

# Ethylene Polymerization Over Supported Titanium-Magnesium Catalysts: Effect of Polymerization Parameters on the Molecular Weight Distribution of Polyethylene

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**ABSTRACT:** The data on the effects of polymerization duration, cocatalyst, and monomer concentrations upon ethylene polymerization in the absence of hydrogen, and the effect of an additional chain transfer agent (hydrogen) on the molecular weight (MW), molecular weight distribution (MWD), and content of vinyl terminal groups for polyethylene (PE) produced over the supported titanium-magnesium catalyst (TMC) are obtained. The effects of these parameters on nonuniformity of active sites for different chain transfer reactions are analyzed by deconvolution of the experimental MWD curves into Flory components. It has been shown that the polymer MW grows, the MWD becomes narrower and the content of vinyl terminal groups in PE increases with increasing polymerization duration. It is assumed to

occur due to the reduction of the rate of chain transfer with  $\text{AlEt}_3$  with increasing polymerization duration. The polydispersity of PE is found to rise with increasing  $\text{AlEt}_3$  concentration and decreasing monomer concentration due to the emergence of additional low molecular weight Flory components. The ratios of the individual rate constants of chain transfer with  $\text{AlEt}_3$ , monomer and hydrogen to the propagation rate constant have been calculated. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 122: 3092–3101, 2011

**Key words:** Ziegler-Natta polymerization; polyethylene (PE); molecular weight distribution/molar mass distribution; kinetics (polym.); polymer synthesis and characterization

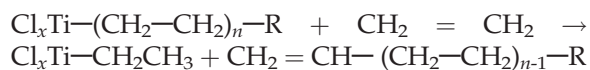
## INTRODUCTION

One of the most important issues upon ethylene polymerization over highly active supported Ziegler-Natta catalysts is the control of molecular weight (MW) and molecular weight distribution (MWD) of polyethylene (PE). The most known supported Ziegler-Natta type catalysts are titanium-magnesium catalysts (TMC), which are widely used in industry for production of PE with various MW and MWD. The active component of these catalysts is titanium chloride supported on magnesium chloride. These catalysts contain several types of active sites differing in their reactivity and these sites produce polymer molecules with different average molecular weights. It is well known that multiple-site titanium-magnesium catalysts (TMC) produce PE with broad MWD ( $M_w/M_n = 3\text{--}8^{1-8}$ ). The polydispersity value and distribution of active sites are de-

pendent upon the catalyst composition, conditions of its preparation, modifying agents being introduced into the catalyst, and polymerization conditions.

The general kinetic scheme of olefin polymerization over heterogeneous Ziegler-Natta catalysts was proposed by Natta<sup>9</sup> and minutely analyzed in work<sup>10</sup> with respect to ethylene polymerization over supported titanium-magnesium catalysts. This scheme comprises four chain transfer reactions (Scheme 1); together with the propagation reaction, they determine the molecular weight of the resultant polymer.

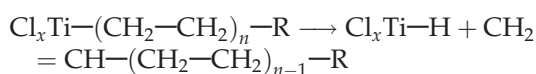
1. Chain transfer to the monomer by transferring a hydrogen atom from the  $\beta$ -carbon atom of the propagating chain to the coordinated monomer:



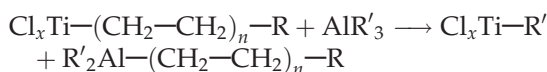
2. Chain transfer by transferring a hydrogen atom from the  $\beta$ -carbon atom of the propagating chain to the transition metal of the active site ( $\beta$ -hydrogen elimination):

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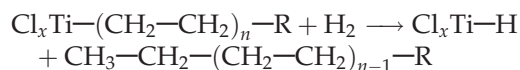
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3. Chain transfer to the aluminum-organic compound (cocatalyst):



4. Chain transfer with molecular hydrogen:



The average polymerization degree  $\bar{v}$  is determined by the ratio of the rate of chain propagation reaction to the sum of the chain transfer rates (eq. 1).<sup>9</sup>

$$\frac{1}{\bar{v}} = \frac{\sum V_{tr}}{V_p} = \frac{k_{tr}^M}{k_p} + \left( \frac{k_{tr}^\beta}{k_p} + \frac{k_{tr}^{Al}[Al]^m}{k_p} + \frac{k_{tr}^H[H_2]^n}{k_p} \right) \times \frac{1}{[M]} \quad (1)$$

where  $\sum V_{tr}$  and  $V_p$  are the sums of the chain transfer rates and of the chain propagation rates, respectively;  $k_p$  is the propagation rate constant;  $k_{tr}^M$ ,  $k_{tr}^\beta$ ,  $k_{tr}^{Al}$  and  $k_{tr}^H$  are the rate constants of transfer to the monomer,  $\beta$ -hydrogen elimination, transfer to trialkylaluminum and hydrogen, respectively;  $[M]$ ,  $[Al]$ , and  $[H_2]$  are the concentrations of the monomer, the cocatalyst and hydrogen, respectively;  $m$ ,  $n$  are the kinetic orders with respect to the cocatalyst and hydrogen.

The ratio of individual rate constants of chain transfer to the propagation rate constant can be determined using eq. (1) and the experimental dependences of the polymerization degree on concentrations of trialkylaluminum, monomer, and hydrogen.

