Polymerization of Ethylene in the Presence of Titanium(IV), Zirconium(IV), and Vanadium(V) Coordination Compounds with Salen Ligands

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Abstract—Coordination compounds of titanium(IV), zirconium(IV), and vanadium(V) with chiral salen ligands have been obtained and characterized, and their catalytic activity in the polymerization reaction of ethylene has been studied. It has been shown that in the presence of polymethylaluminoxane as a cocatalyst, the activity of the titanium-containing catalyst system reaches 944 kgPE $mol(Ti)^{-1} h^{-1}$ and leads to the preparation of ultrahigh-molecular-weight polyethylene.

Keywords: titanium, zirconium, and vanadium compounds, salen ligands, polymerization of ethylene, ultrahigh-molecular-weight polyethylene, olefins, organoaluminum compounds

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INTRODUCTION

Polyolefins are the largest group of polymer materials; the volume of the world output is estimated as 140 million tons per year and has a consistent trend to growth. In this group of polymers, the lion share accounts for polyethylene (about 100 million tons per year) which is explained by the availability of the monomer, ethylene, the main petrochemical process in the world. A promising variety of polyethylene (PE) is ultrahigh-molecular-weight polyethylene (UHM-WPE) characterized by the molecular weight of 1 to 10 mln g/mol and possessing a unique set of properties. It is known that if the synthesis of UHMWPE is performed in the suspension mode with the use of specific catalysts, in particular, postmetallocene catalysts, it turns out to be possible, in some cases, to obtain a nascent reactor powder in a high yield, the morphology of which is close to the morphology of monocrystalline PE mats. For the materials of such a type, the implementation of a continuous technique of solution-free solid-phase formation of ultrahigh-strength (the tensile strength at break of above 2.5 GPa) and ultrahigh-modulus (the Young modulus of above 150 GPa) orientated varns and fibers [1, 2] is possible. UHMWPE can be obtained in the presence of catalysts based on complexes of transition metals with salen ligands.

Salens, the products of condensation of salicylic aldehydes with various diamines including chiral, are

one of the most studied groups of organic ligands. The simplicity of the synthesis, relative resistance to nucleophilic reagents, and simplicity of variation of the geometry and electronic characteristics defined by the need for changing the properties of the metallic site, e.g., in the case of the use of salen complexes in catalytic reactions, can be considered as the obvious advantages of salen ligands over their other types. Indeed, these compounds are widely used in asymmetric synthesis for the catalysis of Henry, Nozaki-Hiyama-Kishi, and Baeyer-Villiger reactions; cycloaddition processes; ring-opening polymerization; activation of a CH bond; and addition of nucleophiles to unsaturated carbonyl compounds [3, 4]. Surprisingly, the examples of the use of complexes of metals of Group IV with salen ligands as the catalysts for the polymerization of ethylene are quite rare (Fig. 1). Thus, it is known that the activity of the systems based on titanium dichloride salen complexes of type A (Fig. 1) and polymethylaluminoxane (MAO) or Et₂AlCl is low and varies within 30-88 kgPE mol(Ti)⁻¹ h⁻¹. Upon the application of the complexes onto a magnesium-containing carrier with the composition MgCl₂(THF)_{0.32}(Et₂AlCl)_{0.36}, the activity increases to 412 kgPE mol(Ti)⁻¹ h⁻¹ [5]. Salen complexes of zirconium activated by Et₂AlCl oligomerize ethylene with the formation of C_4-C_{10} products and



Fig. 1. Examples of complexes with salen and salfen ligands active in the oligo- and polymerization of ethylene.

good selectivity with respect to linear α -olefins (LAOs); the value of TOF reaches 4.93 × 10⁴ h⁻¹ [6]. Complexes with salfen ligands (type **B**, Fig. 1) catalyze the polymerization of ethylene in the presence of MAO with the activity of up to 21.5 kgPE mol(Zr)⁻¹ h⁻¹ [7].

