Kinetics of ethylene polymerization over titanium-magnesium catalysts: The reasons for the observed second order of polymerization rate with respect to ethylene

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ABSTRACT

The data on the effect of ethylene concentration on polymerization rate for several modifications of modern highly active titanium–magnesium catalysts $TiCl_4/MgCl_2$ are presented. These catalysts differ in titanium content and conditions of support preparation, activities, and the shape of kinetic curves. It is found that the observed order of polymerization rate with respect to ethylene in the range of ethylene pressures of 0.5–6 bar is 1.8-2.1 for all catalysts used (polymerization at 80°C, $AlEt_3$ used as a cocatalyst). When $AlEt_3$ was replaced with $Al(i-Bu)_3$, the reaction order decreased to 1.3-1.4. In order to elucidate the possible reasons for the observed high order with respect to ethylene, we analyzed the data on the effect of monomer concentration on the molecular weight of polyethylene. The results gave grounds for suggesting that the observed order with respect to monomer is attributable to the effect of ethylene concentration on the number of active sites. The possible reaction scheme explaining the nonlinear dependence of the polymerization rate on monomer concentration was proposed based on these data. **Polyolefins J (2015) 2: 27-38**

Keywords: polyethylene (PE); polymerization kinetics; Ziegler-Natta polymerization; molecular weight distribution / molar mass distribution.

INTRODUCTION

Ziegler–Natta catalysts are known for over 50 years and are widely used for polyolefin production. Although numerous studies have been devoted to the analysis of the kinetics of polymerization over these catalysts, many problems still remain to be solved. In particular, the problem regarding the dependence of polymerization rate on monomer concentration is rather controversial. For propylene polymerization, the results of a number of studies indicate that the reaction rate depends linearly on monomer concentration [1-7]. Meanwhile, some authors have reported a higher order of the reaction with respect to propylene (in particular, at low monomer pressures) [8-15]. According to refs. [5, 7, 11, 16-23] ethylene polymerization is also characterized by the reaction rate order greater than 1. Different authors have reported different reaction rate orders. Thus, the values of 1.24–1.68 were reported in refs. [7, 20, 23, 24], while the observed reaction rate order with respect to ethylene reported in refs., [17-19]

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was 1.8–2.0.

Several hypotheses have been proposed to explain this phenomenon. Karol [17] proposed the dynamic equilibrium kinetic model suggesting that ethylene acts as a coordinated ligand of an active site. Chien [18] studied the kinetics of ethylene polymerization over metallocene catalysts and has put forward a hypothesis that a complex may be formed between one or two ethylene molecules and the active site. The interpretation of the observed second-order reaction with respect to ethylene based on the "trigger" mechanism proposed by Ystenes [16] has become commonly used. According to the Ystenes' model, an ethylene molecule is coordinated to an active site; however, it can be incorporated into the propagating chain only when a second ethylene molecule is coordinated. Shimizu [25] has proposed that the trigger mechanism assumes that it is a "newly coming" ethylene molecule that is incorporated rather than the one that was previously coordinated by the active site. Kissin studied ethylene polymerization [26-28] and assumed that there is a strong β-agostic interaction between the methyl proton and the titanium atom in the $Cl_2Ti-CH_2-CH_3$ site, which considerably reduces the polymerization rate in the presence of hydrogen. As a result, the observed reaction rate order with respect to ethylene is greater than 1.

Resconi et al. [12, 29-31] proposed that the emergence of the second-order reaction with respect to monomer is attributable to kinetic heterogeneity of active sites, which may be characterized by different constants of chain propagation.

The physical processes of heat and mass transfer have also been discussed as a possible reason for the second-order of polymerization reaction with respect to monomer in the dependence of polymerization rate. [14] Another explanation to the second order of polymerization rate with respect to propylene has been proposed by Busico et al. [32-34]. According to his hypothesis, 2-1-incorporation of a propylene molecule converts the active site to the "dormant" state due to the impeded coordination of the following propylene molecule. This effect may result in a greater order with respect to propylene in the expression for polymerization rate. However, this mechanism does not explain the second order upon ethylene polymerization with respect to monomer.

In order to explain the second-order dependence between the polymerization rate of olefins and monomer concentration or the mixed (between the first and the second) order, a kinetic model was proposed in refs. [7-9, 22, 35]. The reversible stage of active site formation with participation of a monomer molecule was added. In this case a complex dependence, Eqn1, between the polymerization rate and monomer concentration was proposed:

$$R_{pol} = K_p.C_p.(K.C_{et}^2)/(1 + K.C_{et}) \qquad (1)$$

where R_{pol} is the polymerization rate; K_p is the propagation rate constant; C_p is the concentration of active sites; K is the ratio between the rate constants of active site formation with participation of monomer and its reverse conversion to the inactive precursor of the active site; and C_{et} is the monomer (ethylene) concentration.

Equation 1 allows one to explain the regions where both the first and second orders of the reaction with respect to monomer are observed. The second order of the reaction with respect to monomer is observed in the low-pressure region ($K \times C_{et} \ll 1$), while in the high-pressure region ($K \times C_{et} \gg 1$) there is a linear dependence between the polymerization rate and monomer concentration. Hence, an intermediate reaction order (between 1 and 2) with respect to monomer will be observed in a certain pressure range. Thus, plenty of data on nonlinear dependence between the polymerization rate and ethylene concentration have been reported and various interpretations to this phenomenon have been proposed in the literature. However, the experimental evidence about these interpretations is scarce. Individual modifications of different catalysts were usually used in the earlier studies. Thus, the possible effect of the composition, structure, and kinetic parameters of the catalyst on the dependence of the polymerization rate on monomer concentration could not be revealed.

The data on the effect of ethylene concentration on polymerization rate over four modifications of modern highly active titanium–magnesium catalysts (TMCs) differing in preparation method and titanium content were obtained in this study. The catalysts were characterized by different activities and different shapes of kinetic curves; furthermore, they yielded polyethylene with different molecular weights. The order of polymerization rate with respect to ethylene was determined for these catalytic systems. A new approach for revealing the possible reasons for

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the observed order of polymerization reaction was proposed. This approach was based on analyzing the data on the effect of monomer concentration on molecular weight of polyethylene. The results provide evidence that the observed reaction order with respect to ethylene (1.3-2.1) is due to the effect of ethylene concentration on the number of active sites. A possible reaction scheme is proposed to explain the nonlinear dependence between polymerization rate and monomer concentration, as well as the high order of polymerization rate with respect to ethylene.