It should be noted that hydrogen is the most efficient chain transfer agent, and the experimental data on the molecular weight characteristics of polyethylene were typically obtained upon ethylene polymerization in the presence of hydrogen.<sup>3,5,11-15</sup> The effects of polymerization duration and concentrations of alkylaluminum and the monomer on the molecular weight have been studied for ethylene polymerization over TMC in the presence of hydrogen.<sup>14,15</sup> In this case, the predominant reaction is the chain transfer with hydrogen, making it infeasible to determine the contribution of chain transfer reactions, (1), (2) and (3) to the control of the molecular weight and MWD of polyethylene. A limited number of works has been known, with the available data on the molecular weight of polyethylene produced over the Ziegler-Natta catalysts upon polymerization in the absence of hydrogen.<sup>16,17</sup> In these

works, the effect of polymerization conditions on the viscosity-average MW was studied, since ethylene polymerization in the absence of hydrogen yields the polymer with high MW. The determination of the MW of this polymer by GPC is complicated. The effect of polymerization duration, and concentrations of the aluminum organic cocatalyst and monomer was studied upon ethylene polymerization over TMC in the absence of hydrogen.<sup>16,17</sup> It was found that the viscosity-average MW of PE increases with increasing polymerization duration and attained the constant value after 1 h of polymerization. An increase in the monomer concentration upon ethylene polymerization over TMC resulted in the enhancement of the viscosity-average MW.

It should be noted that the assumption concerning the constant value of polydispersity for polymers produced under these conditions places limits on the analysis of the results presented in refs.<sup>16,17</sup> As it will be shown in this work, the polydispersity of PE produced upon ethylene polymerization in the absence of hydrogen may be considerably changed under varying polymerization conditions.

In this work, the data on the effect of polymerization duration and concentrations of the cocatalyst and the monomer on the MW and MWD of PE produced over the supported TMC in the absence of hydrogen were obtained using the GPC technique. The ratios of the individual rate constants of chain transfer with AlEt<sub>3</sub>, monomer, and hydrogen to the propagation rate constant have been calculated. The influence of these parameters on nonuniformity of active sites of this catalyst for different chain transfer reactions was analyzed by deconvolution of the experimental MWD curves into Flory components.

## EXPERIMENTAL

Catalyst TMC-I (3.0 wt % of Ti) was synthesized via the procedure described earlier<sup>5</sup> by supporting titanium tetrachloride on highly dispersed magnesium dichloride with the average particle size of 10  $\mu\text{m}$  and narrow particle size distribution. TMC-II (2.6 wt % of Ti) was synthesized via a procedure described elsewhere<sup>18</sup> by supporting titanium tetrachloride on the support (with the average particle size of 10  $\mu\text{m}$ ) prepared by interaction of a solution of organomagnesium compound Mg<sub>3</sub>Ph<sub>4</sub>Cl<sub>2</sub> in dibutyl ether and PhCl with the mixture of PhSiCl<sub>3</sub> and Si(OEt)<sub>4</sub>.

Ethylene slurry polymerization was performed in a 0.85 L steel reactor with stirring at 1000 rpm in heptane (250 mL) at constant ethylene pressure and polymerization temperature (80°C); triisobutylaluminum (Al(*i*-Bu)<sub>3</sub>) and triethylaluminum (AlEt<sub>3</sub>) were used as cocatalysts, catalyst concentration was 0.028–0.034 g/L. The agents were added in the

TABLE I  
Data<sup>a</sup> on the Catalyst and Cocatalyst Effect on the Yield and Intrinsic Viscosity of Produced Polyethylene

Catalyst	Ti, wt %	Exp. No	AOC	Yield, kg PE/g <sub>cat</sub>	Yield, kg PE/g <sub>Ti</sub>	[η], dL/g	$M_n \times 10^{-6}$ , g/mol
TMC-I	3.0	1	Al( <i>i</i> -Bu) <sub>3</sub>	10.6	350	13.1	2.5
		2	AlEt <sub>3</sub>	7.9	260	10.7	1.8
TMC-II	2.6	3	Al( <i>i</i> -Bu) <sub>3</sub>	6.1	240	10.5	1.8
		4	AlEt <sub>3</sub>	4.7	180	6.2	0.8

<sup>a</sup> Polymerization conditions: ethylene pressure = 4 bar, [AOC] = 4.8 mmol/L, 80 °C, 1 hour.

following sequence: heptane, cocatalyst, hydrogen (if used), ethylene, catalyst. Concentrations of ethylene and hydrogen were calculated from their partial pressures with the Henry's Law  $C = K_H P$ , where  $C$  is the ethylene or hydrogen concentration (mol/L),  $K_H$  is the Henry's constant (mol/(L × bar)),  $P$  is the ethylene or hydrogen pressure (bar). The Henry's constants for ethylene at 80°C  $K_H = 0.071$  M/bar, according to ref.<sup>19</sup> The Henry's constant for hydrogen weakly depends on temperature and is 0.011 M/bar, according to ref. 9.

MWD measurements were performed using a WATERS-150C instrument (Waters Corp., USA). Run conditions were as follows: temperature 140°C; 1,2,4-trichlorobenzene (TCB) was used as a eluent at a flow rate of 1 cm<sup>3</sup>/min. Four mixed bed TSK-gel columns (GMHXL-HT, Tosoh Corp., Japan) were used. The conventional calibration was made using the Polystyrene and PE standards with narrow MWD.

Viscosity ( $\eta$ ) of the polymers was measured in decalin at 135°C on an Ubbelohde viscosimeter. The viscosity-average molecular weight  $M_\eta$  was calculated according to the Mark-Houwink equation:  $M_\eta = (\eta/K)^{1/\alpha}$ , where the Mark-Houwink coefficients  $K = 67.7 \times 10^{-5}$ ;  $\alpha = 0.67$ , according to ref. 20.

The number of double bonds was determined by IR spectroscopy on a Shimadzu FTIR 8400 S as described in ref. 21. The content of vinyl groups was estimated according to the 909 cm<sup>-1</sup> band.

Deconvolution of MWD curves procedure was described in refs. 7,22.

