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# The kinetic evidence for the formation of multiple active species in a bis(phenoxy-imine) zirconium dichloride/MAO catalyst during ethylene polymerization

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ABSTRACT

The effects of polymerization time and temperature on the molecular weight and molecular weight distribution of polyethylene, produced over homogeneous catalyst bis[*N*-(3-*tert*-butyl salicylidene)anilinato]zirconium(IV) dichloride $^t$Bu-$L_2ZrCl_2$/MAO have been studied. The data on the number of active centers ($C_P$) and propagation rate constants ($k_P$) at different polymerization time have been obtained as well. It was found that at a short polymerization time two types of active centers, producing low molecular weight PE ($M_w = (4–10) \times 10^3$ g mol$^{-1}$) are formed. The number of these centers was estimated to be 11% of total zirconium complex and their reactivity is very high (the $k_P$ value was found to be $54 \times 10^3$ L mol$^{-1}$ s$^{-1}$ at 35 °C). High initial activity of the catalyst fell with the increase in polymerization time, whereas the polydispersity values of the resulting PE increase due to formation of new centers, producing high molecular weight PE ($M_w = (30–1300) \times 10^3$ g mol$^{-1}$). It was found that the decrease in activity is caused by reducing the initial active centers number and lower reactivity of the new-formed centers ($k_P = 17 \times 10^3$ L mol$^{-1}$ s$^{-1}$).

## 1. Introduction

Generally homogeneous catalysts based on the complexes of transition metals (metallocene-, bis(imino)pyridyl-, phenoxy–imine complexes and others) demonstrate high initial activity at olefin polymerization that falls with the increase in polymerization time. For catalytic systems containing only one type of active center (for example catalysts based on metallocenes [1] or cobalt 2,6-bis(imino)pyridyl complexes [2]) the decrease in polymerization activity is caused by lowering of the active centers number. In contrast to the mentioned catalytic systems, homogeneous catalysts based on iron 2,6-bis(imino)pyridyl complexes produce polyethylenes with broad MWD. The kinetic studies of 2,6-bis(imino)pyridyl iron and cobalt catalysts [3,4] have shown that the decay of the reaction rate with the increase in polymerization time can be attributed both to lowering of the active centers number and to the decrease of their average reactivity (propagation rate constant, $k_P$). These data evidence, that a set of active centers with different stability and reactivity is formed in these catalytic systems, being the reason of formation of PE with broadened MWD in prolonged polymerization runs. Thus, in case of the catalysts, characterized by non-stationary type of the kinetic curves, the data on the effect of polymerization time on the molecular weight distribution and polydispersity of the produced PE are needed to determine whether or not the single-center mode of these catalysts is retained throughout the polymerization.

In the past decade there has been much interest in highly active catalytic systems based on bis(phenoxy-imine) complexes of zirconium and titanium (FI catalysts) [5–22]. For the catalysts of this family the polymerization rate as a function of time is strongly unstable. As it was shown in refs. [6,10,11], the molecular structure (MW and MWD) of polymers, prepared with these catalysts, is strongly affected by composition of bis(phenoxy-imine) complex: complexes bearing one substituent in the phenoxy-group of the ligand produce polymers with narrow unimodal MWD, whereas complexes with two substituents allow to get PE with broad bi- and trimodal MWD. Among the catalysts of this family, the systems based on (bis[*N*-(3-*tert*-butylsalicylidene)anilinato]zirconium dichloride, $^t$Bu-$L_2ZrCl_2$) exhibited the highest activity. The catalysts formed upon activation of $^t$Bu-$L_2ZrCl_2$ with MAO produce PE with narrow MWD ($M_w/M_n \cong 2$), indicating their single-site character. It should be noted, that for this catalytic system the kinetic data obtained only in a very short polymerization runs (less than 5 min) are represented in the literature [6,10,11]. Recently we have found

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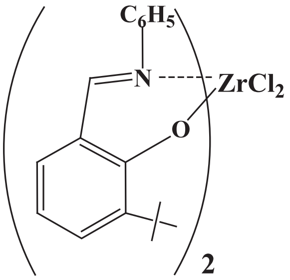


**Scheme 1.** Structure of (bis[*N*-(3-*tert*-butylsalicylidene)anilinato]zirconium dichloride, used in the study.

that the molecular weight and polydispersity of PE, produced over the catalyst $^t$Bu-$L_2ZrCl_2$/MAO, depends on polymerization time. Thus we have studied this effect in more detail.

Herein, the data on the effect of polymerization conditions (time and temperature) on the activity of $^t$Bu-$L_2ZrCl_2$/MAO catalyst and MW and MWD values of the resulted PE are presented and discussed together with the data on the number of active centers and propagation rate constants, determined at different polymerization time.