EXPERIMENTAL

The support S-1 was obtained according to ref.,[36] via the interaction between organomagnesium compound $Mg_3Ph_4Cl_2$ dissolved in diisoamylether and $PhSiCl_3$. The supports S-2 and S-3 were prepared according to ref., [37] via the interaction between organomagnesium compound $Mg_3Ph_4Cl_2$ dissolved in dibutylether and a mixture of $Si(OEt)_4$ and $PhSiCl_3$ at different $Si(OEt)_4$/$PhSiCl_3$ molar ratios. The supports were washed with heptane and used to prepare catalysts with various titanium contents.

The supported catalysts TMC-1 (1 wt% of Ti), TMC-2 (2.6 wt% of Ti), and TMC-3 (2.6 wt % of Ti) were prepared through the reaction of $TiCl_4$ (the Ti/Mg molar ratio being 1) at 60°C with the supports S-1, S-2 and S-3, respectively (see Table 1). The catalysts were washed thrice with heptane to remove the excess of $TiCl_4$.

The preparation of TMC-4 catalyst with low titanium content (0.12 wt % of Ti) included preliminary treatment of the support S-2 with a solution of diethyl aluminum chloride in heptane (the Al/Mg

molar ratio being 1.5) at 40°C followed by washing with heptane and treatment with CCl_4 to convert the adsorbed $AlEt_2Cl$ to $AlCl_3$ (supports S-4). The catalyst was prepared by deposition of the calculated amount of titanium tetrachloride on magnesium-containing support S-4 modified by $AlCl_3$ (TMC-4).

All the obtained catalysts have a spherical shape with the average particle size of 4-6μm and a narrow particle size distribution.

The titanium contents in catalysts were determined by AES-ICP using an Optima 4300 DV spectrometer.

Ethylene slurry polymerization runs were performed in a 0.85 L steel reactor under stirring in heptane with catalyst concentration 0.02-0.08 g/L. A sealed glass ampoule with suspension of a catalyst in heptane was placed in the reactor. The reactor was heated at 80°C under vacuum for 1.5 h and cooled to 20°C. After that, the reactor was filled with 250 mL of heptane and a solution of AlR_3 (R = Et, i-Bu) ([AlR_3] = 1.3-4.8 mmol/L). The reaction mixture was heated to 80°C and saturated with ethylene (0.5-10 bar). The reaction was started by breaking the ampoule with the catalyst. During polymerization, ethylene pressure was maintained constant through an automatic computer-controlled system for the ethylene feed; ethylene consumption to the reaction medium was measured a few seconds apart. The temperature in the reactor was permanently measured with a thermo cell and kept constant through water-jacket cooling. All relevant data (temperatures, mass flows, pressure, and power of the internal heating element) were measured, monitored, and controlled in real-time through a computer system. The rate of polymerization was monitored online by accurately measuring the monomer mass flow. Ethylene concentrations were calculated from their partial pressures using the Henry law (0.071 mol/(L bar) for 80°C) [38].

MWD measurements were performed using a PL 220C gel permeation chromatograph with refractive index and viscosity detectors. Run conditions were as follows: temperature was 160°C; 1,2,4-trichlorobenzene was used as a solvent at a flow rate of 1 cm³/min. A set of Olexis-gel columns was employed. Calibration was performed using narrow Polystyrene standards and PE standards.

Viscosity (η) of the polymers was measured in decalin at 135ºC on an Ubbelodhe viscometer. The viscosity-average molecular weight M_v was calculated according to the Mark-Houwink equation: $M_v = (η/K)1/α$, where

Table 1. Data on titanium content and activities of titanium–magnesium catalysts used in this study as well as the molecular weight of polyethylene obtained[(a)]

Catalyst	Ti content (wt%)	V_1[(b)] [kg PE/(g_{cat}.h.bar)]	V_2[(b)] [g PE/(g_{Ti}.h.bar)]	MW×10⁻³
TMC-1	1.0	3.2	320	M_v[(c)] = 1600
TMC-2	2.6	1.4	50	M_w[(d)] = 590
TMC-3	2.7	5.8[(e)]	220[(e)]	M_w[(d)] = 590
TMC-4	0.12	1.6	1300	M_v[(c)] = 1200

[(a)] Polymerization conditions: 80°C, Ethylene pressure 4 bar, [TEA] = 1.3-2.6 mmol/L; [(b)] Maximum polymerization rate; [(c)] M_v – viscosity average molecular weight; [(d)] M_w – weight average molecular weight; [(e)] Ethylene pressure 2 bar.

the Mark-Houwink coefficients were as follows: K = 67.7x10^{-5}; α = 0.67 according to ref.,[39].

RESULTS AND DISCUSSION

Effect of ethylene concentration on polymerization rate for catalysts of different compositions

Table 1 lists the data on titanium content and activities of the four modifications of titanium–magnesium catalysts used in this study. These catalysts differ in titanium content and the way $MgCl_2$ supports had been prepared. We have selected these catalysts for kinetic study because of the following reasons:

1) These catalysts have the small particle size (4-6μm) and narrow particle size distribution. According to the literature data[40-42], it is important to exclude the effect of intro particle ethylene diffusion in the growing polymer particle on the polymerization rate.

2) TMC-4 catalyst with low titanium content has the lowest polymerization rate calculated per gram of catalyst (Table 1). That proceeds to low probability of intro particle ethylene diffusion on the polymerization rate.

3) Kinetic study in the case of catalysts with different shapes, if kinetic curves allows to elucidate the possible effects of fragmentation of catalysts, formation of active sites and deactivation of active sites on the observed order of polymerization rate with respect to ethylene.