## RESULTS AND DISCUSSION

### Selection of the catalytic system

Table I lists the data on the yield and molecular weight of PE produced over TMC-I and TMC-II catalysts upon hydrogen-free polymerization in the presence of various cocatalysts (Al(*i*-Bu)<sub>3</sub>, AlEt<sub>3</sub>). Both catalysts are highly active; however, they differ in molecular weight of the resultant polymer. The polymer with the higher MW ( $M_n = 2.5 \times 10^6$  g/mol with Al(*i*-Bu)<sub>3</sub> as a cocatalyst,  $M_n = 1.8 \times 10^6$  g/mol with AlEt<sub>3</sub> as a cocatalyst) is produced over the TMC-I catalyst. It is an appreciably difficult task to reliably measure the MWD using GPC at such

high molecular weight. On the other hand, PE with the lower MW is produced over the TMC-II catalyst. For both catalysts, the MW depends on the cocatalyst composition and is considerably lower upon polymerization in the presence of AlEt<sub>3</sub>. For the TMC-II/AlEt<sub>3</sub> catalytic system, the  $M_n$  value is  $0.8 \times 10^6$  g/mol (Table I, exp.4), which makes it possible to more reliably measure the MWD of PE by GPC. The TMC-II/AlEt<sub>3</sub> catalytic system was used for the more comprehensive study of the effect of polymerization conditions on the molecular weight and the MWD of PE produced in the absence of hydrogen.

### Polymerization duration

Figure 1 shows the kinetic curve of ethylene polymerization over the TMC-II/AlEt<sub>3</sub> catalyst (exp. 5 in Table II). As seen, the activity increases during one hour; then it reaches the stationary level. Active sites of different types may form and deactivate during the polymerization process. Moreover, the rates and ratios of the rates of different chain transfer reactions may change in the course of polymerization. As a result, polymer properties, such as the MW, MWD, stereocomposition (for polypropylene), and copolymer composition may depend on the reaction duration.<sup>3,23,24</sup>

Table II and Figure 2 show the data on the effect of polymerization duration on the MW and MWD of PE produced, and the data on content of terminal

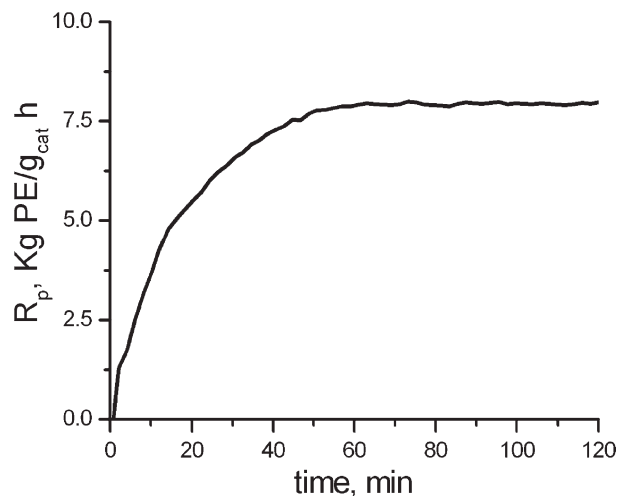


Figure 1 Kinetic curves of ethylene polymerization over TMC-II/AlEt<sub>3</sub> in the absence of hydrogen (exp. 5 in Table II).

**TABLE II**  
Data<sup>a</sup> on Effect of Polymerization Duration on the Molecular Weight and MWD of PE

Exp. No	Reaction time, min	$M_n \times 10^{-3}$	$M_w \times 10^{-3}$	$M_z \times 10^{-3}$	$M_w/M_n$	[C=C] <sup>b</sup>
1	2	57	350	1100	6.1	0.20
2	5	68	370	1200	5.4	0.24
3	15	88	450	1340	5.1	0.31
4	60	145	690	2300	4.8	0.46
5	120	150	680	1800	4.5	0.58
6 <sup>c</sup>	15	27	135	410	5.0	0.14
7 <sup>c</sup>	60	29	140	430	4.8	0.19

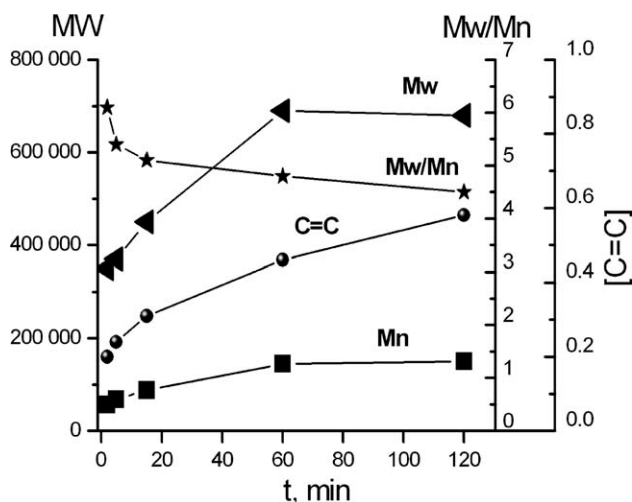
<sup>a</sup> Polymerization conditions: ethylene pressure = 4 bar, 80 °C, [AlEt<sub>3</sub>] = 2.4 mmol/L.

<sup>b</sup> Content of vinyl groups calculated per one polymer chain.

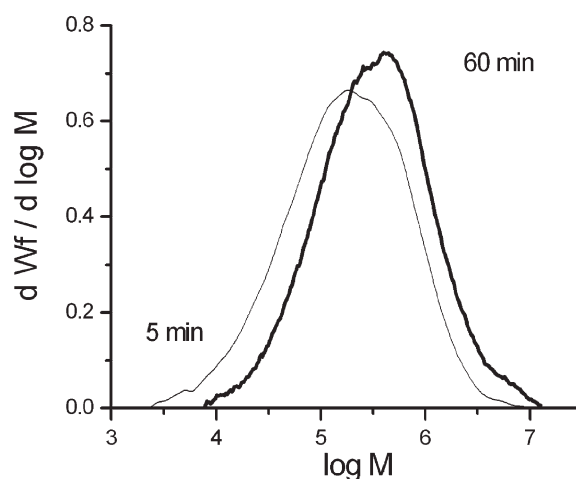
<sup>c</sup> Hydrogen pressure = 1 atm.

vinyl groups calculated per one polymer chain. As seen from these data, with the polymerization duration increasing from 2 to 60 min, the MW increases, the MWD becomes narrower (the  $M_w/M_n$  ratio decreases from 6.1 to 4.8) and amount of terminal double bonds in polymers increases. With the reaction duration increasing from 60 to 120 min, the MW and MWD of the resultant polymer remain virtually the same.

