymerization processes is still a challenging task. Among relevant publications, noteworthy is the review by Delferro and Marks[28] focused on the design of olefin polymerization catalysts based on polynuclear transition metal complexes. These catalysts are a special case of multisite catalysts.

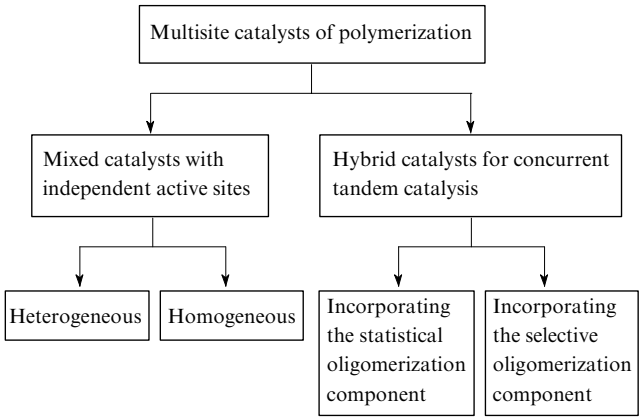
Here, we also survey polynuclear complexes as a special case of multisite catalysts; however, for getting complete information on studies in this area carried out so far, it is advisable to become acquainted with the mentioned review.[28] The authours reflected great progress in designing polynuclear complexes, olefin polymerization catalyst precursors; however, last-decade advances in design of multisite and hybrid catalysts have not been considered. The latest review on this topic[26] was published in 2004 and is already outdated.

The synthesis of polynuclear complexes is rather complicated; therefore, they are unsuitable for industrial use. At the same time, mixed catalysts especially addressed in the present work are widely used in polyethylene production. In addition, we consider catalysts for concurrent tandem catalysis. At present, this concept has not been implemented in processes catalyzed by polynuclear complexes; however, it is promising for the *in situ* preparation of ethylene–olefin copolymers.

II. Mixed catalysts with independent active sites

Mixed catalysts with independent active sites are used for preparing PE with a wide (including bimodal) MWD. The major advantage of such catalysts is the possibility to easily control the MWD by varying the molar ratio of the catalyst component and, hence, to obtain polymers with tailored MWD by the 'reactor blending' method. The accepted classification of such catalysts (Scheme 1) places heterogeneous catalysts that can be used in the existing gas-phase ethylene polymerization processes into a separate group.

Scheme 1



1. Homogeneous catalysts

Polymers obtained by ethylene polymerization catalyzed by a combined catalyst based on the titanium-containing constrained-geometry complex $[Me_2Si(\eta^5\text{-}Me_4C_5)(NEt)].Ti(NMe_2)_2$ and the zirconium complex $[En(Ind)_2]ZrCl_2$ (En = CH_2CH_2, Ind is η^5-inden-1-yl) contain up to four long-chain branches per 10 000 carbon atoms[29] and their MWD depends on the molar ratio of catalyst precursors and corresponds to the calculated data obtained by the Monte Carlo method[30] using the kinetic model of the catalytic process suggested by the authors.

Homopolymerization of ethylene and its copolymerization with 1-hexene catalyzed by a 1 : 1 mixture of the $(\eta^5\text{-}1,2,4\text{-}Me_3C_5H_2)_2ZrCl_2$ and $(\eta^5\text{-}Me_5C_5)_2ZrCl_2$ metallocene complexes activated by polymethylalumoxane (MAO) have been studied.[31] The activity of the catalyst system is intermediate between the activities of the individual metallocene catalysts. There are several interesting features typical of this system:

— a smaller (by ~30%) content of hexene units in the copolymer;

— an increase in M_w as compared to the M_w values of the polymers obtained in the presence of the initial catalytic systems;

— chain transfer to trimethylaluminium (TMA), its contribution decreasing with an increase in the 1-hexene concentration;

— an increase in the number of vinyl and *trans*-vinylidene groups in the copolymer with an increase in the 1-hexene concentration.

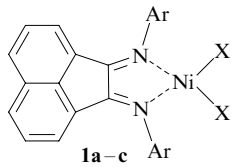
As suggested,[31] there is no 1,2-insertion of hexene into the polymer chain. The MWD of the copolymers remains narrow ($M_w : M_n = 2-3$), which is explained by chain transfer between two types of active sites, and it is assumed that the chain transfer agent is TMA contained in MAO. The MW of the product can be controlled by introducing hydrogen into the gas phase. Analysis of the resulting polymers by the CRYSTAF (Crystallization Analysis Fractionation) method showed that they contained two fractions corresponding to the polymers produced under the action of the individual catalytic systems.[32]

Copolymers of ethylene and propylene produced with the use of a mixed system based on *rac*-$[Me_2Si(2\text{-}Me\text{-}4\text{-}(1\text{-}Naph)Ind)_2]ZrCl_2$/$[Me_2Si(Ind)(Flu)]ZrCl_2$/MAO (Naph is naphthyl, Flu is fluoren-9-yl) differ from the polymers

obtained under the action of the corresponding individual catalysts: the former have higher M_w values and a bimodal MWD (the active sites of both types function independently).[25] The content of propylene units in the copolymer is intermediate between their contents in the copolymers obtained in the presence of the individual catalysts, and it can be controlled by varying the molar ratio of metallocene precursors.

The addition of hydrogen to a mixed catalytic system based on $[En(Ind)_2]ZrCl_2/Cp_2HfCl_2$ (Cp is cyclopentadienyl) (Ref. 33) or a titanium-containing constrained-geometry complex and $[En(Ind)_2]ZrCl_2$ (Ref. 34) modifies the MWD of the product: with increasing hydrogen concentration, the MWD changes from bimodal to unimodal. Analysis of MWD curves and CRYSTAF data has demonstrated that superposition of MWD and microstructure data for the polymers obtained in the presence of each of the components of the mixed catalytic system (with taking into account the molar ratio of titanocene to zirconocene) enables the determination of the microstructure and MWD of the end product. This is possible since the active sites of two types function independently from each other and differ in the susceptibility to the change in process conditions.

Combining nickel bis(arylimino)acenaphthene complex **1a** (Ar = 2,6-$Pr^i_2C_6H_3$, X = Cl) with $[En(Ind)_2]ZrCl_2$ gives catalytic system **I**; being activated by MAO, the latter enables the synthesis of a mixture of linear and branched PE.[35]



1a–c

When the reaction is carried out at 30 °C, a nonlinear correlation is observed between the catalytic system performance and the content of the zirconocene component of the catalyst; at 0 and 50 °C, this correlation is linear (Fig. 2).[36]

The MWs of the resulting polymers are within $(220-470)\times10^3$, the polydispersity coefficient is 2, and the system activity‡ at 30 °C is $\sim1.3\times10^6$ (g PE) mol^{-1} h^{-1}. The strain–strength properties of polymers significantly depend on the zirconocene content in the catalyst.[35] Scanning electron microscopy (SEM) studies have shown that the polymers produced at 0 °C are more homogeneous in composition and are characterized by smaller inclusions of branched amorphous PE in the matrix of the crystalline linear polymer as compared with the products obtained at 30 °C.[36]

It has been shown that different active sites in a mixed catalytic system based on complex **1b** (R = 2,6-$Pr^i_2C_6H_3$, X = Br)/MMAO and $[En(Ind)_2]ZrCl_2$/MMAO (where MMAO is modified methylalumoxane) function independently at temperatures from 30 to 100 °C.[37] The differential scanning calorimetry (DSC) curves of the polymers synthesized at 60 °C and an ethylene pressure of 0.7 MPa show two peaks identical to the melting peaks in the DSC curves

‡ In this review, the catalyst activities are reported in the same units as in the original works, mainly in grams of PE per mole of a metal per hour [(g PE) mol^{-1} h^{-1}].

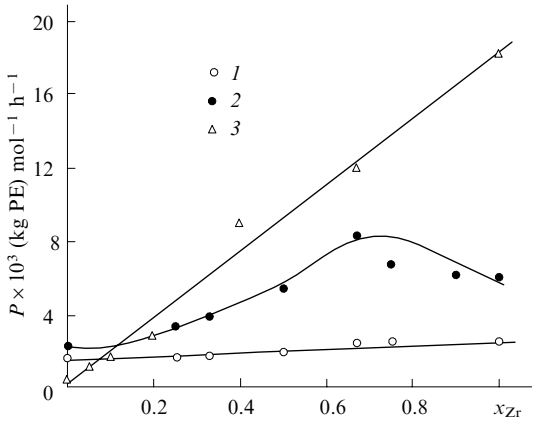
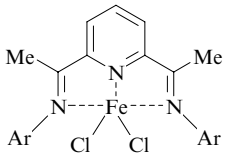


Figure 2. Productivity (P) of catalytic system **I** *vs.* temperature and zirconium mole fraction (x_{Zr}).[36]
Temperature/°C: (*1*) 0, (*2*) 30, (*3*) 50.

of the polymers obtained with the use of the corresponding individual catalytic systems. The polymers produced in the presence of the mixed system have a unimodal MWD with a small polydispersity coefficient ($M_w:M_n = 2.1-3.5$). Depending on the component ratio in the catalyst and temperature, the M_w value can change from 67×10^3 to 588×10^3 and the crystallinity (according to DSC), from 1.2% to 65%. The system activity at 60 °C, a pressure of 0.7 MPa and an equimolar content of the catalyst components is as high as 10.5×10^6 (g PE) mol^{-1} h^{-1}.

The formation of PE with $M_w:M_n = 11.2-17.3$ under the action of a combined catalytic system based on $[En(Ind)_2]ZrCl_2$ and iron bis(imino)pyridyl complex **2a** (Ar = 2,6-$Me_2C_6H_3$) has been reported.[38]



2a–i

With an increase in the Fe : Zr molar ratio in the catalyst, the crystallinity of the polymer decreases and, according to SEM, more compact domains of high-crystallinity PE are formed. Thus, varying the composition of the catalytic system makes it possible to control the polymer morphology. The system activity is as high as 4.5×10^6 (g PE) mol^{-1} h^{-1} at 50 °C.

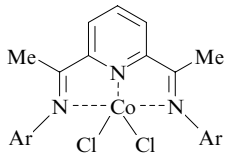
It has been shown that mixed catalysts can be designed on the basis of early and late transition metal compounds.[39] Iron bis(iminopyridyl) and nickel diimine complexes are combined well with both different zirconocene catalysts and each other.

A mixed catalytic system based on Fe(II) bis(iminopyridyl) complex and nickel(II) diimine complex activated by $AlEt_3$ or $AlBu^i_3$ has enabled the synthesis of polymers with a bimodal MWD ($M_w:M_n = 96.8-148.8$) containing the same amounts of the branched and linear PE.[40] It has been shown that, in the temperature range 0–35 °C, the active sites of different types in these systems function independently. The system activity can be as high as

4.48×10^6 (g PE) mol^{-1} h^{-1} in hexane at 0 °C and an ethylene pressure of 0.1 MPa.