Possibly, the shortage of interest in these compounds is determined not only by the relatively low activity of the systems but also by the established view that the transoid position of the halogens in salen precatalysts does not favor the formation of stable catalytically active cationic particles [8]. However, as is shown by the published data, the potential of salen complexes as the precatalysts for the polymerization of ethylene and α -olefins is far from exhausted. Thus, the authors of [9] have found that the activity of zirconium complexes (type C, Fig. 1) increases with both a growth in the length of the carbon linker reaching the maximum at n = 6 and an increase in the volume of the substituent in the ortho-position to the phenol hydroxyl. Increasing the temperature of the polymerization reaction to 75°C leads to a sharp growth in the activity of the system reaching an unthinkable value of 103800 kgPE mol(Zr)⁻¹ h⁻¹ for precatalyst C (R = adamantyl, n = 6) [9]. In some cases, high- or ultrahigh-molecular-weight PE with a wide MWD was obtained over these systems.

The aim of the work was the preparation of new coordination compounds of the metals of Groups IV and V with salen ligands and investigation of their catalytic activity in the polymerization reaction of ethylene in the presence of MAO upon varying the conditions of the catalytic process.

EXPERIMENTAL

Synthesis of Coordination Compounds

The complexes were synthesized in a dry argon atmosphere in dehydrated solvents. Reagent grade dichloromethane, toluene, hexane, and ethyl acetate were additionally purified according to a known procedure [10]. A solution of polymethylaluminoxane in toluene, TiCl₄, and VOCl₃ (Aldrich) were used without additional purification. ¹H and ¹³C NMR spectra were recorded on Bruker WP-300 and Bruker AMX-400 instruments. X-ray fluorescence analysis was performed on a VRA-30 instrument (Carl Zeiss). The calorimetric studies were performed on a DSC-822e calorimeter (Mettler Toledo) at a rate of heating of 10 deg/min in air.

Chiral tetradentate salen ligands were synthesized by the interaction of the corresponding salicylic aldehydes with cyclohexanediamine in toluene in the presence of *p*-toluenesulfonic acid and further crystallization of obtained substances **1L** [11], **2L** [12, 14], and **3L** [13]. The properties of the obtained compounds fully conformed to the published data.

Ligand 1L. $[a]_D^{25} -359^\circ$ (c = 1, CHCl₃) [ref. [53]: $[a]_D^{25} -359.5^\circ$ (c = 1, CHCl₃)]. Found, %: C, 74.69; H, 6.97; N, 8.32. Calculated for C₂₀H₂₂N₂O₂, %: C, 74.51; H, 6.88; N, 8.69. ¹H NMR spectrum (CDCl₃, ppm): 1.69–1.90 (m, 8H), 3.21–3.40 (t, 2H), 6.93–7.35 (br, 8H), 8.20 (s, 2H, CH=N), 13.6 (s, 2H, OH).

Ligand 2L. $T_{\rm m}$ 63–64°C, $[a]_{\rm D}^{25}$ –250° (c = 1, CHCl₃). Found, %: C, 79.01; H, 9.91; N, 5.10. Calculated for C₃₆H₅₄N₂O₂, %: C, 79.07; H, 9.95; N, 5.12. ¹H NMR spectrum (CDCl₃, ppm): 1.20–1.42 (m, 36H), 3.26 (s, 2H), 3.66 (m, 6H), 6.78–6.88(m, 4H), 8.22 (s, 2H, CH=N), 13.21 (s, 2H, OH).

Ligand 3L. $[a]_D^{25} - 288^\circ$ (c = 1, CHCl₃). Found, %: C, 80.96; H, 6.33; N, 5.86. Calculated for $C_{32}H_{30}N_2O_2$, %: C, 80.98; H, 6.37; N, 5.90. ¹H NMR spectrum (CDCl₃, ppm): 2.21–2.45 (m, 8H), 3.47– 3.50 (m, 2H), 7.51–8.24 (m, 18H, Ar), 12.2 (s, 2H). The complexes were synthesized according to the following procedure:

Complex 1. A solution of ligand **1L** (0.32 g, 1 mmol) in toluene (10 mL) was placed into a Schlenk tube filled with argon, 0.23 g (1 mmol) of $TiCl_2(Oi-Pr)_2$ was added upon stirring, and it was stirred for 20 h. Then the solution was evaporated in vacuum, and the obtained crystalline substance was recrystallized from a toluene–hexane mixture (1 : 1).