## 2. Experimental part

### 2.1. Materials

Toluene was dried over molecular sieves (4 Å), purified by refluxing over sodium metal, distilled in dry argon and degassed in vacuum. Methylene chloride was dried over $P_2O_5$ and distilled under vacuum. All solvents and prepared solutions were stored and handled in vacuum. All the experiments were carried out in sealed high vacuum systems using breakseal techniques.

Bis[*N*-(3-*tert*-butylsalicylidene)anilinato]zirconium(IV) dichloride ($^t$Bu-$L_2ZrCl_2$) (Scheme 1) was prepared as described in ref. [6].

Methylaluminoxane (MAO) – commercial sample (Crompton GmbH (Bergkamen)) purchased as a toluene solution (total Al content 1.8 M).

### 2.2. Ethylene polymerization

Ethylene polymerization was performed in a 0.5 L steel reactor, equipped with a mechanical stirrer and a water-jacket for cooling. A sealed glass ampoule with $^t$Bu-$L_2ZrCl_2$ complex solution in $CH_2Cl_2$ (1.1 μmol$_{Zr}$ mL$^{-1}$, 0.5 mL) was placed into the reactor. The reactor was heated at 80 °C in vacuum for 1 h and cooled to 25 °C. Then the reactor was charged with 150 mL of toluene solution of MAO to provide molar ratio MAO/Zr = 1000. The reaction mixture was heated to the desired temperature (25–55 °C), saturated with ethylene (2, 3 or 5 bar) and the ampoule with Zr complex solution was broken to start the reaction. During the reaction the ethylene pressure was maintained constant through automatic computer-controlled system for the ethylene feed. The temperature in the reactor was permanently measured by a thermocell and kept constant through water-jacket cooling. After a prescribed time the reactor was vented, the obtained solid product separated and dried at ambient conditions to the constant weight.

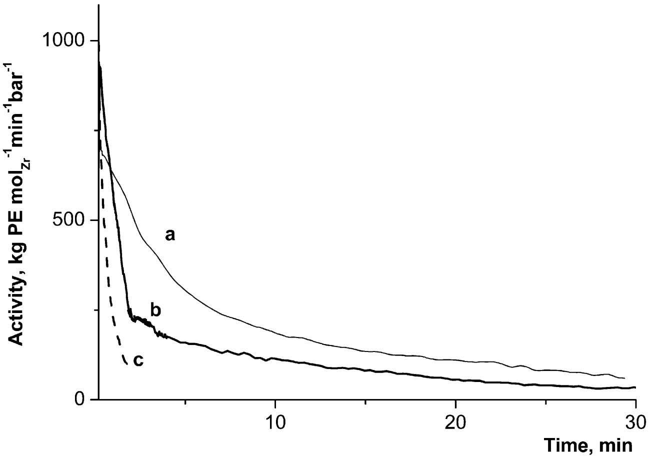


**Fig. 1.** Kinetic curves of ethylene polymerization over $^t$Bu-$L_2ZrCl_2$/MAO catalyst (in experiments from Table 1): (a) exp. 2 (25 °C); (b) exp. 5 (40 °C) (c) exp. 6 (55 °C).

### 2.3. Determination of $C_P$ and $k_P$

To determine the $C_P$ and $k_P$ values the method of polymerization quenching by $^{14}CO$ was applied [23–28]. The experimental conditions of quenching (time of contact ($\tau_{CO}$), $^{14}CO$/M) were used as in refs. [2–4]. To remove labeled by-products [26], the obtained polymers were twice re-precipitated from decane as described in ref. [3].

SL-4000 scintillation counter was used for measuring of the polymers radioactivity. The number of active centers was calculated via the radioactivity of PE and the propagation rate constants – from equation (1):

$$k_P = \frac{R}{C_P \cdot [C_2H_4]} \qquad (1)$$

where $R$ is the rate of polymerization at the moment of $^{14}CO$ introduction, $[C_2H_4]$ is ethylene concentration in toluene, calculated according to ref. [29].

### 2.4. PE molar weight and MWD measurements

GPC measurements were made using a WATERS-150C High Temperature Chromatograph equipped with the 4 mixed bed TSK-gel columns set (GMHXL-HT, Tosoh Corp.). Run conditions used:

**Table 1**
Ethylene polymerization over homogeneous catalyst $^t$Bu-$L_2ZrCl_2$/MAO.

| Exp. No.[a] | T, °C | $\tau_{pol}$, min | Maximum activity,[b] kg(PE)·mol$_{Zr}^{-1}$ min$^{-1}$ bar$^{-1}$ | PE yield, kg(PE)·mol$_{Zr}^{-1}$ | Average activity, kg(PE)·mol$_{Zr}^{-1}$ min$^{-1}$ bar$^{-1}$ | $M_w \times 10^{-3}$, g mol$^{-1}$ | $M_w/M_n$ | $M_z \times 10^{-3}$, g mol$^{-1}$ | $M_z/M_w$ |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 25 | 3 | 1050 | 8930 | 500 | 7.9 | 2.5 | 19 | 2.4 |
| 2 | 25 | 30 | 760 | 20 360 | 230 | 32 | 8.0 | 880 | 28 |
| 3 | 40 | 1.5 | 870 | 5360 | 600 | 9.4 | 2.2 | 15 | 1.6 |
| 4 | 40 | 7 | 1300 | 10 360 | 500 | 14 | 3.3 | 90 | 6.4 |
| 5 | 40 | 30 | 930 | 24 820 | 280 | 140 | 30.4 | 2200 | 15.7 |
| 6 | 55 | 2 | 1000 | 3570 | 600 | 10 | 2.8 | 35 | 3.5 |

