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Metal salen complexes as ethylene polymerization catalysts — effect of catalytic system composition on its activity and properties of polymerization products

Summary — The series of salen-type complexes differing in the metal center (M = Ti, Zr, V) and in the coordination spheres (different substituent at salen ligands) after activation with methylalumoxane (MAO) or Et_2AlCl were studied as catalytic systems in ethylene polymerization. The vanadium and titanium complexes were found to be more active in combination with alkylaluminum compound (Et_2AlCl) then with MAO, while zirconium complex was active only in combination with MAO. The activity of complexes activated by Et_2AlCl decreases in the order V > Ti >> Zr ≅ 0, and when MAO is used as the cocatalyst the activity changes the order: Ti > Zr > V. The substituent type in the salen ligand also affects the catalyst activity; the best results were obtained for the catalyst having Cl or Br as substituents. The type of substituent has no significant effect on polyethylene properties, while the type of cocatalyst and the type of metallic centre play here the essential role. The salen titanium complexes in combination with Et_2AlCl usually produce low molecular weight polyethylene with narrow polydispersity, also accompanied by oligomers. Other catalytic systems give linear high molecular weight polyethylene (M_w = 200 000—700 000).

Key words: polyethylene, polymerization, post-metallocene catalysts, salen complexes of metals, activity, oligomers.

SALENOWE KOMPLEKSY METALI JAKO KATALIZATORY POLIMERYZACJI ETYLENU — WPŁYW SKŁADU KATALIZATORA NA JEGO AKTYWNOŚĆ I NA WŁAŚCIWOŚCI PRODUKTÓW POLIMERYZACJI

Streszczenie — Zsyntetyzowano i zastosowano [po aktywacji metyloaluminoksanem (MAO) lub Et_2AlCl] w charakterze katalizatorów niskociśnieniowej polimeryzacji etylenu serię salenowych kompleksów metali przejściowych różniących się rodzajem atomu centralnego (M = Ti, Zr lub V) i budową chemiczną ligandu (schemat A). Stwierdzono, że salenowe kompleksy cyrkonu są aktywne w polimeryzacji jedynie wówczas, gdy aktywator stanowi MAO, natomiast kompleksy tytanu i wanadu są aktywniejsze w przypadku gdy kokatalizatorem jest typowy związek glinoorganiczny — dietylochloroglin. Aktywność kompleksów w układzie z Et_2AlCl zmienia się w szeregu V > Ti >> Zr ≅ 0, podczas gdy w odniesieniu do kompleksów aktywowanych MAO maleje ona w kolejności Ti > Zr > V (tabela 1). Na efektywność katalizatora wywiera również wpływ rodzaj podstawnika w ligandzie salenowym. Najkorzystniejszymi prekatalizatorami okazały się mianowicie kompleksy zawierające w ligandzie atomy halogenu (Cl, Br) w położeniu *para*, najmniej pożądana jest zaś obecność dużego, stwarzającego zawady przestrzenne podstawnika (np. grupy *t*-butylowej) w pozycji *orto* (rys. 3). Rodzaj podstawnika nie wpływa w istotnym stopniu na właściwości otrzymywanego polietylenu (tabela 2), ważną natomiast rolę odgrywa dobór kokatalizatora i centrum metalicznego. Wobec kompleksów tytanowych aktywowanych Et_2AlCl powstaje PE o niewielkim ciężarze cząsteczkowym i wąskim jego rozkładzie; polimeryzacji towarzyszy tworzenie się oligomerów (rys. 2). Pod wpływem pozostałych układów uzyskuje się liniowy polietylen o dużym ciężarze cząsteczkowym (M_w = 200 000—700 000) i większej polidyspersyjności (tabele 1 i 2).

Słowa kluczowe: polietylen, polimeryzacja, katalizatory postmetalocenowe, salenowe kompleksy metali, aktywność, oligomery.

