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CATALYTIC REACTION MECHANISMS

New Bis(arylimino)pyridyl Complexes as Components of Catalysts for Ethylene Polymerization

S. S. Ivanchev*, G. A. Tolstikov, V. K. Badaev*, I. I. Oleinik**, N. I. Ivancheva*, D. G. Rogozin*, I. V. Oleinik**, and S. V. Myakin***

** Boreskov Institute of Catalysis (St. Petersburg Branch), Siberian Division, Russian Academy of Sciences, St. Petersburg, Russia*

*** Vorozhtsov Institute of Organic Chemistry, Siberian Division, Russian Academy of Sciences, Novosibirsk, Russia*

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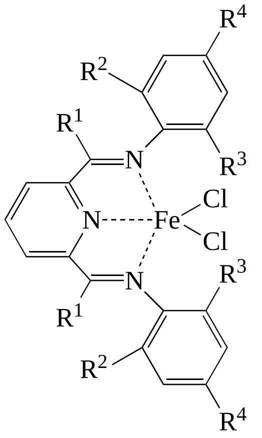
Abstract—A new series of 2,6-bis(arylimino)pyridineiron(II) complexes with cycloaliphatic (cyclopentyl, cyclohexyl, cyclooctyl, and cyclododecyl) substituents in the *ortho* position of the aryl ring are synthesized and studied as components for ethylene polymerization catalysts. Methylaluminoxane is used as an activator for the complexes. The resulting catalytic systems are more active in polymerization at elevated temperatures (60–80°C) than previously described systems based on substituted 2,6-bis(arylimino)pyridines. The influence of the number of CH_2 groups in a cycloaliphatic substituent on the efficiency of the catalytic system is studied. Polymers formed are characterized by an increased molecular weight, high density, and high crystallinity.

INTRODUCTION

First bis(arylimino)pyridines with the general structure



have recently been synthesized and studied as components of catalysts for olefin polymerization by two independent research groups in the United States[1, 2] and Great Britain [3, 4]. The related catalysts turned out to be very attractive due to their high activity (at the level of metallocene catalysts), accessibility, and low sensitivity to admixtures in a monomer (moisture, CO, and others). During a short period, extensive experimental data were accumulated on the synthesis of various ligand structures of bis(arylimino)pyridine complexes based on iron and cobalt halides and on the study of their catalytic activity in α-olefin polymerization. These were generalized in two reviews [5, 6].

The 2,6-bis(arylimino)pyridine derivatives had a certain limitation for their wide-spread use as reported in [3] and then in [7, 8]: a decrease in the activity of the related catalysts at polymerization temperatures above 40–50°C.

In this work, we attempted to synthesize new 2,6-bis(arylimino)pyridineiron(II) chloride complexes retaining (in combination with methylaluminoxane as a cocatalyst) their catalytic activity at temperatures higher than the 40–60°C used in this technology. With this purpose we synthesized, for the first time, a series of 2,6-bis(arylimino)pyridineiron complexes containing one or two cycloaliphatic *ortho*-substituents in the aryl group [9]. This study is based on our first experiment on studying 2,6-bis(arylimino)pyridines with cyclopentyl substituents [10].

EXPERIMENTAL

Reagents and Solvents

Toluene (special purity grade) was dried for 24 h over calcined alumina, distilled in an argon flow over metallic sodium, and stored in the presence of metallic sodium in argon.

Isopropyl alcohol (reagent grade) was used without additional purification.

Ethylene with a purity of at least 99.5% and **argon** (special purity grade) were dried by passing through columns packed with calcined Al_2O_3 before supplying to a reactor. After drying the moisture content of ethylene was at most 10–20 ppm and that of argon was at most 10 ppm.

Polymethylaluminoxane from SL Witko GmbH (Eurecen® Al 5100/10T) was used as a 10% solution in toluene. According to analyses of the reagent producer, the total aluminum content of polymethylaluminoxane was 4.6–5.6 mol %, and the relative concentration of Al recalculated per trimethylaluminum was 32–36 mol %.

Synthesis of 2,6-Bis(arylimino)pyridyl Ligands and Corresponding Complexes

2,6-Bis(arylimino)pyridyl ligands, for example, 2,6-bis[1-(2-methyl-6-cycloalkylphenylimino)ethyl]pyridines, were synthesized in 80–85% yields by heating 2-methyl-6-cycloalkylanilines with 2,6-diacetylpyridine in methanol in the presence of catalytic amounts of formic acid using a modified procedure described in [11].

