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Kinetics of Ethylene Polymerization in the Presence of a Homogeneous Catalyst Based on a Bis(phenoxyimine) Complex of Zirconium(IV)

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Abstract—Changes in the molecular-weight characteristics of the product of ethylene polymerization in the course of reaction in the presence of a homogeneous catalytic system and in the number and reactivity of catalyst active sites were studied. The catalytic system consisted of bis[*N*-(3-*tert*-butylsalicylidene)anilinato]zirconium dichloride and methylalumoxane as an activator. This catalytic system exhibited the signs of unsteady-state conditions: the rate of polymerization dramatically decreased as the reaction time increased. At the onset of polymerization (to 5 min), the catalyst was single-site, and it produced low-molecular-weight polyethylene with $M_w = (4–10) \times 10^3$ g/mol. The fraction of active sites at the initial point in time was as high as 11% based on the initial amount of the zirconium complex. The reactivity of these centers was very high (the rate constant of polymer chain growth was 5.4×10^4 l mol^{-1} s^{-1} at 35°C). As the polymerization time increased, the number of active sites decreased and the molecular-weight distribution of polyethylene broadened because of the decay of a portion of initial centers and the formation of new centers that produced high-molecular-weight polyethylene with M_w to 130×10^4 g/mol. The propagation rate constant measured at a sufficiently long polymerization time (20 min) was lower than that at the initial point in time; this fact suggests the much lower reactivity of the new active sites.

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INTRODUCTION

Highly active catalytic systems based on bis(phenoxyimine) complexes of zirconium and titanium have attracted considerable attention of researchers in the past decade [1–7]. A catalytic system based on a bis(phenoxyimine) complex of zirconium containing a *tert*-butyl substituent at the phenoxy group of the ligand—bis[*N*-(3-*tert*-butylsalicylidene)anilinato]zirconium dichloride (^{t}Bu-L$_2$ZrCl$_2$)—exhibited the highest activity in the process of ethylene polymerization. In the presence of this complex activated by methylalumoxane (MAO), a polymer with a narrow molecular-weight distribution ($M_w/M_n \approx 2$) was formed; this fact suggests the single-site structure of this catalytic system. However, note that the published kinetic data [2, 6, 7] were obtained only at a very short polymerization time (<5 min). At the same time, we experimentally found that the reaction rate dramatically decreased as the time of polymerization on this catalyst increased to 30 min. It was found previously that the duration of ethylene polymerization on single-site metallocene complexes [8], bis(imino)pyridyl complexes of cobalt [9], and polycentric bis(imino)pyridyl complexes of iron [10, 11] can considerably affect the number and reactivity of catalyst active sites. The decrease in the activity of single-site catalysts in the course of polymerization was due to only a decrease in the number of their active sites (C_p), whereas both C_p and the average propagation rate constant (k_p) decreased in the course of polymerization on multi-site catalysts and the molecular-weight characteristics of the resulting polymer also changed noticeably.

Thus, it seems important to obtain data on the molecular-weight characteristics of a polymer and on the number and reactivity of active sites at different points in time during polymerization because of the unsteady-state kinetic behavior of the ^{t}Bu–L$_2$ZrCl$_2$–MAO system.

Here, we report the effect of polymerization time (τ_p) on the activity of the ^{t}Bu–L$_2$ZrCl$_2$ + MAO catalyst, the molecular weight and molecular-weight distribution of polyethylene (PE), and changes in the number of active sites and the rate constant of polymer growth in the course of the process. A combined analysis of these data allowed us to make conclusions on transformations that occurred in the test unsteady-state catalytic system during polymerization.