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CATALYSTS FOR LOW-PRESSURE POLYMERIZATION OF OLEFINS — CLASSIFICATION AND GENERAL DESCRIPTION

A very wide and diversified group of transition metal complexes have been employed nowadays as catalysts for low-pressure polymerization of olefins. According to the type of ligands present around the metallic centre, those complexes can be classified into one of three fundamental groups of catalytic systems: Ziegler—Natta catalysts, metallocene catalysts and post-metallocene ones. All these systems have been continually inspiring researchers to elaborate better and better catalysts [*e.g.* 1—6]. The revolutionary development of the catalytic systems can be considered as the key of huge evolution within the field of olefins' polymerization processes [7—10].

Traditional heterogeneous Ziegler—Natta systems are expected to remain the dominant catalytic route for the production of polyolefins, despite of their numerous disadvantages. For the reason of multiple catalytic sites, heterogeneous catalytic systems produce polymers with broad molecular weight distributions and nonhomogeneous comonomer incorporation. Moreover, heterogeneous catalysts have also limitations in terms of stereocontrol and ability to incorporate comonomers containing functional groups.

Homogeneous metallocene systems, in contrast to heterogeneous Ziegler—Natta catalysts, made possible to change their ligand skeletons and thus to control stereochemical aspects of a reaction. As a result, there are formed the products with uniform properties, *i.e.* with a narrow molecular weight distributions. Those catalytic systems made also possible to synthesize highly isotactic polypropylene (PP) as well as some new materials like syndiotactic or hemiisotactic PP and stereoblock (isotactic-atactic) materials [11]. It should be stressed, however, that metallocene systems offer high activities in polymerization processes only after having been activated by a large excess of methylalumoxane (MAO) in relation to a precursor compound.

The first post-metallocene catalysts are the nickel complexes with diimine ligands discovered by Brookhart *et al.* in 1995 [12—15]. Their discovery accelerated the study on post-metallocene catalysts. In 1996 it was shown [16, 17], that chelating diamide complexes of titanium exhibited high catalytic activity for higher α-olefin polymerizations. Then, iron and cobalt complexes possessing diimine-pyridine ligands appeared to be very high active catalysts in ethylene polymerization [18]. Shortly after nickel complexes with phenoxyimine ligands [19, 20] and then group 4. transition metal (mainly Zr and Ti) complexes containing two phenoxyimine chelate ligands and activated with MAO were discovered [21—27]. The latter new family complexes, named FI catalysts, exhibit high catalytic performance in olefin polymerization. It was also established, that the activity of the catalysts depends, alike polymer molecular weight, on the metal type, on the size of the group attached to the imino nitrogen atoms, and on the *ortho* substituent [21, 22, 28]. Additionally, with the use of this type catalyst having fluorine substituents, living polymerizations of ethylene or propylene have been achieved [25, 29]. Recently, FI catalysts and related compounds have been intensively investigated as olefin polymerization catalysts.

The related complexes, principally of zirconium and not so often of titanium, based on bis(phenoxy)amino ligands with additional donors, on bis(phenoxy)bis(amino) and bis(salicylideneiminate) ligands bearing four donor atoms, were also used in polymerization of olefins, after activation with MAO or with boron compounds [11, 29—31]. Their catalytic performance, alike that of the previously mentioned group of catalysts, is predominantly dependent on the type of metal and structure(s) of ligand(s).

In our research we used — as catalyst precursors — the new complexes of groups 4. or 5. metals (Ti, V, Zr) with *N,N'*-ethylenebis(salicylideneiminate) ligands (so called salen complexes) which contained various substituents at aromatic rings. The effect of the activator type — common organoaluminum compound or MAO — was studied as well as the effects of the central atom type and the ligand structure on the yield of the polymerization process and on some properties of the obtained products, *i.e.* molecular weight and its distribution, polymer structure, melting temperature, crystallinity and bulk density, were verified.

EXPERIMENTAL PART

All manipulations described below were performed under inert atmosphere (nitrogen or argon) using standard Schlenk and glove box techniques.

Materials

Ethylene (Orlen SA, Poland) was purified by passing over a column of sodium metal supported on Al_2O_3.

Toluene was distillated from sodium, and CH_2Cl_2 was distillated from CaH_2 prior to use.

