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Homogeneous catalysts for ethylene polymerization based on bis(imino)pyridine complexes of iron, cobalt, vanadium and chromium

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Results of a comparative study of ethylene polymerization activity and the structure of polyethylene (PE) produced over homogeneous catalysts based on bis(imino)pyridine complexes with close ligand frameworks and different transition metal centers (Fe(II), Co(II), Cr(III) and V(III)) are reported. The effects of the activator nature and polymerization conditions on the activity of these complexes and the resulting PE structure (molecular weight, molecular weight distribution, content of methyl and vinyl groups) have been studied. The experimental data obtained under comparable conditions demonstrate a pronounced effect of transition metal center on the catalytic properties of bis(imino)pyridine complexes (polymerization activity, copolymerization reactivity, thermal stability, PE structure, composition of optimal activator, formation of single-site or multiple-site catalytic system).

1. Introduction

At present, complexes of transition metals with polydentate nitrogen-containing ligands are considered as one of the most promising families of post-metallocene catalysts for olefin polymerization [1,2]. In the last 10 years, it was shown that 2,6-bis(imino)pyridine complexes of Fe(II) and Co(II) ($LMCl_2$, where M = Fe(II) or Co(II), L = 2,6-bis(imino)pyridine ligand) activated with methylaluminoxane (MAO) form extremely active homogeneous catalysts for ethylene polymerization to linear polyethylene (PE) [3–5].

Later, it was shown [6,7] that these complexes can be activated with common aluminum trialkyls ($AlMe_3$, $Al(i\text{-}Bu)_3$, $Al(n\text{-}Oct)_3$), which substantially simplifies the catalytic systems based on bis(imino)pyridine complexes and broadens the possibilities of their use in the polymerization processes. Highly linear PE samples are obtained with iron and cobalt bis(imino)pyridine complexes. The values of molecular weight (M_w) and molecular weight distribution of the resulting PEs are governed by the substituents in phenyl rings of the ligand [5,8–10], giving the possibility to obtain polymers with different values of M_w—from oligomers to high-molecular-mass PE. Following the initial discovery of highly active iron and cobalt catalysts for olefin polymerization, both vanadium(III) [11–13] and chromium(III) [14–16] complexes with bis(arylimino)pyridine ligands have also been identified as promising catalysts for catalytic polymerization applications.

Commonly, the data on the catalytic properties of systems based on bis(imino)pyridine complexes of various composition are discussed separately in the literature. Such an approach hinders ascertainment of patterns in the catalytic properties of these systems since the catalytic activity and molecular structure of the resulting PE are affected by polymerization conditions (catalyst concentration, the nature and amount of the activator, polymerization temperature, etc.). A comparison of Fe-, Cr- and V-based bis(imino)pyridine complexes immobilized on $MgCl_2$ support [17] shows that the nature of transition metal centers of the bis(imino)pyridine complexes has a pronounced impact on the catalytic properties of these systems. Anchoring of bis(imino)pyridine complexes on the supports of different composition (silica, alumina, $MgCl_2$) noticeably affects their catalytic properties, giving rise to less active but more stable sites to produce PE with higher molecular weight in comparison with that of corresponding homogeneous catalysts [17–19]. In this study we summarize the known data and present new results on the polymerization properties of homogeneous catalysts based on Fe(II), Co(II), V(III) and Cr(III) bis(imino)pyridine complexes with close ligand framework. A detailed study of the effect of the activator nature on catalytic behavior of bis(imino)pyridine complexes and the resulting PE structure has been undertaken. The experimental data have been obtained under comparable conditions allowing us to reveal the effect of transition metal on the catalytic properties of homogeneous catalysts based on bis(imino)pyridine complexes.

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2. Experimental

2.1. Materials

Toluene and heptane were dried over molecular sieves (4 Å), purified by refluxing over sodium metal, distilled in dry argon, and then degassed in vacuum. All solvents and prepared solutions were stored and handled in vacuum. All the experiments were carried out in sealed high vacuum systems using breakseal techniques.

Bis(imino)pyridine complexes: 2,6-(2,6-$(Me)_2C_6H_3N{=}CMe)_2C_5H_3NFeCl_2$ ($LFeCl_2$), 2,6-(2,6-$(Me)_2C_6H_3N{=}CMe)_2C_5H_3NCoCl_2$ ($LCoCl_2$), 2,6-(2,6-$(Et)_2C_6H_3N{=}CMe)_2C_5H_3NVCl_3$ ($LVCl_3$) and 2,6-(2,4,6-$(Me)_3C_6H_3N{=}CMe)_2C_5H_3N\ CrCl_3$ ($LCrCl_3$), were prepared according to Refs. [5,12,14].

Activators: MAO-commercial sample (Crompton) purchased as a toluene solution with total Al content 1.8 M and Al as $AlMe_3$ ~0.5 M).

MAO samples with the reduced content of $AlMe_3$: MAO(20) ($AlMe_3$ content ca. 0.01 M) and MAO(50) ($AlMe_3$ content ca. 0.001 M) were prepared by evacuating the commercial MAO at 20 and 50 °C, respectively. Thus obtained solid products were dissolved in toluene (total Al concentration 0.1 M).

MMAO–MAO modified with $Al(i\text{-}Bu)_3$ (commercial sample (AKZO) purchased as a heptane solution with total Al content 1.7 M).

