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MECHANISMS
OF CATALYTIC REACTIONS

Ethylene Polymerization on Titanium Phenoxyimine Complexes with Different Structures

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Abstract—The kinetics of ethylene polymerization in the presence of catalytic systems based on methylaluminoxane-activated titanium bis(phenoxyimine) complexes with different structures has been investigated in the temperature range 30–70°C. The structures of the complexes have different substituents at the imine nitrogen atom and in the phenoxy group in the ligand, which affect the activity of the system and the molecular weight of polyethylene resulting from polymerization over at least 1 h. The polymerization kinetics is most sensitive to the structure of the substituent at the imine nitrogen atom and to bulky substituents in the *ortho* position of the phenoxy group. The results obtained are explained. An attempt is made to classify the influence of the substituents in the ligands. Process conditions ensuring living polymerization have been found. The physicochemical properties and structural features of the polyethylenes obtained have been determined.

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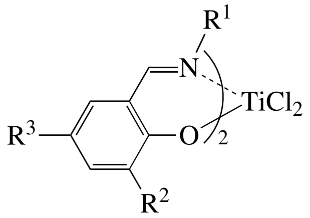
INTRODUCTION

Catalytic systems based on zirconium, titanium, and hafnium bis(phenoxyimine) complexes were discovered rather recently [1, 2]. They have attracted attention from many researchers owing to their availability, structural diversity, and low oxophilicity, as well as the opportunity to obtain polyolefins with various molecular weights and structures and to perform living polymerization [3–8].

Quite extensive experimental data on the synthesis of transition metal (Zr, Ti, Hf, etc.) phenoxyimine complexes with various ligand structures and on their catalytic activity in the polymerization of ethylene and some α-olefins have been accumulated within a short period of time. The results are systematized in two reviews [3, 4], which present conceptions of the influence of substituents in the ligands of bis(phenoxyimine) complexes on the polymerization activity of these complexes. Bulky substituents *ortho* to the oxygen atom of the phenoxy group enhance the activity of the catalytic system through steric protection of the phenoxy group [3]. Less bulky substituents at the imine nitrogen atom are preferable for higher catalytic activity because they do not prevent monomer incorporation into the growing polymer chain. These conclusions as to the activity of the catalytic systems were derived from polymer accumulation data collected over a certain, usually short, period of time (5–15 min), without studying the polymerization kinetics, and the activity was expressed in terms of (kg PE) (mol Cat)$^{-1}$ h^{-1} (PE = polyethylene, Cat = catalyst). This shortcut method of activity determination has not provided reliable data for a number of structures differing substantially in terms of polymerization kinetics and, accordingly, polymer accumulation. For this reason, we undertook a detailed study of the kinetics of ethylene polymerization over a time period of 1 h in the presence of titanium phenoxyimine complexes with the general formula



varying either the substituents at the imine nitrogen atom for a fixed structure of the phenoxy group or the structure of the phenoxy group for a fixed structure of the imine group.

EXPERIMENTAL

Chemicals and Solvents

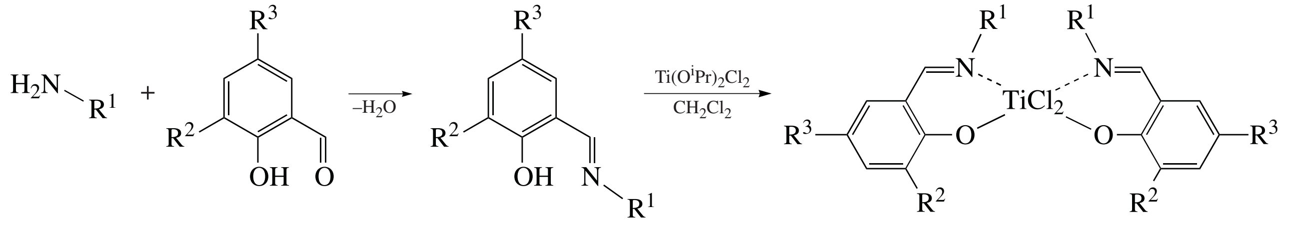
Toluene (special-purity grade) was dried for 24 h over calcined alumina, distilled in flowing argon from sodium metal, and stored in the presence of sodium metal in an inert gas atmosphere.