MAO (Witco, 10.0 wt. %), Et_2AlCl (Aldrich, 1 M), $TiCl_4$, VCl_4, $ZrCl_4$ (Aldrich) were used without further purifications.

Synthesis of metal-salen complexes and their characterization

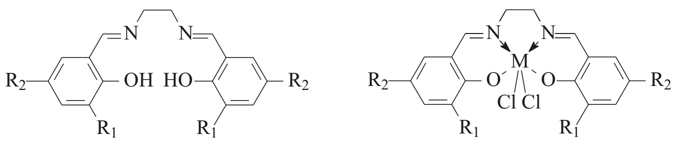
In this study, transition metal complexes with *N,N'*-ethylenebis(salicylideneiminate) ligands were used as ethylene polymerization precursors. Those tetra-dentate ligands [O,N,N,O] are often called salen ligands because they are formed in the reaction of ethylenediamine with salicylaldehyde or with its adequate derivative. All ligand

(L) in this study were synthesized by the research team of prof. W. Bukowski (Rzeszów Technical University); their structures and designations are shown in Scheme A.

The general synthesis route for the salen complexes consists of complexation of MCl_4 (M = Ti, V, Zr) with the ligand at the molar ratio 1:1 in CH_2Cl_2 for a few hours:

$$L + MCl_4 \xrightarrow[-2\,HCl]{} LMCl_2 \qquad (1)$$

The complexes were usually produced with the yields of 60 to 95 %. The structures of the obtained complexes $LMCl_2$ are also presented in Scheme A. All synthesized titanium complexes were red-brown, those of vanadium were dark-green, while the zirconium complexes were yellow-coloured. The FT-IR spectra of those complexes revealed that the specific band for ν vibrations (C=N) was shifted in relation to its location for free ligands. In the case of complex **1a** and ligand a, that band was recorded at 1653 and 1635 cm^{-1}, respectively.



Ligands:
a: $R_1 = R_2 = H$
b: $R_1 = OCH_3$; $R_2 = H$
c: $R_1 = OC_2H_5$; $R_2 = H$
d: $R_1 = R_2 = t$-Bu
e: $R_1 = H$; $R_2 = Cl$
f: $R_1 = H$; $R_2 = Br$

Complexes:
1a: M = Ti; $R_1 = R_2 = H$
1b: M = Ti; $R_1 = OCH_3$; $R_2 = H$
1c: M = Ti; $R_1 = OC_2H_5$; $R_2 = H$
1d: M = Ti; $R_1 = R_2 = t$-Bu
1e: M = Ti; $R_1 = H$; $R_2 = Cl$
1f: M = Ti; $R_1 = H$; $R_2 = Br$
2b: M = V; $R_1 = OCH_3$; $R_2 = H$
3b: M = Zr; $R_1 = OCH_3$; $R_2 = H$

Scheme A. Structure and designations of salen ligands and complexes used in this study

Polymerization conditions

The ethylene polymerization was carried out in a 1 L Büchi autoclave equipped with a magnetic stirrer. The autoclave was charged with toluene (0.15 L), 10.5 mmol of MAO or 7.9 mmol of Et_2AlCl and the salen complex as the catalyst precursor. After catalyst injection, ethylene was added and its pressure, 0.5 MPa, was kept constant during polymerization. The polymerization reaction was continued for 0.5 hour and then stopped by the addition of acidic methanol solution. The polymer was subsequently filtered off, washed several times with methanol and dried in vacuum.

Polymer characterization

Molecular weight values and molecular weight distributions ($\overline{M}_w/\overline{M}_n$) were determined by high temperature size exclusion chromatography (Waters, model 150C) at 142 °C, using 1,2,4-trichlorobenzene (0.8 mL/min) as a solvent. For calibration, the narrow molecular weight distribution polystyrene standards were used.

DSC analyses were carried out using a 2010 DSC calorimeter from TA Instruments. The heat of fusion (ΔH_f) and melting temperature (T_m) values were measured for the samples which had been previously melted and re-crystallised at the heating rate of 5 K/min. From the ΔH_f value crystallinity (X_c) in % was calculated as: $X_c = \Delta H_f \cdot (100/290)$ [32].