EXPERIMENTAL

Catalyst Preparation

The starting bis(phenoxyimine) complex of zirconium ^{t}Bu–L$_2$ZrCl$_2$ (^{t}Bu–L:[(C$_6$H$_5$–N=CH)(^{t}Bu-

Table 1. Effect of polymerization time on the yield, MW, and MWD of PE prepared in the presence of the ^{t}Bu-L_2ZrCl_2–MAO homogeneous catalyst

Experiment no.	τ_p, min	Yield of PE, kg/(mol Zr)	r_{av}, (kg PE) (mol Zr)$^{-1}$ min^{-1} bar^{-1}	$M_n \times 10^{-3}$, g/mol	$M_w \times 10^{-3}$, g/mol	$M_z \times 10^{-3}$, g/mol	M_w/M_n
1	1.5	5360	600	4.2	9.4	15	2.2
2	7	10360	500	4.2	14	90	3.3
3	30	24820	280	4.6	140	2200	30

Note: Polymerization conditions: temperature, 40°C; C_2H_4 pressure, 2 bar; toluene volume, 150 ml; MAO/Zr = 1000; [^{t}Bu-L_2ZrCl_2] = 3.7 μmol/l.

C_6H_3)O]) was prepared in accordance with a published procedure [2].

A commercial sample of MAO from Crompton GmbH (Bergkamen) as a solution in toluene with a total aluminum concentration of 1.8 mol/l was used as an activator.

Ethylene Polymerization

The polymerization of ethylene was performed in a 0.5-l steel autoclave, in which a solution of ^{t}Bu-L_2ZrCl_2 in CH_2Cl_2 (1.1 (μmol Zr)/ml, 0.5 ml) was placed in a sealed glass ampoule. Then, the autoclave was evacuated at 80°C for 1.5 h; thereafter, it was cooled to 20°C and a solution of MAO in toluene (150 ml; MAO/Zr = 1000) was introduced into the autoclave at room temperature. The reaction mixture was heated to 40°C and saturated with ethylene (2–3 bar). To initiate the reaction, the ampoule with the solution of the complex was crushed. The temperature and pressure of ethylene in the autoclave were maintained at a constant level with the use of an automated system. The rate of polymerization was measured based on ethylene consumption; the measurements were performed at regular intervals of a few seconds. After the completion of polymerization, the ethylene pressure was relieved, and the resulting solid product was filtered off and dried at room temperature to constant weight.

Determination of C_p and k_p

To determine C_p and k_p, we used a polymerization inhibition method by the introduction of ^{14}CO. Previously, we used this method to study catalysts based on the bis(imino)pyridine complexes of cobalt [9] and iron [10, 11]. Labeled by-products [12] were removed from the polymer by double reprecipitation from decane in accordance with a procedure described elsewhere [10, 11]. The radioactivity of PE was measured on an SL-4000 scintillation counter, and the number of active sites was calculated based on these data. The propagation rate constant was determined using the equation

$$k_p = \frac{r}{C_p[C_2H_4]}, \quad (1)$$

where r is the rate of polymerization at the point in time when ^{14}CO was introduced, and $[C_2H_4]$ is the concentration of ethylene in toluene calculated with consideration for the Henry constant [13].

Determination of the Molecular Weight and Molecular-Weight Distribution of Polyethylene

The molecular weight (MW) and the molecular-weight distribution (MWD) were determined by gel permeation chromatography on a Waters 150 C instrument with TSKgel GMHXL-HT columns (Tosoh) at 140°C and a solvent (trichlorobenzene) flow rate of 1 cm^3/min. The Viscotec GPC Software (Version 3.0) was used for data processing. The instrument was calibrated using standard PE and polystyrene samples with narrow MWDs.

RESULTS AND DISCUSSION

Effect of Polymerization Time on the MWD of PE

Figure 1 shows the kinetic profiles of ethylene polymerization in the presence of the ^{t}Bu–L_2ZrCl_2 + MAO homogeneous system. The rate of polymerization (r) at the initial point in time was very high; however, it dramatically decreased in the course of reaction. The most significant decrease in the rate occurred at the onset of the reaction: in the first 5 min, it decreased by a factor of 1.5–2 (curve *1*); then, it decreased more smoothly (curve *2*). As a result, the average rate of polymerization (r_{av}) in long-term experiments decreased (Table 1).