Ortho-cycloalkenylanilines necessary for the synthesis of 2,6-bis(arylimino)pyridyl ligands, for example, 2-methyl-6-(cyclo-2'-alkenyl)anilines, were synthesized by the reaction of 3-halocycloalkenes with 2-methylaniline by the amino-Claisen rearrangement of the primarily formed *N*-(cyclo-2'-alkenyl)-2-methylanilines [12].

Ortho-cycloalkylanilines necessary for the synthesis of 2,6-bis(imino)pyridyl ligands, for example, 2-methyl-6-(cyclo-2'-alkenyl)anilines, were prepared by the hydrogenation of the corresponding 2-methyl-6-cyclo-2'-alkenylanilines in the presence of Raney nickel under mild conditions with a 95–98% yield.

2,6-Bis(arylimino)pyridyl complexes of metal halides, for example, 2,6-bis[1-(2-methyl-6-cycloalkylphenylimino)ethyl]pyridineiron(II) chloride, were synthesized in high yields by the reaction of the corresponding 2,6-bis(arylimino)pyridyl ligand, for example, 2,6-bis[1-(2-methyl-6-cycloalkylphenylimino)ethyl]pyridine, with $FeCl_2 \cdot 4H_2O$ in THF at room temperature in argon using a modified procedure described in [11].

2-Methyl-6-cyclopentylaniline. Yield 98%, b.p. 98–100°C at 0.5 mm Hg. $C_{12}H_{17}N$ anal. calcd. (%): C, 82.23; H, 9.78; N, 7.99. Found (%): C, 82.51; H, 9.77; N, 7.98.

2-Methyl-6-cyclohexylaniline. Yield 96%, b.p. 100–102°C at 0.5 mm Hg. $C_{13}H_{19}N$ anal. calcd. (%): C, 82.46; H, 10.12; N, 7.40. Found (%): C, 82.51; H, 10.15; N, 7.41.

2-Methyl-6-cyclooctylaniline. Yield 98%, b.p. 129–130°C at 0.5 mm Hg. $C_{15}H_{23}N$ anal. calcd. (%): C, 82.89; H, 10.67; N, 6.44. Found (%): C, 82.91; H, 10.64; N, 6.41.

2-Methyl-6-cyclododecylaniline. Yield 95%, b.p. 170–172°C at 0.5 mm Hg. $C_{19}H_{31}N$ anal. calcd. (%): C, 83.45; H, 11.43; N, 5.12. Found (%): C, 83.48; H, 11.45; N, 5.15.

2,4-Dimethyl-6-cyclopentylaniline. Yield 98%, b.p. 134–136°C at 0.5 mm Hg. $C_{13}H_{19}N$ anal. calcd. (%): C, 82.70; H, 10.12; N, 7.40. Found (%): C, 82.48; H, 10.15; N, 7.41.

2,4-Dimethyl-6-cyclohexylaniline. Yield 97%, b.p. 133–135°C at 0.5 mm Hg. $C_{14}H_{21}N$ anal. calcd. (%): C, 82.70; H, 10.41; N, 6.89. Found (%): C, 82.73; H, 10.45; N, 6.85.

2,4-Dimethyl-6-cyclooctylaniline. Yield 98%, b.p. 145–147°C at 0.5 mm Hg. $C_{16}H_{25}N$ anal. calcd. (%): C, 83.06; H, 10.89; N, 6.05. Found (%): C, 83.10; H, 10.92; N, 6.08.

2,4-Dimethyl-6-cyclododecylaniline. Yield 96%, b.p. 180–182°C at 0.5 mm Hg. $C_{20}H_{33}N$ anal. calcd. (%): C, 83.56; H, 11.57; N, 4.87. Found (%): C, 83.59; H, 11.60; N, 4.85.

2,6-Bis[1-(2-methyl-6-cyclopentylphenylimino)ethyl]pyridine. Yield 85%, m.p. 170–172°C. $C_{33}H_{39}N_3$ anal. calcd. (%): C, 82.97; H, 8.23; N, 8.80. Found (%): C, 82.94; H, 8.26; N, 8.84. ^1H NMR ($CDCl_3$, CCl_4) δ: 8.54 (d, 2 H, Py–H_m), δ 7.96 (t, 1 H, Py–H_p), δ 7.13–6.88 (m, 6 H, Ar–H), 2.26 (s, 6 H, N=C–CH_3), 2.03 (s, 6 H, C_{Ar}–Me), 1.78, 1.6 (d, 16 H, cyclopentyl).