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

Ethylene (≥99.5%) and argon (high-purity grade) were dried in columns packed with calcined alumina before being fed into the reactor. The moisture content of the thus-dried ethylene and argon was no higher than 10–200 and 10 ppm, respectively.

Polymethylaluminoxane (MAO) (CK Witko GmbH, trade name Eurecen® Al 5100/10T) was used as a 10% solution in toluene. According to an assay provided by Witko, the total aluminum content of MAO was 4.6–5.6 mol % and the relative aluminum content in terms of trimethylaluminum was 32–36 mol %.

The catalysts to be examined were prepared from titanium bis(phenoxyimine) complexes synthesized at the Vorozhtsov Institute of Organic Chemistry, Siberian Branch, Russian Academy of Sciences (Novosibirsk). The ligands and complexes were synthesized according to the scheme



using published procedures [6, 9–11].

The structures of the ligands and complexes were confirmed by elemental analysis and ^{1}H NMR and IR spectroscopy.

Ethylene Polymerization

Ethylene polymerization was carried out at pressures up to 0.6 MPa and $T = 30$–80°C in a 150-ml stainless steel reactor fitted with a removable jacket and a propeller-type magnetic stirrer. The pressure in the reactor was maintained automatically, and the temperature regime was controlled by supplying water with an appropriate temperature from an ultrathermostat to the reactor jacket.

Before polymerization, the reactor was vacuumized for 1 h to achieve a residual pressure of 1×10^{-1} Torr at 150–170°C and was then flushed with dry argon three times.

After the reactor was cooled to room temperature, appropriate amounts of toluene and of the components of the catalytic system were syringed into the reactor through the charging port under counterflowing argon. The reaction mixture was saturated with ethylene while bringing the reactor to the working temperature and pressure. After a certain time, the reaction was terminated by adding isopropyl alcohol. The liquid phase was separated on a Büchner funnel, and the resulting polymer was washed with isopropyl alcohol and dried to constant weight at 60°C in vacuo.

Physicochemical Properties of the Resulting Polyethylenes

The molecular weight (MW) of polymers was determined by viscometry and was calculated using the equation [12]

$$[\eta] = 6.2 \times 10^{-4}\, M^{0.70}.$$

The polydispersity of the polyethylenes was determined by gel permeating chromatography using an Alliance GPCV 2000 chromatograph (Waters, United States) with HT3 and HT5 styrogel columns (Waters) and 1,2,4-trichlorobenzene (Merck) as the solvent. The elution rate was 0.5 ml/min. Universal calibration was carried out using polystyrene standards (Waters) with MW = 1100–10100000.

The thermal properties of polymers were studied by scanning calorimetry. The specific heats of phase transitions and characteristic temperatures were measured on a DSC-60 differential scanning calorimeter (Shimadzu) at a heating rate of 10 K/min using 5- to 10-mg samples. The melting point was determined by examining the initial polymer.

The structures of the synthesized polymers were studied by FTIR spectroscopy on an FTIR-8300 spectrophotometer (Shimadzu).

RESULTS AND DISCUSSION

The structures of the substituents in the titanium phenoxyimine complexes are presented in Table 1.

Temperature-dependent ethylene polymerization data for three phenoxyimine complexes containing a cyclohexyl substituent at the imine nitrogen atom and different substituents in the phenoxy group are given in Table 2. As can be seen from these data, the bulky substituent cumyl (complex **I**) in the *ortho* position of the phenoxy group provides a higher activity than *tert*-butyl (complexes **II** and **III**). The replacement of the substituents in the *para* position of the phenoxy group exerts a slight effect on the catalytic activity but increases the MW of the resulting PE.

