

A Comparative Study of Ethylene and Propylene Polymerization Over Titanium–Magnesium Catalysts of Different Composition

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ABSTRACT: New data on the molecular weight characteristics of polypropylene (PP) and polyethylene (PE) were obtained from the polymerization over supported titanium–magnesium catalysts differing in their compositions (presence and absence of internal and external donors). Internal and external donors were found to affect the molecular weight of polymers in a different manner for ethylene and propylene polymerization. The introduction of the internal donor increases the molecular weight of PP and does not affect the molecular weight of PE. The effect of external donor introduced to catalytic system on the polymer molecular weight depends on catalyst composition: for a catalyst without internal donor, the introduction of the external donor increases the molecular weight of PP and does not affect that of PE. In the case of catalyst with the internal donor, the introduction of the external donor increases the molecular weight of PP and substantially decreases that of PE. The data on polymerization degree of the polymers produced under conditions when chain transfer with hydrogen was the dominant reaction were used to calculate the k_{tr}^H/k_p values for ethylene polymerization over the catalysts of different composition. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40658.

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INTRODUCTION

Supported titanium–magnesium catalysts (TMCs) belonging to the Ziegler–Natta (ZN) catalytic systems are widely used to produce polyethylene (PE), polypropylene (PP) and copolymers of ethylene with α -olefins. In most cases, kinetic studies of olefin polymerization over these catalysts and investigation of the molecular weight characteristics of the resulting polymers are performed separately for polymerization of propylene and that of ethylene. Catalysts of different composition are usually employed in polymerization of these olefins. In particular, the catalysts containing stereoregulating electron donor compounds are used for propylene polymerization, while their presence is not mandatory in the case of ethylene polymerization. Meanwhile, it is of interest to reveal the general kinetic regularities and distinctions observed during propylene and ethylene polymerization, first of all those concerning the control of molecular weight characteristics of the polymers produced over the catalysts of identical composition. These data can be obtained by a comparative study of PP and PE produced over TMCs of a similar composition.

Comparative data on propylene and ethylene polymerization in the presence of the conventional ZN catalyst ($\text{TiCl}_3 + \text{AlEt}_3$) and TMCs ($\text{TiCl}_4/\text{dibutylphthalate}/\text{MgCl}_2\text{-AlEt}_3/\text{PhSi}(\text{OEt})_3$) are

reported in Refs. [1,2]. According to these studies, polymerization of propylene over the catalytic system ($\text{TiCl}_3 + \text{AlEt}_3$) gave rise to polypropylene with a broad molecular weight distribution (MWD) ($M_w/M_n = 14.6$) and low isotacticity (70%), while polymerization of ethylene yielded polyethylene (PE) with a much narrower MWD ($M_w/M_n = 5.3$). Propylene polymerization over TMC gave rise to PP with $M_w/M_n = 5.0\text{--}6.5$; no data on the molecular weight characteristics of PE were presented in these works. The comparative kinetic data on ethylene and propylene polymerization over a commercial TMC in a gas phase stirred-bed reactor are considered in Ref. [3]. However, only the kinetic features of ethylene and propylene polymerization are reported in this article, molecular weight characteristics of the polymers being neglected.

As shown in Refs. [4–6], the introduction of the external donor (ED) into the catalyst already containing the internal donor gives narrower MWD values for atactic polypropylene in propylene polymerization, but does not affect MWD of isotactic fraction. Studies^{7,8} were devoted to the effect of external donor (methyl-*p*-toluate) as a constituent of TMC ($\text{MgCl}_2/\text{ethylbenzoate}/p\text{-cresol}/\text{AlEt}_3/\text{TiCl}_4\text{-AlEt}_3$) on ethylene polymerization. In the presence of external donor, the number of active sites decreased twofold and M_w of PE increased. However, in

Table I. Molecular Weight Characteristics of PP Produced Over TMC with Different Composition (TMC-PE and TMC-PP Catalysts)

Catalyst ^a	Polymer No	τ_p (min)	Al/PTMS	Yield (kg PP/g _{cat})	M_n ($\times 10^{-3}$)	M_w ($\times 10^{-3}$)	M_w/M_n	APP ^b (%)	PP (%)	T_m (°C)
TMC-PE	PP1	19	-	2.6	14	105	7.5	35.1	64.9 ^c (19.2* + 45.7**) ^d	151.7/160.7
	PP2	60	20	1.7	42	210	5.0	4.6	95.4 ^c (10.5* + 84.9**) ^d	160.5
TMC-PP	PP3	6	-	1.7	29	150	5.2	10.5	89.5 ^c (14.7* + 74.8**) ^d	155.2/163.0
	PP4	7	20	2.3	49	230	4.7	1.2	98.8 ^c (2.1* + 96.7**) ^d	163.2

^a TMC-PE does not contain an ID, TMC-PP contains DBPh as an ID.