2,6-Bis[1-(2-methyl-6-cyclohexylphenylimino)ethyl]pyridine. Yield 81%, m.p. 215–217°C. $C_{35}H_{43}N_3$ anal. calcd. (%): C, 83.12; H, 8.57; N, 8.31. Found (%): C, 83.15; H, 8.54; N, 8.34. ^1H NMR ($CDCl_3$, CCl_4), δ: 8.48 (d, 2 H, Py–H_m), δ 7.9 (t, 1 H, Py–P_p), 6.99–6.86 (m, 6 H, Ar–H), δ 2.2 (s, 6 H, N=C–CH_3), 1.98 (s, 6 H, C_{Ar}–Me), δ 1.76–1.23 (m, 20 H, cyclohexyl).

2,6-Bis[1-(2-methyl-6-cyclooctylphenylimino)ethyl]pyridine. Yield 85%, m.p. 140–142°C. $C_{39}H_{51}N_3$ anal. calcd. (%): C, 83.37; H, 9.15; N, 7.48. Found (%): C, 83.78; H, 9.11; N, 7.45.

2.6-Bis[1-(2-methyl-6-cyclododecylphenylimino)ethyl]pyridine. Yield 83%, m.p. 178–180°C. $C_{47}H_{67}N_3$ anal. calcd. (%): C, 83.75; H, 10.02; N, 6.23. Found (%): C, 83.39; H, 10.04; N, 6.18.

2,6-Bis[1-(2,4-dimethyl-6-cyclopentylphenylimino)ethyl]pyridine. Yield 81%, m.p. 183–185°C. $C_{35}H_{43}N_3$ anal. calcd. (%): C, 83.12; H, 8.57; N, 8.31. Found (%): C, 83.13; H, 8.58; N, 8.30. ^1H NMR ($CDCl_3$, CCl_4) δ 8.46 (d, 2 H, Py–P_m), δ 7.86 (t, 1 H, Py–H_p), δ 6.78 (d, 4 H, Ar–H), δ 2.27 (s, 6 H, N=C–CH_3), δ 2.19 (s, 6 H, C_{Ar}–Me), 1.93 (s, 6 H, C_{Ar}–Me), δ 1.73, 1.56 (d, 16 H, cyclopentyl).

2,6-Bis[1-(2,4-dimethyl-6-cyclohexylphenylimino)ethyl]pyridine. Yield 82%, m.p. 234–236°C. $C_{37}H_{47}N_3$ anal. calcd. (%): C, 83.25; H, 8.87; N, 7.87. Found (%): C, 83.27; H, 8.85; N, 7.85. ^1H NMR ($CDCl_3$, CCl_4), δ: 8.46 (d, 2 H, Py–H_m), 7.88 (t, 1 H, Py–H_p), δ 6.80 (d, 4 H, Ar–H), 2.27 (s, 6 H, N=C–CH_3), δ 2.19 (s, 6 H, C_{Ar}–Me), δ 1.94 (s, 6 H, C_{Ar}–Me), δ 1.76–1.23 (m, 20 H, cyclohexyl).

2,6-Bis[1-(2,4-dimethyl-6-cyclooctylphenylimino)ethyl]pyridine. Yield 80%, m.p. 128–130°C. $C_{41}H_{55}N_3$ anal. calcd. (%): C, 83.48; H, 9.40; N, 7.12. Found (%): C, 83.50; H, 9.43; N, 7.10.

2,6-Bis[1-(2,4-dimethyl-6-cyclododecylphenylimino)ethyl]pyridine. Yield 80%, m.p. 168–169°C. $C_{49}H_{55}N_3$ anal. calcd. (%): C, 83.82; H, 10.19; N, 5.98. Found (%): C, 83.85; H, 10.22; N, 5.95.