[a] Polymerization conditions: catalyst load: 0.56 μmol; 150 mL of toluene; MAO/Zr = 1000; ethylene pressure 5 bar in exps. 1, 3, 6 and 2 bar in exps. 2,4,5.
[b] Calculated from PE yield for 1.5 min of polymerization.

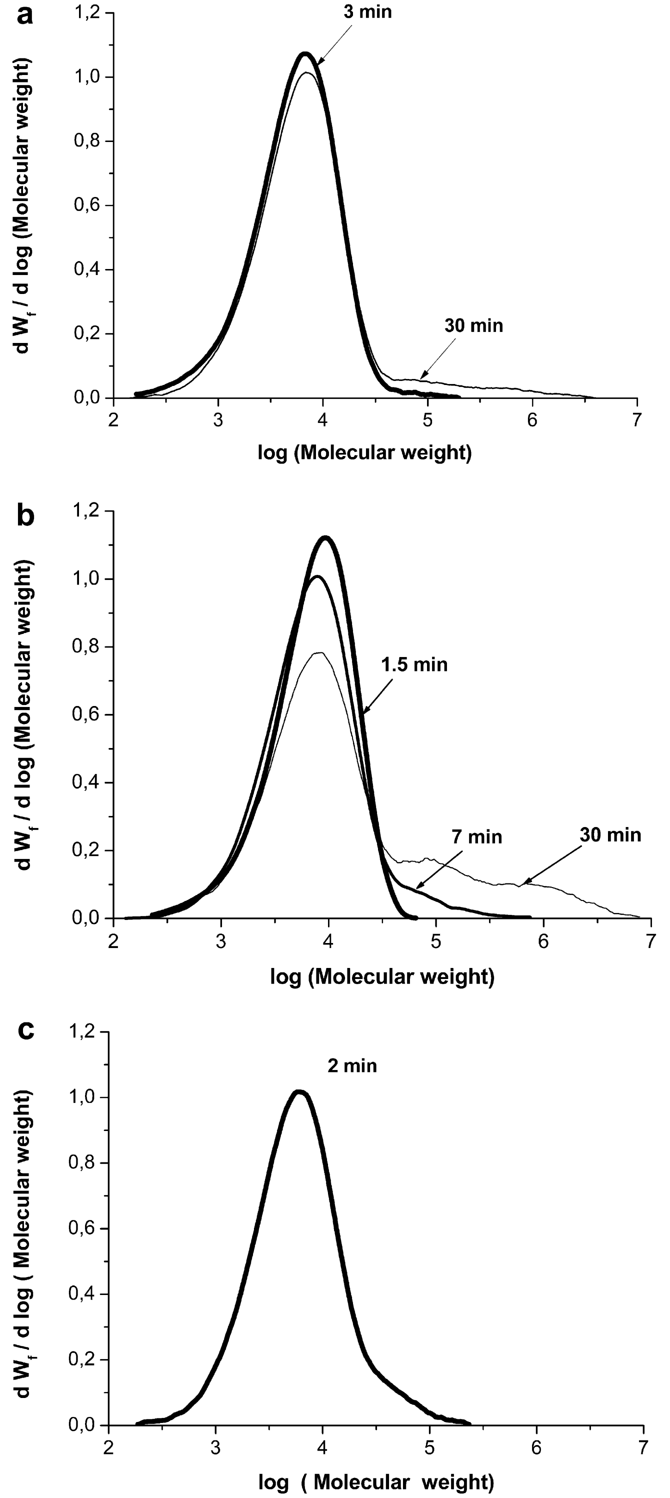


**Fig. 2.** MWD curves of PE produced with $^t$Bu-L$_2$ZrCl$_2$/MAO catalyst in experiments with different polymerization temperature and time (Table 1): (a) 25 °C; (b) 40 °C, (c) 55 °C.

140 °C; flow rate of 1 cm$^3$ min$^{-1}$; 1,2,4-trichlorobenzene (TCB) was used as a solvent. The data were collected and processed with a Viscotek GPC Software version 3.0. Conventional calibration was made using narrow PS and PE standards.

Deconvolution of the experimental MWD curves was performed as described in ref. [30].