Terminal double bonds and the number of chain branches were analysed with the use of Nicole Nexus, 2002 FT-IR spectrometer. The samples were investigated in the form of tablets made of polymer powder and KBr. The numbers of $-CH_3$ groups were found from the ratio of the absorption band with the maximum at 1379.3 cm^{-1} and the absorption value for methylene ($-CH_2-$) group with the peak at 1368.7 cm^{-1}. The relative content of unsaturated groups was found from the ratio of the absorption band of C=C and absorption band of the internal standard [A(C=C)/A(2020)].

Distributions of liquid oligomers and their structures were determined by GC-MS analysis of the solution obtained, with the use of HP 5890/2 instrument.

Bulk density was measured according to standard PN 80/C-04532.

RESULTS AND DISCUSSION

Influence of metal center in the salen complex and activator type on ethylene polymerization

The effects of the central metal atom (Ti, V, Zr) in a complex and of the type of organoaluminum activator (MAO or Et_2AlCl) on ethylene polymerization process were investigated for only one selected salen ligand (b) which had $-OCH_3$ group substituted at the 3,3′-position. The complexes of titanium, vanadium or zirconium with this *N,N′*-ethylenebis(3-methoxysalicylideneiminate) ligand (**1b**, **2b**, **3b**), after activation with methylalumoxane or common organoaluminum compound, were employed in ethylene polymerization. The reactions were carried out at various temperatures, optimized for the specific metal complex, *i.e.* polymerization in the presence of titanium complex was conducted at 50 °C, vanadium complex needed the temperature of 30 °C, while the temperature of 80 °C was set up for zirconium complex. The conditions and results of these processes are presented in Table 1. As can be seen, both the type of metallic centre in a catalyst and the type of activator affect essentially the course of polymerization. The zirconium salen complex (**3b**) activated by MAO offers moderate activity in ethylene polymerization and it is less efficient than the corresponding titanium-based catalyst (**1b**). The lowest yield of polymer is observed for the vanadium complex (**2b**) activated by MAO. The change of the activator used from MAO to a common organo-

Table 1. Conditions and results of ethylene polymerization promoted by salen complex of Ti, V or Zr

Salen complex mmol	Cocatalyst mmol	Reaction temp., °C	Yield g	Activity kg/(mol$_{Mt}$ · 0.5 h)	T_m, °C	Crystal-linity, %	nCH$_3$/1000C	C=C/2020	Bulk density g/dm^3	M_w	M_w/M_n
1b, 0.08	MAO, 10.5	50	1.76	21.3	134.2	72.8	9.1	1.8	nd*)	360 000	6.9
1b, 0.08	Et$_2$AlCl, 7.9	50	3.65	44.1	109; 121.5	—	nd	nd	103.5	2500	1.5
2b, 0.11	MAO, 10.5	30	0.31	2.9	136.6	42.3	4.2	3.5	nd	725 000	5.3
2b, 0.08	Et$_2$AlCl, 7.9	30	5.19	62.9	137.3	64.4	0.04	1.1	90.9	nd	nd
3b, 0.16	MAO, 15.2	80	1.84	11.2	134.7	65.6	7.4	3.6	nd	nd	nd
3b, 0.16	Et$_2$AlCl, 7.9	80	0	—	—	—	—	—	—	—	—

*) nd — not determined.