Data given in Table 1 and Fig. 2 indicate that the polymerization time considerably affected the molecular-weight characteristics of the resulting polymer. At short τ_p (1.5 min), PE with a narrow MWD (M_w/M_n = 2.2; Table 1) and a low MW ($M_w = 9.4 \times 10^3$ g/mol) was formed; this is consistent with published data [6, 7]. However, as the polymerization time was increased to 30 min, the weight-average MW increased (to 1.4×10^5 g/mol) and the MWD of the resulting PE broadened ($M_w/M_n = 30$) because of the formation of additional high-molecular-weight fractions with MW of 10^5–10^6 g/mol (Fig. 2). This manifests itself in a dramatic increase of the value of M_z from 15×10^3 to 2200×10^3 g/mol (Table 1). Note that, as the polymer-

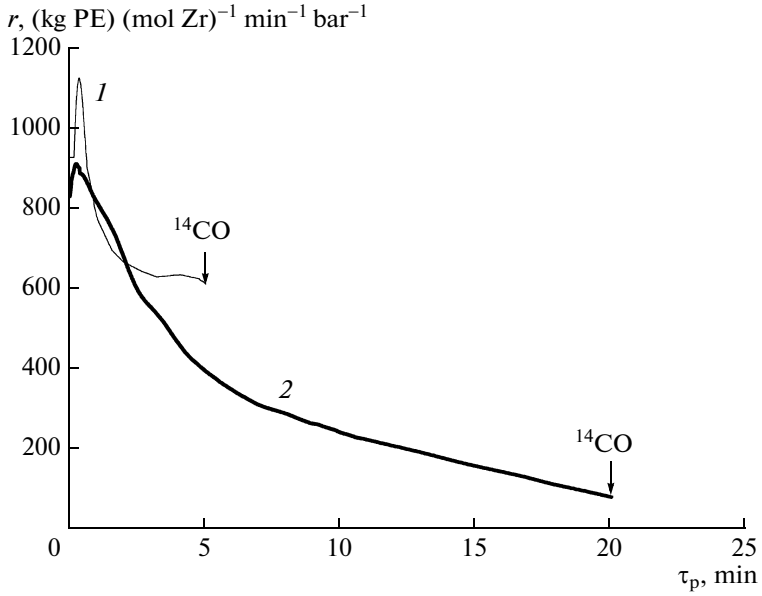

Fig. 1. Dependence of the rate of ethylene polymerization on reaction time on the ^{t}Bu-L_2ZrCl_2 + MAO catalyst obtained in experiments with the introduction of a ^{14}CO inhibitor: (*1*) after 5 min and (*2*) after 20 min.

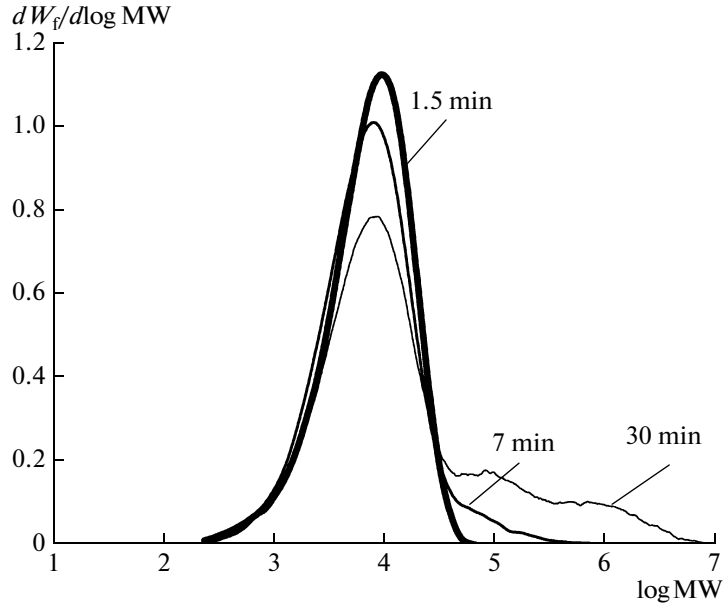

Fig. 2. MWD curves for PE prepared on the ^{t}Bu-L_2ZrCl_2 + MAO catalyst at various polymerization times.

ization time was increased, the main peak position in the distribution curve (near 10^4 g/mol) remained almost unchanged (Fig. 2), and only the peak intensity decreased; that is, the fraction with MW of ~10^4 g/mol in the total product decreased.