As a whole, the data presented in Table 2 agree with earlier reported results [3], indicating that the catalytic

Table 1. Structures of the synthesized titanium phenoxyimine complexes

Catalyst	R^1	R^2	R^3
I	cyclohexyl	cumyl	methyl
II	cyclohexyl	*tert*-butyl	methyl
III	cyclohexyl	*tert*-butyl	*tert*-butyl
IV	phenyl	*tert*-butyl	*tert*-butyl
V	2-cyclohexylphenyl	*tert*-butyl	*tert*-butyl
VI	1-(1-adamantyl)ethyl	*tert*-butyl	*tert*-butyl
VII	2-isobornyl	*tert*-butyl	*tert*-butyl
VIII	*n*-butyl	*tert*-butyl	methyl
IX	pentafluorophenyl	*tert*-butyl	cumyl
X	pentafluorophenyl	2-isobornyl	H

activity increases upon the introduction of a bulky *ortho* substituent into the phenoxy group. This is likely due to the steric protection of the phenoxy group against the electrophilic attack of Lewis acids and the hindered interaction between the active cationic form of the complex and the anionic cocatalyst.

Ethylene polymerization data obtained for the phenoxyimine catalytic systems with different substituents at the imine nitrogen atom are presented in Table 3.

The data in Table 3 demonstrate the ambiguity of the influence of the substituents at the imine nitrogen atom on the ethylene polymerization efficiency of the catalyst. For instance, **III** and **IV**, the most active complexes, contain cyclohexyl and phenyl at the imine nitrogen atom, respectively. However, for complex **IV**, the temperature dependence of catalytic activity passes through a maximum at 50°C, whereas the activity of complex **III** decreases by a factor greater than 3 as the temperature is raised from 30 to 50°C. At 30°C, the efficiency of the cyclohexyl substituent is higher than the efficiency of phenyl, while, at 50°C, the efficiency of the phenyl substituent at the imine nitrogen atom is several times higher than the efficiency of the cyclohexyl substituent. The catalytic activity decreases sharply as the bulkiness of the substituent at the imine nitrogen atom is increased, for example, by introducing 2-cyclohexylphenyl (complex **V**), 1-(1-adamantyl)ethyl (**VI**), or 2-isobornyl (**VII**). However, it should be mentioned that, for complex **V**, the catalytic activity grows with increasing temperature (up to 70°C). Catalyst **VIII** synthesized by our group, with the smallest substituent volume (*n*-butyl), has the smallest volume and shows low efficiency as compared to complex **III** or **IV**. By studies of the influence of the structure of complexes [13] on the energies (ΔE) of the formation of the catalyst–MAO cationic complex (step 1), active site formation (step 2), chain propagation (step 3), and β-hydride transfer with α-olefin elimination (step 4), it was demonstrated that, for step 4, ΔE is most exothermic for catalyst **VIII** (−34.1 kcal/mol) and is less exothermic for **III** and **IV** (–31.0 kcal/mol). As a consequence, the catalytic complex in the case of **VIII** is less active and affords PE with a much smaller molecular weight: MW = 1760000 for **III** and 300000 for **VIII**.

Thus, complexes **III**–**VIII**, which contain the same substituent in the phenoxy group and different substituents at the imine nitrogen atom, behave differently in ethylene polymerization, whereas complexes **I**–**III**, which contain the same substituent at the imine nitrogen atom and different substituents in the phenoxy group, show the same catalytic behavior: their catalytic activity decreases with increasing temperature.

The FTIR spectroscopic and DSC studies of the structural and thermal properties of the resulting polymers showed that all the PEs are highly linear. This is indicated by the low fraction of terminal CH_3 groups (<0.05) and T_m = 139–142°C. We were interested in the perfection of polymer chain packing during the synthesis, so T_m was determined for the initial PE.

Table 2. Results of ethylene polymerization on titanium phenoxyimine complexes with different substituents in the phenoxy group

Catalyst	Polymerization temperature, °C	Amount of Ti, μmol	Yield, g	Activity, kg (mol Cat)$^{-1}$ MPa^{-1} h^{-1}	$M_\eta \times 10^{-3}$	$M_n \times 10^{-3}$	$M_w \times 10^{-3}$	$\frac{M_w}{M_n}$
I	30	1.10	20.9	64000	783	333.6	1134.9	3.40
	50	1.10	10.1	30700	658	313.0	1087.0	3.50
II*	30	2.00	8.9	22250	1090	254.3	978.4	3.85
	50	2.15	8.2	12713	800	–	–	–
III	30	2.00	10.2	17000	1761	607.6	2179.2	3.60
	50	2.00	3.0	5000	1300	–	–	–

Note: Polymerization conditions: τ = 60 min, MAO/Ti = 250 : 1, $P_{ethylene}$ = 0.3 MPa, and $V_{toluene}$ = 50 ml.
* The duration of the run is 40 min.