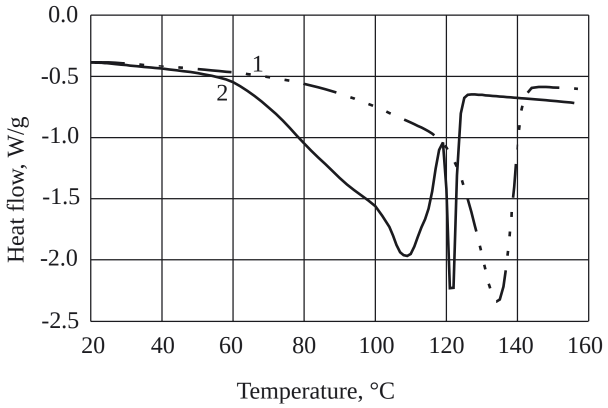


*Fig. 1. DSC curves corresponding to PE produced in the presence of salen-titanium complex (**1b**) activated by MAO (1) or Et$_2$AlCl (2)*

aluminum compound, Et$_2$AlCl, leads to changed efficiencies of the studied systems, *i.e.* the V catalyst becomes more active than Ti catalyst, while the zirconium complex after its activation with Et$_2$AlCl is practically inactive in ethylene polymerization. It should be emphasised that the tested Ti and V catalysts offer higher activities when a simple organoaluminum compound is used as an activator; the most active system (**2b**/Et$_2$AlCl) may yield as high as 62.9 kg PE/ (mol$_V$ · 0.5 h). It is advantageous for the tested catalytic systems that they can be activated by diethylchloroaluminum, *i.e.* the compound which is much simpler and cheaper than MAO and has well defined structure.

The type of the transition metal in a complex and the type of activator are decisive not only for the activity of the catalytic system but they also affect significantly the properties of the products obtained (Table 1). The Ti, V and Zr complexes activated by MAO, and V complex activated by Et$_2$AlCl, produce polyethylene showing high melting temperature (134—137 °C) and linear structures of macromolecules: the number of CH$_3$ groups per 1 000 carbon atoms is not higher than 10.

On the other hand, the DSC curve of polyethylene produced with the use of Ti complex activated with Et$_2$AlCl shows clearly the appearance of two peaks in distinct temperature regions: one at 121.5 °C and one (very broad) with the minimum at 109 °C (Fig. 1). The GPC analysis of that polymer revealed, however, its very narrow molecular weight distribution (M_w/M_n = 1.5) and also its very low molecular weight, of the order of a few thousand. So, we verified whether the process gives oligomers in addition to the principal solid product.

A gas chromatogram of the polymerization liquid product (**1b**/Et$_2$AlCl) is shown in Fig. 2. The compounds were identified by comparing their retention

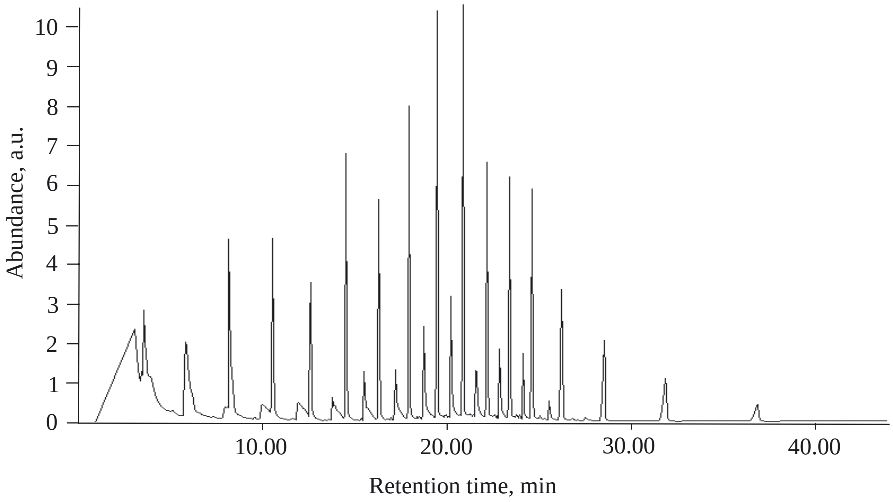


*Fig. 2. GC plot of oligomers obtained in the presence of salen-titanium complex (**1b**)/Et$_2$AlCl*

times with those obtained for the corresponding analytical standards under the same conditions. As can be seen, the GC analysis of the oligomer mixture shows the formation of olefins with the even carbon number from 12 to 42, and also the presence of isomers. No oligomers with lower numbers of carbon atoms were detected or identified. However, a wide peak appearing at short retention times, and representing the solvent used, could disturb the correct interpretation of the obtained analytical findings.