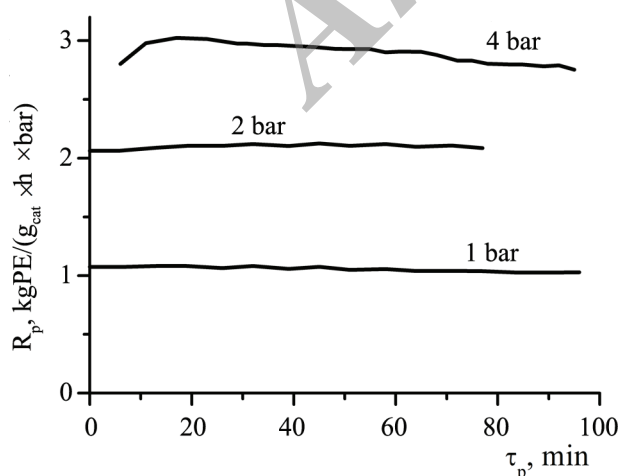Table 1 also lists the molecular weights of polyethylene

samples produced over these catalysts. Due to different preparation conditions and compositions, the catalysts exhibit different activities both per gram of catalyst (from 1.4 to 5.8 kg PE/(g$_{cat}$.h.bar)) and per gram of titanium (from 50 to 1300 kg PE/(g$_{Ti}$.h.bar). Furthermore, they produce polyethylene with different molecular weights (from 6×10^5 to 1.6×10^6).The shapes of the kinetic curves in ethylene polymerization over these catalysts also differ. The kinetic curves of ethylene polymerization over these catalysts at different ethylene pressures are shown in Figures 1–4 (the polymerization rate was related to pressure of 1 bar). Figure 1 shows that the kinetic curves observed for TMC-1 catalyst at different pressure were almost steady-state. In the case of polymerization over TMC-2 catalyst, an acceleration stage was observed on the kinetic curves (Figure 2); the time required achieving
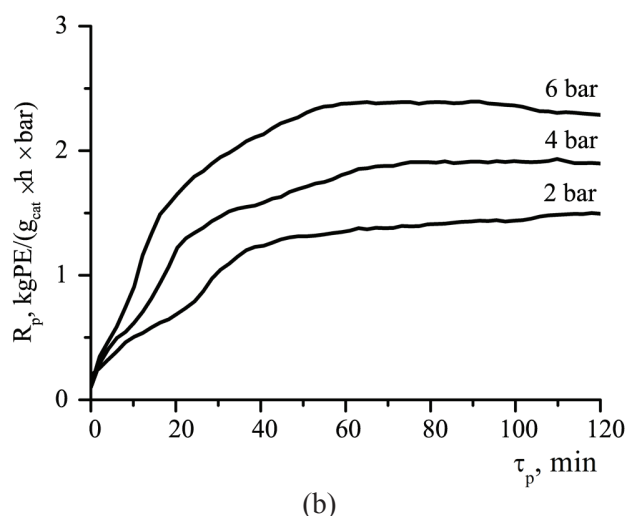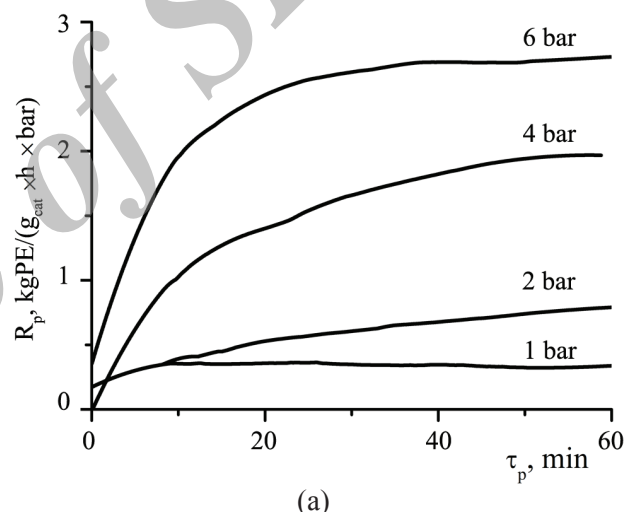

(a)

(b)

Figure 2. Kinetic curves of ethylene polymerization over TMC -2 at different ethylene pressures: A: with TEA (2.6 mmol/L) as cocatalyst; B: with TIBA (4.8 mmol/L) as cocatalyst
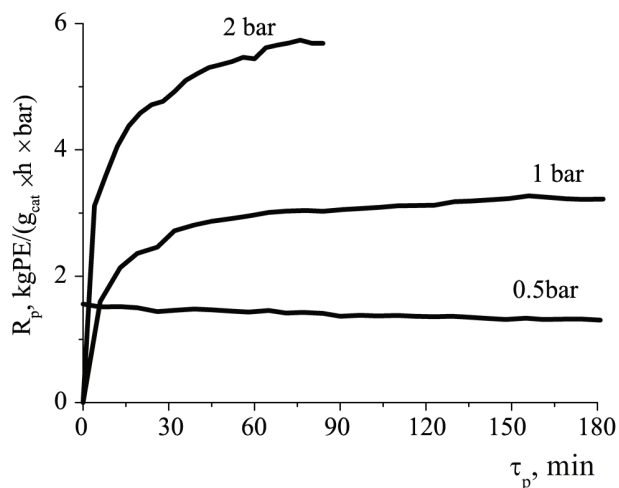

Figure 1. Kinetic curves of ethylene polymerization over TMC -1 at different ethylene pressures. Polymerization conditions: 80°C, [TEA] = 1.3 mmol/L

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Figure 3. Kinetic curves of ethylene polymerization over TMC-3 at different ethylene pressures. Polymerization conditions: 80°C, [TEA] = 1.3 mmol/L

the maximum polymerization rate decreased with increasing pressure. The most active catalyst TMC-3 (if calculated per gram of catalyst), was characterized by an almost steady-state kinetic curve at ethylene pressure of 0.5 bar (Figure 3).

When polymerization was carried out at ethylene pressures of 1 and 2 bar, the acceleration stage (60-90 min) has been observed (Figure 3). The most active catalyst (if calculated per gram of titanium), TMC-4, was characterized by virtually steady-state kinetic curves at ethylene pressures of 1 and 2 bar (Figure 4). Meanwhile, when polymerization was conducted at ethylene pressure of 4 bar, the polymerization rate reached its maximum within 25 min and subsequently decreased with time (Figure 4). Thus, the catalysts
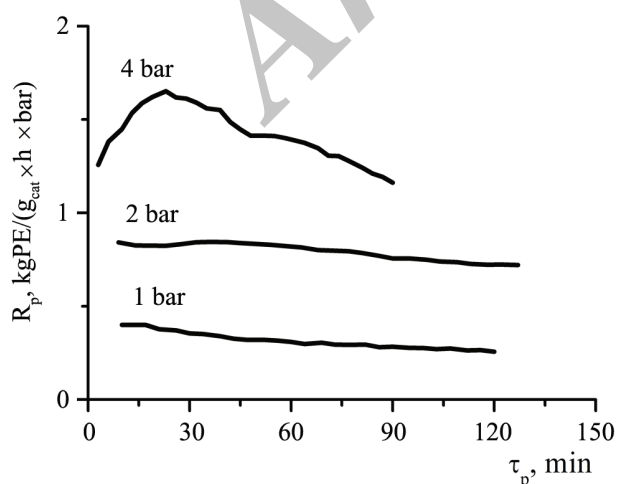