Figure 3 shows the MWD curves for the PE samples produced during 5 and 60 min (exp. 2, 4, Table II). Table III lists the results of the deconvolution of the MWD curves of these samples into Flory components. The MWD curves for these PE samples are fairly well described by four Flory components. With polymerization duration increasing from 5 to 60 min, the MW of each component increases, and the contributions of individual components are redistributed.



**Figure 2** Data on effect of polymerization duration on the molecular weight, MWD of polyethylene and the content of vinyl groups calculated per one polymer chain ([C=C]).



**Figure 3** MWD curves of PE produced upon different polymerization duration (exps. 2 and 4 from Table II).

With increasing polymerization duration, an increase in content of terminal vinyl bonds in the polymer calculated per one polymer chain is observed (Table II, Fig. 2). According to Scheme 1, double bonds are formed during chain transfer to the monomer and  $\beta$ -hydrogen elimination (Reactions 1 and 2). The results presented attest to the fact that the ratio between the reaction rates of chain transfer to the cocatalyst and the rates of chain transfer to the monomer changes with the polymerization duration: the contribution of the reaction of chain transfer to the cocatalyst decreases, while the contribution of the reaction of chain transfer to the monomer increases. Short polymerization duration results in predominance of the chain transfer reaction with AlEt<sub>3</sub> and a low content of vinyl groups in the polymer. As polymerization duration increases, the contribution of this reaction decreases, while the contribution of the reaction of chain transfer to the monomer increases. This probably is due to the fact that AlEt<sub>3</sub> concentration on the catalyst surface (inside the polymer particle) decreases with polymerization time due to formation of polymer on the

**TABLE III**  
Effect of Polymerization Duration on the Distribution of Flory Components

Reaction time, min	5		60		
	Flory component	Fraction weight, %	$M_w \times 10^{-3}$	Fraction weight, %	$M_w \times 10^{-3}$
I		10.0	30	21.8	100
II		33.6	105	40.0	330
III		38.5	350	28.5	860
IV		17.3	980	9.0	3000
Sum <sup>a</sup>					
polymer	$M_w \times 10^{-3}$		330		645
	$M_w/M_n$		5.0		4.6

<sup>a</sup> The sum of Flory components.

**TABLE IV**  
**Data<sup>a</sup> on TEA Concentration Effect on the Yield, MW, and MWD of Produced PE**

Exp. No	[AlEt <sub>3</sub> ], mmol/L	Yield, kg PE/g <sub>cat</sub>	M <sub>n</sub> × 10 <sup>-3</sup>	M <sub>w</sub> × 10 <sup>-3</sup>	M <sub>z</sub> × 10 <sup>-3</sup>	M <sub>w</sub> /M <sub>n</sub>	M <sub>z</sub> /M <sub>w</sub>	[C=C] <sup>b</sup>
1	1.2	6.5	250	910	2500	3.6	2.7	0.89
2	2.4	6.1	145	690	2300	4.8	3.3	0.46
3	4.8	4.7	93	580	2900	6.2	5.0	0.33

<sup>a</sup> Polymerization conditions: ethylene pressure = 4 bar, 80 °C, 1 hour.

<sup>b</sup> Content of vinyl groups calculated per one polymer chain

catalyst surface. As a result, the reaction rate of chain transfer with triethylaluminum decreases. We believe that the MW of the polymer increases with the increasing polymerization duration due to the same reason. In the case of polymerization in the presence of hydrogen, the predominant reaction is the chain transfer with hydrogen. In this case, the MW and MWD of the polymer are independent of the polymerization duration (exp. 6, 7, Table II). To eliminate the effect of polymerization duration on the MW and MWD of the polymer, the polymers produced by polymerization during 1 h were studied in the subsequent sections of this work.

### Triethylaluminum concentration

Table IV lists the data on the effect of AlEt<sub>3</sub> concentration on the polymer yield, MW and MWD of the PE produced, and the content of terminal vinyl groups. As seen from these data, a certain decrease in the polymer yield is observed with AlEt<sub>3</sub> concentration increasing, which was earlier noted in works.<sup>17,25</sup> The MW of the resultant PE decreases and the MWD broadens as AlEt<sub>3</sub> concentration increases (Table IV, Fig. 4). The resultant data on the decrease in the MW and content of terminal vinyl groups in the polymer with increasing AlEt<sub>3</sub> concentration attests to the fact that the reaction of chain transfer with AlEt<sub>3</sub> under these conditions is considerable. Using these data, we estimated the rate constant of chain transfer with AlEt<sub>3</sub>. With this view, expression (1) can be written as:

$$\frac{1}{\nu} = \frac{k_{tr}^M}{k_p} + \frac{k_{tr}^{\beta}}{k_p M} + \frac{k_{tr}^{Al}[Al]^m}{k_p M} = A + \frac{k_{tr}^{Al}[Al]^m}{k_p M} \quad (2)$$

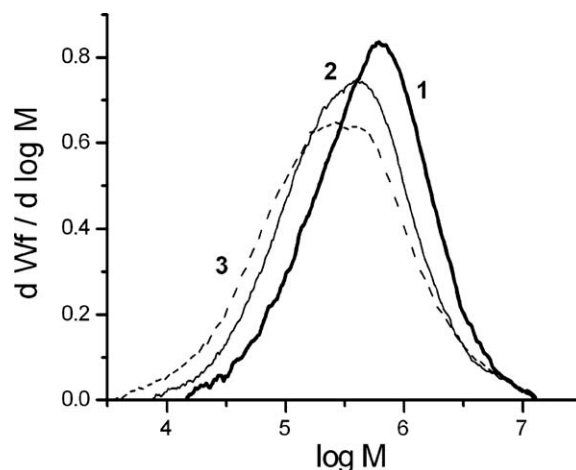
Using the logarithmic form of expression, (2) we determined the kinetic order of the chain transfer reaction with respect to AlEt<sub>3</sub>; it appeared to be equal to 0.5, which agrees with the literature data.<sup>9</sup> In accordance with expression, (2) using the linear dependence of the polymerization degree  $1/\nu$  versus the  $[Al]^{0.5}/M$  ratio, we calculated the  $k_{tr}^{Al}/k_p$  ratio ( $1.6 \times 10^{-3}$ ) and the value of  $A = (k_{tr}^M/k_p + k_{tr}^{\beta}/k_p M)$ , which was equal to  $1 \times 10^{-5}$ .