The presented data confirm the formation of different catalytic species in the investigated catalytic systems, *i.e.* those responsible for the formation of polyethylene and the mixture of liquid oligomers at the same time. The production of the latter results from the definitely higher contribution of the chain transfer reaction in relation to the chain propagation reaction.

The molecular weight of polyethylene produced in the presence of titanium/MAO catalyst (360 000) is clearly higher than that obtained for Et_2AlCl cocatalyst (2500), and it is also clearly more diversified (M_w/M_n = 6.9). Similar polydispersity (5.3) is specific for PE produced in the presence of vanadium/MAO catalyst, but its molecular weight is much higher, *i.e.* 725 000. The effect of the transition metal type on the molecular weight value of the product is similar to that observed for other post-metallocene catalysts, namely for the systems which contain complexes with tris(pyrazolyl)borate ligands [33].

Effect of the ligand structure on ethylene polymerization

It was found for metallocene catalysts that the catalytic activities and polymer parameters, such as molecular weight and molecular weight distribution, can be tailored through a rational ligand design at the transition metal centre. It seems true that — also in the case of post-metallocene catalysts — the ligand structure can be one of the factors which affect the polymerization behavior of those systems. Since the salen ligands have multiple sites available for introducing and/or changing substituents, we decided to check the impact of ligand structure on activity of the titanium catalysts activated with MAO or Et_2AlCl, and on the properties of the polymerization products. When analyzing the effects of ligands, it should be taken into account that both the steric and electronic effects of ligand substituents influence the behavior of the complex, and that they cannot be considered in isolation. Six different titanium complexes were employed in our research: two with substituents at 3,3′-positions: $-OCH_3$ (**1b**) or $-OC_2H_5$ (**1c**), another two with substituents at 5,5′-positions: -Cl (**1e**) or -Br (**1f**), the complex **1d** with *t*-Bu groups at 3,3′- and 5,5′-positions, and the complex with no substituents (**1a**) as reference.

As it is apparent from Fig. 3, nearly all complexes become more active in the polymerization process when diethylchloroaluminum is used as an activator — their average activities are about twice higher than those for the systems activated by MAO. Irrespective ot the type of activator, the use and change of substituents affect the polymerization activity of the catalyst. The findings suggest that the presence of an electron-acceptor substituent (Cl or Br, **1e** and **1f**) in the 5,5′- position is advantageous. The catalytic efficiency is also improved when an electron-donor substituent ($-OCH_3$, **1b**) is placed in 3,3′-position, but this advantageous effect is reduced for the increasing size of such substituent ($-OC_2H_5$, **1c**). It seems true that the essential factor is the steric hindrance connected with that substituent — coordination of the monomer to the metallic active site becomes harder then. This conclusion is confirmed by low activity specifications of the complexes which contain spatially expanded substituents *e.g.* *t*-butyl groups at 3,3′- position (**1d**).

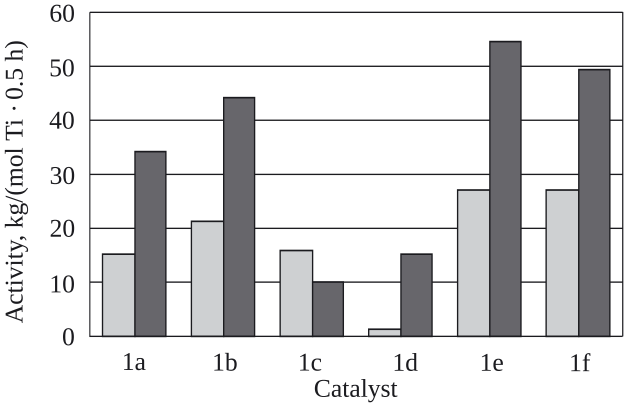


*Fig. 3. The effect of ring substituents on activity of salen complex of titanium/MAO (░) (conditios: 0.08 mmol of complex **1b**, **1d**, **1e**, **1f**, 0.13 mmol of **1a** or 0.10 mmol of **1c**) and salen complex of titanium/Et_2AlCl (■) catalysts (conditions: 0.08 mmol of complex **1b**, **1c**, **1e**, **1f**, 0.095 mmol of **1a** or 0.03 mmol of **1d**)*