Triphenylmethyl tetrakis(pentafluorophenyl)borate ($Ph_3C[B(C_6F_5)_4]$) was a commercial sample (Strem Chemicals) used as a 0.1 M toluene solution.

Aluminum trialkyls $AlMe_3$ (TMA), $Al(i\text{-}Bu)_3$ (TIBA), $Al(n\text{-}Oct)_3$ (TOA) were commercial samples.

2.2. Ethylene polymerization and ethylene-1-hexene copolymerization

Ethylene polymerization was performed in a 0.5 L steel reactor. A sealed glass ampoule with the weighed amount of bis(imino)-pyridine complex (0.001 g, 2×10^{-6} mol) was placed into the reactor. The reactor was heated at 80 °C in vacuum for 1 h and then cooled to 25 °C. Then the reactor was charged with the appropriate amount of activator to provide a molar ratio Al/M = 500 dissolved in 150 mL of toluene (MAO, TMA) or heptane (TIBA, TOA). The reaction mixture was heated to the desired temperature (35–70 °C), saturated with ethylene (2–5 bar), and the ampoule with the bis(imino)pyridine complex was broken to start the reaction. 1-Hexene was introduced into the reactor once at the beginning of the polymerization run. During the reaction the ethylene pressure was maintained constant through automatic computer-controlled system for the ethylene feed, recording the ethylene consumption and providing the kinetic curve output both in the form of a table and as a graph.

2.3. Polymer characterization

GPC measurements of PE molecular weight (M_w, M_n) and molecular weight distribution (M_w/M_n, MWD) were performed using a WATERS-150C High Temperature Chromatograph equipped with the four mixed bed TSK-gel columns set (GMHXL-HT, Tosoh Corp.). Run conditions: 140 °C; flow rate of 1 cm^3/min; 1,2,4-trichlorobenzene (TCB) used as a solvent. The data were collected and processed with a Viscotek GPC Software version 3.0. Conventional calibration was made using narrow PS standards and PE standards.

The microstructure of the obtained polymers was analyzed using high temperature ^{13}C NMR spectroscopy. The weighed amount of PE (50–100 mg) was dissolved in 3 mL of diclorobenzene, and inverse gated $^{13}C\{^1H\}$ spectra were recorded on a Bruker AVANCE 400 spectrometer at 100.613 MHz in 10 mm standard glass tubes at either 90 or 100 °C. Operating conditions used: spectral width 30 kHz; spectrum accumulation frequency 0.1–0.05 Hz; number of transients 500–2000. The content of terminal propyl groups was determined from the integral intensities of ^{13}C signals at δ 13.6 ($-CH_2CH_2\mathit{C}H_3$), 22.4 ($-CH_2\mathit{C}H_2CH_3$), and 31.7 ($-\mathit{C}H_2CH_2CH_3$). To determine the content of terminal vinyl groups the integral intensities of ^{13}C signals at δ 113.7 ($-CH_2CH{=}\mathit{C}H_2$), 138.6 ($-CH_2\mathit{C}H{=}CH_2$), 33.4 ($-\mathit{C}H_2CH{=}CH_2$) were measured.

The content of $-CH_3$ groups and double bonds in high molecular weight PE samples and ethylene-1-hexene copolymers was measured according to Ref. [20] using IR spectroscopy with a FTIR-8400S SIMADZU Fourier spectrometer.

3. Results and discussion

3.1. Catalysts based on $LFeCl_2$

The data on the activity of homogeneous catalytic systems composed of $LFeCl_2$ with different activators and structure of the resulting PE are summarized in Table 1. The kinetic curves for corresponding polymerization runs are shown in Fig. 1. All the systems examined exhibited low thermal stability and virtually lost polymerization activity at temperatures above 50 °C. At 35 °C highly active catalytic systems providing high PE yield were formed upon activation of $LFeCl_2$ with both different MAO samples and aluminum trialkyls (TMA, TIBA and TOA) (Table 1). In contrast to metallocene catalysts, a borate activator was not effective for iron bis(imino)pyridine based catalysis (Table 1, run 7). The examined catalysts exhibited high initial activity decreasing in the course of polymerization (Fig. 1). The system stability and PE yield depended on the activator nature. The catalyst obtained upon activation of iron complex with commercial MAO exhibited very high initial activity, but the latter rapidly fell with the polymerization time (Fig. 1, curve 1). The systems formed by $LFeCl_2$

Table 1
Ethylene polymerization using homogeneous catalysts based on $LFeCl_2$.

Run no.	Activator	Yield (kg PE/mol Fe bar)	[a]Maximum activity (kg PE/mol Fe bar min)	M_w ($\times 10^{-3}$)	M_w/M_n	[b]Content per 1000C		[b]Content per PE molecule	
						CH_3	$CH{=}CH_2$	CH_3	$CH{=}CH_2$
1[c]	MAO	9,100	500	71	8.3	1	0.8	1.2	0.9
2[c]	MAO(50)	11,000	330	75	4.6	0.8	1.0	1.0	1.2
3[d]	MMAO	6,800	430	–	–	–	–	–	–
4[c]	TMA	12,300	300	106	12.0	1.9	0.7	1.5	0.5
5[d]	TIBA	7,600	250	115	10.8	1.5	0.6	1.4	0.6
6[c]	TOA	12,300	320	46	6.3	1.4	1.2	1.1	0.9
7[c]	$Ph_3C[B(C_6F_5)_4 + Al(i\text{-}Bu)_3$	470	20	–	–	–	–	–	–

[a] Calculated according to Fig. 1.