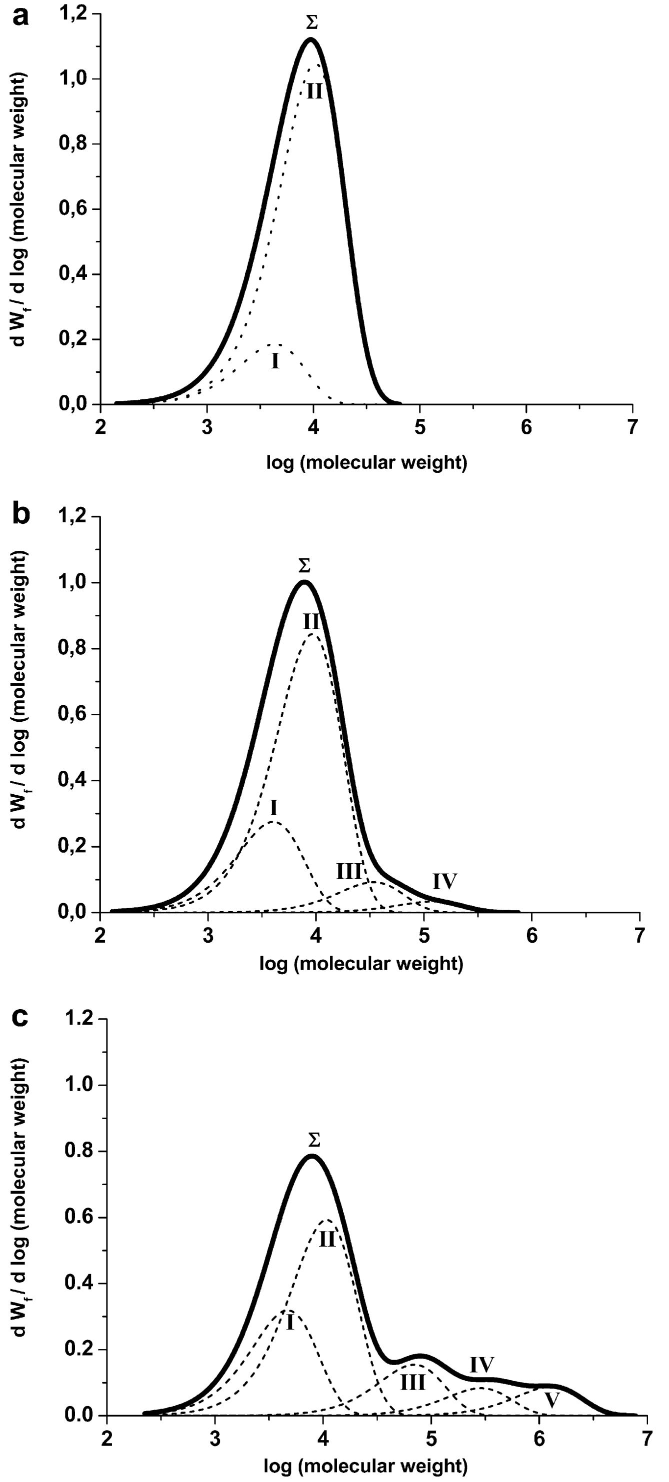


**Fig. 3.** MWD curves deconvolution for PE produced at different polymerization time over $^t$Bu-L$_2$ZrCl$_2$/MAO catalyst (exps. 3–5 from Table 1): (a) 1.5 min; (b) 7 min; (c) 30 min.

## 3. Results and discussion

### *3.1. Effect of time and temperature on the catalyst $^t$Bu-L$_2$ZrCl$_2$/MAO activity at ethylene polymerization and MWD of PE*

The data on the activity of homogeneous catalyst $^t$Bu-L$_2$ZrCl$_2$/MAO at different time and temperatures and the MW and MWD

**Table 2**
Data on the MMD curves deconvolution.

| Exp. No.[a] | $\tau_{pol}$,min | MWD data[b] | Flory component |  |  |  |  |  | **Experimental MWD curve** |
|---|---|---|---|---|---|---|---|---|---|
|  |  |  | I | II | III | IV | V | $\Sigma$ |  |
| 3 | 1.5 | Portion of Flory component, % | 15 | 85 |  |  |  | **100** | **100** |
|  |  | $M_w \times 10^{-3}$, g mol$^{-1}$ | 4.2 | 10 |  |  |  | **9.5** | **9.4** |
|  |  | $M_w/M_n$ | 1.9 | 2.0 |  |  |  | **2.2** | **2.2** |
| 4 | 7 | Portion of Flory component, % | 22.1 | 67.8 | 7.4 | 2.7 |  | **100** | **100** |
|  |  | $M_w \times 10^{-3}$, g mol$^{-1}$ | 4 | 9.3 | 34 | 120 |  | **13** | **14** |
|  |  | $M_w/M_n$ | 1.9 | 1.9 | 2.0 | 2.0 |  | **3.3** | **3.3** |
| 5 | 30 | Portion of Flory component, % | 25.6 | 47.6 | 12.4 | 6.7 | 7.1 | **100** | **100** |
|  |  | $M_w \times 10^{-3}$, g mol$^{-1}$ | 4.6 | 10.8 | 70 | 288 | 1300 | **130** | **140** |
|  |  | $M_w/M_n$ | 1.8 | 1.9 | 2.0 | 2.0 | 2.0 | **25** | **30** |

[a] Experiments from Table 1.
[b] Data from Fig. 3.