Independent functioning of two types of active sites has been demonstrated [41] for mixed catalytic systems composed of complex **1a** and $Tp^{Ms*}VCl_2(NBu^t)$ [Tp^{Ms*} is hydridobis(3-mesitylpyrazol-1-yl)(5-mesitylpyrazol-1-yl)borate] activated by MAO. Changing the molar ratio of the components in the catalytic system can give blends of branched PE and high-density PE with melting points (T_m) within 135–144 °C and different degrees of crystallinity. For the reaction in toluene at 0–50 °C and in hexane at 0 °C, there is a linear correlation between the fraction of the nickel component and the catalytic system activity. When the reaction is carried out in hexane at elevated temperatures (30–50 °C), the activity of the system first decreases with an increase in the mole fraction of nickel, which is thought [41] to be a result of the spontaneous phase separation in the course of polymerization owing to the difference in properties of the polymers formed by different types of active sites. The maximal activity of the system at the equimolar component ratio is observed in toluene at 0 °C being 1.012×10^6 (g PE) mol^{-1} h^{-1}. PE with a bimodal MWD can be produced by reactor blending of the branched PE (formed in the presence of nickel complex **1a**) and the high-density PE (formed in the presence of $Tp^{Ms*}TiCl_3$).[42] This catalytic system can be activated by MAO and/or triisobutylaluminium (TIBA).[43] In the course of ethylene polymerization at 30 and (to a greater extent) 55 °C, there is observed the synergistic effect of different types of active sites on each other, which is manifested in a nonlinear dependence of the activity and kinetic parameters of polymerization on the mole fractions of the catalytic system components. With an increase in the Al : (Ti + Ni) molar ratio in the system, the polymer MW noticeably decreases,[43] presumably due to chain transfer to the organoaluminium compound. The melting point of the polymers (132 ± 3 °C) is roughly independent of the polymerization conditions and catalytic system composition.

A mixed catalyst composed of cobalt bis(imino)pyridyl complex **3a** (Ar = 2,6-$Me_2C_6H_3$) and nickel complex **1b** has been described.[44]

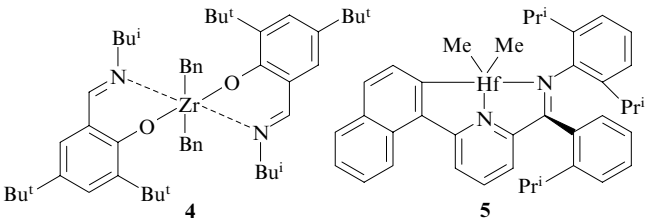


3a–c

The PE produced by this catalyst has a bimodal MWD ($M_w : M_n$ = 8.11–10.36), and the catalyst activity is as high as 2.1×10^6 (g PE) mol^{-1} h^{-1}. The polymer contains branched (formed owing to the nickel precursor) and linear fractions, the branching of the polymer being a linear function of the nickel content in the catalyst, which is evidence on the independent functioning of the active sites. This fact can be used for tailoring the properties of a polymer.

An analogous catalyst composed of complexes **1c** and **2b** (Ar = 2,4-Me_2-6-CyC_6H_2, Cy is cyclohexyl, X = Br) has been reported [45]. The catalyst allows producing polymers with different degree of branching (up to 49.7 Me/1000 CH_2);§ depending on the molar ratio of the catalyst components, the MW of the polymer can vary from 22.0×10^3 to 220.0×10^3. The resulting polymers have a bimodal MWD ($M_w : M_n > 25$). Optimal conditions for the functioning of catalysts of this type have been worked out.[45]

Using a catalyst containing zirconium phenoxyimine derivative **4** and hafnium amidopyridyl complex **5**



and activated by a mixture of MAO and $ZnEt_2$ (the chain transfer agent), researchers at the Dow Chemical Company pioneered the synthesis of block copolymers of ethylene with α-olefins containing segments with different degrees of branching, owing to chain shuttling between two active sites.[17, 18] The polymer densities change within the range from 0.86 to 0.94 g cm^{-3}, whereas the MWD of PE produced at different catalyst component ratios remains unimodal. The system activity is as high as 0.3×10^6 (g PE) mol^{-1} h^{-1}.

A similar approach has been developed by other researchers. A hyperbranched-linear multiblock PE has been prepared in the presence of binary catalyst system **I**.[46] The branched and linear segments (identified by NMR) are a result of the addition of the $ZnEt_2$ agent responsible for chain shuttling between different active sites in the course of polymerization. The system activity is as high as 0.97×10^6 (g PE) mol^{-1} h^{-1} at 20 °C and an ethylene pressure of 0.1 MPa. The M_n values of the polymer is $\sim 10^5$, and the polydispersity coefficient is $M_w : M_n$ = 1.94–2.54.

The largest number of recent studies have dealt with binary systems containing nickel diimine complexes (Table 1). Interest in similar systems stems, first of all, from the possibility that these catalysts yield polymers with short-chain branches owing to the chain walking effect.[47] Thus, binary catalytic systems containing nickel α-diimine complexes enable the preparation of reactor blends composed of branched low-crystallinity PE (low-density linear PE) and linear high-crystallinity PE with a bimodal MWD.

As follows from the data in Table 1, the highest activity is exhibited by the systems in which both components are zirconium metallocene derivatives (No. 1), as well as by the zirconocene–nickel diimine complex (No. 5) and iron bis(imino)pyridyl complex–nickel diimine complex (No. 13, this system yields polymers with the broadest MWD) systems. The activity of the binary systems in toluene is higher than in hexane (see, for example, systems Nos 12 and 13). For the systems based on vanadium and nickel complexes (Nos 8–10), the activity decreases with increasing temperature from 0 to 50 °C. In all cases, the MW characteristics of the end products can be finely regulated by varying the composition of the catalytic system and polymerization conditions.

Markel *et al.*[48] compared the properties of block copolymers obtained by two methods: (1) successive formation of a macromonomer at a high metallocene concentration and a low Al : Zr(Ti) molar ratio and its subsequent copolymer-

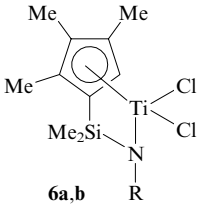
§ nMe/$m$$CH_2$ is the ratio of the methyl and methylene groups.

Table 1. Characteristics of soluble bifunctional catalytic systems.

No.	Catalytic system		$A \times 10^{-6}$ (see [a])	$MW \times 10^{-3}$	$M_w : M_n$	Solvent	T/ °C	p/ MPa	Ref.
	first component	second component							
1	$(\eta^5\text{-}1,2,4\text{-}Me_3C_5H_2)_2ZrCl_2$	$(\eta^5\text{-}Me_5C_5)_2ZrCl_2$	33	97 – 311	2 – 3	toluene	80	0.2	31, 32
2	$[En(Ind)_2]ZrCl_2$	Cp_2HfCl_2	–	69 – 264	4.13	"	50	0.7	33
3	$[En(Ind)_2]ZrCl_2$	**1a**	1.3	220 – 470	~ 2	hexane	30	0.1	35, 36
4	$[En(Ind)_2]ZrCl_2$	**1a**	2.4	–	–	"	50	0.1	35, 36
5	$[En(Ind)_2]ZrCl_2$	**1a**	10.5	67 – 558	2.1 – 3.5	toluene	60	0.7	37
6	$[En(Ind)_2]ZrCl_2$	**1a** + Et_2Zn	0.97	100	1.9 – 2.5	"	20	0.1	46
7	$[En(Ind)_2]ZrCl_2$	**2a**	4.5	40 – 79	11.2 – 17.3	"	50	0.1	38
8	$Tp^{Ms*}VCl_2(NBu^t)$	**1a**	1	–	–	hexane	0	0.1	41
9	$Tp^{Ms*}VCl_2(NBu^t)$	**1a**	0.5	–	–	"	30	0.1	41
10	$Tp^{Ms*}VCl_2(NBu^t)$	**1a**	0.3	–	–	"	50	0.1	41
11	$Tp^{Ms*}TiCl_3$	**1a**	1.4	305 – 1000	3.1 – 53	"	30	0.1	42, 43
12	**2a**	**1a**	4.5	–	96.8 – 148.8	"	0	0.1	40
13	**2b**	**1a**	13.2	22 – 220	> 25	toluene	50	0.3	45
14	**3a**	**1a**	2.1	111 – 240	8.1 – 10.4	"	20	1	44
15	**4**	**5**	261 [b]	100	~2	"	80	0.7	17, 18

[a] Hereinafter, expressed in (kg PE) mol^{-1} h^{-1}; [b] in (g PE) (g metal)$^{-1}$ h^{-1}.

ization with ethylene catalyzed by another catalyst under other conditions and (2) *in situ* preparation of macromonomers and copolymerization in the presence of mixed catalytic systems. As catalyst precursors, Cp_2ZrCl_2 and titanium complex **6a** (R = n-$C_{12}H_{23}$) activated with MAO were used.



6a,**b**

Copolymers of both types had an inverse MW distribution of comonomer units. The polymers prepared by the second method had a lower tensile strength at 20 and 80 °C; however, the ultimate strain (606%) for these polymers considerably exceeded the value found for the block copolymers prepared by the first method (489%). It is worth noting that the tensile strength and ultimate strain for both types of block copolymers are considerably higher than for the linear polymers. Thus, both methods are applicable for preparing new elastomers and enable the control of their rheological properties.

2. Heterogeneous catalysts

a. Heterogeneous catalysts containing conventional Ziegler – Natta systems

Comparison of characteristics of the polymers obtained with the use of hybrid (both components are applied to the same support) and mixed (mechanical mixture of heterogeneous particles) catalysts based on $TiCl_4/MgCl_2$ and Cp_2ZrCl_2,[49, 50] has shown that, in both cases, both types of active sites function independently. This leads to the formation of a product with a bimodal MWD, which can be easily controlled by varying the molar ratio of catalyst components or organoaluminium activators (TIBA : MAO). The M_w value as a function of the catalyst composition changes within wide limits (from 0.5×10^5 to 8×10^5). Hybrid catalysts with these components were prepared by an original procedure,[51] involving the preparation of a bisupport ($SiO_2/MgCl_2$) by the sol – gel method.

A blend of an INPETUS® (Ref. 52), a commercial Ziegler – Natta catalyst, with different metallocene catalysts (Cp_2TiCl_2, Cp_2ZrCl_2, Cp_2HfCl_2, $[En(Ind)_2]ZrCl_2$) activated with MAO leads to PE with a narrow MWD.[53] The bimodal MWD of the resultant polymer is observed only when the $CpZrCl_3$/MAO system is used (Table 2).

Table 2. Activity and MW characteristics of the products obtained with the use of two-site catalytic systems based on an INPETUS® titanium – magnesium catalyst and metallocenes.