[b] IRS data.

[c] Polymerization in toluene at 35 °C, ethylene pressure 2 bar, for 30 min, [Fe] = 1.4×10^{-5} mol/l, Al/Fe = 500.

[d] Polymerization in heptane, all other conditions being the same.

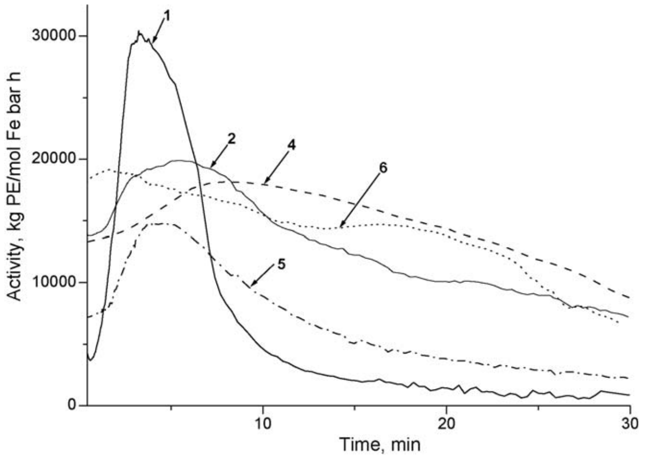

Fig. 1. Time dependence of the ethylene polymerization activity over homogeneous catalysts based on $LFeCl_2$ and different activators: (1) MAO, (2) MAO(50), (4) TMA, (5) TIBA, (6) TOA. (Number on the curve corresponds to the number of experiment in Table 1.)

interaction with aluminum trialkyls (TMA, TOA) provided a higher PE yield (Table 1, runs 4 and 6) than that obtained in the presence of MAO and MMAO (Table 1, runs 1 and 3) due to the higher stability of these systems (Fig. 1, curves 4 and 6). The catalysts formed by interaction of iron complex with TIBA and MMAO, soluble in aliphatics, show high initial activity in the polymerization in heptane medium (Table 1, runs 3 and 5). These systems were less stable than those prepared using MAO(50), TMA and TOA (Fig. 1), causing the reduced yield of PE.

The obtained polyethylene samples were highly linear (about one $-CH_3$ and one $-CH{=}CH_2$ group per one PE molecule) (Table 1). The values of molecular weight and polydispersity (M_w/M_n values) depend on the activator nature. The data of Table 1 and Fig. 2 show that in the presence of MAO(50) purified from TMA, PE with the lowest polydispersity was obtained ($M_w/M_n = 4.6$, Table 1, run 2 and Fig. 2, curve 2), whereas the M_w/M_n value of PE sample prepared using commercial MAO was noticeably higher ($M_w/M_n = 8.3$, Table 1, run 1 and Fig. 2, curve 1). Polymers prepared with the systems ($LFeCl_2$ + TIBA) and ($LFeCl_2$ + TMA) were characterized with the highest M_w values (Table 1, runs 4 and 5), whereas using TOA as activator, PE sample with the lowest molecular mass was obtained (Table 1, run 6). Broad molecular weight distribution of the polymers formed in the presence of catalysts composed of $LFeCl_2$ and different activators indicates that a set of different active sites is formed in these catalytic systems, so the catalysts of this type should be regarded as multiple-site catalysts.

A kinetic study of the ethylene polymerization catalyzed by ($LFeCl_2$ + Al(i-Bu)$_3$) and ($LFeCl_2$ + MAO) [21] showed the average value of propagation rate constant (k_P), the number of active centers (C_p), M_w and M_w/M_n values of the obtained PE samples to depend on the polymerization time. As it was shown in [21], for the catalyst system ($LFeCl_2$ + Al(i-Bu)$_3$), with the increase in polymerization time from 2 to 15 min the M_w value of the produced PE increases from 39,000 to 100,000 and the M_w/M_n value—from 7.6 to 9.6. The polydispersity and M_w of PE obtained with ($LFeCl_2$ + MAO) catalyst also increase with the polymerization time. It was concluded that at the initial stage of polymerization, highly active but unstable centers are formed in both systems. These centers produce the low molecular mass PE. The number of these centers decreases with the polymerization time, at the same time the less active and more stable centers appear in the system, producing PE with high M_w.

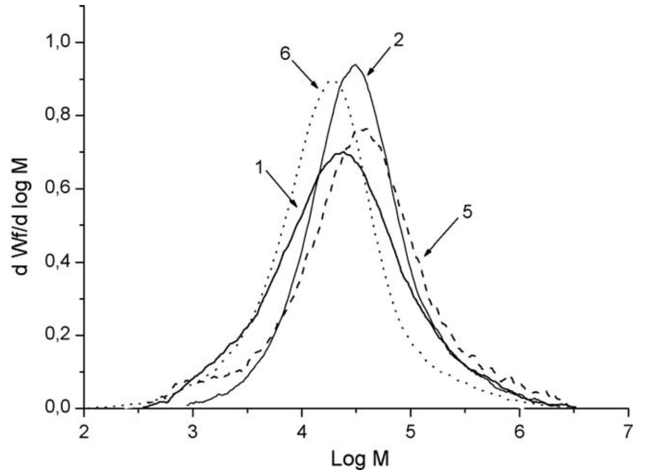

Fig. 2. MWD of PE produced with homogeneous catalysts based on $LFeCl_2$ and different activators: (1) MAO, (2) MAO(50), (5) TIBA, (6) TOA. (Number on the curve corresponds to the number of experiment in Table 1; W_f = weight fraction, M = molecular weight.)