Table 3. Results of ethylene polymerization on titanium phenoxyimine complexes with different substituents at the imine nitrogen atom

Catalyst	Polymerization temperature, °C	Amount of Ti, μmol	Yield, g	Activity, kg (mol Cat)$^{-1}$ MPa^{-1} h^{-1}	$M_\eta \times 10^{-3}$	$M_n \times 10^{-3}$	$M_w \times 10^{-3}$	$\frac{M_w}{M_n}$
III	30	2.00	10.20	17000	1761	607.6	2179.2	3.60
	50	2.00	3.00	5000	1300	–	–	–
IV	30	2.01	8.80	14594	640	351.4	940.7	2.68
	50	1.94	14.10	24227	590	194.0	636.3	3.28
	70	2.07	5.10	8212	520	–	–	–
V*	30	4.00	0.77	321	4430	–	–	–
	50	4.00	0.67	558	735	–	–	–
	70	4.00	1.43	1192	381	–	–	–
VI	30	1.96	0.03	51	–	–	–	–
VII	30	1.85	0.02	36	–	–	–	–
VIII	30	1.13	0.39	1150	300	–	–	–
	50	0.85	1.20	4700	–	–	–	–
	70	1.60	1.50	3130	–	–	–	–

Note: For the polymerization conditions, see Table 2.
* The duration of the run is 2 h.

Table 4. Results of ethylene polymerization in the presence of titanium phenoxyimine complexes with pentafluorophenyl substituents at the imine nitrogen atom

Catalyst	Polymerization temperature, °C	Time, min	Amount of Ti, μmol	Yield, g	Activity, kg (mol Cat)$^{-1}$ MPa^{-1} h^{-1}	$M_\eta \times 10^{-6}$
IX	30	6	1.13	7.45	219764	6.5
	30	14	1.36	12.14	127520	15
	30	30	1.41	16.94	80095	20
	50	60	1.35	20.30	50123	16
	70	60	2.10	10.54	16730	11
X	20	10	2.08	1.50	14420	1.7
	20	20	2.27	2.83	12470	3.1
	30	60	2.10	9.55	15160	6.0
	50	60	2.26	12.00	17700	6.9
	70	60	2.25	10.34	15320	6.9

Note: For the polymerization conditions, see Table 2.

The ethylene polymerization rate as a function of time for four active titanium phenoxyimine complexes is plotted in the figure.

The titanium phenoxyimine complexes are capable of maintaining the polymerization rate virtually constant for a rather long time (figure), whereas similar Zr complexes lose their catalytic activity within 5 min [13, 14].

We studied two titanium phenoxyimine complexes containing the same substituent pentafluorophenyl at the imine nitrogen atom and cumyl (**IX**) or 2-isobornyl (**X**) in the phenoxy group. The results of ethylene polymerization in the presence of these complexes are presented in Table 4.

The data listed in Table 4 show that complexes **IX** and **X** are very active. This is likely due to the electron-donating effect of the fluorine-containing substituents enhancing the electrophilicity of the titanium center and resulting in a decrease in the activation energy of ethylene insertion, as described in [15].

The very high polymerization activity of complex **IX** (200000 kg PE (mol Cat)$^{-1}$ MPa^{-1} h^{-1}) and the ultrahigh MW of the resulting PE over the first 6 min of the reaction confirm the aforesaid. The high efficiency of