^b Content of fraction which is soluble in heptane at polymerization (70°C).

^c Content of PP powder which does not contain fraction soluble in polymerization heptane.

^d Content of fraction soluble in boiling heptane* and content of fraction insoluble in boiling heptane**.

Refs. [7,8] molecular weights of PE and PP were calculated using intrinsic viscosity, which does not allow one to estimate the MWD of the polymers being produced.

The authors of Ref. [9] presented the data on molecular weight characteristics of PP and PE produced over the catalysts strongly differing in their composition: PP was obtained over a supported $\text{TiCl}_4/\text{MgCl}_2/\text{diisobutylphthalate}/\text{AlEt}_3$ catalyst, while PE was produced over a ZN catalyst with composition $\text{TiCl}_4/\text{VOCl}_3/\text{AlEt}_3$.

Thus, the literature provides very scarce comparative data on the molecular weight characteristics of PE and PP produced over TMCs of identical composition and for the cases when the effect of catalyst composition on molecular weight characteristics of both PE and PP can be estimated. In this article, we conducted a comparative study of the molecular weight characteristics of PP and PE produced by polymerization of ethylene and propylene over two modifications of supported TMCs. One of these catalysts (TMC-PP) contains the internal donor, while the other catalyst (TMC-PE) does not contain any. In addition, the effect of external donor was investigated in propylene and ethylene polymerization over both catalysts.

EXPERIMENTAL

Catalyst TMC-PE (3.5 wt % Ti) was synthesized by supporting of TiCl_4 on a highly dispersed MgCl_2 with the average particle size of 5 μm and a narrow particle size distribution.^{10,11}

Catalyst TMC-PP (2.3 wt % Ti) was prepared by a method reported elsewhere;¹² it comprises TiCl_4 on a MgCl_2 support and 12 wt % dibutyl phthalate (DBPh) as the internal stereoregulating donor. The catalyst has a narrow particle size distribution with the average size of 18 μm .

Ethylene polymerization was performed in a 0.85 L steel reactor under stirring at 1000 rpm in heptane (250 mL) at a constant ethylene pressure (4 bar) with hydrogen (1 bar) as a chain transfer agent; the polymerization temperature of 80 °C and polymerization time of 1 h were employed; triethylaluminum was used as a cocatalyst ($[\text{AlEt}_3] = 3.2$ mmol/L), the catalyst concentration was 0.022 g/L. Propyltrimethoxysilane (PTMS) was added as the external donor in some experiments. The components were added in the following sequence: heptane, cocatalyst, external donor (if needed), hydrogen, ethylene, and catalyst.

Propylene polymerization was performed in a 0.85 L steel reactor under stirring at 1000 rpm in heptane (300 mL) at constant propylene (6 bar) and hydrogen (0.14 bar) pressure. The polymerization temperature was 70°C, triethylaluminum was used as a cocatalyst ($[\text{AlEt}_3] = 4$ mmol/L), the catalyst concentration was 0.032 g/L. Propyltrimethoxysilane was added as the external donor in some experiments. In propylene polymerization, the hydrogen concentration decreases considerably with increasing the polymer yield. Thus, in order to prevent substantial changes in hydrogen concentration in the course of the reaction, we limited the polymerization time and, correspondingly, the polymer yield (not longer than 20 min and not higher than 20 g of polymer).

After polymerization, heptane containing the PP fraction (atactic fraction, APP), which is soluble during the polymerization, was separated from the polymer powder.

Prepolymerization was performed by the following procedure. The reactor was loaded with heptane, AlEt_3 , PTMS (if needed), propylene (0.5 bar) and catalyst at 20°C, and the mixture was then stirred for 5 min. We used prepolymerization step in the following cases: (a) propylene polymerization over TMC-PE and TMC-PP (PP1-PP4, Table I); (b) ethylene polymerization over TMC-PP (PE3, PE4, Table III).