The active intermediates of the catalysts based on bis(imino)pyridine iron complex with different activators (MAO, TMA, TIBA, TOA) were studied by ^1H, ^2H NMR and EPR spectroscopy [7,22–25]. The authors of [22] reported that upon interaction of $LFe(II)Cl_2$ with an excess of MAO, the intermediates containing iron in the +3 oxidation state might be formed (however, the question how iron(II) catalyst precursors could afford iron(III) catalysts in the presence of such reducing agents as $AlMe_3$ and MAO was not considered). Later on, by a comparative study of $LFeCl_2$/MAO and $LFeCl_3$/MAO catalysts, it was shown that the closest precursors of the active centers in both catalysts are ferrous complexes containing iron in the +2 oxidation state [24].

The structure of the intermediates was determined from ^1H and ^2H NMR spectra. It was reported that under the conditions approaching a real polymerization, neutral heterobinuclear complexes of the type $[LFe(II)Cl(\mu\text{-}R)_2AlR_2]$ or $[LFe(II)R(\mu\text{-}R)_2AlR_2]$ dominate in the reaction solution in $LFeCl_2 + AlR_3$ systems, whereas in $LFeCl_2$/MAO systems the ion pairs $[LFe(II)(\mu\text{-}Me)(\mu\text{-}Cl)AlMe_2]^+[Me{-}MAO]^-$(at $Al/Fe < 200$) and $[LFe(II)(\mu\text{-}Me)_2AlMe_2]^+[Me{-}MAO]^-$(at $Al/Fe > 500$) were the predominant species [23–25].

Thus, the main characteristics of iron bis(imino)pyridine complex as an active component of the homogeneous ethylene polymerization catalyst are as follows: (1) high activity at activation with different organoaluminum activators and especially with aluminum trialkyls; (2) low thermal stability; (3) formation of linear PE with high M_w and broad MWD; (4) noticeable effect of the organoaluminum activator on the M_w and M_w/M_n values of the resulting PE; (5) formation of the catalysts with multiple active sites upon interaction of $LFeCl_2$ with both MAO and aluminum trialkyls.

3.2. Catalysts based on $LCoCl_2$

Table 2 presents the data on catalytic activity for ethylene polymerization over Co(II) bis(imino)pyridine complex ($LCoCl_2$) with different activators and the characteristics of the obtained PE samples. The results of Table 2 (runs 1–3) show that, when activated with the same co-catalysts (Table 1, runs 1, 2, and 4), $LCoCl_2$ exhibited a noticeably lower activity than the analogous Fe(II) bis(imino)pyridine complex. The catalytic system ($LCoCl_2$ + TIBA) was almost inactive (Table 2, run 4). Like the $LFeCl_2$-based systems, catalysts with $LCoCl_2$ as the active component were inactive at polymerization temperatures above 50 °C. The time-dependent polymerization activities with the catalysts based on $LCoCl_2$ are shown in Fig. 3. As in the case of iron, the catalysts based

Table 2
Ethylene polymerization using homogeneous catalysts based on $LCoCl_2$.

Run no.	Activator	Yield (kg PE/mol Co bar)	[a]Maximum activity (kg PE/mol Co bar min)	M_w ($\times 10^{-3}$)	M_w/M_n	[b]Content per 1000C		[b]Content per PE molecule	
						CH_3	$CH{=}CH_2$	CH_3	$CH{=}CH_2$
1[c]	MAO	3.100	80	1.5	1.8	25.0	23.0	1.0	1.0
2[c]	MAO(50)	2.700	100	1.9	1.9	16.0	16.8	1.0	1.0
3[c]	TMA	3.600	60	1.6	1.8	16	16	1.0	1.0
4[d]	TIBA	20	10	–	–	–	–	–	–

[a] Calculated according to Fig. 3.

[b] ^{13}C NMR data.

[c] Polymerization in toluene at 35 °C, ethylene pressure 5 bar, for 30 min, [Co] = 1.4×10^{-5} mol/l, Al/Co = 500.

[d] Polymerization in heptane, all other conditions being the same.