As already noted above, the content of terminal vinyl bonds in the polymer decreases with increasing AlEt<sub>3</sub> concentration (Table IV). It may be concluded

on the basis of these data that the reaction of chain transfer with AlEt<sub>3</sub> is prevailing (content of terminal vinyl bonds is less than 0.5 [C=C] per one polymer chain) only at high concentrations of AlEt<sub>3</sub> (above 2.4 mM). Figure 4 shows the MWD curves of the polymers produced at different AlEt<sub>3</sub> concentrations. Table V lists the results of deconvolution of these curves into Flory components. The MWD curves of PE are described by four and five Flory components. With AlEt<sub>3</sub> concentration increasing from 1.2 mM to 4.8 mM, an additional low molecular weight component I emerges, the contribution of Component II increases, and the contribution of high molecular weight Components III–V decreases, resulting in the observable broadening of the MWD. The data presented in Figure 4 and Table V attest to the considerable nonuniformity of active sites of the catalyst with respect to the reaction of chain transfer with AlEt<sub>3</sub>. The active sites on which high molecular weight PE is formed (Components IV–V) almost do not participate in the reaction of chain transfer with AlEt<sub>3</sub> and are partially deactivated as the AlEt<sub>3</sub> concentration increases. The chain transfer with AlEt<sub>3</sub> occurs predominantly on the active sites that produce the lower molecular weight PE (Components II and III).

### Monomer concentration

Table VI and Figure 5 show the data on the effect of ethylene pressure on the polymer yield, MW and



**Figure 4** MWD curves of PE produced with different AlEt<sub>3</sub> concentration (exps. 1, 2 and 3 in Table IV).

TABLE V  
TEA Concentration Effect on the Distribution of Flory Components

[AlEt <sub>3</sub> ], mmol/L		1.2		2.4		4.8	
Flory component		Fraction weight, %	$M_w \times 10^{-3}$	Fraction weight, %	$M_w \times 10^{-3}$	Fraction weight, %	$M_w \times 10^{-3}$
I						7.7	39
II		14.2	135	21.8	100	28.3	120
III		42.5	470	40.0	330	38.6	390
IV		34.6	1100	28.5	860	18.8	1070
V		8.9	3170	9.0	3000	6.6	3500
Sum <sup>a</sup>	$M_w \times 10^{-3}$	905		645		590	
polymer	Mw/Mn	3.6		4.6		6.1	

<sup>a</sup> The sum of Flory components.

MWD of the resultant PE. An increase in the MW and the noticeable narrowing of the MWD are observed (the  $M_w/M_n$  ratio decreases from 11.0 to 4.8) with increasing ethylene pressure. A considerable increase in the content of terminal vinyl bonds per one polymer molecule is also observed with increasing ethylene pressure. These data attest to the decrease in contribution of the reaction of chain transfer with AlEt<sub>3</sub> and increase in contribution of  $\beta$ -hydride transfer and chain transfer with the monomer as the ethylene pressure increases. It should also be noted that in this range of ethylene pressures the catalyst activity (polymer yield) increases considerably higher than it appears from the first-order propagation reaction with respect to the monomer. The monomer probably participates in the formation of catalyst active sites, their number increasing with the increasing ethylene pressure.

The  $k_{tr}^M/k_p$  ratio can be estimated using eq. (1) in form (3) and the data on the effect of monomer concentration on the  $M_n$  value.

$$\frac{1}{\bar{v}} = \frac{k_{tr}^M}{k_p} + \left( \frac{k_{tr}^\beta}{k_p} + \frac{k_{tr}^{Al}[Al]^{0.5}}{k_p} \right) \times \frac{1}{[M]} \quad (3)$$

The ratio of the rate constant of transfer to the monomer ( $k_{tr}^M$ ) to the propagation rate constant ( $k_p$ ) was calculated from the linear dependence of  $1/\bar{v}$  on  $1/[M]$ . This value was equal to  $2 \times 10^{-5}$ .

TABLE VI  
Data<sup>a</sup> on Ethylene Pressure Effect on the Yield, MW, and MWD of PE

Exp. No	P C <sub>2</sub> H <sub>4</sub> , bar	Yield, kg PE/g <sub>cat</sub>	$M_n \times 10^{-3}$	$M_w \times 10^{-3}$	$M_z \times 10^{-3}$	$M_w/M_n$	$M_w/[C=C]^b$
1	1	0.4	39	430	2050	11.0	0.08
2	2	1.2	76	690	3700	9.1	0.22
3	4	6.1	145	690	2300	4.8	0.46

<sup>a</sup> Polymerization conditions: [AlEt<sub>3</sub>] = 2.4 mmol/L, 80 °C, 1 hour.

<sup>b</sup> Content of vinyl groups calculated per one polymer chain.