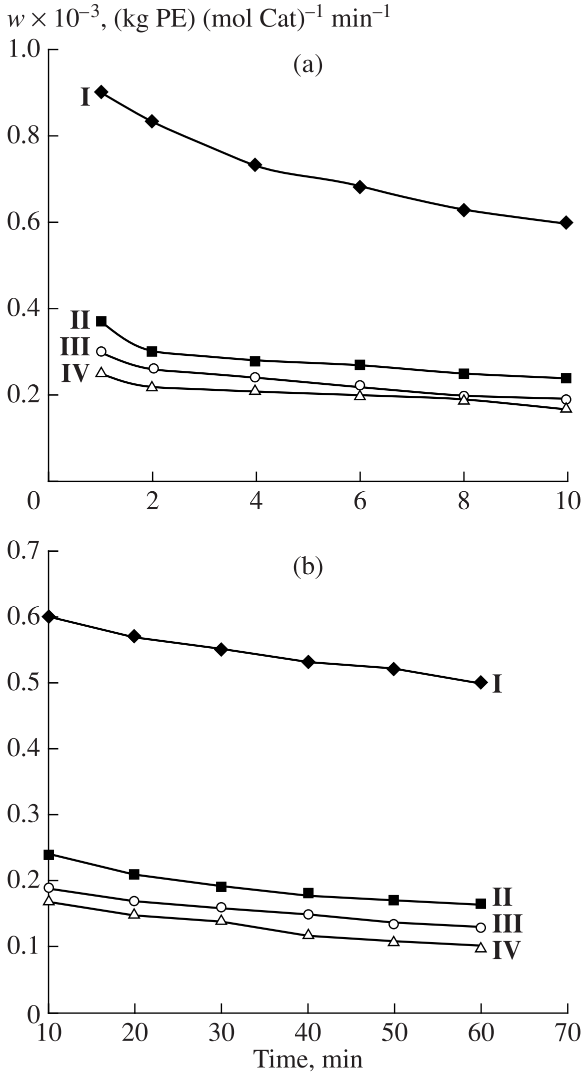


Fig. 1. Kinetics of ethylene polymerization on selected titanium phenoxyimine complexes. Polymerization conditions: $T_{\text{pol}} = 30°\text{C}$, [Ti] = (**I**) 2.2×10^{-5} and (**II**–**IV**) 4×10^{-5} mol/l, MAO/Ti = 250 : 1, $P_{\text{ethylene}} = 0.3$ MPa, and $V_{\text{toluene}} = 50$ ml. The duration of the process is (a) 10 and (b) 10–60 min.

complex **IX** is retained at 50°C, and a decrease in the polymerization rate is observed only at 70°C.

Equally interesting are the results of ethylene polymerization on analogous complex **X**, whose phenoxy group contains R^2 = 2-isobornyl in the *ortho* position, a substituent bulkier than the corresponding substituent in complex **IX**. The activity of complex **X** remains virtually invariable (on average, 15000 kg (mol Cat)$^{-1}$ MPa^{-1} h^{-1}) as the polymerization temperature is raised from 20 to 70°C, regardless of the reaction time.

The ultrahigh MW of the resulting PE throughout the polymerization process and its increase with reaction time suggest a living polymerization behavior. This is in agreement with an earlier article [11], whose authors claim that the presence of fluorine-substituted phenyl groups in the imine group ligand is an important condition for living polymerization to occur. In ethylene polymerization, the fluorine atom in the active site interacts with β-hydrogen in the polymer chain, thus preventing β-hydride transfer, particularly at the early stages of the reaction.

Thus, this study of the ethylene polymerization activity of ten synthesized titanium phenoxyimine complexes with different substituents at the imine nitrogen atom and in the phenoxy group in the presence of MAO has demonstrated the following:

The substituents at the imine nitrogen atom in the ligand exert a substantial effect on the activity of the catalytic complex, on the optimum temperature interval for active operation of the complex, and on the MW of the resulting PE. The reference data suggesting that small substituents at the imine nitrogen atom in the ligand are preferable since they do not prevent ethylene access to the active site need to be revised.

The steric volume of the substituents in the *ortho* position of the phenoxy group and its influence on the activity of the catalytic system based on the complex confirm, on the whole, the widespread conception of its role. However, one should allow for the existence of some optimum substituent volume above which the stimulating effect of the substituent on the activity of the catalytic system is lower or is not observed all.

The polyethylenes obtained are linear and have a high melting point (139–142°C) and crystallinity and a high or ultrahigh MW.

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