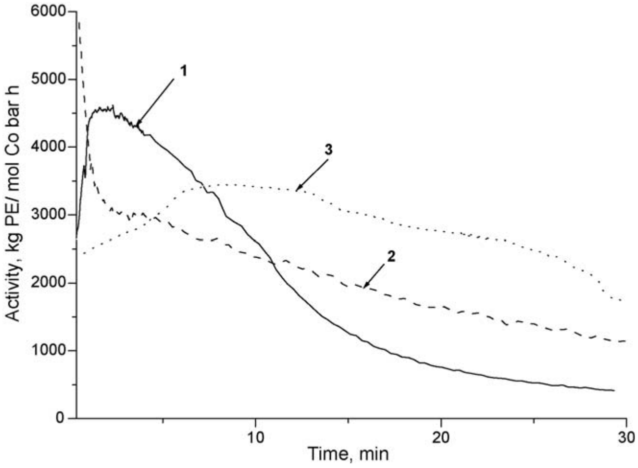

Fig. 3. Time dependence of the ethylene polymerization activity over homogeneous catalysts based on $LCoCl_2$ and different activators: (1) MAO, (2) MAO(50), (3) TMA. (Number on the curve corresponds to the number of experiment in Table 2.)

on $LCoCl_2$ demonstrated high initial activity that fell with the increase in polymerization time. The values of the initial activity and the rate of deactivation depend on the activator composition. Similar to $LFeCl_2$, $LCoCl_2$ activated by MAO demonstrated the highest initial activity (Table 2, run 1 and Fig. 3, curve 1) and the highest deactivation rate. The catalyst formed by interaction of cobalt complex with TMA was characterized by a noticeably higher stability (Fig. 3, curve 3).

The PE samples obtained with homogeneous catalysts based on $LCoCl_2$ were characterized by low M_w and narrow MWD (M_w/M_n = 1.8–1.9, Table 2). These polymers were extremely linear, containing only one terminal $-CH_3$ and one $-CH{=}CH_2$ group per polymer molecule (Table 2). M_w and MWD values of the polymers produced with $LCoCl_2$ activated by different activators (commercial MAO, MAO with reduced content of TMA–MAO(50), and pure TMA) were comparable. Thus, at the interaction of $LCoCl_2$ with different activators only one type of active center is formed, and in contrast to $LFeCl_2$, the homogeneous catalysts based on $LCoCl_2$ can be regarded as the single-site catalysts.

The intermediates formed upon $LCoCl_2$ activation with MAO and TMA have been studied by ^1H and ^2H NMR spectroscopy [7]. Formation of Co(I) and Co(II) species has been identified in these systems. However, the detailed assignment of the ^1H NMR resonances of these species is still not completed and the real structures of the active intermediates of these catalysts remain unclear.

3.3. Catalysts based on $LVCl_3$

The data about ethylene polymerization with the homogeneous catalysts based on V(III) bis(imino)pyridine complex ($LVCl_3$) are presented in Table 3 and Fig. 5. In contrast to the iron and cobalt-based catalysts (inactive at polymerization temperatures above 50 °C), catalytic systems based on $LVCl_3$ were highly active at 60 °C (Table 3, runs 1 and 3), indicating a higher thermal stability of the active centers formed in these systems. At 35 °C, $LVCl_3$ activated with commercial MAO gave a stable kinetic curve (Fig. 4, curve 1). In polymerization runs at 60 °C, the catalyst ($LVCl_3$ + MAO) showed high initial activity (Fig. 4, curves 2 and 3) that rapidly fell with the polymerization time. Reducing the free TMA content in MAO samples used for vanadium complex activation (MAO(20)) (Table 3, run 4) led to a decrease in the initial activity and PE yield. In the presence of MAO completely purified from free TMA (MAO(50)) or with TMA as activator, $LVCl_3$ was inactive.

PE prepared with the catalysts ($LVCl_3$ + MAO) displayed high linearity and low M_w (Table 3). The value of PE polydispersity depends on the polymerization conditions (temperature and polymerization time). PE with narrow MWD (M_w/M_n = 2.4) was obtained in polymerization run at 35 °C (Table 3, run 1). The increase in polymerization temperature up to 60 °C resulted in the formation of PE with noticeably broader MWD (M_w/M_n = 4.8, Table 3, run 3 and Fig. 5, curve 3). PE with narrow MWD (M_w/M_n = 2.1) and lower M_w formed at short polymerization time (4 min, Table 3, run 2 and Fig. 5, curve 2). Evidently, interaction of $LVCl_3$ with MAO at the increased temperature generates highly

Table 3
Ethylene polymerization using homogeneous catalysts based on $LVCl_3$.

Run no.	Activator	T_{pol} (°C)	Polymerization time (min)	[a]Yield (kg PE/mol V bar)	[b]Maximum activity (kg PE/mol V bar min)	M_w ($\times 10^{-3}$)	M_w/M_n	[c]Content per 1000C		[c]Content per PE molecule	
								CH_3	$CH{=}CH_2$	CH_3	$CH{=}CH_2$
1	MAO	35	30	3,300	170	6.7	2.4	–	–	–	–
2	MAO	60	4	3,250	350	5	2.1	–	–	–	–
3	MAO	60	30	11,000	360	12	4.8	4.2	4.2	1.0	1.0
4	MAO(20)	60	30	6,500	260	–	–	–	–	–	–

[a] Polymerization in toluene at ethylene pressure 2 bar, [V] = 1.4×10^{-5} mol/l, Al/V = 500.

[b] Calculated according to Fig. 4.

[c] ^{13}C NMR data.