In the previous section, we calculated the value of  $(k_{tr}^M/k_p + k_{tr}^\beta/k_p M) = 1 \times 10^{-5}$ , using the data on the effect of AlEt<sub>3</sub> concentration on the  $M_n$  value. It may be concluded by comparing the calculated values of  $k_{tr}^M/k_p$  and  $(k_{tr}^M/k_p + k_{tr}^\beta/k_p M)$  that the  $k_{tr}^\beta/k_p M$  value is smaller than  $k_{tr}^M/k_p$  value; therefore, the reaction rate of  $\beta$ -hydrogen elimination is low relative to the reaction rate of chain transfer to the monomer.

Table VII lists the results of deconvolution of the MWD curves (Fig. 5) into Flory components. As seen from the data in Table VII, with increasing ethylene pressure the number of Flory components decreases from six at ethylene pressure of 1 bar to four at pressure of 4 bar.

The data in Table VII demonstrate that two new low molecular weight Components I and II emerge and the contribution of Components IV–VI decreases with decreasing ethylene pressure. Thus, polymerization under low ethylene pressure, when the predominant transfer reaction is the chain transfer with AlEt<sub>3</sub>, is characterized by a stronger nonuniformity of active sites (six Flory components). The nonuniformity of active sites decreases (four Flory components) with increasing ethylene pressure (enhanced contribution of the reaction of chain transfer to the monomer).

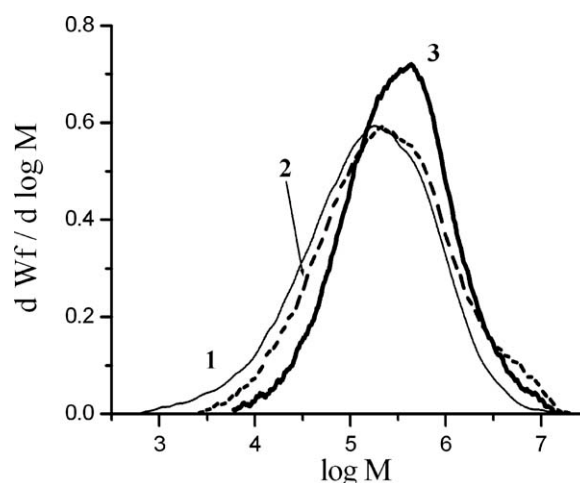


Figure 5 MWD curves of PE produced under different ethylene pressure (exps. 1, 2, and 3 in Table VI).

TABLE VII  
Ethylene Pressure Effect on the Distribution of Flory Components

P (C <sub>2</sub> H <sub>4</sub> ), bar		1		2		4	
Flory component		Fraction weight, %	$M_w \times 10^{-3}$	Fraction weight, %	$M_w \times 10^{-3}$	Fraction weight, %	$M_w \times 10^{-3}$
I		3.2	6.8	–	–	–	–
II		12.9	30	10.5	32	–	–
III		26.7	100	28.2	113	21.8	100
IV		27.2	275	33.1	366	40.0	330
V		23.2	690	19.1	1041	28.5	860
VI		6.4	2100	9.0	4264	9.0	3000
Sum <sup>a</sup>	$M_w \times 10^{-3}$	410		690		645	
polymer	$M_w/M_n$	9.2		9.0		4.6	

<sup>a</sup> The sum of Flory components.

It was found in work<sup>26</sup> that upon ethylene polymerization over TMC, the  $K_p$  value is equal to  $1.2 \times 10^4$  L/(mol s). Taking this into consideration, we calculated the values of  $k_{tr}^{Al}$  and  $k_{tr}^M$  (Table VIII). Using these data, the ratio of the reaction rates of chain transfer with AlEt<sub>3</sub> and the monomer for various polymerization conditions can be estimated according to eq. (4):

$$R = \frac{V_{tr}^{Al}}{V_{tr}^M} = \frac{k_{tr}^{Al} c_p [Al]^{0.5}}{k_{tr}^M c_p M} = \frac{k_{tr}^{Al} [Al]^{0.5}}{k_{tr}^M M} \quad (4)$$

The ratios of the reaction rate of chain transfer to AlEt<sub>3</sub> to the reaction rate of chain transfer to the monomer ( $R$ ) were calculated for the boundary conditions (the data in Table IV, exp. 1 and Table VI, exp. 1):

- (1) P = 4 bar, [AlEt<sub>3</sub>] = 1.2 mM,  $R \sim 10 M_w/M_n = 3.6$
- (2) P = 1 bar, [AlEt<sub>3</sub>] = 2.4 mM,  $R \sim 55 M_w/M_n = 11.0$

As seen from these data, the reaction of chain transfer to cocatalyst is dominating even at low AlEt<sub>3</sub> concentrations; however, that contradicts the data on the content of terminal vinyl bonds for this polymer (Table IV, exp. 1). For PE produced at low AlEt<sub>3</sub> concentration, 0.89 terminal double bonds were found per 1 polymer chain, i.e., there is a terminal vinyl bond almost in each polymer molecule. These data attest to the predominant contribution of the reactions of chain transfer to the monomer under these conditions. We believe that this can be attributed to the fact that the bulk concentration of AlEt<sub>3</sub> is used for calculations of the reaction rate of chain transfer to AlEt<sub>3</sub>, while a decrease in AlEt<sub>3</sub> concentration on the catalyst surface takes place during the reaction due to the fact that the polymer formed on the catalyst surface impedes the AlEt<sub>3</sub> diffusion to the catalyst surface. As a result, the actual reaction rate of chain transfer with AlEt<sub>3</sub> is considerably

lower, and this phenomenon should be taken into account when considering the actual contribution of this reaction to the processes of chain transfer. It can be noted that in the case when the reaction rate of chain transfer to AlEt<sub>3</sub> far exceeds that of chain transfer to the monomer, appreciable nonuniformity of active sites (broadening of the MWD due to the formation of additional low molecular weight components) is observed.

### The effect of hydrogen

The data on the effect of hydrogen concentration on the polymer yield, MW, and MWD of PE are presented in Table IX and Figure 6. Introduction of hydrogen results in a decrease in activity and considerable decrease in the MW; the polymer polydispersity (the  $M_w/M_n$  ratio) remains virtually unchanged.