Figure 4. Kinetic curves of ethylene polymerization over TMC -4 at different ethylene pressures. Polymerization conditions: 80°C, [TEA] = 1.3 mmol/L
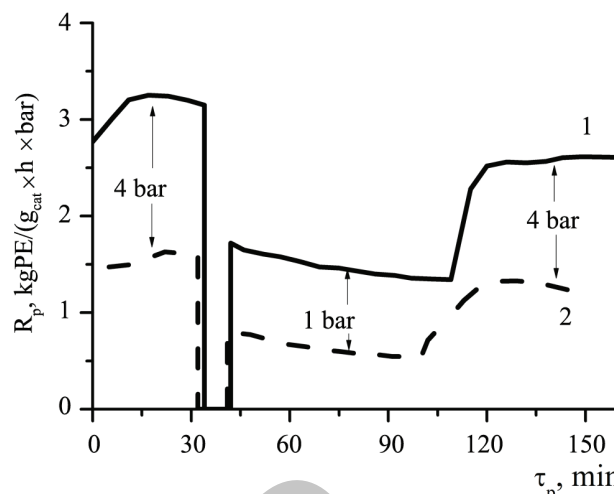

Figure 5. Kinetic curves of ethylene polymerization over TMC-1 (1) and TMC-4 (2) at varied ethylene pressure during the same run. Polymerization conditions: 80°C, [TEA] = 1.3 mmol/L

selected for the kinetic study differ both in their activities and shapes of kinetic curves.

Despite the evident differences in the shape of kinetic curves shown in Figures 1–4, it is clear that the maximum polymerization rate related to ethylene pressure of 1 bar increases abruptly with increasing ethylene pressure for all catalysts.

Figure 5 shows the data of polymerization over TMC-1 and TMC-4 catalysts at varied ethylene pressure in the same run. It is clear that with ethylene pressure reduced from 4 to 1 bar, the polymerization rate related to ethylene pressure of 1 bar decreased; the reverse transition of pressure from 1 bar to 4 bar increased the polymerization rate again. So, pressure variation in a single experimental run results in reversible changes in polymerization rate.

In order to determine the observed reaction order with respect to ethylene, the dependence of polymerization rate on monomer concentration can be written as:

$$R_{pol} = K_p . C_p . C_{et}^n \qquad (2)$$

where R_{pol} is the polymerization rate; K_p is the propagation rate constant; C_p is the concentration of active sites; C_{et} is the monomer (ethylene) concentration; and n is the reaction order with respect to monomer.

Figure 6 shows the data obtained by determining the observed reaction order with respect to ethylene (n) upon ethylene polymerization over catalysts TMC-1, TMC-2, TMC-3, and TMC-4 using the logarithmic form of Eqn 2. The maximum polymerization rates in
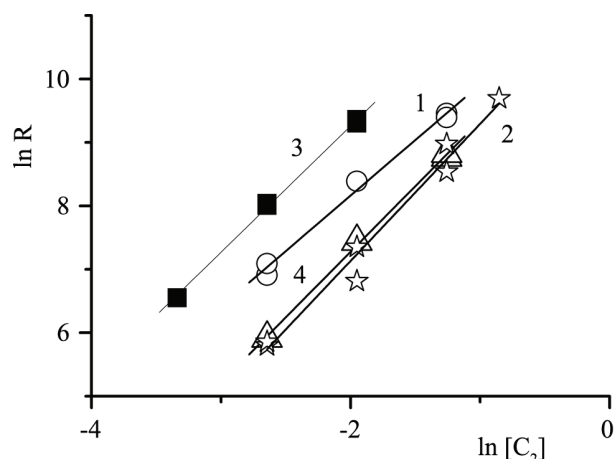
Figure 6. Logarithmic dependence of maximum polymerization rate versus ethylene concentration for catalysts of different composition: (1) – TMC-1, (2) – TMC-2, (3) – TMC-3, (4) – TMC-4. Data on the reaction order with respect to ethylene (n) are presented in Table 2

all the experimental runs were used for calculations. The resulting reaction orders for catalysts of different compositions are summarized in Table 2. The results show that the observed reaction order with respect to monomer in the pressure range of 0.5–6 bar for catalysts TMC-1, TMC-2, TMC-3, and TMC-4 was close to 2 (1.8–2.1).

Figure 7 and Table 3 show the data on the order of polymerization rate with respect to ethylene at polymerization over TMC-1 and TMC-2 catalysts with different cocatalysts. The observed reaction order with respect to monomer was lower (1.3–1.4) for both catalysts, TMC-1 and TMC-2, when TIBA was used as a cocatalyst. These values considerably differ from the data obtained over these catalysts in the experiments with TEA (n = 1.8–2.1, Table 3). Thus, the order of the polymerization reaction with respect to ethylene upon ethylene polymerization in the pressure range of 0.5–6 bar over catalysts of different compositions characterized by different activities and shapes of kinetic curves with TEA used as a cocatalyst was found to be close to 2 (n = 1.8–2.1). When TIBA

Table 2. The observed reaction order with respect to ethylene (n) upon ethylene polymerization[a] on TMC of different composition (calculated according to data on Figure 6)

Catalyst	Ethylene pressure interval (bar)	n
TMC -1	1-4	1.8
TMC -2	1-6	2.1
TMC -3	0.5-2	2
TMC -4	1-4	2.1

[a] Polymerization conditions: 80°C, [TEA] = 1.3 mmol/L, heptane (for TMC-2 [TEA] = 2.6 mmol/L)

Table 3. The observed reaction order with respect to ethylene (n) upon ethylene polymerization on TMC-1 and TMC -2 with different cocatalysts (calculated according to data on Figure 7)