Concentrations of ethylene, propylene and hydrogen were calculated from their partial pressures using the Henry law.^{1,13}

MWD measurements were made on a PL 220C Gel Permeation Chromatograph with refractive index and viscosity detectors. Run conditions were as follows: temperature of 160°C and 1,2,4-trichlorobenzene (TCB) used as a solvent at a flow rate of 1 mL/min. The polymers were analyzed on set of Olexis gel columns. The instrument was calibrated using polyethylene and polystyrene standards with narrow MWD.

The melting temperature (T_m) was determined on a Differential Scanning Calorimeter (DSC 204 F1, Netzsch) according to ASTM D3418-82 and ASTM D3417-83 procedures in an argon atmosphere. Samples were examined by means of the melting—crystallization—melting program in the temperature range 30–210°C at a rate of 10°C/min. The melting temperature (T_m) was found from data of the second melting.

Deconvolution of MWD curves was performed as described in Refs. [14,15].

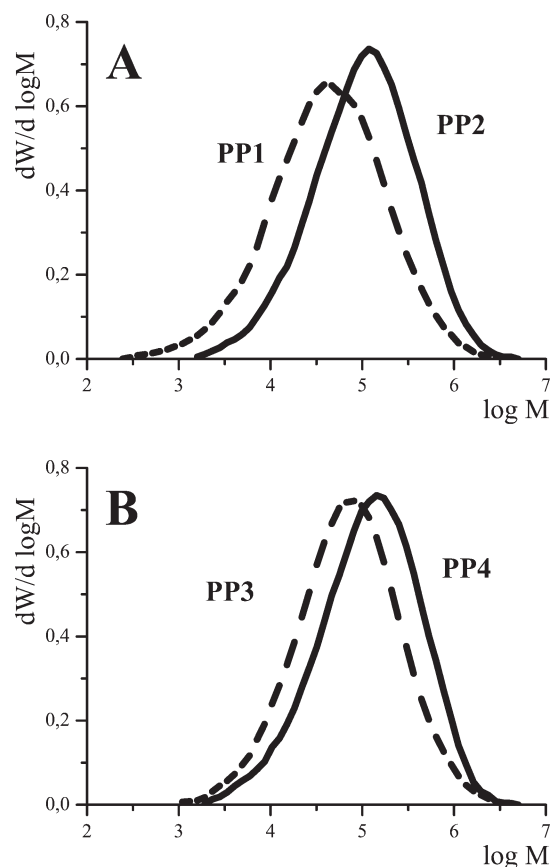


Figure 1. MWD curves of PP produced over TMC-PE (curves 1, 2) and TMC-PP (curves 3, 4). Curve numbers correspond to the numbers in Table I.

RESULTS AND DISCUSSION

Propylene Polymerization

The data on activity of TMC-PE and TMC-PP catalysts, content of atactic polypropylene (APP) fraction (which is soluble in heptane during polymerization) and molecular weight characteristics of PP produced over TMCs of different composition are listed in Table I. The MWD curves for PP1-PP4 samples are displayed in Figure 1.

In the absence of internal and external donors, the TMC-PE catalyst (sample PP1) gave rise to PP with a high content of APP fraction (35.1 %) and the lowest M_w value, the M_w/M_n value is 7.5. When the external donor was introduced, the content of APP fraction decreased abruptly (to 4.6%) and the M_w value of the resulting PP increased. This was accompanied by narrowing of the MWD value ($M_w/M_n = 5.0$) for sample PP2.

Furthermore, the presence of the internal donor in the TMC-PP catalyst decreased the content of APP fraction as compared to sample PP1 (to 10.5%), increased M_w and gave a narrower MWD ($M_w/M_n = 5.0$) (sample PP3, Table I). When the external donor was added in polymerization over the catalyst comprising the internal donor (sample PP4, Table I), the content of APP fraction strongly diminished (to 1.2%) and the M_w of the resulting PP increased, the MWD width remained virtually constant. Thus, the introduction of the external donor to both

TMC-PE and TMC-PP catalysts increased the M_w of PP and substantially reduced the content of APP fraction. PP produced over the catalysts of different composition either in the presence or in the absence of the external donor had close values of M_w/M_n ($M_w/M_n = 4.7$ – 5.2 , samples PP2–PP4). The only exception was sample PP1, which was produced over TMC-PE without internal and external donor ($M_w/M_n = 7.5$).