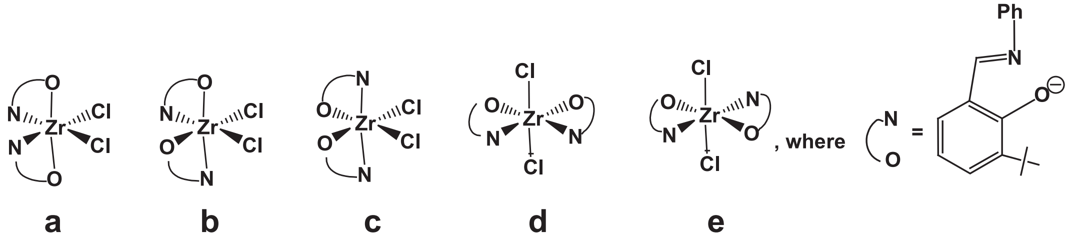
values of the produced polymers are summarized in Table 1. The kinetic curves of ethylene polymerization over $^t$Bu-$L_2ZrCl_2$/MAO at different temperatures are plotted in Fig. 1.

It is seen, that the values of the initial activity are very high. As polymerization proceeds, the catalyst activity rapidly decreases. The most substantial drop of the activity is observed in the beginning of the reaction (for example, for the polymerization run at 40 °C, the value of the initial activity decreases five time within 3 min, Fig. 1, curve b). Further decrease of polymerization rate occurs slower. Such unsteady character of the kinetic curves causes noticeable decrease in the catalyst average activity in the prolonged polymerization runs (30 min) in comparison with that in a short-time experiments (1.5–3 min, Table 1, exps. 1 and 2, 3 and 5). With the increase of polymerization temperature the rate of catalyst deactivation also increases (Fig. 1).

The polymerization time and temperature greatly affect the molecular weight characteristics of the produced polymers. Data on Fig. 2a and b shows the changes in MWD of PE with the increase in polymerization time at different polymerization temperatures (25 and 40 °C). In a short-time polymerizations ($\leq$3 min) polymers with narrow MWD ($M_w/M_n = 2.2–2.8$, Table 1, exps. 1, 3 and 6) and low molecular weight ($M_w = (7.9–10) \times 10^3$ g mol$^{-1}$) are formed, being in a good agreement with the literature [10,11]. With the increase in polymerization time, the $M_w$ value of the resulted PE rises and MWD broadens ($M_w/M_n = 3.3–30$, Table 1, exps. 2, 4 and 5) due to formation of the additional high-molar-weight fractions in $10^5–10^6$ g mol$^{-1}$ region (Fig. 2a and b).

The experimental MWD curves of polymers, obtained at 40 °C (Fig. 2b, Table 1, exps. 3–5) were analyzed by deconvolution into Flory components ($M_w/M_n = 2$, $M_z/M_w = 1.5$), corresponding to polymer, produced with the only one type of active center (Fig. 3). The content and the molecular weight of each component were calculated (Table 2). Note, that the experimental molecular weight characteristics (Table 2, column Experimental MWD curve) are close to the values, calculated from the envelope of the theoretical curves (Table 2, column $\Sigma$), proving the validity of the theoretical MWD deconvolution procedure for analysis of the experimental data. The results of deconvolution of the experimental MWD curves (Table 2) show, that polymers contain two low molecular weight components: I ($M_w = 4 \times 10^3$ g mol$^{-1}$, 15–26% of total PE) and II ($M_w = 1 \times 10^4$ g mol$^{-1}$, 48–85% of total PE). Only these two components are observed at short polymerization time (1.5 min, Table 2, exp. 3). The additional high molecular weight components III–V with $M_w$ values within the range $(3–130) \times 10^4$ g mol$^{-1}$ appear in the resulted polymers with the increase of polymerization time (Fig. 3c, Table 2, exps. 4 and 5). The content of components III–V in total PE grows with polymerization time up to 26%, whereas the ratio of the main components II and I diminishes from 5.6 (1.5 min) to 1.9 (30 min) due to decrease of the proportion of component II. The obtained results indicate, that in the initial moment of polymerization over the catalytic system $^t$Bu-$L_2ZrCl_2$/MAO two types of the active centers, producing low molecular weight PE (fractions I and II), are formed. These centers undergo gradual deactivation or transformation into the other centers, producing high molecular weight PE (fractions III–V). It was noted in refs. [11,31] that bis(phenoxy-imine) complexes have different isomers arising from coordinating mode of the ligand (Scheme 2). According to $^1$H NMR spectroscopy data, the solution of $^t$Bu-$L_2ZrCl_2$ contain mainly two isomers (*trans*-O (a) and *cis*-O (b)) in the ratio *trans*-O/*cis*-O$\approx$5 [31]. The other isomers are presented in the reaction medium in much lower concentrations.