Metallocene	$A \times 10^{-6}$ (see [a])	$MW \times 10^{-3}$	$M_w : M_n$
Cp_2TiCl_2	0.61	110	2.6
Cp_2ZrCl_2	0.53	133	2.9
Cp_2HfCl_2	0.29	100	2.6
$CpZrCl_3$	0.45	697	11.2
$[En(Ind)_2]ZrCl_2$	1.1	100	2.7

[a] In 10^5 (g PE) mol^{-1} h^{-1}.

The productivity of a hybrid catalyst based on $TiCl_4/MgCl_2$ and $CpTiCl_3$ in ethylene polymerization can be as high as 5 (kg PE) (g catalyst)$^{-1}$ (Ref. 54). It has been shown that the interaction of the components on the (100) plane of $MgCl_2$ can result in catalytically active $CpTiBu^iCl_2$ particles. The interaction between the metallocene catalyst and the Ziegler – Natta catalysts is responsible for the increase in the activity of the latter. A 2^3 full factorial experiment employed in studying of this system[55] has shown that the effect of the components on each other and on the total productivity of the system considerably depends on the molar ratio between the catalytic system components and the Al : Ti ratio.

Magnesium chloride can serve as a support for mixed catalysts based on Cp_2ZrCl_2 and conventional Ziegler –

Natta catalysts.[56] The best success in controlling the MWD of the resultant PE has been achieved with a catalytic system prepared by succesively applying MAO, Cp_2ZrCl_2 and $TiCl_4$ to water-treated $MgCl_2$ at 70 °C and an ethylene pressure of 0.13 MPa. The polymerization resulted in PE with a bimodal MWD ($M_w : M_n = 26.7$), and the system productivity was 14.4 (kg PE) (g catalyst)$^{-1}$, which is 4.5 times higher than the productivity of the corresponding zirconocene-free catalyst. It has been demonstrated[57] that $MgCl_2$ can be used as a component of a bisupport obtained through the sol–gel route in combination with SiO_2 and that the MWD of the polymers can be controlled by varying the composition of a cocatalyst containing MAO and TIBA.

When a conventional Zigler–Natta catalyst ($TiCl_4$) and Cp_2ZrCl_2 are jointly applied to $MgCl_2 \cdot n$ EtOH, the metallocene catalyst can be activated with triethylaluminium.[58] The resulting polymer has a bimodal MWD, which is not observed in the absence of Cp_2ZrCl_2. This fact is evidence that Cp_2ZrCl_2 is involved in polymerization as a precursor of the active site functioning independently of the titanium–magnesium catalyst. The heterogenized catalyst activated with MAO also yields a polymer with a bimodal MWD. The activity of this catalytic system at 60 °C and a pressure of 2 bar is as high as 23.6×10^6 (g PE) mol^{-1} h^{-1}. SEM has revealed fragmentation of the initial catalyst particles in the course of polymerization, which, according to Ahmadi *et al.*,[58] accounts for the induction period observed in the ethylene consumption curves.

A combined [En(Ind)$_2$]$ZrCl_2$/$TiCl_4$/MAO catalyst applied to a mixed $SiO_2/MgCl_2$ support has been used[59] in synthesis of ethylene copolymers with 1-hexene. The presence of two melting peaks in DSC curves and a broadened MWD demonstrate that there are two types of active sites functioning in the system. Study of the lamellar structure of the resulting copolymer has shown that the size distribution of lamellas in the case of the combined catalyst is narrower than in the case of the corresponding individual catalytic systems. The Al : Zr ratio has an effect on the polymer composition: at Al : Zr = 300, 400 and 500, the product has two melting temperatures (~110 and 130 °C), whereas, at Al : Zr = 200, the DSC curves show one peak at 136 °C. This is due to fact that, under these conditions, the metallocene catalytic system does not form an active site. An increase in the Al : Zr molar ratio is accompanied by an increase in the number of ethylene–hexene–ethylene sequences and by a decrease in the number of ethylene–hexene–hexene sequences in the copolymer backbone,[60] which is evidence of the possibility of preparing both block and alternating copolymers with the use of this catalytic system.

A bimodal PE has been obtained with the use of [En(Ind)$_2$]$ZrCl_2$ applied to the TiO_2 (anatase) surface activated with MAO.[61] As compared with an analogous soluble metallocene catalytic system, the polydispersity coefficient of the PE obtained with the use of the supported system increased from 2.1 to 5.0. The MWD broadening is observed for the TiO_2 support and is not observed for the SiO_2 support. It is evident that this example is a special case of a mixed multisite catalytic system in which the active site precursors are the zirconocene complex and titanium atoms on the support surface. It has been shown that the anatase surface contains quadruply and triply charged titanium cations, which are believed[61] to be precursors of the active site of ethylene polymerization and ethylene copolymerization with 1-hexene.

The broadening of the MWD of PE synthesized with the use of a mixed catalytic system based on titanium–magnesium and zirconocene catalysts in the presence of hydrogen has been reported.[62] The $M_w : M_n$ ratio for such polymers can be as large as 45, which is explained by a different effect of hydrogen additions on the MW of polymer fractions formed under the action of active sites of different types.

The copolymerization of ethylene with 1-butene in the presence of the catalytic system $TiCl_4$/**1a**/$MgCl_2/SiO_2$ activated with AlR_3 has been studied.[63] Varying the Ni : Ti molar ratio leads to a change not only in the content of 1-butene units in the backbone but also in the MW of the end product. The resulting copolymers are characterized by branching values from 10 to 55 Me/1000 CH_2 and $M_w = (1.5–7.5) \times 10^4$. It has been shown that polymerization is also accompanied by oligomerization and formation of olefin macromonomers, which leads to the appearance of long-chain branches in the polymer.[64]

As follows from the data in Table 3, the best studied systems are combinations of zirconocene and titanium–magnesium catalysts. They exhibit moderate activity with respect to the transition metal concentration [up to 23.6×10^6 (g PE) mol^{-1} h^{-1} (see system No. 19)]; however, the productivity of such catalysts can be rather high [14.4 (kg PE) (g catalyst)$^{-1}$ at high MW values, $(620–2150) \times 10^3$ (No. 18)]. Introducing hydrogen into the reactor gas phase enables the control of the MW and MWD of the polymer (compare the data for systems Nos 16 and 22).

Table 3. Mixed catalytic systems of ethylene polymerization containing a titanium–magnesium catalyst as one of the components.

No.	Catalytic system		$A \times 10^{-6}$	P (see [a])	MW $\times 10^{-3}$	$M_w : M_n$	T/ °C	p/ MPa	Ref.
	first component	second component							
16	$TiCl_4/MgCl_2$	Cp_2ZrCl_2	15.7	–	50–800	3.4–42	70	0.13	49–51
17	$TiCl_4/MgCl_2$	$CpTiCl_3$	–	8.3	–	–	75	0.7	54, 55
18	$TiCl_4/MgCl_2$	$Cp_2ZrCl_2/MgCl_2$	–	14.4	620–2150	8.8–27	70	0.13	56, 57
19	$TiCl_4/MgCl_2 \cdot$ EtOH	$Cp_2ZrCl_2/MgCl_2 \cdot$ EtOH	23.6	–	–	–	60	0.2	58
20	$TiCl_4/SiO_2/MgCl_2$	[En(Ind)$_2$]$ZrCl_2/SiO_2/MgCl_2$	–	–	–	–	55	0.13	59, 60
21	TiO_2	[En(Ind)$_2$]$ZrCl_2$	1.3	–	26	5.5	70	0.35	61
22	$TiCl_4/MgCl_2$	Cp_2ZrCl_2	1.2	–	228	45 [a]	40	0.1	62
23	$TiCl_4/MgCl_2$	**1a**	–	6.2 [b]	150–750	–	–	0.1	63, 64

[a] Expressed in (kg PE) (g catalyst)$^{-1}$; [b] in the presence of hydrogen.

b. Heterogeneous catalysts based on several multisite complexes

Mixed catalysts based on SiO_2-supported catalytic systems based on $(Bu^nCp)_2ZrCl_2$ (Bu^nCp is n-butylcyclopentadienyl) and Cp_2ZrCl_2 activated with MAO have been reported.[65] The systems prepared by sequential grafting of the components have a more uniform distribution of a transition metal into a catalyst particle (according to electron probe microanalysis). It has been shown that varying the molar ratio of the metallocene components (from 1 : 1 to 3 : 1) affects the productivity of the catalytic system, whereas the sequence of their layers on SiO_2 has no noticeable effect. The maximal productivity of the system at 60 °C and the molar ratio $Cp_2ZrCl_2 : (Bu^nCp)_2ZrCl_2 = 1 : 3$ was 4.26×10^6 (g PE) $mol^{-1}\ h^{-1}$ in toluene. Unimodal polymers with a polydispersity coefficient of ~ 2 were synthesized. The activity of these catalytic systems and properties of the produced polymers (including polydispersity) significantly depend on the support characteristics, such as the particle size, specific surface and pore volume.[66]

Being activated with butyloctylmagnesium, hybrid system **6b** ($R = Bu^t$)/$(Bu^nCp)_2ZrCl_2$ heterogenized on the SiO_2 surface catalyzes the copolymerization of ethylene with 1-hexene, which leads to a product with a bimodal MWD ($M_w : M_n = 5.05 - 6.32$) and an inverse comonomer distribution.[67] The activity of this system at 70 °C and an ethylene pressure of 4 MPa in an isobutane medium is as high as 1.44 (kg PE) (g catalyst)$^{-1}$ 90 min^{-1} at a titanium and zirconium content of 55 and 10 μmol (g catalyst)$^{-1}$, respectively. The true density of the copolymer can change from 0.9160 to 0.9268 g cm^{-3} depending on the catalyst composition and polymerization conditions. The introduction of 0.02 vol.% of hydrogen into the reactor gas phase leads to a decrease in the product density to 0.9080 g cm^{-3}. It is worth noting that such a system based on metallocene precursors does not require expensive and unavailable MAO for activation, which make them attractive for commercial use.

A hybrid catalyst based on a nickel diimine derivative and Cp_2TiCl_2 can be immobilized on the surface of MCM-41 aluminosilicate particles. The catalyst thus obtained was used for producing reactor blends of linear and branched PE.[68] The length of branches in the polymer depends on reaction temperature (the polymerization catalyzed by the nickel-containing component leads to a polymer with long branches at 50 °C and short branches at 0 °C). SEM has demonstrated that the polymerization temperature also has a considerable effect on the homogeneity of the product since different polymer fractions are characterized by different miscibility.