Using the data on the effect of hydrogen concentration on the  $M_w$  value, we estimated the order of the reaction of chain transfer with hydrogen ( $n$ ), which appeared to be close to 1 (0.81). In our further calculations we used the value  $n = 1$ , as it was earlier done in works.<sup>5,27</sup> The data on the effect of hydrogen content on the MW allow estimating the ratio of the rate constant of transfer with hydrogen to the propagation rate constant in accordance with expression (5):

$$\frac{1}{v} = \left( \frac{k_{tr}^M}{k_p} + \frac{k_{tr}^{Al} [Al]^{0.5}}{k_p [M]} \right) + \frac{k_{tr}^H [H_2]^n}{k_p [M]} \quad (5)$$

The calculated values of  $k_{tr}^H/k_p$  and  $k_{tr}^H$  are given in Table VIII. The value of  $k_{tr}^H$  is considerably higher

TABLE VIII  
Data on the Chain Transfer Reaction Constants at Ethylene Polymerization Over TMC/AlEt<sub>3</sub> Catalyst (80°)

$k_{tr}^{Al}/k_p$ , mol <sup>0.5</sup> /L <sup>0.5</sup>	$k_{tr}^{Al}$ , L <sup>0.5</sup> /mol <sup>0.5</sup> × s	$k_{tr}^M/k_p$	$k_{tr}^M$ , L/mol × s	$k_{tr}^H/k_p$	$k_{tr}^H$ , L/mol × s
$1.6 \cdot 10^{-3}$	19	$2 \cdot 10^{-5}$	0.24	$1.5 \cdot 10^{-2}$	180

TABLE IX  
Data<sup>a</sup> on Hydrogen Effect on the Yield, MW, and MWD of PE

Exp. No	$P_{\text{total}} (P_E + P_H)$ , bar	$P (H_2)$ , bar	Yield, kg PE/g <sub>cat</sub>	$M_n \times 10^{-3}$	$M_w \times 10^{-3}$	$M_z \times 10^{-3}$	$M_w/M_n$	[C=C] <sup>b</sup>
1	4	0	6.1	145	690	2300	4.8	0.46
2	5	1	5.1	29	140	430	4.8	0.19
3	6	2	3.7	19	91	310	4.8	0.11
4	8	4	4.7	11	54	180	4.9	0.07

<sup>a</sup> Polymerization conditions: ethylene pressure = 4 bar, 80 °C, [AlEt<sub>3</sub>] = 2.4 mmol/L, 1 hour.

<sup>b</sup> Content of vinyl groups calculated per one polymer chain.

than the values of  $k_{tr}^{Al}$  and  $k_{tr}^M$ . It is reasonable that in this case the reaction of chain transfer with hydrogen becomes predominant even at low hydrogen content (20% of H<sub>2</sub> in the gas phase, exp. 2, Table VIII).

Table X lists the results of deconvolution of the MWD curves into Flory components for PE samples produced at different hydrogen concentrations. The MWD curves of all PE samples are fairly well described by four Flory components. After the introduction of hydrogen, the redistribution of Flory components takes place: the contribution of low molecular weight components decreases, while the contribution of high molecular weight components increases (Table X, exps. 1 and 2). However, this does not result in a considerable change in the polymer polydispersity. Hydrogen concentration further increasing, all Flory components shift toward the low molecular weight region without any considerable change in the contribution of individual components.

Earlier,<sup>5</sup> we studied the effect of hydrogen on the MW and MWD of PE upon polymerization over TMC-I type catalysts (Table I) with various contents of titanium; Al(*i*-Bu)<sub>3</sub> was used as a cocatalyst. It was revealed for these catalytic systems that when using the catalyst with low titanium content (0.1 wt %), the polymer polydispersity remains constant with changing hydrogen content, while when using the catalyst with high titanium content (5 wt %), the polydispersity increases (the  $M_w/M_n$  ratio rises from 4.8 to 8.3) with increasing hydrogen content.

It follows from these data that TMC-II catalyst studied in the present work, similar to the low titanium content TMC-I that was studied in work,<sup>5</sup> is more homogeneous with respect to the reaction of chain transfer with hydrogen as compared with the TMC-I catalyst with high titanium content.

## CONCLUSIONS

The catalytic system, which makes it possible to produce the polymer with the molecular weight of less than  $1 \times 10^6$  g/mol upon polymerization in the absence of hydrogen was selected for comprehensive study of the separate chain transfer reactions upon

ethylene polymerization over supported titanium-magnesium catalysts; this polymer being suitable for reliable determination of molecular weight characteristics by GPC.

The effect of polymerization conditions (polymerization duration, concentrations of the AlEt<sub>3</sub> cocatalyst and the monomer) on the molecular weight and molecular weight distribution of polyethylene and the content of terminal vinyl groups in the polymer was studied upon polymerization in the absence of hydrogen.

It was found that the molecular weight of the polymer increases, while its polydispersity decreases as polymerization duration increases. Simultaneously with the rise in polymerization duration, the content of terminal vinyl groups calculated per one polymer chain increases. We believe that these results are connected with a decrease in the reaction rate of chain transfer with AlEt<sub>3</sub> with increasing polymerization duration (polymer yield) due to the decrease in AlEt<sub>3</sub> concentration on the catalyst surface. It probably occurs due to the fact that the polymer formed on the surface of catalyst impedes the AlEt<sub>3</sub> diffusion to the catalyst surface. As a result, the ratio of the reaction rate of chain transfer with AlEt<sub>3</sub> to the reaction rate of transfer with monomer changes; the contribution of the latter reaction to the chain transfer processes increases with

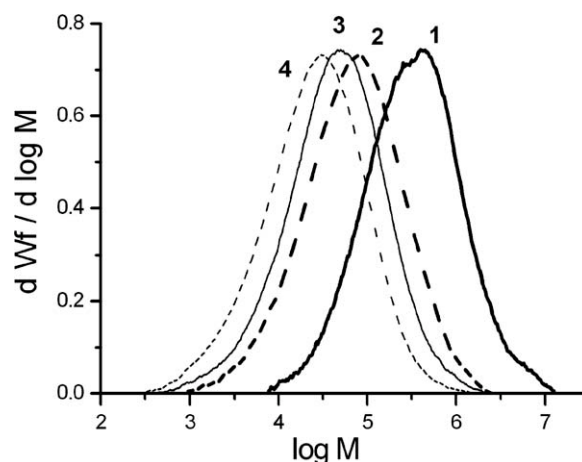


Figure 6 MWD curves of PE produced under different hydrogen pressure (exps. 1, 2, 3, and 4, Table IX).