Yield 0.38 g (87%). $T_{\rm m}$ 250–300°C. $[a]_{\rm D}^{25}$ +390 (c = 0.033, CHCl₃). Found, %: C, 54.67; H, 4.53; N, 6.32; Cl, 16.10; Ti, 10.86. Calculated for C₂₀H₂₀Cl₂N₂O₂Ti (438), %: C, 54.70; H, 4.59; N, 6.38; Cl, 16.15; Ti, 10.90. IR spectrum ($v_{\rm max}$ (Nujol), cm⁻¹): 1618 s, 1583 m, 1560 m. ¹H NMR spectrum (CDCl₃, ppm): 1.72–1.88 (m, 8H), 3.32–3.41 (t, 2H), 6.98–7.40 (br, 8H), 8.14 (s, 2H, CH=N). ¹³C NMR spectrum (CDCl₃): 24.1, 28.4, 29.8, 35.4, 122.2, 126.2, 133.5, 133.7, 137.6, 160.2, 161.7.

Complex 2. A solution of ligand **2L** (0.55 g, 1 mmol) in toluene (10 mL) was placed into a Schlenk tube filled with argon, 0.23 g (1 mmol) of TiCl₂(*Oi*-Pr)₂ was added upon stirring, and it was stirred for 20 h. Then the solution was evaporated in vacuum, and the obtained crystalline substance was recrystal-lized from hexane. Yield 0.56 (84%). Found, %: C, 65.10; H, 7.85; N, 4.17; Cl, 10.65; Ti, 7.19. Calculated for C₃₆H₅₂Cl₂N₂O₂Ti (662), %: C, 65.16; H, 7.90; N, 4.22; Cl, 10.69; Ti, 7.21. IR spectrum (v_{max} (Nujol), cm⁻¹): 1618, 1583, 1560. ¹H NMR spectrum (CDCl₃, ppm): 1.29–1.47 (m, 36H), 3.36 (s, 2H), 3.78 (m, 6H), 6.90–7.21 (m, 4H), 8.15 (s, 2H, CH=N).

Complex 3. A solution of ligand **3L** (0.47 g, 1 mmol) in toluene (10 mL) was placed into a Schlenk tube filled with argon, 0.23 g (1 mmol) of TiCl₂(O*i*-Pr)₂ was added upon stirring, and it was stirred for 20 h. Then the solution was evaporated in vacuum, and the obtained crystalline substance was recrystal-lized from toluene. Yield 0.41 (69%). Found, %: C, 64.92; H, 4.70; N, 4.70; Cl, 11.91; Ti, 8.03. Calculated for $C_{32}H_{28}Cl_2N_2O_2Ti$ (590), %: C, 64.99; H, 4.77; N, 4.74; Cl, 11.99; Ti, 8.09. IR spectrum (v_{max} (Nujol), cm⁻¹): 1620, 490, 547. ¹H NMR spectrum (CDCl₃, ppm): 2.43–2.55 (m, 8H), 3.41–3.59 (m, 2H), 7.36–7.98 (m, 18H, Ar).

Complex 4. A solution of ligand **2L** (0.55 g, 1 mmol) in toluene (10 mL) was placed into a Schlenk tube filled with argon, 0.38 g (1 mmol) of $ZrCl_4 \cdot 2THF$ was added upon stirring, and it was stirred for 24 h upon heating. Then the solution was evaporated in vacuum, and the obtained crystalline substance was recrystallized from a toluene–hexane (2 : 1) mixture.

Yield 0.61 g (87%). Found, %: C, 61.13; H, 7.36; N, 3.92; Cl, 9.97; Zr, 12.85. Calculated for $C_{36}H_{52}$ -Cl₂N₂O₂TiZr (704), %: C, 61.16; H, 7.41; N, 3.96; Cl, 10.03; Zr, 12.90. IR spectrum (v_{max} (Nujol), cm⁻¹): 1623, 1589, 1562. ¹H NMR spectrum (CDCl₃, ppm): 1.32–1.40 (m, 36H), 3.31 (s, 2H), 3.62 (m, 6H), 6.99–7.30 (m, 4H), 8.11 (s, 2H, CH=N).