Exp. No.	Catalyst	AlR$_3$	[AlR$_3$] (mmol/L)	n
1	TMC -1	TEA	1.3	1.8
2		TIBA	2.4	1.3
3	TMC -2	TEA	2.6	2.1
4		TIBA	4.8	1.4

was used as a cocatalyst, the n value decreased to 1.3–1.4. The order of the polymerization reaction with respect to ethylene in Eqn 2 higher than 1 may result either from the fact that the propagation reaction has a reaction order with respect to ethylene greater than 1 or be attributable to the effect of ethylene pressure
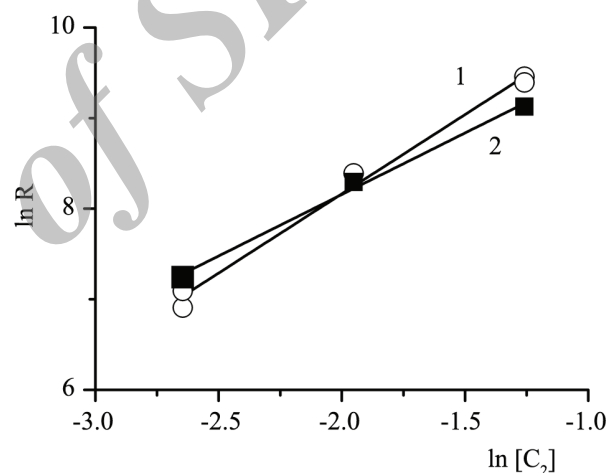
(a)
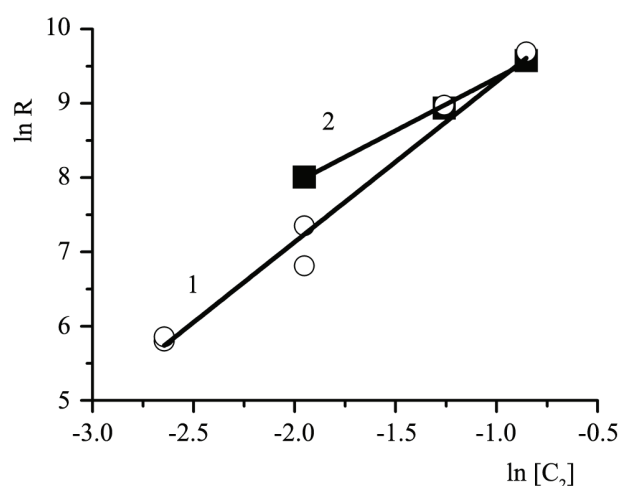
(b)

Figure 7. Data on the reaction order with respect to ethylene (n) determination for TMC -1 (Figure A), and TMC -2 (Figure B) with different cocatalysts: TEA (1) and TIBA (2). Calculated results are presented in Table 3

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on the number of active sites. In order to elucidate the possible reasons for the observed order of the reaction with respect to ethylene, we studied the effect of ethylene pressure on the molecular weight of PE.

Effect of ethylene concentration on the molecular weight of polymers.

The degree of polymerization is known to be determined by the ratio between the rates of chain propagation and transfer reactions. We have previously demonstrated [43] that chain transfer with triethylaluminum is the predominant transfer reaction upon ethylene polymerization over TMC-3 catalyst in the absence of hydrogen (especially at low monomer pressures). The equation for the degree of polymerization can be written for these conditions in a simplified form:

$$P_n = \frac{V_p}{V_{tr}^{Al}} = \frac{K_p . C_p . C_{et}^m}{V_{tr}^{Al} . C_p . C_{Al}} = \frac{K_p}{K_{tr}^{Al} . C_{Al}} . C_{et}^m \quad (3)$$

where V is the propagation rate; R_{tr}^{Al} is the rate of chain transfer with organoaluminum cocatalyst; K_p is the propagation rate constant; C_p is the concentration of active sites; C_{et} is the monomer (ethylene) concentration; m is the order of chain propagation reaction with respect to monomer; K_{tr}^{Al} is the rate constant of chain transfer with an organoaluminum catalyst; and C_{Al} is the cocatalyst concentration.

In accordance with Eqn3, if the chain propagation rate is the first-order reaction with respect to ethylene (m = 1), the degree of polymerization is expected to increase linearly with ethylene pressure. In order to study the dependence of the molecular weight of polyethylene on ethylene pressure upon polymerization without hydrogen, we used TMC-2, TMC-3, and TMC-4 catalysts producing a lower molecular weight polymer (being more convenient to measure the molecular weight by high-temperature gel permeation chromatography).

Table 4 lists the data on the molecular weights of polyethylene produced over these catalysts at different ethylene pressures. Figure 8 (lines 1, 2, and 3) shows the data on the effect of ethylene concentration on the polymerization degree plotted using the results from Table 4. It is clear from Figure 8 (lines 1, 2, and 3) that Eqn3 provides a good fit to the linear dependences of the degree of polymerization on monomer concentration at m close to 1. It follows from these results that the propagation reaction is first-order with respect to monomer.

Chain transfer with hydrogen is the predominant reaction upon ethylene polymerization in the presence of hydrogen [43]. Earlier we have found that the order of chain transfer reaction with respect to hydrogen is close to 1 [43, 44]. In this case, the equation for degree polymerization can be written in another simplified form as follows :

$$P_n = \frac{V_p}{V_{tr}^H} = \frac{K_p . C_p . C_{et}^m}{V_{tr}^H . C_p . C_H} = \frac{K_p}{K_{tr}^H} . \frac{C_{et}^m}{C_H} \quad (4)$$

where V_p is the propagation rate; V_{tr}^H is the rate of

Table 4. The molecular weight distribution of polyethylene produced over catalysts of different composition at different ethylene pressures upon polymerization without hydrogen (TEA as cocatalyst)

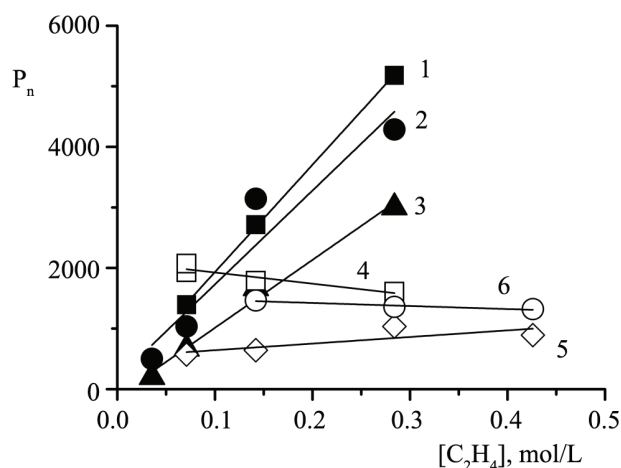| Exp. No.	Catalyst	[TEA] (mmol/L)	P C₂H₄ (bar)	$M_n \times 10^{-3}$	$M_w \times 10^{-3}$	M_w / M_n
1	TMC -2	2.6	1	39	430	11.0
2			2	76	690	9.1
3			4	145	690	4.8
4	TMC -3	2.6	0.5	14	390	28
5			1	29	490	17
6			2	88	530	6
7			4	120	590	4.9
8	TMC -4	4.5	0.5	4.8	180	38
9			1	16	330	21
10			2	40	400	10
11			4	72	470	6.5

Figure 8. Data on the polymerization degree dependence as functions of ethylene concentration at polymerization with and without hydrogen (Polymerization conditions are presented in Tables 4 and 5). Polymerization without hydrogen, TEA as cocatalyst: (1) ■ – TMC-2, (2) ● – TMC -3, (3) ▲ – TMC -4. Polymerization with hydrogen: (4) □– TMC -1; TEA as cocatalyst, (5) ○– TMC -2; TEA as cocatalyst, (6) ◇- TMC -2; TIBA as cocatalyst

chain transfer with hydrogen; K_p is the propagation rate constant; C_p is the concentration of active sites; C_{et} is the monomer (ethylene) concentration; m is the order of chain propagation with respect to monomer; K_{tr}^H is the rate constant of chain transfer with hydrogen; and C_H is the hydrogen concentration.