The intermediates formed upon activation of bis(phenoxy-imine) complexes of zirconium R-$L_2ZrCl_2$ (R = $^t$Bu, Me, H) with MAO and $AlMe_3/[CPh_3]^+[B(C_6F_5)_4]^-$ were studied by $^1$H and $^{13}$C NMR spectroscopy [32]. It was shown that immediately after mixing of $^t$Bu-$L_2ZrCl_2$ with activator, two types of the heterobinuclear ion pairs $[^t\text{Bu-}L_2Zr(\mu\text{-}Me)_2AlMe_2]^+[\text{Me-MAO}]^-$ are formed. The ratio of the resonances intensities, ascribed to these complexes, was found to be 5:1, that corresponds to the ratio of *trans*-O/*cis*-O isomers in $^t$Bu-$L_2ZrCl_2$ solutions [31]. The intermediates, observed in ref. [32] are unstable and at room temperature irreversibly turn into the new complexes with resonances, similar to that, observed for $LAlMe_2$ [31]. It should be noted that the ratio of *trans*-O/*cis*-O isomers in the initial $^t$Bu-$L_2ZrCl_2$ complex is close to the ratio of the components I and II in the PE, obtained with $^t$Bu-$L_2ZrCl_2$/MAO catalyst in the short-time polymerization run (Table 2, exp. 3).



**Scheme 2.** Possible coordinating mode of the ligands in $^t$Bu-$L_2ZrCl_2$ [11].

**Table 3**
Effect of time on the MWD, $C_P$ and $k_P$ data in ethylene polymerization over homogeneous catalyst $^t$Bu-$L_2ZrCl_2$/MAO.

| Exp. No.[a] | $\tau_{pol}$, min | $R$,[b] kg (PE)·$mol_{Zr}^{-1}$ $min^{-1}$ $bar^{-1}$ | $C_P$, mol $mol_{Zr}^{-1}$ | $k_P$, L $mol^{-1}$ $s^{-1}$ | $M_n \times 10^{-3}$, g $mol^{-1}$ | $M_w \times 10^{-3}$, g $mol^{-1}$ | $M_w/M_n$ |
|---|---|---|---|---|---|---|---|
| 1 | 5 | 610 | 0.057 | 53 900 | 3.6 | 9.6 | 2.7 |
| 2 | 20 | 80 | 0.022 | 17 650 | 3.9 | 63 | 16.2 |

[a] Polymerization conditions: 35 °C; ethylene pressure 3 bar; 150 mL of toluene; catalyst load: 0.55 $\mu$mol; MAO/Zr = 1000; $1.3 \cdot 10^{-5}$ mol of $^{14}CO$; $^{14}CO$/Zr = 22.
[b] $R$: polymerization rate in the moment of $^{14}CO$ introduction.

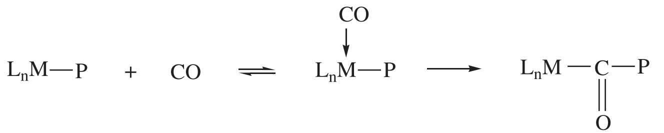
These data allow to conclude, that at a short time of polymerization (<3 min), the active centers, derived both from *cis*-O and *trans*-O isomers of $^t$Bu-$L_2ZrCl_2$ complex participate in the reaction. Probably, the active centers, producing the component I of the polymer, are generated from *cis*-O isomer, whereas the precursors of the active centers, giving component II are derived from *trans*-O isomer of the zirconium bis(phenoxy-imine) complex. The centers I and II are rapidly deactivated, at the same time the new centers, differing from the initial ones by reactivity in the reactions of chain propagation and transfer, appear in the polymerization medium. The nature of these centers is still unclear. Probably, these centers are formed due to chemical rearrangement of the initial ones or originate from the other isomers of $^t$Bu-$L_2ZrCl_2$.

Thus, in course of polymerization the active centers, formed upon interaction of $^t$Bu-$L_2ZrCl_2$ with MAO, undergo transformations and by variation of the polymerization time it is possible to affect the molecular weight and polydispersity of the resulted polymer.

Earlier it was reported [6,10,11] that the molecular weight of PE, obtained with the catalyst $^t$Bu-$L_2ZrCl_2$/MAO at a short polymerization time weakly depends on the reaction temperature. The results presented in Table 1 (exps. 1, 3 and 6) are in agreement with these data. In the case of long-run polymerizations (30 min) the polymer with noticeably higher $M_w$ value was obtained at higher polymerization temperature (40 °C, Table 1, exps. 2 and 5). This result looks to be strange, because it is well known that the increase of polymerization temperature leads to the decrease of molecular weight of polymers. This unusual effect of polymerization temperature on the molecular weight of PE can be explained on the base of the results, presented in Table 2 and Figs. 2 and 3. In case of long-run polymerization $M_w$ values depend greatly on the formation of high molecular weight components III–V. The proportion of these components increases with polymerization temperature (Table 1, Fig. 2a and b), leading to increase in the value of PE $M_w$.