The experimental data suggest that active sites of only one type occurred at the initial point in time of polymerization in the ^{t}Bu–L_2ZrCl_2 + MAO catalytic system. These active sites produced low-molecular-weight PE (the main peak in MWD curves occurred near 10^4 g/mol). These centers can undergo gradual deactivation or transformation into new centers that produce higher molecular weight PE (maximums in the region of 10^5–10^6 g/mol in Fig. 2). As a result, a product with a broad MWD is formed. Thus, the ^{t}Bu–L_2ZrCl_2 + MAO single-site catalytic system is converted into a multi-site system in the course of polymerization; in this case, PE fractions formed at cen-

Table 2. Values of C_p and k_p measured in the polymerization of ethylene on the ^{t}Bu–L_2ZrCl_2–MAO homogeneous catalyst

Experiment no.	τ_p, min	r*, (kg PE) (mol Zr)$^{-1}$ min^{-1} bar^{-1}	C_p, mol/(mol Zr)	k_p, l mol^{-1} s^{-1}
1	5	610	0.057	53900
2	20	80	0.022	17650

Note: Polymerization conditions: temperature, 35°C; C_2H_4 pressure, 3 bar; toluene volume, 150 ml; [^{t}Bu-L_2ZrCl_2] = 3.3 μmol/l; MAO/Zr = 1000; amount of added ^{14}CO, 1.3×10^{-5} mol; ^{14}CO/Zr = 22. Figure 1 shows the kinetic curves of the experiments.

* The rate of polymerization at the instant ^{14}CO was introduced.

ters of different types differed in MWs by a factor of >100.

Makio and Fujita [14] noted that the starting bis(phenoxyimine) complexes can have at least five different isomers. According to ^{1}H NMR-spectroscopic data, the main species are *trans*-O and *cis*-O isomers, and the ratio between them is 5 : 1. Signals from two types of intermediates (**I** and **II**) were observed in the ^{1}H NMR spectra of samples obtained by the interaction of ^{t}Bu-L_2ZrCl_2 with MAO at 25–75°C. The authors ascribed complexes **I** to the outer-sphere ion pairs [^{t}Bu-L_2ZrMe(S)]$^+$[Me-MAO]$^-$ (where S is the solvent). They are analogous to those observed in the (bis[*N*-(3-*tert*-butylsalicylidene)-2,3,4,5,6-pentafluoroanilinato]titanium dichloride–MAO system. As the temperature was increased, complexes **I** irreversibly converted into complexes **II** as a result of ligand transfer to aluminum. These complexes **II** are aluminum compounds with a phenoxyimine ligand ($LAlMe_2$), which are inactive in the polymerization reaction [14].

Kravtsov et al. [15] used ^{1}H and ^{13}C NMR spectroscopy to study the activation of the bis(phenoxyimine) complexes of zirconium R-L_2ZrCl_2 (R = ^{t}Bu, Me, and H) under the action of MAO and the perfluoroarylborate activator $AlMe_3$/[CPh_3]$^+$[$B(C_6F_5)_4$]$^-$. They found that, upon the interaction of ^{t}Bu-L_2ZrCl_2 with MAO, the heterobinuclear ion pairs [^{t}Bu-$L_2Zr(\mu$-$Me)_2AlMe_2$]$^+$[Me-MAO]$^-$ of two types in a ratio of 5 : 1 were mainly formed at the initial point in time; this ratio is consistent with the ratio between *trans*-O and *cis*-O isomers in the solutions of the starting ^{t}Bu-L_2ZrCl_2 complex [14]. The intermediates detected by Kravtsov et al. [15] are unstable, and they irreversibly converted into a new complex at room temperature; the signals of this complex coincided with the signals of the $LAlMe_2$ complex [14]. These data suggest that, at the onset of reaction (1.5 min), polymerization mainly occurred at active sites formed from the *cis*-O and *trans*-O isomers of the phenoxyimine complex. These centers partially decayed (probably, as a result of ligand transfer to aluminum [14]); however, new centers were formed in the course of polymerization. These new centers differed from the initial ones in reactivity toward polymer chain growth and transfer reactions. It is believed that the new centers were formed from other possible ^{t}Bu–L_2ZrCl_2 isomers, which occurred in a reaction medium in much lower concentrations and whose activation required a longer time.