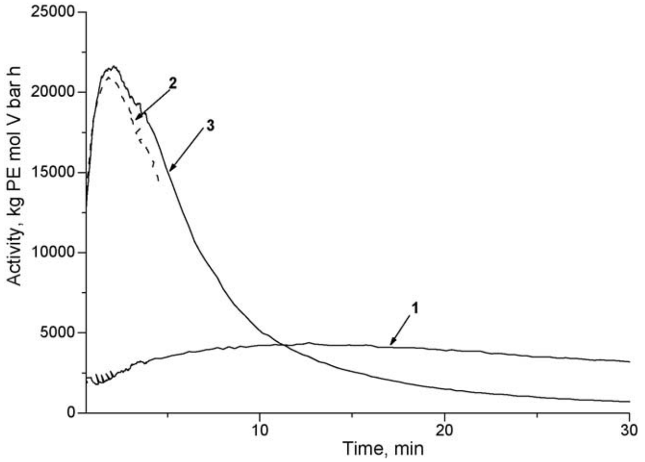

Fig. 4. Time dependence of the ethylene polymerization activity over homogeneous catalysts $LVCl_3$ + MAO: (1) polymerization at 35 °C, (2) polymerization at 60 °C for 4 min, (3) polymerization at 60 °C for 30 min. (Number on the curve corresponds to the number of experiment in Table 3.)

active but unstable centers of only one type. These centers are responsible for the formation of PE with low M_w and narrow MWD at the beginning of polymerization. As the polymerization proceeds, the new centers that produce PE with higher M_w are formed. As a result, M_w and M_w/M_n values of the resulting PE increase.

The nature of active species formed upon interaction of $LVCl_3$ with MAO remains unclear. The ($LVCl_3$ + MAO) samples display broad unresolved NMR and EPR spectra that hinder assignment of the signals.

Thus, MAO is an effective activator for $LVCl_3$. The reduction of free TMA content in MAO reduces the catalytic activity of $LVCl_3$ + MAO system. The active centers formed by the interaction of $LVCl_3$ with MAO demonstrated higher thermal stability in comparison with those of $LFeCl_2$ and $LCoCl_2$-based systems. The catalyst ($LVCl_3$ + MAO) acts as a single-site system at low polymerization temperatures (35 °C). At high temperature (60 °C) it acts as a single-site catalyst only at a short polymerization time, but as the polymerization proceeds it turns out to be a multi-site catalyst.

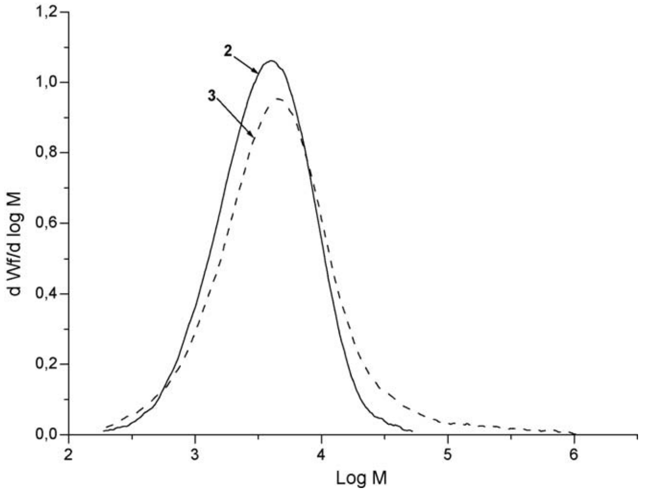

Fig. 5. Effect of time on the MWD of PE produced with homogeneous catalyst $LVCl_3$ + MAO. Polymerization at 60 °C: (1) 4 min, (2) 30 min. (Number on the curve corresponds to the number of experiment in Table 3; W_f = weight fraction, M = molecular weight.)

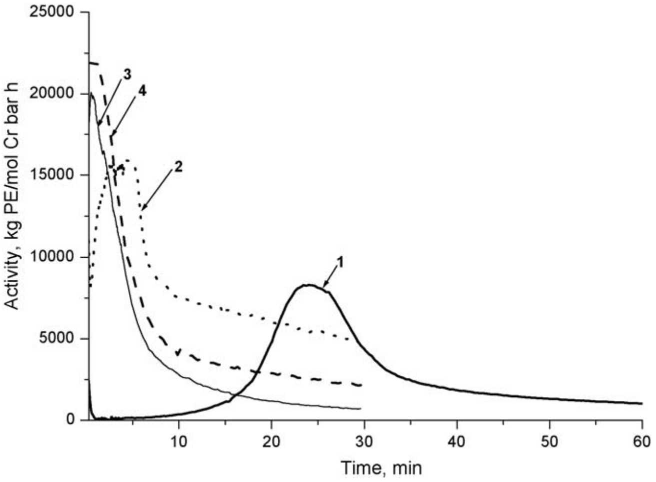

Fig. 6. Time dependence of the ethylene polymerization activity over $LCrCl_3$ at various preactivation modes and polymerization temperatures: (1) polymerization in toluene without preactivation with MAO as co-catalyst, at 70 °C and 5 bar of C_2H_4, (2) preactivated with MAO (T. pol 35 °C), (3) preactivated with MAO (T. pol 70 °C), (4) preactivated with MAO(50) (T. pol 70 °C) (preactivation at $Al_{MAO}/Cr = 200$, polymerization in heptane with TIBA as co-catalyst (TIBA/Cr = 1000), 5 bar of C_2H_4). (Number on the curve corresponds to the number of experiment in Table 4.)