Three-site systems consisting of Cp_2ZrCl_2, Cp_2TiCl_2 and bis(aryliminopyridyl)iron complex heterogenized on the SiO_2 and MCM-41 surface have been suggested as catalysts of ethylene polymerization.[69] A specific feature of these catalysts is that both the zirconocene and titanocene active sites can catalyze ethylene copolymerization with higher α-olefins so that the end product is a blend of branched copolymers with a bimodal MWD. The activity of these systems is as high as 2.3×10^6 (g PE) $mol^{-1}\ h^{-1}$ at 60 °C and an ethylene pressure of 1 MPa. The polydispersity coefficient of the polymers is 30, $T_m = 122 - 135$ °C, and the crystallinity is within the range from 30% to 52%. The method of application of the catalyst components to the support surface has a decisive effect on the product MWD: successive application of the components to the same support basically leads to a product with a narrow unimodal MWD, whereas separate application of the components to different support portions results in a polymer with a bimodal MWD.[69]

Coimmobilization of a nickel α-diimine complex and iron complex **2c** (Ar = 2-Me-5-ClC_6H_3) on the $MgCl_2$ support has been reported to lead to a considerable increase in the catalyst activity as compared with the activity of each of the individual components.[70] This has been claimed to be a result of reduction of diffusion limitations at the stage when the monomer approaches an active site owing to easier fragmentation of catalyst particles in the course of formation of highly branched PE under the action of the nickel complex. At low nickel complex contents in the hybrid catalyst, the synergistic effect is also observed, which enables the preparation of highly active catalysts that can catalyze the synthesis of both branched and linear high-density polymers. The activity increase caused by the synergistic effect can also be observed for other mixed catalysts containing nickel diimine compounds as one of the components. In particular, when a nickel derivative is added to a titanium–magnesium catalyst, the productivity of the latter increases more than twofold.[71] At the same time, additions of nickel compounds have no noticeable effect on the MW characteristics and other properties of the products.

Catalytic systems based on nickel and iron complexes **1c** and **2b**, respectively, heterogenized on silica (the complexes are identical to those used in soluble system No. 13, Table 1) have been considered.[72] It has been shown that the activity of binary catalytic systems and the MW and short-chain branching of PE samples depend on the method of application of the catalyst components to the support:

— concurrent deposition;

— successive deposition of the first and second component (and *vice versa*) on the same support;

— the use of the components separately deposited on SiO_2.

The highest activity is exhibited by a catalyst obtained by separate deposition on SiO_2 of the components with the relative molar content of the iron complex

$$\frac{[Fe]}{[Fe] + [Ni]} \times 100 = 50\%$$

[$A = 42 \times 10^6$ (g PE) $mol^{-1}\ h^{-1}\ atm^{-1}$]. The polymerization results in PE with low branching (3.7 Me/1000 CH_2), high MW ($M_n > 10^6$) and $T_m = 141$ °C. The highest branching level (15 Me/1000 CH_2, $T_m = 133$ °C) is observed in polymers synthesized in the presence of a catalyst obtained by separate deposition of the components (first, the iron derivative and then, the nickel compound) on the same support.[72]

The active sites of mixed catalytic systems based on complexes **1a** and $Tp^{Ms*}TiCl_3$ deposited on MAO-modified silica function independently, which follows from a linear correlation between the catalyst activity and the content of the first component in the catalyst.[73] This fact has been interpreted as a result of the presence of MAO aggregates in the catalyst structure, which safely isolate different active sites from each other. However, the melting point of the product depends on the sequence of immobilization of transition metal complexes on a support (if the titanium

compound is deposited first, the melting point of the polymers is higher). The activity of the catalytic systems at 30 °C in a toluene medium is no more than 0.7×10^6 (g PE) mol^{-1} h^{-1}, and the crystallinity (according to DSC data) is 20%–40%.

The substitution of the $(Bu^nCp)_2ZrCl_2$ zirconocene for the nickel derivative in the above heterogenized system leads to the formation of linear high-MW PE.[74] The overall catalyst activity is close to the activity of SiO_2-supported zirconocene. An increase in the titanium derivative concentration leads only to an increase in the polymer MW. This has been assigned to the decrease in the probability of hydride shift between two active sites because of the appearance of separating titanium complex molecules.

The microstructure of PE with a bimodal MWD obtained with the use of a mixed catalytic system based on [1-(8-Quin)Ind]$CrCl_2$ [1-(8-Quin)Ind is 8-(inden-1-yl)quinoline] and iron complex **2d** (Ar = 2,4-Me_2-6-ClC_6H_2) heterogenized on $MgCl_2/AlR_n(OR')_{3-n}$ has been studied.[75] In the presence of high-MW fractions of high-density PE in a bimodal polymer ($M_w : M_n$ = 8.4–29.4), high-temperature crystallization induced by shear strain can lead to formation of 'shish-kebab' structures. It has been shown that PE obtained in the presence of mixed catalytic systems can be used as models in studying crystallization processes in polymers with a bimodal MWD.

Hybrid catalysts consisting of $(Bu^nCp)_2ZrCl_2$ and Cp_2NbCl_2 heterogenized on silica gel are highly active [up to 4.5×10^6 (g PE) mol^{-1} h^{-1}] in ethylene polymerization.[76] The activity of the catalyst significantly depends on the method of its preparation: the highest activity was achieved when the support was pretreated with MAO and then successively impregnated with niobocene and zirconocene solutions. The resulting polymers had a narrow MWD ($M_w : M_n < 2$).

Super-acids based on Al_2O_3 treated with ammonium hexafluorozirconate or hexafluorotitanate solutions can be used for activation of $(Bu^nCp)_2ZrCl_2$, an ethylene polymerization catalyst.[77] The resulting polymer has a bimodal MWD, which points to the formation of active sites based on both the metallocene precursor and transition metal atoms in the cocatalyst. There is no need in additional activation of such catalysts with organoaluminium compounds.

It has been suggested to deposit layer-by-layer the catalytic system components on a support, separating these layers with nanofilms of different inert materials (in particular, with polystyrene films).[78]

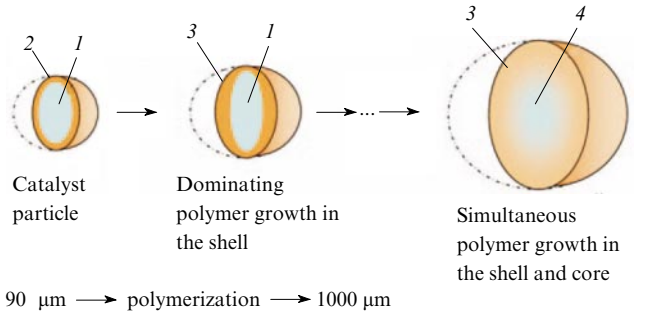


Figure 3. Growth of a polymer particle on the surface of a catalyst prepared by layer-by-layer deposition of components.[78] (*1*) Catalyst A [$(\eta^5$-$MeC_5H_4)_2ZrCl_2$], (*2*) catalyst B {[Me_2Si.(2-MeBenz[*e*]Ind)$_2$]$ZrCl_2$, 2-MeBenz[*e*]Ind is 2-methylbenzo[*e*]inden-1-yl}, (*3*) catalyst B + polymer B (isotactic polypropylene), (*4*) catalyst A + polymer A (atactic polypropylene).

Polymerization of olefins on such catalysts yields polymer particles of inhomogeneous composition since different polymer molecules are formed in the core and shell of the growing polymer particle (Fig. 3). This strategy enables the control of the morphology of a growing polymer particle by varying the composition and structure of the initial catalyst particle.

The data in Table 4 demonstrate that different combinations of single-site catalysts allow synthesizing PEs with different properties. High activity is exhibited by catalytic systems based on both metallocene (No. 26) and non-metallocene (No. 30, No. 31) precursors. However, PE obtained with the use of metallocene precursors is characterized by a narrow MWD (Nos 24–27, 29, 32), which is evidence that the character of the active sites in these systems is close to the single-site one.

3. Catalysts based on polynuclear complexes

Specific hybrid catalysts of ethylene polymerization are those based on polynuclear metal complex precursors. In a molecule of such precursors, two (or more) transition metal atoms can form different active sites of polymerization. The close spatial arrangement of these sites and electronic interactions between them can be responsible for different effects observed when studying the kinetic behaviour of polymerization and properties of resulting polymers ('proximity effect').[79] Similar effects can also emerge if a cocatalyst molecule is polynuclear. Possible variants of

Table 4. Mixed heterogeneous catalytic systems of ethylene polymerization based on several single-site complexes.

No.	Catalytic system		$A \times 10^{-6}$	MW $\times 10^{-3}$	$M_w : M_n$	T/°C	p/MPa	Ref.
	first component	second component						
24	$(Bu^nCp)_2ZrCl_2$	Cp_2ZrCl_2	4.26	100–420	2	60	0.1	65, 66
25	$(Bu^nCp)_2ZrCl_2$	Cp_2NbCl_2	4.5		< 2			76
26	$(Bu^nCp)_2ZrCl_2$	**6b**	22.2	507–900	5.0–6.3	70	4.0	67
27	**1a**	Cp_2TiCl_2	1.3	187–219	~ 2	50	0.1	68
28	**1a**	$Tp^{Ms*}TiCl_3$	0.7			30	0.3	73, 74
29	**2c**	Cp_2TiCl_2, Cp_2ZrCl_2	2.3	23–104	30	60	1.0	69
30	**2a**	**1a**	20			60	0.5	70, 71
31	**2b**	**1c**	42	1000		50	0.3	72
32	**2d**	[1-(8-Quin)Ind]$CrCl_2$	5.5	151–686	8.4–29.4	50	0.5	75

combination of several types of active sites *via* covalent and electrostatic bonding in the system of polynuclear catalyst (cocatalyst) precursors are shown in Fig. 4.

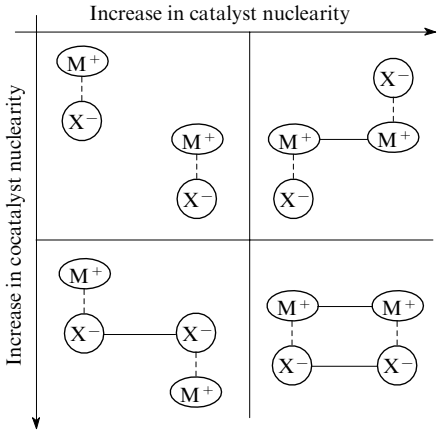
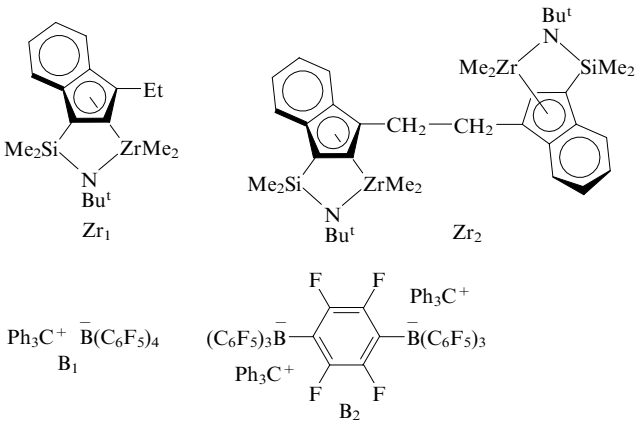


Figure 4. Matrix of combinations of binuclear precursors of catalysts and cocatalysts.[79]

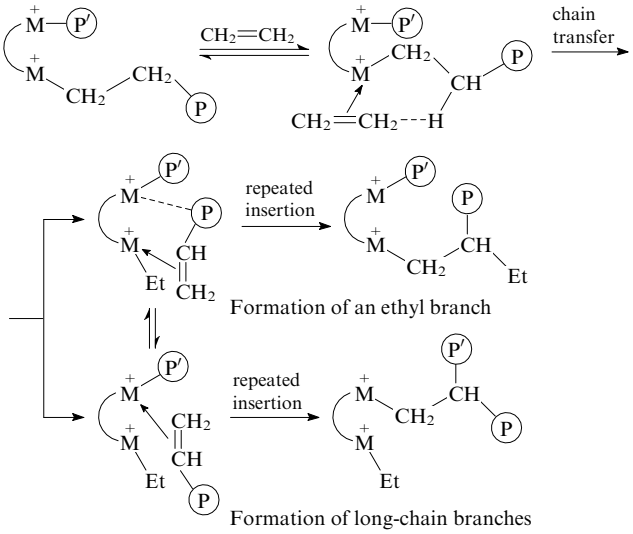
Binuclear constrained-geometry zirconocenes (Zr_2) and binuclear perfluorophenylboronate cocatalysts (B_2) and their mononuclear analogues Zr_1 and B_1, respectively, have been synthesized.[79] An increase in nuclearity (of both the catalyst and cocatalyst) is accompanied by an increase in content of ethyl and butyl branches in the resulting polymers. The most branched polymers have been synthesized with the use of a catalytic system in which both the catalyst and cocatalyst are binuclear ($Zr_2 + B_2$).