Number and Reactivity of Active Sites

To better understand processes that occur in a catalyst in the course of reaction, we determined the number of active sites and the rate constants of chain growth at different polymerization times. For this purpose, we used the inhibition of polymerization by radioactive carbon monoxide. Previously, we used this method in a kinetic study of the bis(imino)pyridine complexes of Fe and Co in order to measure the number and reactivity of the active sites of these catalysts [9–11]. Note that the introduction of ^{14}CO into the reaction atmosphere resulted in the rapid (for approximately 2 min) and complete inhibition of ethylene polymerization on the ^{t}Bu–L_2ZrCl_2 + MAO catalyst; this is a necessary prerequisite for the correct determination of C_p and k_p.

Table 2 summarizes the results of the determination of C_p and k_p at various ethylene polymerization times. Figure 1 shows the kinetic curves. By the instant of inhibition (5 min after the onset of reaction), the rate of polymerization was 610 (kg PE) (mol Zr)$^{-1}$ min^{-1} bar^{-1} (curve *2*). In this case, C_p = 0.057 mol/(mol Zr). Note that the measurement of C_p at the point in time when the catalyst activity reached a maximum (τ_p = 1–2 min) is a technically difficult problem because of a dramatic unsteady-state character of the kinetic curve. However, knowing the maximum activity (in experiment 1 from Table 2, it was 1180 (kg PE) (mol Zr)$^{-1}$ min^{-1} bar^{-1} (see Fig. 1)) and the value of k_p, we can calculate the number of centers C_p^{max} = 0.11 mol/(mol Zr). Thus, at the onset of polymerization, the fraction of active sites was to 11% on a basis of the total initial amount of the zirconium complex. In terms of reactivity at 35°C, these centers ($k_p = 5.4 \times 10^4$ l mol^{-1} s^{-1}) are comparable with the active sites of homogeneous catalysts based on bis(imino)pyridyl complexes of iron ($k_p = (2.5–5.0) \times 10^4$ l mol^{-1} s^{-1} [11]) and much superior to the centers of the bis(imino)pyridyl complex of cobalt ($k_p = 3.5 \times 10^3$ l mol^{-1} s^{-1} [9]). As the polymerization time was increased to 20 min (Table 2, experiment 2), the catalyst activity decreased as a result of a decrease in both C_p and k_p. Taking into account the fact that the ^{t}Bu-

L_2ZrCl_2–MAO single-site catalyst was converted into a multi-site catalyst in the course of polymerization (centers that produce low-molecular-weight PE fractions were partially deactivated to form new centers that produce high-molecular-weight PE), we assume that the value of k_p at the initial stage of polymerization (5 min) characterized the reactivity of active sites in the initial single-site catalyst, whereas the constant k_p measured at a polymerization time of 20 min corresponded to the average reactivity of active sites in the catalytic system that operated for a sufficiently long time. The decrease in k_p at a long polymerization time (Table 2, experiment 2) suggests a much lower reactivity of new centers that produce higher molecular weight PE, as compared with that of the initial centers that produce low-molecular-weight PE.

Thus, it was found that the polymerization of ethylene in the presence of the ^{t}Bu–L_2ZrCl_2 + MAO homogeneous catalytic system has an unsteady-state character: the rate of polymerization dramatically decreases in the course of polymerization. In this system at short ethylene polymerization times (<2 min), active sites of only one type occur; these active sites produce PE with a low molecular weight ($M_w \approx 10^4$ g/mol). The fraction of these centers is 11% on a basis of the initial amount of the zirconium complex, and their reactivity is very high (the rate constant of polymer chain growth at 35°C is 5.4×10^4 l mol^{-1} s^{-1}). In the course of polymerization, the single-site system converts into a multi-site system. In this case, a portion of the initial active sites decays and new centers that produce high-molecular-weight PE ($M_w \approx 10^5$–10^6 g/mol) are formed; this causes a broadening of the MWD of the resulting PE. The reactivity of the new active sites is much lower than that of the initial centers, as evidenced by a decrease in the rate constant of polymer chain growth, as compared with the initial value.

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