The presence and the type of a substituent at the ring have no significant effects on the properties of the products obtained in the presence of the salen complex/MAO catalysts (Table 2). The process always yields polyethylene with 5 to 9 branches per 1 000 carbon atoms, melting temperature within the range of 133—135 °C and crystallinity of about 70 %. The obtained polyethylene is characterized by the molecular weight of the order of a few hundred thousand and the broad molecular weight distribution — from 3.7 to 7.6.

In contrast to previous catalytic systems, all complexes activated by Et_2AlCl produced solid PE with low molecular weight and narrow polydispersity; oligomers were also formed with the range of molecular weights similar to that for the catalyst **1b**/Et_2AlCl (see Fig. 2).

It is also worth to mention, that on the DSC curves of the polymers synthesized with all titanium complexes activated by Et_2AlCl multiple melting peaks are present.

Tables 1 and 2 indicate that all the catalysts, independently on the ligand structures and the types of me-

Table 2. Properties of PE produced in the presence of salen complexes of Ti activated by MAO or Et_2AlCl cocatalysts

Salen complex	Activator	Maximum of melting temperature, °C	Crystallinity %	$nCH_3/1000C$	C=C/2020	Bulk density g/dm^3	M_w	M_w/M_n
1a	MAO	133.2	67.8	6.1	2.9	nd*)	348 000	4.9
1b		134.2	72.8	9.1	1.8	nd	nd	—
1c		134.9	68.4	4.7	3.2	nd	228 000	3.7
1d		135.1	—	6.1	2.0	nd	695 000	7.6
1e		133.1	72.0	8.3	2.1	nd	nd	nd
1f		133.6	70.6	9.1	2.2	101.5	nd	nd
1a	Et_2AlCl	98.0; 108.0; 121.2	—	nd	nd	nd	2800	1.8
1b		109.0; 121.5	—	nd	nd	103.5	2500	1.5
1c		101.0; 110.0; 122.0	—	nd	nd	90.4	nd	nd
1d		98.3; 110.9; 122.2	—	nd	nd	nd	nd	nd
1e		110.5; 124.3	—	nd	nd	98.0	1.4	1.5
1f		107.6; 123.0	—	nd	nd	115.7	nd	nd

*) nd — not determined.

tallic centres, produced polyethylene with the relatively low bulk density, *i.e.* in the range of 90—115 g/dm^3, which however is about twice higher than that available with use of unsupported metallocene catalysts [34].

CONCLUSIONS

We have shown that the compositions of salen complex/activator catalytic systems directly affect their activities in ethylene polymerization and properties of products. The performance of these catalysts was found to be affected by all the factors covered by our investigation, *i.e.* type of metallic centre in a complex, type of activator used, and also (to somewhat lower extent) the structure of the ligand employed. The vanadium and titanium complexes were found to be more active in combination with alkylaluminum compound than with MAO, while zirconium complexes were active only in combination with MAO. The activity of complexes activated by Et_2AlCl decreases in the order $V > Ti >> Zr \cong 0$, and when MAO is used as cocatalyst, the activity changes the order: $Ti > Zr > V$. The substituent type in the salen ligand also affects the catalyst activity; the best results were obtained for the catalyst having Cl or Br substituents at 5,5′-position. The type of substituent has no significant effect on polyethylene properties, while the type of cocatalyst and the type of metallic centre play the essential role. The salen titanium complexes in combination with Et_2AlCl usually produce polyethylene with low molecular weight and narrow polydispersity, also accompanied by oligomers. Other investigated by us catalytic systems give linear high molecular weight polyethylene (M_w = 200 000—700 000).

The authors wish to thank Professor W. Bukowski from the Rzeszów Technical University for the preparation and supplies of salen ligands.

This work was financially supported by the funds within the 2005—2008 science support programme, as the research project No T 09A 168 29.

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