In this case, the M_n value of the polymer is also the largest. The increase in polymer branching has been claimed [79] to be a result of coordination of a macromonomer that forms in the β-hydride transfer reaction on one of the active sites 'close' to active sites in the same molecule due to agostic interactions. This facilitates the subsequent repeated 1,2-insertion of the macromonomer, which accounts for the appearance of branches (Scheme 2).

The cooperative effect of two covalently bonded active sites is also manifested in ethylene copolymerization with α-olefins;[80] when binuclear components of the catalytic system are used, the rate of insertion of the olefin comonomer increases more than threefold.

Scheme 2



(P) and (P′) are polymer units of different length, M is a metal.

A decrease in the distance between the zirconium atoms in a binuclear metal complex molecule (the substitution of a methylene bridge for the ethylene bridge between two indenyl ligands) leads to an increase in M_w from 2.5×10^5 to 3.3×10^5 (activation with MAO).[81] This is also evidence of the proximity effect of active sites. The ^{13}C NMR spectra of these complexes activated with MAO show signals corresponding to Zr—(μ-Me)—Zr bridging structures, which points to the possibility of direct interaction between the metal sites and leads to stable conformations with the shortest distance between the metal atoms. When the reaction is carried out in a polar solvent (chlorobenzene), the cooperative effect vanishes, presumably, due to the coordination of a solvent molecule to one of the transition metal atoms of the catalytic precursor.[82]

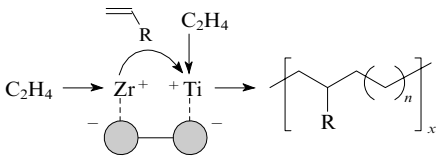
Thus, the proximity effect is sensitive to the nature of both the cocatalyst and the solvent, which is associated with the conformational effect in a molecule of the binuclear organometallic compound. This effect is also observed for styrene polymerization catalyzed by such catalysts, which is explained by coordination of the phenyl group of the monomer to the second transition metal atom in the complex molecule.[82] The proximity effect is caused by both steric and electronic factors in a polynuclear molecule of the catalytic precursor, which supported by quantum chemical density functional theory calculations.[83]

The proximity effect was also observed for binuclear *ansa*-zirconocenes and *ansa*-hafnocenes;[84,85] however, all tested compounds exhibit moderate catalytic activity.

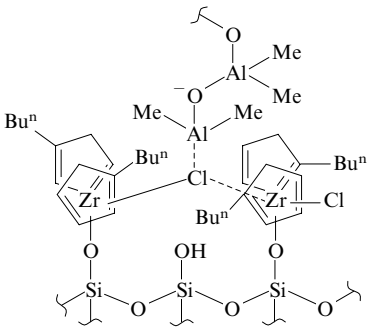
Heterogenization of different polynuclear metallocene complexes [86] on silica gel leads to a considerable increase in the productivity of related catalysts.[87] This is likely related to steric factors that determine the possibility of outer-sphere coordination of a monomer and the probability of chain transfer processes.

Heteropolynuclear complexes containing atoms of both early (Ti, Zr, V) and late (Ni, Pd, Co) transition metals can be used for synthesis of branched polymers.[88] In this case, different active sites in one molecule function as a tandem catalyst system. Using binuclear cocatalysts makes it possi-

ble to enhance the control of the PE composition and homogeneity.[89] In particular, ethylene polymerization under the action of a mixed system containing $[Me_2Si(3\text{-}EtInd)(Bu^tN)]ZrMe_2$ (3-EtInd is 3-ethylinden-1-yl) and $[Me_2Si(\eta^5\text{-}Me_4C_5)(NBu^t)]TiMe_2$ activated with $[Ph_3C^+][B(C_6F_5)_4^-]$ yields PE with a bimodal MWD. The use of the binuclear activator $[Ph_3C^+]_2[1,4\text{-}(C_6F_5)_3.BC_6F_4B(C_6F_5)_3^{2-}]$ rather than the mononuclear one leads to the formation of PE with a unimodal MWD. The DSC curves of this polymer have a single well-pronounced peak corresponding to the melting of a monophase system. The use of the binuclear activator instead of $[Ph_3C^+][B(C_6F_5)_4^-]$ enables the synthesis of products with considerably higher M_n values. The manifestation of these effects can be treated as a result of growing chain exchange between the active sites of different catalysts. It is believed that, in ion pairs formed by the binuclear activator anion and different metallocene cations, such an exchange is mainly intramolecular.[89]



The possibility of formation of mixed binuclear active sites with a common counterion in the heterogenized mixed metallocene catalytic system $Cp_2ZrCl_2/(Bu^nCp)_2ZrCl_2/SiO_2$ has been suggested on the basis of experimental results and extended Hückel calculations.[90]



The zirconium atoms in similar active sites should compete with each other for the coordination to ethylene molecules, and this accounts for the effect of metallocene precursors on each other.

Currently, polynuclear catalyst and cocatalyst precursors are being actively studied. These studies have been described in detail in comprehensive review.[28]

III. Hybrid catalysts for concurrent tandem catalysis

Concurrent tandem catalysis enables the synthesis of ethylene copolymers with α-olefins prepared *in situ* from ethylene. The branching and, hence, crystallinity and true density of similar polymers can be easily controlled by varying the composition of a hybrid catalytic system. It is worth noting that a necessary condition for producing the polymer of constant composition (composition homogeneity) is the same rate of oligomer formation and consumption in the course of copolymerization. This condition considerably complicates the task of creating such systems.

The classification of similar systems is based on the principle of selectivity of the component responsible for ethylene oligomerization, since the systems involving a high-selectivity oligomerization component lead to copolymers with high degree of composition homogeneity. The properties of such copolymers are easy to predict and control. It is also worth noting that the possibility of heterogenization of these systems is favourable from the industrial standpoint (the use in available suspension and gas-phase processes). Joint deposition of the components responsible for oligomerization and copolymerization can result in the formation of a zone with a high comonomer concentration near the catalyst surface. This will be manifested in effects similar to the above proximity effect for catalysts based on polynuclear complexes.[91]

1. Hybrid catalytic systems containing statistical ethylene oligomerization catalysts

Denger *et al.*[92] attempted to synthesize branched PEs using catalytic systems composed of a SHOP-type (Shell Higher Olefins Process) nickel catalyst of ethylene oligomerization and a heterogeneous ethylene polymerization catalyst being a mixture of MgH_2 and α-$TiCl_3$ treated with a Cp_2TiCl_2 solution. The resulting copolymer contained ethyl and butyl branches (the product of copolymerization with 1-butene and 1-hexene, respectively); however, their content was no more than 0.5 mol.%. The low content of comonomer units was explained by the authors as a result of isomerization of the oligomerization products under the action of the Ziegler–Natta catalyst to give 'internal' olefins incapable of further copolymerization with ethylene.

An attempt to combine a SHOP-type nickel catalyst with zirconocene catalytic systems[92] led to a change in the properties of the oligomerization catalyst itself: in the presence of MAO, such a catalyst promotes the isomerization of 1-butene into 2-butene.

The Phillips Petroleum company has patented a chromium oxide catalyst CrO_3 deposited on an inorganic support. Such a catalyst makes it possible to obtain linear low-density PE.[93] Substoichiometric pyrrole (or pyrrole derivative) additions modify some of the active sites. The modified sites catalyze ethylene oligomerization, whereas the non-modified sites catalyze ethylene copolymerization with the oligomerization products. A similar strategy has been used in Ref. 94, where the chromium oxide was modified by $Cr_4(CH_2SiMe_3)_4$. The authors believe that the reduction of some chromium atoms on the catalyst surface converts them into active sites of ethylene oligomerization.

The use of the heterogeneous Cr^{II}/SiO_2 catalyst (a SHOP-type catalyst) yielded PE with long-chain branches.[95] Upon an increase in the Ni : Cr molar ratio, the polymer melting point and density decrease. The branch content of the products has, unfortunately, not been reported.

A combined Ziegler–Natta catalyst ($TiCl_4/MgCl_2$) with iron complex **2e** (Ar = 4-Me-2-ClC_6H_3) enabled the synthesis of branched PE containing from 8 to 29 branches per 1000 carbon atoms.[96] The catalytic system was activated with a mixture of triethylaluminium and MAO. The MW of the polymer was as large as 700 600, and the polydispersity coefficient changed from 8.1 to 12.1. In addition to ethyl

and butyl branches, the polymer contained longer aliphatic substituents, which is indicative of low selectivity of ethylene oligomerization in the presence of iron bis(imino)pyridyl complex under given conditions.

It has been shown that a titanium–magnesium catalyst in combination with iron bis(imino)pyridyl complexes **2** can also be used for preparing branched PE.[97] The activity of such a hybrid catalyst is as high as 2.28×10^6 (g PE) (mol Ti)$^{-1}$ h^{-1}, and the polymer branching is 59 Me/1000 CH_2, branches being mainly short-chain (C_2 and C_4). The polymers obtained at low Fe : Ti ratios have better morphological characteristics, which is associated with their lower solubility in the reaction medium (toluene).

The metallocene catalytic system $[Me_2C(Cp)_2]ZrCl_2$/MAO leads to the formation of ethylene oligomers with M_w up to 4500 and the content of terminal double bonds >96%. Combining this system with titanium complex **6b** allows one to synthesize polymers with long-chain branches (the branch length is up to 350 carbon atoms).[98] The polymer is easy to separate from olefin macromonomers by the Kumagawa extraction method. Polymers obtained by ethylene copolymerization with macromonomers isolated after the ethylene oligomerization with the use of the above zirconocene have also been studied.[98] The distribution of macromonomers in the products obtained by successive synthesis is more homogeneous than in the products prepared *in situ*.