3.4. Catalysts based on $LCrCl_3$

Fig. 6 (curve 1) shows the time-dependent ethylene polymerization activity at 70 °C over chromium(III) bis(imino)pyridine complex activated with MAO. In contrast to the previously described catalysts based on iron, cobalt and vanadium complexes, and in line with the results of Esteruelas et al. [14], a long period of acceleration is observed for polymerization run with the catalyst $LCrCl_3$ + MAO.

An effective method to form the active component of the homogeneous catalysts based on chromium bis(imino)pyridine complex by preliminary interaction of $LCrCl_3$ with MAO solution at a low molar ratio of components ($Al_{MAO}/Cr = 100–200$) was suggested in Ref. [14]. Thus prepared solution of the chromium complex is very stable and could be used for ethylene polymerization at 70 °C in heptane with TIBA as an additional co-catalyst. In the case of pre-activation of $LCrCl_3$ with MAO at the molar ratio $Al_{MAO}/Cr = 200$, the polymerization starts immediately with high activity (Fig. 6, curve 2), providing higher PE yield in comparison with that of the system without preactivation (Table 4, runs 1 and 3).

The EPR studies of the catalyst systems $LCrCl_3$ + activator (where activator was MAO, MMAO) have shown the appearance of EPR spectra after mixing the reagents. These spectra are characteristic of $S = 3/2$ chromium(III) complexes [26]. However, the initial signals of Cr(III) disappeared within 5–30 min, depending on the nature of the co-catalyst used. Apparently, the activation of $LCrCl_3$ with MAO leads to the formation of the active centers via the reduction of Cr(III) to a lower oxidation state.

The data of Table 4 show that the preactivated systems ($LCrCl_3$/MAO) + TIBA are highly active at the increased polymerization temperature (70 °C, Table 4, runs 2–5). The yield of PE obtained in polymerization run at 35 °C was 1.5 times higher than that obtained in polymerization at 70 °C (compare runs 2 and 6, Table 4) due to a higher stability of the catalyst at lower polymerization temperature (Fig. 6, curves 2 and 3). Catalytic systems based on $LCrCl_3$ preactivated by different samples of MAO were characterized by close kinetic curves (Fig. 6, curves 3 and 4) and produced highly linear PE with narrow MWD ($M_w/M_n = 1.7–1.9$) and close M_w values ($1.2–1.5 \times 10^3$) (Table 4, runs 1–4).

Table 4
Effect of preactivation mode on the ethylene polymerization activity of $LCrCl_3$.

Run no.	[a]Pre-activator	[Cr] (μmol/l)	Yield (kg PE/mol Cr bar)	[b]Maximum activity (kg PE/mol Cr bar min)	M_w ($\times 10^{-3}$)	M_w/M_n	[c]Content per 1000C		[c]Content per PE molecule	
							CH_3	$CH{=}CH_2$	CH_3	$CH{=}CH_2$
1[d]	–	20.0	4,740	140	1.3	1.9	–	–	–	–
2[e]	MAO	3.3	7,880	330	1.5	1.9	17.0	15.6	1.0	1.0
3[e]	MAO(20)	5.0	9,680	400	–	–	–	–	–	–
4[e]	MAO(50)	5.0	9,920	360	1.2	1.7	17.2	15.9	1.0	1.0
5[e]	MMAO	5.0	2,870	300	–	–	–	–	–	–
6[f]	MAO	5.0	12,400	260	1.1	1.9	–	–	–	–

[a] Molar ratio Al/Cr = 200.
[b] Calculated according to Fig. 6.
[c] ^{13}C NMR data.
[d] Polymerization in toluene at 70 °C, ethylene pressure 5 bar, for 60 min, co-catalyst MAO ($Al_{MAO}/Cr = 500$).
[e] Polymerization in heptane at 70 °C, ethylene pressure 5 bar, for 30 min, co-catalyst TIBA (TIBA/Cr = 1000).
[f] Polymerization at 35 °C, ethylene pressure 5 bar, for 30 min, co-catalyst TIBA (TIBA/Cr = 1000).

Table 5
Ethylene/1-hexene copolymerization with homogeneous catalysts based on bis(imino)pyridine complexes.

Catalyst	T_{pol} (°C)	[a]C_6H_{12}/C_2H_4	[b]Bu/1000 C	Maximum activity (kg PE/mol M bar min)	r_1
$LFeCl_2$ + TIBA, Al/Fe = 500	35	3.2	<1.0	140	>1000
$LVCl_2$ + MAO, MAO/V = 500	60	3.2	4.8	270	200
$LCrCl_2$ + MAO + TIBA, MAO/Cr = 200, TIBA/Cr = 800	70	2.0	2.4	350	400
[c]$Me_2Si(Ind)_2ZrCl_2$ + MAO	60				25

[a] Co-monomer molar ratio in the polymerization medium.
[b] 1-Hexene content in the obtained polymer (^{13}C NMR data).
[c] Data of Ref. [28].

Table 6
Comparison of bis(imino)pyridine complexes as homogeneous catalysts for ethylene polymerization.