Table 1. Characteristics of the structures of the synthesized complexes

Catalyst	Substituents in aryl ring			
	R^1	R^2	R^3	R^4
P-1	CH_3	cyclopentyl	H	H
P-2	CH_3	cyclopentyl	CH_3	H
P-3	CH_3	cyclopentyl	CH_3	CH_3
P-4	CH_3	cyclopentyl	cyclopentyl	H
H-1	CH_3	cyclohexyl	H	H
H-2	CH_3	cyclohexyl	CH_3	H
H-3	CH_3	cyclohexyl	CH_3	CH_3
H-4	CH_3	cyclohexyl	cyclohexyl	H
O-1	CH_3	cyclooctyl	H	H
O-2	CH_3	cyclooctyl	CH_3	H
O-3	CH_3	cyclooctyl	CH_3	CH_3
D-1	CH_3	cyclododecyl	CH_3	H
D-3	CH_3	cyclododecyl	CH_3	CH_3
Catalyst for comparison*	CH_3	*iso*-C_3H_7	*iso*-C_3H_7	H

* According to published data [3].

2,6-Bis[1-(2-methyl-6-cyclopentylphenylimino) ethyl]pyridineiron(II) chloride. Yield 88%. $C_{33}H_{39}Cl_2FeN_3$ anal. calcd. (%): C, 65.57; H, 6.50; Cl, 11.73; N, 6.95. Found (%): C, 65.32; H, 6.25; Cl, 11.9; N, 6.51.

2,6-Bis[1-(2-methyl-6-cyclohexylphenylimino) ethyl]pyridineiron(II) chloride. Yield 87%. $C_{35}H_{43}Cl_2FeN_3$ anal. calcd. (%): C, 66.46; H, 6.85; Cl, 11.21; N, 6.64. Found (%): C, 66.24; H, 6.75; Cl, 11.45; N, 6.47.

2,6-Bis[1-(2-methyl-6-cyclooctylphenylimino) ethyl]pyridineiron(II) chloride. Yield 86%. $C_{35}H_{51}Cl_2FeN_3$ anal. calcd. (%): C, 68.03; H, 7.47; Cl, 10.30; N, 6.10. Found (%): C, 67.88; H, 7.37; Cl, 10.53; N, 6.01.

2,6-Bis[1-(2-methyl-6-cyclododecylphenylimino) ethyl]pyridineiron(II) chloride. Yield 88%. $C_{47}H_{67}Cl_2FeN_3$ anal. calcd. (%): C, 70.49; H, 8.43; Cl, 8.85; N, 5.25. Found (%): C, 70.21; H, 8.24; Cl, 9.03; N, 6.48.

2,6-Bis[1-(2,4-dimethyl-6-cyclopentylphenylimino) ethyl]pyridineiron(II) chloride. Yield 85%. $C_{35}H_{43}Cl_2FeN_3$ anal. calcd. (%): C, 66.46; H, 6.85; Cl, 11.21; H, 6.64. Found (%): C, 66.23; H, 6.76; Cl, 11.43; N, 5.08.

2,6-Bis[1-(2,4-dimethyl-6-cyclohexylphenylimino) ethyl]pyridineiron(II) chloride. Yield 88%, $C_{37}H_{47}Cl_2FeN_3$ anal. calcd. (%): C, 67.28; H, 7.17; Cl, 10.73; N, 6.36. Found (%): C, 67.04; H, 7.00; Cl, 10.95; N, 6.18.

2,6-Bis[1-(2,4-dimethyl-6-cyclooctylphenylimino) ethylpyridineiron(II) chloride. Yield 80%. $C_{41}H_{55}Cl_2FeN_3$ anal. calcd. (%): C, 68.71; H, 7.74; Cl, 9.89; N, 5.86. Found (%): C, 68.52; H, 7.51; Cl, 9.99; N, 5.68.

2,6-Bis[1-(2,4-dimethyl-6-cyclododecylphenylimino)ethyl]pyridineiron(II) chloride. Yield 83%. $C_{49}H_{71}Cl_2FeN_3$ anal. calcd. (%): C, 71.00; H, 8.63; Cl, 8.55; N, 5.07. Found (%): C, 70.89; H, 8.50; Cl, 8.86; N, 4.91.

Designations and compositions of the synthesized bis(arylimino)pyridyliron(II) chloride complexes are presented in Table 1.

Ethylene Polymerization

Ethylene was polymerized in a stainless steel reactor equipped with a demountable jacket and a propeller mixer with a magnetic driving gear operating at pressures below 0.6 MPa and temperatures from 30 to 80°C. The pressure in the reactor was maintained automatically, and the temperature regime was controlled by a water supply (at the corresponding temperature) from an ultrathermostat into the reactor jacket.

Before polymerization, the reactor was evacuated to a residual pressure of 1×10^{-1} mm Hg at 150–170°C for 1 h along with triple purging with dry argon (moisture content lower than 10 ppm).