The **2**/MAO catalytic system (Ar = 2-MeC_6H_4 (**2f**), 2-EtC_6H_4 (**2g**) and 2-$Pr^iC_6H_4$ (**2h**) exhibits high selectivity in ethylene oligomerization resulting in higher olefins, mainly in liquid α-olefins.[99] A combination of this system with metallocene catalysts of ethylene polymerization $[Me_2Si(Ind)_2]ZrCl_2$/MAO and $[En(Ind)_2]ZrCl_2$/MAO (Ref. 100) gives bifunctional catalysts that enable the synthesis of linear low-density PE with T_m = 100–126 °C and a comonomer content of up to 3 mol.%. The use of the $[Me_2Si(Ind)_2]ZrCl_2$/MAO catalyst leads to a polymer with a bimodal MWD, and an increase in the Fe : Zr molar ratio entails an increase in the content of the high-MW fraction. At the same time, the polydispersity coefficient of the polymers changes from 9.1 to 16.1 at $M_w = (29.9–80.5) \times 10^3$. The maximal activity achieved for this system was 21×10^6 (g PE) (mol Zr + mol Fe)$^{-1}$ h^{-1} bar^{-1}. Conversely, the use of a system containing $[En(Ind)_2]ZrCl_2$ results in polymers with a unimodal MWD ($M_w : M_n$ = 1.56–1.91), which at $M_w = (65.1–81.2) \times 10^3$ remains roughly unaltered with a change in the molar ratio of the catalyst components. The observed maximal activity was 34×10^6 (g PE) (mol Zr + mol Fe)$^{-1}$ h^{-1} bar^{-1}. ^{1}H and ^{13}C NMR showed that the resulting polymers had ethyl, butyl and long-chain branches.[101] In some cases, while long-chain branches were identified, the existence of short-chain branches was not confirmed. At large Fe : Zr molar ratios, unreacted low-molecular-weight α-olefins were identified in the products.

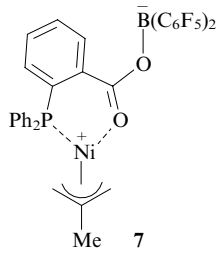
Study of a combination of catalytic systems based on complexes **2i** (Ar = 2,6-$F_2C_6H_3$) and $[En(Ind)_2]ZrCl_2$[102] showed, that at some ratios of catalytic system components, polymers with two melting points can form (bimodal DSC curves). The authors explained this fact by the formation of a blend of polymers with different contents of side groups (branches). The activity of the system was as high as 20.93×10^6 (g PE) (mol Fe + mol Zr)$^{-1}$ h^{-1} atm^{-1}, the branching of polymers was 36 Me/1000 CH_2, T_m = 97.9–121.0, density was 0.915–0.935 g cm^{-3}, the MW of polymers was within the range (162–276) 10^3, and the polydispersity coefficient ($M_w : M_n$ = 1.67–2.65) corresponded to a unimodal MWD.

A system differing from the above one in that the zirconocene component was immobilized on the montmorillonite surface has been studied.[103] The activity of such a system can be as high as 5.92×10^6 (g PE) (mol Fe + mol Zr)$^{-1}$ h^{-1} atm^{-1}. With a change in the Fe : Zr molar ratio, the polymer density changes from 0.9282 to 0.9650; T_m, from 86.2 to 131.1 °C; and the crystallinity (according to DSC data), from 11.6% to 69.6%. A decrease in the Fe : Zr molar ratio in the catalyst leads to a decrease in the MW of a polymer. At large ratios, the GPC curves are bimodal with a low-molecular-weight peak $M_w \approx 1000$, which is explained by assuming that the polymer contains high-molecular-weight ethylene oligomerization products not involved in the copolymerization reaction on the zirconocene catalyst. The size distribution of polymer particles shows that heterogenization of the zirconocene component improves the morphology of the end product.

Iron bis(imino)pyridyl complexes can be used not only as soluble catalytic systems of ethylene oligomerization but also as major components for preparation of heterogenized catalytic systems. A heterogenized bifunctional catalyst of ethylene polymerization was created,[104] both components (iron complex **2i** and $[En(Ind)_2]ZrCl_2$) being fixed on a support. The support was calcosilicate of composition 0.28 K_2O : 0.13 CaO : 1.00 SiO_2 : 22 H_2O. The activity of the heterogenized catalytic system containing the above iron complex is as high as 4.43×10^6 (g oligomers) (g Fe)$^{-1}$ h^{-1}. The activity of the tandem catalytic system is comparable with this value. Noteworthy are the increase in M_w [from 2.9×10^4 to $(5.5–6.5) \times 10^4$] and the MWD broadening (from 1.8 to ~3.5), which is explained[104] by partial washout of the catalyst from the support surface and formation of two types of active sites : heterogenized and soluble. The melting point of the resultant polymers changes in the range from 105.6 to 118.3 °C and the degree of branching changes from 22 to 67 Me/1000 CH_2 (according to ^{13}C NMR).

A mixture of $Tp^{Ms}NiCl$ [Tp^{Ms} is hydridotris(3-mesitylpyrazol-1–yl)borate] and the supported Cp_2ZrCl_2/MAO/SiO_2 catalyst has been studied.[105] The system exhibited an activity of 12.3–309.1 (kg PE) mol^{-1} h^{-1} atm^{-1}. The properties of the resultant polymers depend on the content of the nickel compound in the catalyst and polymerization temperature; for example, the MW of the PE significantly depends on the nickel compound content and can change from 30×10^3 to 507×10^3, while the MWD remains unimodal. Heterogenization of the metallocene component leads to a decrease in the content of 1-butene and 1-hexene units in the copolymer as compared with the copolymer obtained with the use of an analogous soluble catalytic system. Studying the morphology of the resulting polymers demonstrates that, as in the case of many other heterogenized systems, the replication effect is observed, *i.e.*, the influence of the catalyst particle morphology on the morphology of the resultant polymer particles.[106]

As is known, titanium monocyclopentadienyl chelate complexes (constrained-geometry complexes) efficiently catalyze ethylene copolymerization with higher α-olefins. A combination of such a catalyst with nickel complex **7**



7

gives a tandem catalytic system, which enables the synthesis of PEs with short branches containing two and four carbon atoms (the products of ethylene copolymerization with 1-butene and 1-hexene).[107] ^{13}C NMR shows that the polymers contain up to 9.1% of ethyl and up to 1.8% of butyl branches. The MW of the products (according to GPC data) decreases with an increase in the Ni : Ti molar ratio and, while the latter changes from 0 to 2, is within $M_w = (329-63)\times10^3$ (Ref. 108). It is worth noting that, as the Ni : Ti molar ratio increases, a bimodal MWD changes to a unimodal MWD of the polymers, while the polydispersity coefficient decreases from 7.43 to 3.35.

Ethylene polymerization catalyzed by nickel complex **1b** results in a blend of α- and β-olefin oligomers with $M_w \approx 460$.[109] A combination of this catalyst with titanium complex **6** (R = Me or Bu^t) supported on pyridylethylsilane-modified silica produces polymers with long-chain branches [$M_w = (15-50)\times10^3$]. When the titanium complex with R = Me is used, the resulting polymers have, depending on the Ni : Ti molar ratio in the catalyst, from 9 to 21 branches per 1000 carbon atoms, T_m = 125.7–140.9 °C, the crystallinity is 38.0%–67.6% (according to DSC) and $M_w : M_n$ = 17.7–20.9. The activity of the tandem system as compared with the initial titanium catalyst decreases more than threefold [from 1426 to 447 (kg PE) mol^{-1} h^{-1}]. In the case of the titanium complex with R = Bu^t, the polymers have from 4 to 10 branches per 1000 carbon atoms, T_m = 119.7–133.3 °C, the crystallinity is 57.0%–79.4% (according to DSC) and $M_w : M_n$ = 10.2–16.4 (the MWD is bimodal, the content of the high-molecular-weight fraction increases with an increase in the Ni : Ti molar ratio). The activities of the systems in the absence and presence of the nickel complex are comparable.

Cobalt iminopyridyl complexes **3b**,**c** [Ar = 2-Me-4-MeOC$_6$H$_3$ (**b**), 2,4-Me$_2$C$_6$H$_3$ (**c**)] coupled with the [En(Ind)$_2$]ZrCl$_2$ zirconocene have been used[110] as a dual catalytic system for the synthesis of branched linear low-density PE. The activity of these catalysts is as high as 11.95×10^6 (g PE) (mol Zr)$^{-1}$ h^{-1} atm^{-1}. The resulting polymers have a narrow unimodal MWD with $M_w \approx 5\times10^4$. Their backbone contains ~4 mol.% of ethyl, butyl and long-chain branches (according to ^{13}C NMR), and the melting points are within the range 109.2–126.5 °C.

A combination of cobalt iminopyridyl complexes with titanium monocyclopentadienyl derivative **6b** gives a productive [up to 4.57×10^6 (g PE) (mol Ti) h^{-1} at an ethylene pressure of 3 bar and 30 °C] soluble tandem catalyst system,[25] which enables the synthesis of branched PEs (copolymers of the ethylene–1-butene–1-hexene composition). Under the above conditions, polymerization leads to a thermoplastic polymer with a density of 0.868 g cm^{-3} and a glass transition temperature of −55 °C.[111] Varying the molar ratio of catalyst components makes it possible to precisely control the degree of branching and synthesize polymers with branching up to 254 Me/1000 CH$_2$ and a melting point from 47 to 110 °C. The MW of the products is $(332-567)\times10^3$, and the MWD is unimodal ($M_w : M_n$ = 1.50–2.40).[112]

PE with long-chain branches can also be prepared in the presence of a combined catalytic system containing the heterogeneous oligomerization catalyst (acac)$_2$ZrCl$_2$/montmorillonite/Et$_2$AlCl (acac is acetylacetonate) and the homogeneous metallocene catalyst of polymerization [En(Ind)$_2$]ZrCl$_2$/MAO.[113] A blend of olefins formed under the action of the first catalyst consists of 80% 1-hexene and 1-octene, which makes it possible to obtain polymers with a fixed branch length. Of special interest is the possibility of joint functioning of catalysts, one of which being a heterogenized catalyst of ethylene oligomerization.

Branched PEs have been synthesized[114] with the use of a dual mixed catalyst based on zirconium acetylacetonate and zirconocene. It has been shown that immobilization of the catalyst components in the porous montmorillonite structure does not reduce the catalytic activity of the system. This fact can be used as a basis for development of the method of preparation of linear low-density PE filled with montmorillonite.