### 3.2. Data on the number of active centers ($C_P$) and propagation rate constants ($k_P$)

For more detailed characterization of the active centers formed at different polymerization time, we have measured the number of active centers ($C_P$) and propagation rate constants ($k_P$) in ethylene polymerization over the catalyst $^t$Bu-$L_2ZrCl_2$/MAO. To determine the $C_P$ and $k_P$ values, method of polymerization inhibition by $^{14}CO$ was used. This method is based on $^{14}CO$ insertion into the metal–polymer bond, causing termination of the polymerization process and formation of labeled polymer [23,24]. Earlier we have applied it for evaluation of $C_P$ and $k_P$ in ethylene and propylene polymerization over Ziegler–Natta catalysts [25–28], homogeneous catalysts based on bis(imino)pyridyl iron [3] and cobalt [2,4] complexes. Method of polymerization quenching can also be used in the studies of metalloorganic complexes of zirconium. It was shown in refs. [33,34] that introduction of CO into the reaction mixture at ethylene polymerization over homogeneous catalysts based on metallocene complexes of Ti and Zr resulted in fast and quantitative CO insertion into the metal–polymer bond (Scheme 3). Depending on the inhibition conditions, the polymer chains with aldehyde or ketone carbonyl group in the polymer chain end are formed [34].



$$L_nM{-}P + CO \rightleftharpoons \overset{CO\downarrow}{L_nM{-}P} \longrightarrow L_nM{-}\underset{\underset{O}{\|}}{C}{-}P$$

$L_n$: ligand, M: Ti or Zr, P: polymer chain.

**Scheme 3.** The insertion of CO into the metal–polymer bond for complexes of Ti and Zr.

It was shown in ref. [35] by DFT calculations that employing some conditions (the excess of $^{14}CO$, small $\tau_{CO}$), the reliable data on the number of active centers formed in homogeneous zirconium metallocene catalysts can be obtained.

Thus, available literature data on the reaction of carbon monoxide with alkyl complexes of zirconium prove feasible application of polymerization inhibition with $^{14}CO$ for determination of the Zr-polymer chain number (number of active centers) in ethylene polymerization over the catalysts based on the alkyl complexes of Zr and, in particular, $^t$Bu-$L_2ZrCl_2$/MAO catalyst.

Fig. 4 represents the kinetic curves obtained in the experiments with polymerization over $^t$Bu-$L_2ZrCl_2$/MAO catalyst quenched by $^{14}CO$. The conditions of inhibition and separation of radioactive by-products [26] were used as earlier [3,4]. It should be mentioned, that introduction of $^{14}CO$ into the reaction mixture causes dramatic decreasing of polymerization rate (about 10-fold in 1 min) and in 5 min the polymerization reaction was fully stopped.

The data obtained in these experiments are presented in Table 3 and Fig. 5. It was found that after polymerization for 5 min about 6% of zirconium was in the active form ($C_P$ = 0.057 mol $mol_{Zr}^{-1}$, Table 2, exp. 1). The reactivity of these centers ($k_P$ = 5.4 × $10^4$ L $mol^{-1}$ $s^{-1}$ at 35 °C, Table 3, exp. 1) is comparable with that of the active centers of homogeneous catalysts based on iron bis(imino)pyridine complexes ($k_P$ = (2.5–5.0) × $10^4$ L $mol^{-1}$ $s^{-1}$ at 35 °C [3]), and noticeably higher than the reactivity bis(imino)pyridine complexes of cobalt ($k_P$ = 3.5 × $10^3$ L $mol^{-1}$ $s^{-1}$ at 35 °C [2,4]). It should be mentioned, that non-stationary kinetic profile hinders

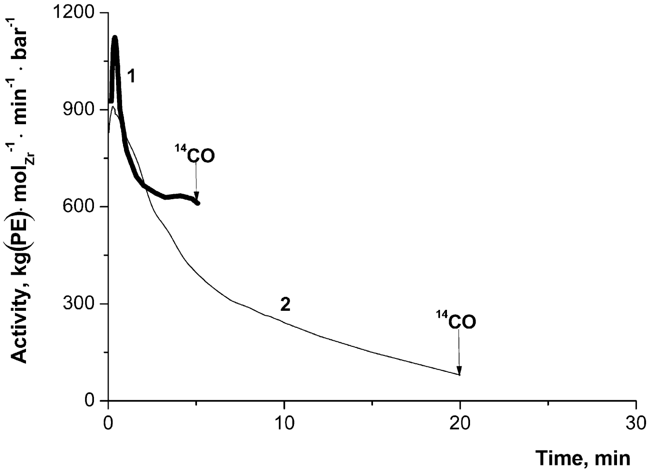


**Fig. 4.** Kinetic curves of ethylene polymerization over $^t$Bu-$L_2ZrCl_2$/MAO catalyst in experiments with quenching polymerization by $^{14}CO$; 35 °C. Curve number corresponds to experiment numbers in Table 3.