After the cooling of the reactor to room temperature, toluene and components of the catalytic system were loaded by medical syringes through a loading outlet in an argon counterflow. The reaction mixture was saturated with ethylene and simultaneously heated to the

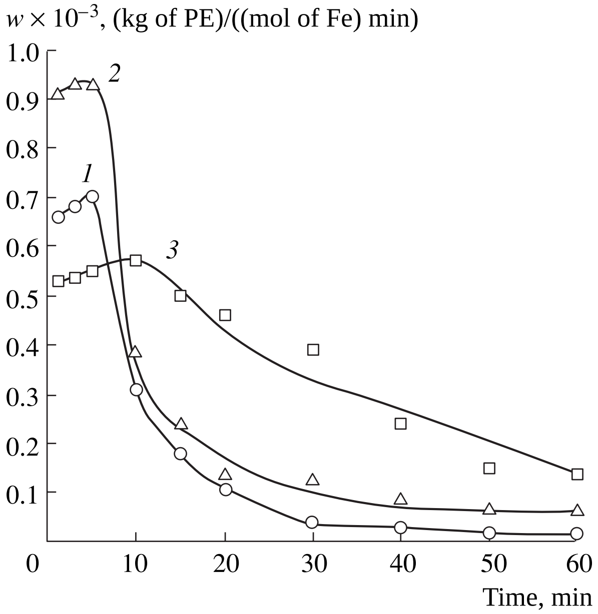


Fig. 1. Changes in the polymerization rate with time of the reaction at 70°C (P_{ethylene} = 0.3 MPa, methylaluminoxane/Fe = 1500 : 1 (mol/mol)): *1*, P-3, $n_{\text{Fe}} = 2.5 \times 10^{-6}$ mol; *2*, H-3, $n_{\text{Fe}} = 2.5 \times 10^{-6}$ mol; *3*, D-3, $n_{\text{Fe}} = 0.9 \times 10^{-6}$ mol.

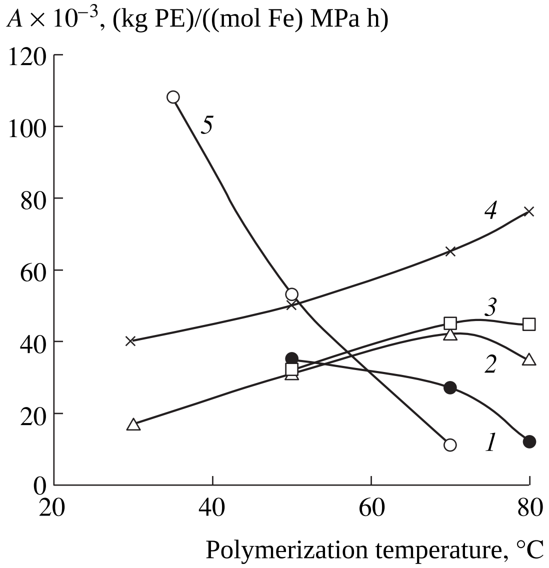


Fig. 2. Plots of the activity of the 2,6-bis(arylimino)pyridyliron(II) chloride complexes vs. temperature of ethylene polymerization: (*1*) P-3, (*2*) H-3, (*3*) O-3, (*4*) D-3, and (*5*) catalyst for comparison (see Table 1). For experimental conditions, see Table 2.

operating temperature. The ethylene pressure was increased to the calculated value, which was automatically maintained during the whole experiment.

The specified regime of the reactor was achieved for ~1 min, after which the polymerization rate was measured.

After 60 min, the reaction was stopped by adding isopropyl alcohol to the reaction medium. The liquid phase was separated on a Büchner funnel, and the resulting polymer was dried at 60°C in a vacuum until it showed a constant weight.

Procedure for Determination of Properties of Prepared Polyethylenes

The melt flow index was determined in order to estimate the molecular weights of the polyethylene samples. It was determined on a standard extrusion-type plastometer at 190°C and loading of 5 kg.

The polymer density was determined by the method of flotation of molded samples with a thickness of 1 mm in an aqueous–alcohol solution at 20 ± 1°C.

The structures of the polyethylenes were analyzed by FTIR spectroscopy on a FTIR-8300 Shimadzu spectrometer.