An interesting example of a tandem catalytic system of ethylene polymerization has been described.[115] The authors used an original approach consisting in combination of two types of active sites (oligomerization and polymerization) that form from the same metallocene precursor under the action of two different organoaluminium compounds. As zirconium-containing precursors, [En(Ind)$_2$]ZrCl$_2$ and bis(dibenzoylmethanato)zirconium dichloride [(dbm)$_2$ZrCl$_2$] were used. It was demonstrated that both complexes in the presence of Et$_2$AlCl exhibit high activity in the ethylene oligomerization to linear α-olefins. The same complexes being activated with MAO catalyze ethylene polymerization. The polymers obtained with the use of the [En(Ind)$_2$]ZrCl$_2$/Et$_2$AlCl/MAO system have T_m from 107.6 to 130.7 °C, $M_w = (104-156)\times10^3$ and the polydispersity coefficient 6.5–7.2. The (dbm)$_2$ZrCl$_2$/Et$_2$AlCl/MAO system enabled the synthesis of PEs with T_m = 117.2–131.7 °C, $M_w = (46-121)\times10^3$ and $M_w : M_n$ = 12.6–27.8. This result is evidence of the wide possibilities of the method of *in situ* preparation of branched PE with the use of catalytic systems in which the active sites are formed from one precursor under the action of different activators.

Branched PEs can be obtained in the presence of the (η^5-Me$_5$C$_5$)Ti(OBz)$_3$/MMAO catalytic system.[116] At a high residual content of trimethylaluminium in MMAO, the Ti^{IV} derivatives undergo deeper reduction to Ti^{III} and Ti^{II} complexes. This leads to the formation of a large number of active sites, which can promote ethylene oligomerization. With an increase in the trimethylaluminium content in alumoxane from 18.6% to 26.1%, the T_m values of the resulting polymers decreases from 139.6 to 117.2 °C (the latter polymer contains 32.6 branches per 1000 carbon atoms as probed by ^{13}C NMR).

According to the data in Table 5, catalysts containing Group VIII metal bis(imino)pyridyl complexes as the component responsible for the statistical ethylene oligomerization have been best studied. They are combined with both high-activity polymerization catalysts based on zirconocenes (Nos 34–39) and titanium-containing constrained-geometry complexes (Nos 40–43) that afford ethylene

Table 5. Characteristics of hybrid catalytic systems containing catalysts of statistical ethylene oligomerization.

No.	Active site precursor		$A \times 10^{-6}$	MW $\times 10^{-3}$	$M_w : M_n$	T / °C	p / MPa	Branching / Me/1000 CH_2	T_m /°C	Ref.
	oligomerization	polymerization								
33	**2e**	$TiCl_4/MgCl_2$	1.95 – 2.28	700 – 830	8.1 – 13.3	50	0.1	8 – 59	–	96, 97
34	**2e**	$(Me_2Cp)(Ind)ZrCl_2$	21	29.9 – 80.5	9.1 – 16.1	60	0.2	3 [a]	100 – 126	100
35	**2e**	$[En(Ind)_2]ZrCl_2$	36	65.1 – 81.2	1.56 – 1.91	60	0.2	–	–	100, 101
36	**2i**	$[En(Ind)_2]ZrCl_2$	21	162 – 276	1.67 – 2.65	50	0.1	36	97.9 – 121.0	102
37	**2i**	$[En(Ind)_2]ZrCl_2$ (see [b])	5.9	64	–	60	0.1	24 – 78	86.2 – 131.1	103
38	**2i**	$[En(Ind)_2]ZrCl_2$ (see [c])	4.43	55 – 65	3.5	80	0.1	22 – 67	105.6 – 118.3	104
39	**3b**	$[En(Ind)_2]ZrCl_2$	12	50	~2	60	0.1	4 [a]	109.2 – 126.5	110
40	**3c**	**6b**	4.8	332 – 567	1.5 – 2.4	30	0.3	254	47 – 110	25, 111, 112
41	$Me_2C(Cp)_2ZrCl_2$	**6b**	3.3	101 – 244	2.1 – 2.3	75	0.1	0.33		98
42	**1a**	**6b**	0.5	15 – 50	17.7 – 20.9	70	0.5	9 – 21	125.7 – 140.9	109
43	**7**	**6b**	0.2	63 – 329	3.4 – 7.4	20	0.3	10 [a]	–	107, 108
44	$Tp^{Ms}NiCl$	Cp_2ZrCl_2/SiO_2	0.3	507	~2	60	0.3	–	–	105, 106
45	$(acac)_2ZrCl_2$ (see [d])	$[En(Ind)_2]ZrCl_2$	1.0	30 – 100	–	50	0.5	–	116 – 133	113, 114
46	$[En(Ind)_2]ZrCl_2 + Et_2AlCl$	$[En(Ind)_2]ZrCl_2$ + MAO	0.9	104 – 156	6.5 – 7.2	110	1.2	–	107.6 – 117.3	115
47	$(dbm)_2ZrCl_2 + Et_2AlCl$	$(dbm)_2ZrCl_2$ + MAO	12.1	46 – 121	12.6 – 27.8	60	0.1	–	117.2 – 131.7	115

[a] In mol %. Support: [b] MCM-41; [c] calcosilicate; [d] montmorillonite.

copolymers with α-olefins containing a larger number of comonomer units and, hence, having a higher degree of branching. Nickel complexes with phosphoylide [SHOP-type catalysts), No. 43] or α-diimine ligands (No. 42) can also act as catalysts of statistical ethylene oligomerization. In many cases, the MW characteristics and branching of the resulting polymers can be regulated within wide limits. The highest activity is exhibited by the systems based on zirconocene complexes (Nos 34 – 36, 39).

2. Hybrid catalytic systems containing selective catalysts of ethylene oligomerization

Key characteristics of hybrid catalytic systems containing selective catalysts of ethylene oligomerization are listed in Table 6. The first attempt to combine ethylene oligomerization and polymerization catalysts with the aim of producing linear low-density PEs with short-chain branches at the backbone has been made by Beach and Kissin.[23, 117] They used mixtures of catalytic systems of selective ethylene dimerization to 1-butene based on titanium tetraalkoxides $Ti(OR)_4$ and triethylaluminium with a conventional titanium – magnesium polymerization catalyst $TiCl_4/MgCl_2$/PE. It was demonstrated that varying the composition of a catalyst mixture makes it possible to obtain polymers with branching from 0 to 80 Me/1000 CH_2; this leads to a change in the crystallinity of the products from 70% to 10% and in the polymer density from 0.95 to 0.90 g cm^{-3}. The product of the constants of ethylene copolymerization with 1-butene for this system, 1.7, found by means of statistical analysis is typical of titanium – magnesium catalysts. Analysis of polymerization kinetics showed that the components of mixed systems have a considerable effect on each other, which generally complicates the construction of the precise kinetic model of polymerization and hinders the development of the scientific basis for control of its parameters.

Joint functioning of the titanium alkoxide catalytic system of selective ethylene dimerization $Ti(OBu^n)_4/AlEt_3$ and the metallocene catalytic system of polymerization $[En(Ind)_2]ZrCl_2$/MAO has been described.[118] In toluene at 50 °C, the combined system leads to unimodal PEs ($M_w/M_n < 2.5$) with extremely low T_m (to 81.9 °C) and true density values (to 0.8801 g cm^{-3}). The system activity is as high as 4.7×10^6 (g PE) mol^{-1} h^{-1}. It is worth noting that an increase in the molar content of titanium in the mixed catalyst leads to narrowing of the MWD of the

Table 6. Characteristics of hybrid catalytic systems containing selective catalysts of ethylene oligomerization.

No.	Active site precursor		$A \times 10^{-6}$	MW $\times 10^{-3}$	$M_w : M_n$	T / °C	p / MPa	Branching / Me/1000 CH_2	T_m /°C	Ref.
	oligomerization	polymerization								
48	$Ti(OBu^n)_4$	$TiCl_4$ / $MgCl_2$	–	–	–	–	–	0 – 80	–	23, 117
49	$Ti(OBu^n)_4$	$[En(Ind)_2]ZrCl_2$	4.7	–	< 2.5	–	–	–	81.9	118
50	$Ti(OBu^n)_4$	$[En(Ind)_2]ZrCl/SiO_2$	5.6	–	–	50	0.5	6.5 [a]	–	119
51	**8**	**6b**	4.6	40 – 568	2.5 – 5.8	–	–	0.3 – 14.2 [a]	60 – 128	123
52	**8**	**6b**	–	40 – 1267	–	–	–	–	88 – 120	124
53	$(SNS)CrCl_3$	$[En(Ind)_2]ZrCl_2$	10	55 – 201	~3	–	–	–	95 – 120	120 – 122
54	$(Ph_2P)_2NCy/Cr(acac)_3$	$[En(Ind)_2]ZrCl_2$	–	79 – 153	–	–	–	–	101.1 – 134.1	127

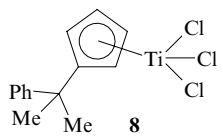
[a] In mol.%.

polymers. A major disadvantage of the system is the necessity of using a combined cocatalyst ($AlEt_3$ / MAO).

A combination of the highly selective ethylene dimerization catalyst $Ti(OBu^n)_4/AlEt_3$ with the heterogenized metallocene catalyst $MAO/SiO_2/[En(Ind)_2]ZrCl_2$, which ensures a high degree of 1-butene insertion into the growing polymer chain, gives an efficient tandem catalyst yielding copolymers with the 1-butene content up to 6.51 mol.%.[119] An increase in the $AlEt_3$: Ti molar ratio in the system leads to a considerable narrowing of the polymer MWD, which is evidence of reversible chain transfer to the organoaluminium compound. The decrease in MW, melting point and crystallinity of the polymer with an increase in the Ti : Zr molar ratio has been explained by the increase in the number of branches in the polymer backbone and the increase in the probability of chain termination. The activity of the hybrid system is as high as 5.57×10^6 (g PE)$^{-1}$ (mol Zr)$^{-1}$ h^{-1} at 50 °C and an ethylene pressure of 0.5 MPa in toluene. The true density of polymers changes in the range from 0.960 to 0.901 g cm^{-3}; *i.e.*, the system enables the synthesis of high-, medium- and low-density PE, depending on the molar ratio of the components.

As a catalytic system for ethylene oligomerization, a system of selective trimerization can be considered (the major comonomer in the composition of the end polymer will be 1-hexene, while short-chain branches at the backbone are exclusively butyl groups). The system containing bis(dodecylsulfanylethyl)amine (SNS)–$CrCl_3$ and the copolymerization catalyst $[En(Ind)_2]ZrCl_2$ in combination with MAO has been studied.[120,121] The copolymerization yields a polymer containing only butyl branches at the backbone with T_m in the range 95–120 °C. The maximal activity of the catalytic system in ethylene polymerization was 10^7 (g PE)$^{-1}$ (mol Zr)$^{-1}$ h^{-1}. Deposition of any of the components on SiO_2 did not improve the activity and selectivity of the system. The MW of the resulting PEs was $(55–201) \times 10^3$, and the polydispersity coefficient was ~3. At low temperatures and high Cr : Zr molar ratios, polymers with a wide MWD (according to DSC curves) were obtained. The introduction of the zirconocene component some time after the onset of the trimerization reaction catalyzed by the chromium-containing complex led to copolymers with a more homogeneous composition, which follows from DSC data.[121] The kinetic model of ethylene polymerization in the presence of the above catalyst has been considered.[122] The results obtained with the use of this model are consistent well with experimental data.