It follows from Eqn4 that at m values close to 1 the degree of polymerization is supposed to be independent of monomer concentration under polymerization conditions with the C_{et}/C_H ratio being constant. Table 5 lists the data on the molecular weights of polyethylene produced over TMC-1 and TMC-2 catalysts at different ethylene pressures and at a constant ratio between ethylene and hydrogen

concentrations (C_{et}/C_H = const). The dependences of the degree of polymerization on ethylene concentration plotted using these data are shown in Figure 8 (lines 4, 5, and 6). It is clear from the data in Figure 8 that an increase in ethylene concentration insignificantly changes the degree of polymerization. Hence, the chain propagation reaction is first-order with respect to ethylene (m = 1).

Thus, the data obtained by analyzing the dependences between the degree of polymerization and ethylene concentration upon polymerization either with or without hydrogen using various catalysts show that the chain propagation reaction is first-order with respect to ethylene. In this case, the observed greater order of the polymerization rate with respect to ethylene is supposed to be due to the fact that the number of active sites depends on ethylene concentration.

When analyzing the possible reasons for the effect of ethylene concentration on the number of active sites, one should take into account the following experimental data obtained in this study:

1. the reversible effect of ethylene concentration on polymerization rate when ethylene concentration is varied during polymerization (Figure 5);
2. organoaluminum cocatalyst affects the observed order of polymerization rate with respect to ethylene; in particular, the replacement of triethylaluminum with triisobutylaluminum reduces the n value from 1.8–2.1 to 1.3–1.4 (Table 3).
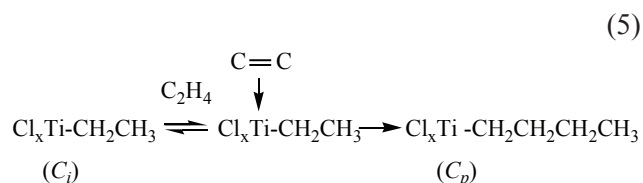
With allowance for these results, we suggest that ethylene polymerization involves the following reactions.

The interaction between the supported titanium–magnesium catalyst (TiCl₄/MgCl₂) and a cocatalyst

Table 5. The molecular weight distribution of polyethylene produced over catalysts of different composition upon polymerization with hydrogen

Exp. No.	Catalyst	Cocatalyst (mmol/L)	P C₂H₄ (bar)	P H₂ (bar)	$M_n \times 10^{-3}$	$M_w \times 10^{-3}$	M_w/M_n
1			1	0.25	58	270	4.7
2	TMC-1	[TEA] = 1.3	2	0.5	50	280	5.6
3			4	1	45	240	5.3
4			1	0.25	16	160	10
5	TMC-2	[TEA] = 2.6	2	0.5	18	130	7.2
6			4	1	29	140	4.8
7			6	1.5	25	140	5.6
8			2	0.5	41	190	4.6
9	TMC-2	[TIBA] = 4.8	4	1	38	190	5.0
10			6	1.5	37	190	5.1

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(AlEt$_3$) yields active site precursors, namely surface compounds with composition Cl$_x$Ti-CH$_2$CH$_3$ (Ci). These compounds can be converted to active sites (C$_p$) via reaction with ethylene (Eqn 5):

(5)

$$Cl_xTi\text{-}CH_2CH_3 \underset{C_2H_4}{\overset{C=C}{\rightleftharpoons}} Cl_xTi\text{-}CH_2CH_3 \longrightarrow Cl_xTi\text{-}CH_2CH_2CH_2CH_3$$
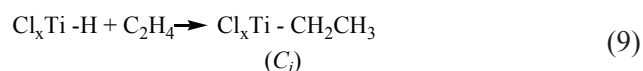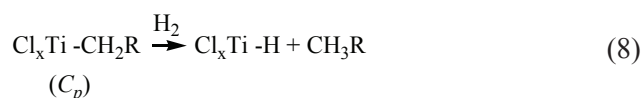$$(C_i) \qquad\qquad (C_p)$$

However, because polymerization is carried out with excess of cocatalyst (AlR$_3$/Ti = 100 – 1000), C$_i$ sites may become inactive (C$_d^{Al}$) as the organoaluminum compound (AOC) is adsorbed on them (Eqn 6):

$$Cl_xTi\text{-}CH_2CH_3 \overset{AlR_3}{\underset{AlR_3}{\rightleftharpoons}} Cl_xTi\text{-}CH_2CH_3$$
$$(C_i) \qquad\qquad (C_d^{Al})$$

(6)
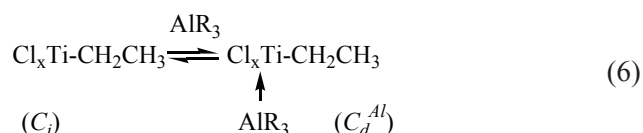
The inactive site (C$_d^{Al}$) may become active via interaction with ethylene (Eqn 7):

(7)

$$C_d^{Al} \underset{AR_3}{\overset{C_2H_4}{\rightleftharpoons}} Cl_xTi\text{-}CH_2CH_3 \longrightarrow Cl_xTi\text{-}CH_2CH_2CH_2CH_3$$
$$(C_p)$$
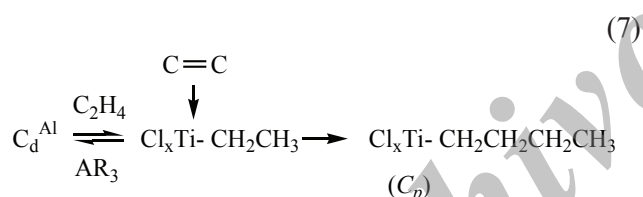
The equilibrium of the reaction of Eqn7 depends on ethylene concentration; the fraction of active sites (C$_p$) increases with increasing of ethylene concentration. Active site precursors (C$_i$) are continuously formed during polymerization via the reactions of chain transfer with AlEt$_3$ or ethylene. If polymerization is carried out with hydrogen, C$_i$ structures are formed via a series of reactions shown in Eqns 8 and 9:

$$Cl_xTi\text{-}CH_2R \overset{H_2}{\longrightarrow} Cl_xTi\text{-}H + CH_3R$$
$$(C_p)$$