The specific heats of phase transitions and characteristic temperatures were measured on a DSC-60 differential scanning calorimeter (Shimadzu) with a heating rate of 10°C/min using a sample of 7 mg. The results were presented as thermograms in the specific thermal flow–temperature coordinates. The temperature of the melting beginning (T_b) and end (T_e) and the position of the maximum of the melting end (T_m) were determined from the thermograms.

The specific melting peak maximum (ΔH_m) was determined as the surface area restricted by the curve of the melting peak and basic line connecting the T_b and T_e points.

RESULTS AND DISCUSSION

The results of ethylene polymerization on the synthesized catalysts are presented in Table 2.

The activities of the synthesized catalytic systems are higher than that of the iron halide complex of 2,6-bis[(2,4-diisopropylarylimino)ethyl]pyridine [3] at temperatures >50°C. Moreover, the activity decreases with temperature only in the case of the cyclopentyl substituents, whereas for the cyclohexyl, cyclooctyl, and cyclododecyl substituents the polymerization rate remains unchanged or increases (the latter is especially the case for the cyclododecyl substituents: samples 21–24 in Table 2).

The ethylene polymerization rate at 70°C in the presence of the bis(arylimino)pyridineiron(II) chloride complexes studied reaches the maximum value 5–10 min after the beginning of the experiment followed by a decrease, which is least pronounced for sample D-3 (Fig. 1). This specific feature is important for the selection of the optimum ligands of the catalytic complex for polymerization in view of the require-

Table 2. Ethylene polymerization in the presence of new bis(arylimino)pyridyliron(II) chloride complexes

No.	Catalyst	Amount of catalyst precursor, μmol	Polymerization temperature, °C	Yield, g	$A \times 10^{-3}$, (kg of PE)/((mol of Fe) MPa h)
1	P-2	1.25	30	12.17	33.9
2	P-2	2.5	50	22.02	29.4
3	P-2	2.5	70	17.83	23.8
4	P-2	2.5	80	4.85	6.5
5	H-2	2.5	30	12.28	16.4
6	H-2	2.5	50	23.92	31.9
7	H-2	2.5	70	26.24	35.0
8	H-2	2.5	80	25.56	34.1
9	O-2	2.0	70	23.2	38.7
10	O-2	2.0	80	19.5	32.5
11	P-3	2.5	50	26.5	35.3
12	P-3	2.5	70	20.92	27.9
13	P-3	2.5	80	7.68	10.2
14	H-3	2.5	30	13.5	18.0
15	H-3	1.25	50	11.38	30.3
16	H-3	1.25	70	15.93	42.5
17	H-3	1.25	80	13.13	35.0
18	O-3	2.5	50	24.5	32.7
19	O-3	2.0	70	27.36	45.6
20	O-3	2.0	80	26.6	44.3
21	D-3	0.9	30	10.8	40.0
22	D-3	0.9	50	13.8	51.0
23	D-3	0.9	70	17.5	64.8
24	D-3	0.9	80	20.7	76.7
25	P-4	2.5	50	24.13	32.2
26	P-4	2.5	70	20.7	27.6
27	P-4	2.5	80	14.13	18.8
28	H-4	2.5	30	11.4	15.2
29	H-4	2.5	50	11.6	15.5
30	H-4	2.5	70	2.6	3.5
31	H-4	2.5	80	0.81	1.1

Note: Duration of experiment 1 h, solvent toluene (50 ml), methylaluminoxane/Fe = 1500 : 1. *A* is activity.

ments regarding the molecular weight of the resulting polyethylene.

The kinetic curves presented in Fig. 2 confirm that, contrary to the previously described [3] catalytic system based on 2,6-bis[(2,4-diisopropylarylimino)ethyl]pyridine (Table 1), which rapidly loses activity with a temperature increase (curve *2*), our new 2,6-bis(arylimino)pyridineiron(II) chloride complexes (in particular, those with H-3 and O-3) at 70°C are more active than at 50°C, and the activity continues to increase with an increase in polymerization temperature to 80°C (curve *4*).

Our study of ethylene polymerization in the 30–80°C temperature interval on the H-1, O-1, and D-1 catalyst precursors in the presence of methylaluminoxane shows that the use of these systems makes it possible to obtain only oligomeric products. The character of the changes in the polymerization rate on these samples is the same as that for their analogs (H-2, D-2, and others).