Complex 5. A solution of ligand **2L** (0.55 g, 1 mmol) in toluene (10 mL) was placed into a Schlenk tube filled with argon, 0.12 g (1 mmol) of VOCl₃ was added upon stirring, and it was stirred for 20 h. Then the solution was evaporated in vacuum, and the obtained crystalline substance was recrystallized from hexane. Yield 0.56 (84%). Found, %: C, 66.75; H, 8.05; N, 4.28; Cl, 5.42; V, 7.80. Calculated for $C_{36}H_{52}$ -ClN₂O₃V (646), %: C, 66.81; H, 8.10; N, 4.33; Cl, 5.48; V, 7.87. IR spectrum (v_{max} (Nujol), cm⁻¹): 1628, 1583, 1560, 995. ¹H NMR spectrum (CDCl₃, ppm): 1.49–1.52 (m, 36H), 3.42 (s, 2H), 3.81 (m, 6H), 6.65–7.17 (m, 4H), 8.11 (s, 2H, CH=N).

The process was performed in toluene in a 100-mL glass reactor at an ethylene pressure of 2 atm. The reactor was preliminarily evacuated for 1 h at 90°C (up to 5×10^{-3} atm), cooled down to ~20°C, and 60 mL of heptane, 6×10^{-4} mol of triisobutylaluminum (TIBA, a sanifying and activating additive), and ethylene were added upon stirring. The polymerization was initiated 15–20 min after the completion of the preparatory operations by breaking a glass ampoule with the preliminarily prepared catalyst in the reactor, and it was terminated by introducing a 10% solution of HCl in ethanol into the reactor. The polymer product was filtered off, repeatedly rinsed with water and alcohol, and dried in vacuum at 50–60°C to a constant weight.

The molecular weight characteristics (M_w , M_n , MWD) of PE were measured for the solutions of the polymers in 1,2-dichlorobenzene at 135°C via gel permeating chromatography on a Waters 150-C instrument equipped with a linear HT- μ -styragel column.

RESULTS AND DISCUSSION

The ligands used in the study were obtained by the interaction of salicylic aldehydes with cyclohexanediamine [11-14]. The complexes presented in Scheme 1 were obtained by the interaction of L,L-bis(salicylidene)cyclohexanediamines with titanium(IV), zirconium(IV), and vanadium(V) halides.



Scheme 1. Synthesis of the complexes of metals of Groups IV and V with ONNO-type ligands.

The investigation of the composition, structure, and properties of the initial substances and reaction products was performed by elemental analysis and CD, IR, and NMR spectroscopy. In the presence of water and organic bases or alkalis, the complexes decompose to release the initial ligand and to form TiO_2 .

According to the ¹H NMR data, complexes 1–5 are in the form of monomeric particles with the C₂ symmetry in chloroform. Thus, for complexes 2 and 4, the characteristic signal of the aldimine protons is a singlet at 8.1 ppm, and two signals of the *tert*-butyl groups and three groups of signals of the protons of the cyclohexanediamine fragment of the chiral ligand are observed. The C₂ symmetry of the chiral tetradentate salen ligand in complexes 2, 4, and 5 manifests itself in the circular dichroism spectra in the form of excitonic coupling at a wavelength of about 350 nm. It is known that the electronic transition occurring at ~350 nm in the electronic spectra of metal complexes with salen ligands belongs to the $\pi \rightarrow \pi^*$ transition of the C=N bond conjugated with the aromatic ring.

The use of compounds 1-5 as precatalysts for the polymerization of ethylene showed that almost all the substances obtained by us exhibited catalytic activity in the presence of MAO (Table 1).

As is seen from the data of Table 1, the catalytic activity of the systems grows with the increase in the concentration of the cocatalyst except for the system with catalyst 5. Here, the maximum catalytic activity is observed for the titanium complex when conducting the polymerization process at 50°C (944 kgPE mol(Ti)⁻¹ h⁻¹).

Unexpectedly, the use of zirconium complex **4** leads to a certain decrease in the catalytic activity of

the system in comparison with the system based on titanium complex **2** under otherwise equal conditions. It is also seen that a decrease in the molecular weights of polyethylene from 1.98×10^6 to 1.17×10^6 occurs with the increase in the concentration of MAO. Here, several bands manifest themselves increasingly clearly in the GPC curves, which is indicative of the polymodality of the polymer, i.e., the multisite nature of the catalyst.