(8)

$$Cl_xTi\text{-}H + C_2H_4 \longrightarrow Cl_xTi\text{-}CH_2CH_3$$
$$(C_i)$$

(9)

The increase in ethylene concentration during polymerization reduces the number of inactive structures (C$_d^{Al}$) as they are converted to active sites

(C$_p$) (Eqn 7). The replacement of the AlEt$_3$ cocatalyst with a bulkier cocatalyst, Al(i-Bu)$_3$ (which exhibits weaker binding to titanium ion and can be substituted by ethylene more easily), reduces the contribution of inactive forms (C$_d^{Al}$). Thus, the proposed scheme attributes the changes in C$_p$ values for the studied catalysts occurring at varied ethylene pressure to adsorption of the AOC on active site precursors (C$_i$). An increase in monomer concentration displaces the equilibrium of these processes towards desorption of AOC, thus increasing the number of active sites and increasing the order of polymerization rate with respect to ethylene to values greater than 1.

CONCLUSION

The data on the effect of ethylene concentration on polymerization rate for several modifications of modern highly active titanium–magnesium catalysts TiCl$_4$/MgCl$_2$ are presented. These catalysts differ in titanium content and conditions of support preparation, activities, and the shape of kinetic curves. It was shown non-linear dependence of polymerization rate with variation of ethylene pressure. The reversible effect of ethylene concentration on polymerization rate was demonstrated when ethylene concentration was varied during polymerization. It is found that the observed order of polymerization rate with respect to ethylene in the range of ethylene pressures of 0.5–6 bar is 1.8-2.1 for all catalysts used (polymerization at 80 C, AlEt$_3$ used as a cocatalyst). When AlEt^3 was replaced with Al(i-Bu)$_3$, the reaction order decreased to 1.3-1.4.

In order to elucidate the possible reasons for the observed high order with respect to ethylene, we analyzed the data on the effect of monomer concentration on molecular weight of polyethylene. The data obtained by analyzing the dependences between the degree of polymerization and ethylene concentration upon polymerization either with or without hydrogen using various catalysts show that the chain propagation reaction is first-order with respect to ethylene. The results gave grounds for suggesting that the observed order with respect to monomer is attributable to the effect of ethylene concentration on the number of active sites. The possible reaction scheme explaining the nonlinear dependence of the polymerization rate on monomer concentration was

proposed based on these data.

REFERENCES

1. Natta G, Pasquon I (1959) The kinetics of stereospecific polymerization of olefins. Adv Catal 11:1-68

2. Natta G (1967) Stereoregular polymers and stereospecific polymerizations, ed. Danusso F, Pergamon Press, Oxford

3. Boor J (1979) Ziegler-Natta catalysts and polymerizations, Academic Press, New York

4. Dumas C, Hsu CC (1989) Propylene polymerization in a semibatch slurry reactor over supported $TiCl_4/MgCl_2$/ethyl benzoate/triethyl aluminum catalyst. 2. A kinetic-study based on a multisite model. J Appl Polym Sci 37: 1625-1644

5. Pasquet V, Spitz R (1993) Irreversible activation effects in ethylene polymerization. Die Makromol Chem 194: 451-461

6. Krentsel BA, Kissin YV, Kleiner VI, Stotskaya SS (1997) Polymers and copolymers of higher α-olefins, Hanser Publishers, New York

7. Hanadebekun GC, Ray WH (1997) Polymerization of olefins through heterogeneous catalysis .17. Experimental study and model interpretation of some aspects of olefin polymerization over a $TiCl_4/MgCl_2$ catalyst. J Appl Polym Sci 65: 1037-1052

8. Natta G, Pasquon I, Svab J, Zambelli A (1962) Cinetica della polimerizzazione del propilene con catalizzatori eterogenei ad elevata stereospecificità. Nota VII: Studio degli stadi di iniziazione delle catene polimeriche. Chim Ind 44: 621

9. Firsov AP, Tsvetkova VI, Chirkov NM (1964) Determination of initiation, propagation and termination reaction rate constants in stationary catalytic propylene polymerization. Izv Akad Nauk, Ser Khim 11: 1956-1964

10. Pino P, Rotzinger B, Vonachenbach E (1985) The Role of some bases in the stereospecific polymerization of propylene with titanium catalysts supported on magnesium-chloride. Makromol Chem: Macromol Chem Phys 13: 105-122

11. Ewen JA, Elder MJ, Jones RL, Curtis S, Cheng HN (1990) Studies in surface science and catalysis. In catalytic olefin polymerization, Ed. Keii T, Soga K, Elsevier, New York, 439

12. Resconi L, Fait A, Piemontesi F, Colonnesi M, Rychlicki H, Zeigler R (1995) Effect of monomer concentration on propene polymerization with the Rac-[ethylenebis(1-indenyl)] zirconium dichloride methylaluminoxane catalyst. Macromolecules 28: 6667-6676

13. Fink G, Herfert N, Montag P (1995) In Ziegler catalysts, Ed. Fink G, Mülhaupt R, Brintzinger HH, Springer-Verlag, Berlin, 159

14. Jungling S, Mulhaupt R, Stehling U, Brintzinger HH, Fischer D, Langhauser F (1995) Propene polymerization using homogeneous Mao-activated metallocene catalysts - Me(2)Si(benz[E]indenyl)(2)ZrCl$_2$/MAO Vs Me(2)Si(2-Me-benz[E]indenyl)(2)ZrCl$_2$/MAO. J Polym Sci Part A: Polym Chem 33: 1305-1317

15. Kaminsky W, Werner R (1999) In metalorganic catalysts for synthesis and polymerization, Ed. Kaminsky W. Springer-Verlag, Berlin, 170

16. Ystenes M (1991) The trigger mechanism for polymerization of alpha-olefins with Ziegler-Natta catalysts - A new model based on interaction of 2 monomers at the transition-state and monomer activation of the catalytic centers. J Catal 129: 383-401

17. Karol FJ, Kao SC, Cann KJ (1993) Comonomer effects with high-activity titanium-based and vanadium-based catalysts for ethylene polymerization. J Polym Sci Part A: Polym Chem 31: 2541-2553