The presented results suggest that

(1) When cycloaliphatic substituents in combination with a methyl group are introduced into the *ortho* position of the arylimine group of the iron halide complexes of the catalytic systems, the activity maximum shifts toward higher temperatures;

(2) The temperature maximum depends on the number of CH_2 groups in the cycloalkyl substituent: it is approximately 50°C for cyclopentyl and 70°C for

Table 3. Characteristics of polyethylenes obtained on new bis(imino)pyridyliron(II) chloride complexes

No.	Catalyst	Polymerization temperature, °C	Flow index of melt*, g/10 min	Density, kg/m^3	T_m, °C	ΔH_m, J/g
1	P-2	30	2.3	–	–	–
2	P-2	50	0.83	–	–	–
3	P-2	70	65.0	–	–	–
4	P-2	80	>4000	–	120.0	–
5	H-2	30	0.53	972.5	–	–
6	H-2	50	71.0	970.0	133.0	202.0
7	H-2	70	6.0	–	138.0	209.0
8	H-2	80	11.0	–	–	–
9	H-2	70	0.43	972.0	133.3	197.0
10	H-2	80	5.9	–	133.3	220.0
11	P-3	50	1.0	–	132.0	–
12	P-3	70	42.0	972.0	–	–
13	P-3	80	>180	–	–	–
14	H-3	30	3.8	972.6	130.0	–
15	H-3	50	0.33			
16	H-3	70	44.0	–	–	–
17	H-3	80	94.0	–	–	–
18	H-3	50	0.98	971.0	–	–
19	H-3	70	0.98	970.0	133.3	–
20	H-3	80	>101	–	134.7	–
21	D-3	30	4.4	968.0	–	–
22	D-3	50	11.4	–	133.0	195.0
23	D-3	70	9.3	–	135.0	205
24	D-3	80	160.0	–	134.0	222.0
25	P-4	50	0.62	972.3	–	–
26	P-4	70	5.6	970.0	–	–
27	P-4	80	16.0	–	–	–
28	H-4	30	115.0	–	130.0	–
29	H-4	50	480.0	–	132.0	–
30	H-4	70	760.0	–	120.0	–

Note: For numbering and conditions of polyethylene preparation, see Table 2.
* Loading 5 kg.

cyclohexyl and cyclooctyl, while for cyclododecyl the polymerization rate does not decrease even at 80°C;

(3) The introduction of two cycloalkyl substituents into the *ortho* position of arylimine substantially decreases the polymerization rate and molecular weight of the product, that is, the melt flow index of the formed polymers increases. This means that the steric effects of two cycloaliphatic substituents favor a decrease in the chain propagation rate constant and an increase in the probability of β-hydride chain transfer;

(4) The presence of only one cycloaliphatic substituent in the *ortho* position (without any substituents in the second *ortho* and *para* positions) along with close results on the dynamics of ethylene absorption produces only oligomeric products and, hence, the experimental data for P-1, H-1, O-1, and D-1 are not included in Table 2.

Available data on the influence of the substituent in the *para* position of the arylimine group are insufficient for a substantiated discussion of this effect.

The molecular characteristics of the polyethylenes were studied by measuring the melt flow index (which is inversely proportional to the molecular weight) and density. The highest molecular weights were obtained in the catalytic systems at 30–50°C (Table 3), and the melt flow index increases in a regular manner with an increase in the polymerization temperature. However, in many cases, polymers appropriate from the viewpoint of the molecular weight are formed at 70–80°C (Table 3, samples 7, 9, 10, and 19). Note that the polyethylenes obtained at 35°C in the presence of the catalytic system based on the 2,6-bis[(2,4-dimethylphenylimino)ethyl]pyridyliron(II) chloride complexes and methylaluminoxane [13] are characterized by a melt flow index equal to 13.6 g/10 min at a loading of 2.16 kg, that is, the molecular weight is much lower than that for polyethylenes synthesized on our catalysts.

The densities of polyethylenes indicate their high crystallinity. This is confirmed by the number of CH_3 groups per 100 carbon atoms determined by IR spectroscopy. This number is within 0.25–0.52 and indicates that short-chain branchings are absent, which agrees with the high density of the polyethylenes and their thermal properties (see Table 3).

CONCLUSIONS

The main result is that the modification of the 2,6-bis(arylimino)pyridyliron(II) chloride complexes by the introduction of cycloaliphatic substituents into the *ortho* position of the aryl groups substantially enlarges the temperature interval of efficient use of the related catalysts for ethylene polymerization under homogeneous conditions. This considerably enhances the potential of using the new catalysts for polyethylene production technologies.

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