The multisite nature of the catalyst systems formed under the action of MAO at 30 and 70°C can be illustrated by the GPC curves presented in Fig. 2. The GPC curve of the sample of PE obtained at 70°C (experiment 9) is trimodal, namely, the main peak (80% by area, $M_w/M_n = 2.06$), low-molecular-weight peak (7%, $M_n = 7000$, $M_w/M_n = 1.20$), and high-molecular-weight peak (13%, $M_n = 986$ 800, $M_w/M_n = 2.12$). The GPC curve of the sample of PE obtained at 70°C is bimodal, namely, the first peak (62%, $M_n = 42000$, $M_w/M_n = 3.52$) and the second peak (39%, $M_n = 471400$, $M_w/M_n = 3.80$). The comparison makes it possible to draw a conclusion about the fact that the main body of PE is formed over two different active sites in both the first and second systems. Here, the nature of these active sites is different from those which are formed at a low temperature and produce ultrahigh-molecular-weight PE (experiment 7).

Apparently, the reason for the occurrence of a lowmolecular-weight "hump" in the GPC curve of Tipolyethylene is the reversible coordination of trimethylaluminum present in MAO which temporarily converts the catalyst to the "dormant" state [5]. The β -hydride shift reaction involving transfer to the monomer determines the lower molecular weights of

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Table 1. Polymerization of ethylene over coordination compounds 1-5 (MAO is the cocatalyst, toluene is the solvent, the total pressure of ethylene and toluene vapors is 1 atm, $[Ti] = 10^{-6}$ mol, and polymerization time is 30 min)

No.	Complex	Al _{MAO} /M (Ti, Zr, V), mol/mol	<i>T</i> , °C	Yield of PE, g	A^1	$T_{\rm m}$, °C	M _w , M _n	M _w /M _n
1	1	1000	30	0.67	268	140	_	_
2	1	2000	30	0.78	312	139	_	_
3	2	500	30	0.83	332	141	$1.98 \times 10^{6},$ 4.85×10^{5}	4.08
4	2	1000	30	1.22	488	143	$1.52 \times 10^{6},$ 2.96×10^{5}	5.13
5	2	1000	50	1.71	684	141	_	I
6	2	1000	70	1.67	668	138	_	
7	2	2000	30	1.99	796	141	$1.17 \times 10^{6},$ 1.92×10^{5}	6.10
8	2	2000	50	2.36	944	139	$1.01 \times 10^{6},$ 1.28×10^{5}	7.89
9	2	2000	70	2.30	920	144	$5.79 \times 10^5,$ 3.71×10^4	15.60
10	3	1000	30	0.36	144	143	_	_
11	3	2000	30	0.89	356	142	_	_
12	4	1000	30	0.73	292	141	$1.85 \times 10^{6},$ 5.66×10^{5}	3.26
13	4	2000	30	0.98	392	140	$1.51 \times 10^{6},$ 3.59×10^{5}	4.20
14	5	1000	30	1.19	476	144	_	_
15	5	2000	30	1.31	424	142	_	_

¹Activity, kgPE mol(M(Ti, Zr, V)) $^{-1}$ h $^{-1}$.

the sample of PE and leads to the occurrence of terminal vinyl groups in the polymer, which is detected by the appearance of the absorption bands at 909 and 995 cm⁻¹ in the IR spectra of the samples of PE. By way of example, Figure 3 presents the comparison of the IR spectra of the samples of the polymer obtained over the system with complex **2** (experiments 7 and 9).

Therefore, comparing the data on the polymerization of ethylene over the titanium catalyst upon activation by MAO at different temperatures raised questions about the deactivation processes that appear over the synthesized catalysts. The analysis of the data on the molecular weight characteristics of the samples of PE is indicative of the fact that, most likely, the modification of the primary neutral or cationic complexes with the formation of active sites with different compositions and structures occurs in the synthesized catalyst systems. This leads to a change in the rates of chain growth and transfer and their ratio, or, in other



Fig. 2. GPC curves of the PE samples obtained over catalyst 2 at 70°C (9 corresponds to experiment 9, Table 1) and 30°C (7 corresponds to experiment 7, Table 1).



Fig. 3. IR spectra of the samples of polyethylene obtained over catalyst 2 at 70°C (9 corresponds to experiment 9, Table 1) and 30° C (7 corresponds to experiment 7, Table 1).

words, to a change in the mechanisms of chain transfer reactions.

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CONFLICT OF INTEREST

The authors declare no conflict of interest to be disclosed in this paper.

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