Run no.	Complex	Activator	T_{pol} (°C)	[a]Yield (kg PE/mol M bar)	Maximum activity (kg PE/mol M bar min)	M_w ($\times 10^{-3}$)	M_w/M_n
1	$LFeCl_2$	MAO	35	9,100	500	[b]44–71	[b]6.9–8.3
2			50	800	50	–	–
3	$LCoCl_2$	MAO	35	3,100	80	1.5	1.8
4	$LVCl_3$	MAO	35	3,300	170	6.7	2.4
5			60	11,000	360	[b]5–12	[b]2.1–4.8
6	$LCrCl_3$	MAO + TIBA	35	12,400	260	1.1	1.9
7			70	7,880	330	1.5	1.9

[a] Polymerization for 30 min at MAO/M = 500 (runs 1–5), MAO/Cr = 200, TIBA/Cr = 1000 (runs 6 and 7).
[b] Increases with polymerization time.

Thus, the obtained data show that the active component of the catalysts based on $LCrCl_3$ can be formed only in the presence of MAO. The active centers of these systems are characterized by higher thermal stability and the catalysts provide high PE yield in polymerization at 70 °C. A narrow MWD of PE samples obtained with the systems ($LCrCl_3$/MAO) + TIBA evidences that the interaction of $LCrCl_3$ with MAO produces only one type of active centers and catalysts of this type can be regarded as single-site catalysts.

3.5. Ethylene-1-hexene copolymerization over the homogeneous catalysts based on bis(imino)pyridine complexes

An important property of polymerization catalysts is their ability to regulate the molecular structure of a growing polymer by copolymerization of ethylene with α-olefins. The data on the ethylene copolymerization with 1-hexene promoted by catalytic systems based on bis(imino)pyridine complexes of Fe(II), V(III) and Cr(III) are presented in Table 5. The copolymerization parameter r_1 was determined using the simplified copolymerization equation ($[C_\alpha]/[C_2H_4]_{pol} = 1/r_1[C_\alpha]/[C_2H_4]_{react}$), where $[C_\alpha]/[C_2H_4]_{pol}$ is the molar ratio between the units of 1-hexene and ethylene in copolymer, and $[C_\alpha]/[C_2H_4]_{react}$ is the molar ratio between the concentrations of co-monomers in the reaction medium [27]. In comparison with the copolymerization parameter for the well-known effective copolymerization catalyst based on zirconocene complex [28], the r_1 values found for iron, vanadium and chromium complexes were noticeably higher (Table 5). The obtained results indicate that catalytic systems based on iron, vanadium and chromium bis(imino)pyridine complexes display very low copolymerization ability.

4. Conclusions

The above data on the ethylene polymerization activity at different temperatures for bis(imino)pyridine complexes with different metal centers and the data on M_w and MWD of the produced polymers are summarized in Table 6. It is evident, that the catalytic behavior of bis(imino)pyridine complexes with close structures of the bis(imino)pyridyl ligands essentially depends on the transition metal center.

The main characteristics of the catalysts based on $LFeCl_2$ are: (1) very high activity at low polymerization temperatures (35 °C) with different activators (both MAO and aluminum trialkyls), (2) formation of multiple active sites and transformation of the active centers in the course of polymerization, (3) low thermal stability of the active sites, and (4) formation of linear PE with high M_w and broad MWD.

Interaction of $LCoCl_2$ with different activators produces only one type of active site, having considerably low activity and low thermal stability. PE with low M_w and narrow MWD is produced with the catalysts based on $LCoCl_2$.

$LVCl_3$ is activated only upon interaction with MAO. Thus formed catalyst is highly active within a broader temperature range (35–60 °C). At low polymerization temperature (35 °C) it can be regarded as a single-site catalyst producing PE with narrow MWD. At higher polymerization temperatures (60 °C) the polymerization kinetics for this catalyst becomes more complex: during the polymerization the catalysts activity sharply decreases, whereas M_w and M_w/M_n values of the produced PE increase. This catalyst acts as a single site in the initial period of polymerization (5 min), but with the increase in polymerization time multiple active sites are formed in the system.

Highly active catalysts based on $LCrCl_3$ are formed upon interaction of chromium complex with MAO at low MAO/Cr molar ratio. The active sites of these systems are characterized by the highest thermal stability. Only one type of active center is formed in the systems $(LCrCl_3/MAO) + TIBA$, producing PE with low M_w and narrow MWD at polymerization temperatures 35–70 °C.

Thus, bis(imino)pyridine complexes of Co(II), V(III) and Cr(III) generate single-site catalysts. However, in the catalysts based on $LVCl_3$, in the course of polymerization simultaneously with deactivation of the initially formed highly active centers, new active centers appear, resulting in broadening of MMD of the obtained PE.

The main difference of $LFeCl_2$ catalysts from the catalysts based on $LCoCl_2$, $LVCl_3$ and $LCrCl_3$ is the formation of multiple active centers upon interaction with activators of different types: MAO or AlR_3.

Active sites of the catalysts based on $LCoCl_2$ are thermally unstable. Cobalt-based systems are inactive at the temperatures higher than 50 °C. Active centers of the catalysts with $LVCl_3$ and $LCrCl_3$ as active component are noticeably stable and these systems exhibit high activity at 60–70 °C. In polymerization experiments run at 35 °C, the value of maximum activity decreases in the order $LFeCl_2 > LCrCl_3 > LVCl_3 > LCoCl_2$, whereas the values of PE yield form another order: $LCrCl_3 > LFeCl_2 > LVCl_3 \approx LCoCl_2$ because of different stability of these catalysts (Table 6). The M_w values of PE produced at 35 °C decrease in the order $LFeCl_2 \gg LVCl_3 > LCoCl_2 \approx LCrCl_3$.

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