Titanium complex **8** in combination with MMAO has been used as an ethylene trimerization catalyst.[123]



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The 1-hexene formed under the action of this catalyst is copolymerized with ethylene on titanium complex **6b**/MAO or zirconocene catalyst *rac*-Me_2Si(2-MeBenz[*e*]Ind)$_2ZrCl_2$/MMAO or their mixture. Varying the molar ratio of the components in the catalytic system makes it possible to obtain polymers with T_m = 60–128 °C, the degree of crystallinity 5.4%–53% (according to DSC data) and the 1-hexene content 0.3%–14.2%. The maximal activity of the catalytic system based on titanocene is 4600 (kg PE) g^{-1} h^{-1}, The MW of the polymers is $(40–568) \times 10^3$ at the polydispersity coefficient 2.5–5.8 (as shown by GPC).

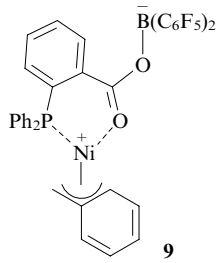
A combination of titanium complexes **6b** and **8** activated with MAO enables the synthesis of ethylene copolymers with 1-hexene almost free of other comonomer units owing to the high selectivity of the component responsible for ethylene trimerization.[124] Such a system allows producing linear low-density PEs with T_m = 88–120 °C and $M_w = (40–1267) \times 10^3$.

Polymers synthesized in the presence of concurrent tandem catalysts can contain long-chain branches in addition to short branches. In particular, studying the rheological properties[125] suggested the presence of long-chain branches in the polymers obtained from ethylene under the action of the catalytic system containing MMAO-activated titanium complexes **6b** and **8**. In the case of polymers synthesized at low temperature (25 °C), the content of long-chain branches increases with a decrease in the molar ratio of the complexes in the catalyst owing to the excessive accumulation of macromonomers that form as the 1-hexene concentration in the system increases. At higher temperature (45 °C), the inverse dependence is observed, which is explained by the increase in mobility and solubility of macromonomers at a limited number of undesired chain terminations.[125]

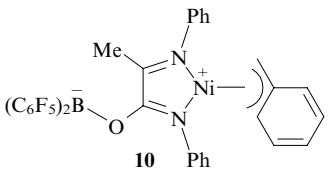
The catalyst of selective ethylene tetramerization to 1-octene based on bis(diphenylphosphinamino)chromium was used[126] in combination with the $[Ph_2C(Cp)(Flu)]ZrCl_2$ and $[En(Ind)_2]ZrCl_2$ metallocene complexes for creating a homogeneous tandem catalytic system for production of linear low-density PE. At 40 °C, the described system mainly leads to ethylene oligomerization products (1-octene and 1-hexene). With an increase in temperature to 100 °C, the major product is a copolymer containing up to 1.5 mol.% of octene and hexene units with a density of 0.922–0.948 g cm^{-3} and T_m = 114–132 °C (depending on the Cr : Zr molar ratio in the catalyst). The polydispersity coefficient of all the polymers is ~2, which is evidence of the multisite character of the polymerization catalytic system.

The synthesis of ethylene copolymers with 1-octene catalyzed by tandem catalysts has been described.[127] Selective tetramerization of ethylene to give 1-octene occurs in the presence of the $(Ph_2P)_2NCy/Cr(acac)_3$/MAO system. The *in situ* copolymerization of this 1-octene with ethylene under the action of $[En(Ind)_2]ZrCl_2$/MAO gives a branched polymer which has, depending on the catalyst composition, T_m = 101.1–134.1 °C, density 0.922–0.950 g cm^{-3} and $M_w = (7.93–15.31) \times 10^4$. In one of the experiments, the distribution of branches was the following: 0.12 mol.% ethyl groups, 0.43 mol.% butyl groups and 1.02 mol.% hexyl groups.

A combination of catalytic systems of three processes — dimerization, oligomerization and ethylene copolymerization — enabled the synthesis of polymers in which not only the total number of branches but also the molar ratio between the ethyl and butyl branches in the copolymer can be controlled[128]. The system containing $[Me_2Si(\eta^5\text{-}Me_4C_5).(NBu^t)]TiMe\}\{MeB(C_6F_5)_3\}$ (a constrained-geometry complex) and nickel complexes **9** (a catalyst of ethylene dimerization to 1-butene) and **10** (a catalyst of statistical oligomerization of ethylene)



9



10

allows producing polyolefins with the comonomer content up to 46%, $T_m = 67-116$ °C, MW = $(75-1522)\times10^3$ and the polydispersity coefficient 3.8–8.3. The content of 1-butene units in the copolymer chain can be changed (from 0.27% to 2.74%) by varying the catalyst composition, the contents of higher olefin comonomers remaining nearly unaltered.

IV. Mathematical simulation of polymerization processes in the presence of mixed catalysts

A kinetic model of polymerization on catalysts containing two types of kinetically different interconvertible active sites was suggested for the first time in Ref. 129. It has been shown that, at different kinetic model parameters, the MWD function can be nonmodal, unimodal or bimodal. Scientific grounds for control of MWD characteristics have been developed.

It has been shown[130] that combination of different soluble metallocene catalytic systems based on Ti, Zr and Hf derivatives makes it possible to prepare polymers with a unimodal and bimodal MWD, and decomposition of the bimodal MWD into modes with the use of the Haarhoff–Van der Linde function

$$y(x) = \frac{a_0 a_2 \exp[-1/2(x - a_1 a_2)]}{\sqrt{2}\pi a_1 a_3 [(a_1 a_3/a_2^2) - 1]^{-1} + 1/2\{1 + \mathrm{erf}[(x-a)/\sqrt{2}a]\}},$$

where $a_0 - a_3$ are empirical parameters, indicates that different active sites in the system can function independently (Fig. 5).

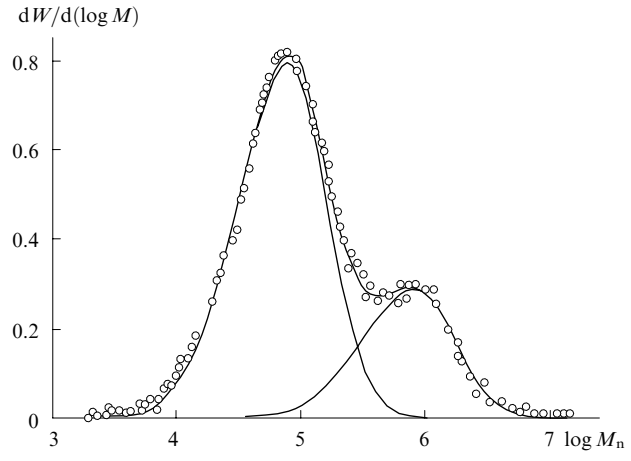


Figure 5. Decomposition of the MWD function into unimodal components.[130]

A mathematical model describing the effect of polymerization conditions and catalytic system composition on PE properties for hybrid metallocene catalysts has been developed.[131] The case in which one of the system components catalyzes the formation of a linear polymer and the second component catalyzes the formation of a polymer with long-chain branches has been considered. The model implies that one of the catalysts catalyzes the formation of macromonomers and the other catalyst catalyzes their copolymerization with ethylene to produce a branched polymer (a cross product). It has been demonstrated that the monomer concentration has no effect on the cross product and the dispersity coefficient of the resulting polymer; however, an increase in the monomer concentration leads to formation of longer chain branches and to a decrease in the statistical probability of branching of the polymer chain. The number of branches, polydispersity coefficient, the content of the cross-product fraction and branch length decrease with an increase in the deactivation rate of each of the components of the catalytic system.

A criterion has been suggested[132] for evaluation of the possibility of synthesis of bimodal PE with the use of mixed catalysts. If the number-average chain lengths of the polymers obtained in the presence of each of the catalysts alone (r_{w1} and r_{w2}) meet the condition

$$\frac{(r_{w1} - r_{w2})^2}{2r_{w1}r_{w2}} > 1,$$

the mixed system will lead to the formation of a bimodal polymer.

The r_w values can be determined by the equation

$$r_w = \frac{2}{\tau},$$

where τ is the ratio of the chain growth and termination rates in the course of polymerization.

A model based on the Galerkin finite element method[133] suggested in Ref. 134 and applied to describe the MWD of the products obtained with the use of the mixed catalytic system based on a constrained-geometry titanium-containing complex and $[En(Ind)_2]ZrCl_2$ gives the results consistent with experimental data. The best fit between the experimental and theoretical values is observed when the model implies the possibility of formation of high-molecular-weight branched polymers *via* copolymerization of linear α-olefin macromonomers, formed in the presence of a zirconocene catalyst, with ethylene under the action of a constrained-geometry complex. The effect of the ratio of the catalytic system components on the MWD of the product and the polymer branching has also been studied.[134] It has been shown that for the most reliable prediction of experimental results, possible interaction of two types of active sites should be considered.

The MWD function for PE obtained with the use of mixed catalytic systems in which one of the components catalyzes formation of a linear polymer and the other, formation of a branched polymer, has been found.[135] In this case, the MWD function is a normalized sum of the MWDs of the polymers formed under the action of each of the catalysts separately. Necessary kinetic parameters for the model can be found with allowance for the degree of branching of the resulting polymer calculated from

^{13}C NMR data. If both catalysts are responsible for branching of the polymer chain, this complicates the problem of constructing a model describing the MWD and branch distribution in the polymer. However, Read and Soares [135] described a recursive algorithm that enables to solve this problem by the Monte Carlo method. The results of modelling with the use of this method [136] confirmed the adequacy of the suggested model.

The distribution of topological sorts of branched polymer chains formed by mixed multisite catalysts can also be predicted by the Monte Carlo method.[137] It has been shown that the chain topology and the branch number and length are an extremal function of the mixed catalyst composition.

* * *

The information reported in this review reveals considerable current interest in developing multisite catalysts of ethylene polymerization, notwithstanding the difficulty of simulation and technological elaboration of polymerization processes promoted by these catalysts. Multisite catalysts make it possible to considerably reduce the price of polymer production; moreover, they enable the smooth control of their consumer properties (density, grain size distribution, melting point, physicomechanical and rheological properties) by varying the component ratio in the catalytic system. In addition, the synergistic effect, which enhances the activity of multisite catalysts and MW characteristics of the products, opens additional possibilities for creation of new high-performance catalytic systems of ethylene polymerization. Similar catalysts are already used in industry.[138]

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[b] — *Kinet. Catal. (Engl. Transl.)*