18. Chien JCW, Yu ZT, Marques MM, Flores JC, Rausch MD (1998) Polymerizations of olefins and diolefins catalyzed by monocyclopentadienyltitanium complexes containing a (dimethylamino)ethyl substituent and comparison with ansa-zirconocene systems. J Polym Sci Part A: Polym Chem 36: 319-328

19. Kissin Y, Mink RI, Nowlin TE, Brandolini AJ (1999) Kinetics and mechanism of ethylene polymerization and copolymerization reactions

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with heterogeneous titanium- based Ziegler-Natta catalysts. In Metalorganic catalysts for synthesis and polymerizations, Ed. Kaminsky W. Springer, Berlin, 60

20. Chakravarti S, Ray WH (2001) Kinetic study of olefin polymerization with a supported metallocene catalyst. II. Ethylene/1-hexene copolymerization in gas phase. J Appl Polym Sci 80: 1096-1119

21. Meshkova IN, Ladygina LA, Ushakova TM, Novokshonova LA (2002) Polymerization of ethylene and propylene with catalysts based on zirconocenes and methylaluminoxane synthesized on a zeolite support. Polym Sci A 44: 824-830

22. Bergstra MF, Weickert G (2005) Ethylene polymerization kinetics with a heterogeneous metallocene catalyst - Comparison of gas and slurry phases. Macromol Mater Eng 290: 610-620

23. Kissin YV (2012) Active centers in Ziegler-Natta catalysts: Formation kinetics and structure. J Catal 292: 188-200

24. Keii T (2004) Heterogeneous Kinetics: Theory of Ziegler–Natta–Kaminsky polymerization, Springer, Berlin

25. Shimizu F (2001) In liquid pool polymerization of propylene and ethylene using a highly active Ziegler-Natta catalyst - Kinetics and polymerization mechanism. University of Twente, Enschede, 77-91

26. Kissin YV, Mink RI, Nowlin TE (1999) Ethylene polymerization reactions with Ziegler-Natta catalysts. I. Ethylene polymerization kinetics and kinetic mechanism. J Polym Sci Part A: Polym Chem 37: 4255-4272

27. Kissin YV, Mink RI, Nowlin TE, Brandolini AJ (1999) Kinetics and mechanism of ethylene homopolymerization and copolymerization reactions with heterogeneous Ti-based Ziegler-Natta catalysts. Top Catal 7: 69-88

28. Kissin YV (2002) Peculiarities of ethylene polymerization reactions with heterogeneous Ziegler-Natta catalysts: Kinetic analysis. Macromol Theory Simul 11: 67-76

29. Fait A, Resconi L, Guerra G, Corradini P (1999) A possible interpretation of the nonlinear propagation rate laws for insertion polymerizations: A kinetic model based on a single-center, two-state catalyst. Macromolecules 32: 2104-2109

30. Resconi L, Cavallo L, Fait A, Piemontesi F (2000) Selectivity in propene polymerization with metallocene catalysts. Chem Rev 100: 1253-1345

31. Moscardi G, Resconi L, Cavallo L (2001) Propene polymerization with the isospecific, highly regioselective rac-Me$_2$C(3-t-Bu-1-Ind)(2)ZrCl$_2$/MAO catalyst. 2. Combined DFT/MM analysis of chain propagation and chain release reactions. Organometallics 20: 1918-1931

32. Busico V, Cipullo R, Corradini P (1993) Ziegler-Natta oligomerization of 1-alkenes - A catalysts fngerprint. 2. Preliminary-results of propene hydrooligomerization in the presence of the homogeneous isospecific catalyst system Rac-(Ebi)ZrCl$_2$/MAO. Makromol Chem: Rapid Commun 14: 97-103

33. Busico V, Cipullo R, Chadwick JC, Modder JF, Sudmeijer O (1994) Effects of regiochemical and stereochemical errors on the course of isotactic propene polyinsertion promoted by homogeneous Ziegler-Natta catalysts. Macromolecules 27: 7538-7543

34. Busico V, Cipullo R, Cutillo F, Vacatello M (2002) Metallocene-catalyzed propene polymerization: From microstructure to kinetics. 1. C$_2$-symmetric ansa-metallocenes and the "trigger" hypothesis. Macromolecules 35: 349-354

35. Tsvetkova VI, Firsov AP, Chirkov NM (1962) Possibility of determination of elementary act's konstans in catalytic polymerization. Dokl Akad Nauk SSSR 142: 149

36. Nikitin VE, Mikenas TB, Zakharov VA (2005) The way of catalyst preparation and process of ethylene polymerization and copolymerization of ethylene with α-olefins using this catalyst. Rus Patent 2257263

37. Zakharov VA, Mikenas TB, Nikitin VE, Mozgunova NV (2009) Catalyst and the way of producing of ultra-high-molecular-weight polyethylene. Rus Patent 2346006

38. Kissin YV (2003) Multicenter nature of titanium-based Ziegler-Natta catalysts: Comparison of ethylene and propylene polymerization reactions. J Polym Sci Part A: Polym Chem 41: 1745-1758

39. Wilson TP, Hurley CP (1963) Kinetics and mechanism of ethylene polymerization by the ziegler-martin catalyst. J Polym Sci Part C: Polym Symp 1: 281-304

40. Skomorokhov VB, Zakharov VA, Kirillov VA (1996) Investigation of the kinetics of ethylene

polymerization with supported titanium-magnesium catalysts of various composition. Macromol Chem Phys 197: 1615-1631

41. Bukatov GD, Zakharov VA, Barabanov AA (2005) Mechanism of olefin polymerization on supported Ziegler-Natta catalysts based on data on the number of active centers and propagation rate constants. Kinet Catal 46: 166-176

42. McKenna TFL, Di Martino A, Weickert G, Soares JBP (2010) Particle growth during the polymerisation of olefins on supported catalysts, 1-Nascent polymer structures. Macromol React Eng 4: 40-64

43. Nikolaeva MI, Mikenas TB, Matsko MA, Echevskaya LG, Zakharov VA (2011) Ethylene polymerization over supported titanium-magnesium catalysts: Effect of polymerization parameters on the molecular weight distribution of polyethylene. J Appl Polym Sci 122: 3092-3101

44. Echevskaya LG, Matsko MA, Mikenas TB, Nikitin VE, Zakharov VA (2006) Supported titanium-magnesium catalysts with different titanium content: Kinetic peculiarities at ethylene homopolymerization and copolymerization and molecular weight characteristics of polyethylene. J Appl Polym Sci 102: 5436-5442