TABLE X  
Hydrogen Pressure Effect on the Distribution of Flory Components

Exp. No	1		2		3		4	
P (H <sub>2</sub> ), bar	-		1		2		4	
Flory component	Fraction weight, %	$M_w \times 10^{-3}$	Fraction weight, %	$M_w \times 10^{-3}$	Fraction weight, %	$M_w \times 10^{-3}$	Fraction weight, %	$M_w \times 10^{-3}$
I	21.8	100	10.0	13	9.0	9.6	10.5	4.7
II	40.0	330	33.3	46	35.1	33	33.5	19
III	28.5	860	39.3	130	41.2	91	40.9	54
IV	9.0	3000	16.8	410	14.0	290	14.4	160
Sum <sup>a</sup>	$M_w \times 10^{-3}$	645		140		90		52
polymer	$M_w/M_n$	4.6		4.8		4.3		4.8

<sup>a</sup> The sum of Flory components.

polymerization duration. In the case of ethylene polymerization in the presence of hydrogen over this catalyst, the MW of the polymer does not depend on polymerization duration.

When studying the effect of AlEt<sub>3</sub> concentration on the molecular weight characteristics of the polymer, it has been shown that the molecular weight decreases, while the polymer polydispersity considerably increases ( $M_w/M_n = 3.6$  at [AlEt<sub>3</sub>] = 1.2 mM and  $M_w/M_n = 6.2$  at [AlEt<sub>3</sub>] = 4.8 mM) with increasing AlEt<sub>3</sub> concentration. The increase in AlEt<sub>3</sub> concentration also results in a considerable reduction of the content of vinyl groups calculated per one polymer chain. It is probably connected with the decrease in contribution of the reaction of chain transfer to the monomer and, correspondingly, with the increase in contribution of the reaction of chain transfer with AlEt<sub>3</sub> to the total sum of reactions of polymer chain transfer. The results of deconvolution of the MWD curves into the individual Flory components demonstrate that the number of components increases from four to five with increasing AlEt<sub>3</sub> concentration due to the emergence of an additional low molecular weight component.

The ethylene pressure was found to have a considerable effect on the molecular weight and polydispersity of the resultant polymer, as well. With pressure increasing from 1 to 4 bar (at [AlEt<sub>3</sub>] = 2.4 mM), the increase in the molecular weight and noticeable narrowing of the MWD (the  $M_w/M_n$  value decreases from 11.0 to 4.8) is observed. Simultaneously, the increasing ethylene pressure results in the considerable increase in the content of vinyl groups in the polymer calculated per one polymer chain. These data point to the considerable rise of the contribution of the transfer reactions resulting in the formation of terminal vinyl groups. On the basis of the results of deconvolution of the MWD curves into the individual Flory components, it was found that the polymer produced under low ethylene pressure (1 bar) comprises six components; an increase in pres-

sure to 4 bar results in the decrease in the number of the individual components to four due to the elimination of low molecular weight components, which in its turn results in the observable MWD narrowing.

The introduction of hydrogen under ethylene pressure of 4 bar results in an abrupt decrease in the molecular weight; the polydispersity of the resultant polymer remaining virtually unchanged. It follows from the results of deconvolution of the MWD curves into Flory components for the polymers produced at various hydrogen contents that the number of Flory components remains unchanged after hydrogen is introduced; however, a decrease in the molecular weight of each component and redistribution of contributions of the individual components to the MWD are observed. With further increase in hydrogen concentration, the molecular weight of the individual components is reduced to appreciably equal extents and the contribution of the individual components to the MWD changes negligibly.

The results given above on the effect of polymerization duration, AlEt<sub>3</sub> concentration, and ethylene pressure on the polydispersity of the resultant polyethylene attest to the fact that in all the cases when the reaction of chain transfer with AlEt<sub>3</sub> becomes predominant, it results in a considerable broadening of the polymer MWD due to the emergence of additional low molecular weight components. Thus, the active sites of supported TMC exhibit appreciable nonuniformity with respect to the reaction of chain transfer with AlEt<sub>3</sub>.

The ratios of the constants of the individual transfer reactions to the propagation rate constant were calculated using the resultant data on the effect of AlEt<sub>3</sub>, ethylene and hydrogen concentrations on the molecular weight of polyethylene. The rate constants of transfer with AlEt<sub>3</sub> ( $k_{tr}^{Al}$ ), the monomer ( $k_{tr}^M$ ), and hydrogen ( $k_{tr}^H$ ) were calculated using these results and the known value of the propagation rate constant ( $k_p$ ) (Table VIII). The relative contribution of

the reactions of transfer with  $\text{AlEt}_3$  and monomer upon polymerization without hydrogen was shown to depend on polymerization duration and concentrations of  $\text{AlEt}_3$  and monomer. It should be noted that the comparison of the  $k_{tr}^M$  values obtained from the experimental data with the  $(k_{tr}^M + k_{tr}^\beta)$  value demonstrates that the  $k_{tr}^\beta$  is small as compared with  $k_{tr}^M$ , and under the selected polymerization conditions the reaction of chain transfer to the monomer is prevailing among the chain transfer reactions resulting in the formation of terminal vinyl groups.

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