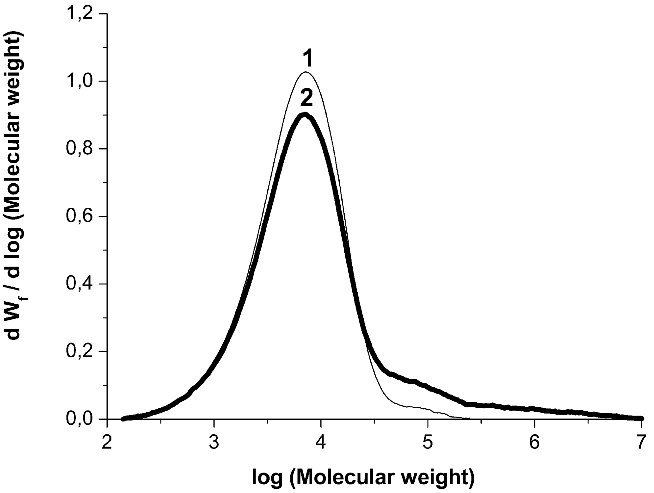


**Fig. 5.** MWD curves of PE produced with $^t$Bu-L$_2$ZrCl$_2$/MAO catalyst in experiments with quenching polymerization by $^{14}$CO; the curve numbers correspond to the experimental numbers in Table 3.

determination of $C_P$ value in the moment of maximal activity. However, using the experimental value of maximal activity (1180 kg(PE)·mol$_{Zr}^{-1}$ min$^{-1}$ bar$^{-1}$) determined from the kinetic profile and the measured $k_P$ value we have calculated the value of $C_P^{max}$, that was found to be 0.11 mol mol$_{Zr}^{-1}$. With the increase in polymerization time to 20 min (Table 2, exp. 2), the catalyst activity rapidly fell due to lowering of both the $C_P$ and $k_P$ values.

The changes in molecular weight and MWD values of the PE samples (Fig. 5 and Table 3) are similar to the results, presented in Table 1: prolongation of polymerization runs results in the increase of the $M_w$ and MWD values due to formation of high-molar-weight PE components. Taking into account the results on the effect of polymerization time on the $M_w$ and MWD values and data on the deconvolution of MWD curves (Tables 1 and 2), it is possible to suppose, that the $k_P$ value determined at a short polymerization time (5 min) characterizes the average reactivity of the active centers of the type I and II, and the $k_P$ value obtained in the long-run polymerization (20 min) can be attributed mainly to the average reactivity of the centers III–V, producing high molecular weight PE.

## 4. Conclusion

Thus, ethylene polymerization over homogeneous catalyst $^t$Bu-L$_2$ZrCl$_2$/MAO at varying reaction time (1.5–30 min) and temperature (25–55 °C) were studied. It has been shown that the reaction time has the pronounced effect on the catalyst activity, molecular weight and polydispersity of the resulted PE. The experimental MWD curves of polymers, obtained at 40 °C and different polymerization time, were analyzed by deconvolution into Flory components. The number and reactivity of the active centers, formed in the system at different reaction time were determined by quenching of polymerization by radioactive carbon monoxide ($^{14}$CO). It was found that activation of $^t$Bu-L$_2$ZrCl$_2$ with MAO gives rise to a set of active centers, producing polymer with molar weights differing more than 100 times. In course of polymerization the ratio between these centers varies. At a short polymerization time (<5 min) the catalytic system contains mainly two types of highly active centers (I and II) (the average $k_P = 5.4 \times 10^4$ L mol$^{-1}$ s$^{-1}$ at 35 °C), producing low molecular weight PE ($M_w = (4–10) \times 10^3$ g mol$^{-1}$). The number of these centers was estimated to be 11% of total zirconium complex content. Comparison of the obtained data and earlier NMR studies on the intermediates, formed upon activation of $^t$Bu-L$_2$ZrCl$_2$ with MAO, makes possible to conclude that these active centers originate from *cis*-O and *trans*-O isomers of the zirconium complex. With the increase in polymerization time the catalyst activity fell due to deactivation of the initial centers I and II. At the same time the new centers (III–V) appear in the reaction medium. The latter are less active (the average $k_P = 1.8 \times 10^4$ L mol$^{-1}$ s$^{-1}$ at 35 °C) and produce high molecular weight PE ($M_w = (3–130) \times 10^4$ g mol$^{-1}$), leading to formation of PE with broadened molecular weight distribution. The increase in polymerization temperature accelerates the processes of the new centers formation and results in the increase of the average molecular weight and polydispersity value of polymers, obtained at the enhanced polymerization temperatures.

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