In theory, each type of active site produces polymer with an MWD that can be described by Flory's most probable distribution. Using the resolution technique,^{14,15} the average molecular weight of polymer produced at each site, as well as the mass fraction of polymer produced at each site, were determined. The MWD curves for samples PP1, PP2, PP3, and PP4 produced over catalysts TMC-PE and TMC-PP (Figure 1) were deconvoluted into Flory components. Results of deconvolution are presented in Table II. All MWD curves for these samples are well described by four Flory components. When the internal donor presented in the catalyst composition (PP1 and PP3 samples, Table II), M_w of low-molecular components I and II increased by a factor of 2–2.5 and M_w of high-molecular components III–IV by a factor of 1.5; the contributions of these components remained virtually unchanged. The introduction of the external donor to TMC-PE without the internal donor (PP1 and PP2, Table II) caused a threefold increase in the M_w of components I–III, and a twofold increase in the M_w of component IV. Meanwhile, the introduction of the external donor to the TMC-PP catalyst containing the internal donor (samples PP3 and PP4, Table II) exerted virtually no effect on M_w of individual Flory components, but led to redistribution of their contributions. A decrease in contribution of low molecular weight components I and II and an increase in contribution of high molecular weight components III and IV were observed, which resulted in an increase in the M_w value of the total polymer. Thus, when the external donor was added to polymerization over TMC-PP catalyst, the portion of active sites producing low molecular weight PP decreased and the portion of active sites producing high molecular weight PP increased.

Table I and Figure 2 show the data on the temperatures of second melting and DSC curves for the produced PP samples. Two peaks are observed on the DSC curve for PP1 and PP3 samples produced over TMC-PP and TMC-PE catalysts in the absence of external donor. In both cases, the introduction of external donor led to disappearance of the low-temperature peaks at 152–155°C (samples PP2 and PP4). Thus, the TMC-PE and TMC-PP catalysts contain active sites with low and high stereospecificity. After external donor was introduced, it was mainly the active sites with increased stereospecificity that remained in the both catalysts. Highly stereospecific active sites in the TMC-PP catalyst with internal donor provided the formation of PP with a higher stereoregularity (samples PP3 and PP4, $T_m = 163^\circ\text{C}$) as compared to samples PP1 and PP2 produced over TMC-PE catalyst in the absence of internal donor ($T_m = 160.5^\circ\text{C}$).

As seen from the molecular weight characteristics of PP1 and PP3, polymers produced over TMC-PE and TMC-PP, the introduction of internal donor to the catalyst composition increases the molecular weight and decreases the M_w/M_n value of PP.

Table II. Results of Deconvolution of MWD Curves into Flory Components for PP Produced Over TMC-PE and TMC-PP Catalyst Without and with External Donor

ID	-		-		+		+	
	PP1 ^a		PP2 ^a		PP3 ^a		PP4 ^a	
ED	-		+		-		+	
Flory component	%	$M_w (\times 10^{-3})$	%	$M_w (\times 10^{-3})$	%	$M_w (\times 10^{-3})$	%	$M_w (\times 10^{-3})$
I	11.2	7.5	13.8	23	11.7	19	7.8	19
II	34.1	27	39.5	86	37.1	57	25.3	64
III	37.9	90	34.3	250	37.8	155	42.0	175
IV	15.4	330	12.6	690	13.5	510	24.5	515
Total polymer ^b	$M_w (\times 10^{-3})$		210		145		215	
	Mw/Mn		4.8		4.2		4.3	

^a Curve numbers correspond to the numbers in Table I.

^b Data for the sum of Flory components.

The increase in polymer M_w is caused by increasing the M_w values for all Flory components. This may occur due to the changes in reactivity of active sites in the chain propagation and transfer reactions. At polymerization over TMC-PP catalyst that has the internal donor already, the introduction of external donor increases the molecular weight of PP due to increasing the contribution (portion) of high molecular weight Flory components, while the molecular weights of all components (Table II) remain constant. Thus, the introduction of external donor does not change reactivity of active sites in chain propagation and chain transfer reactions with hydrogen, but increases the portion of active sites producing high molecular weight PP. The close Mw/Mn values for polymers PP2, PP3, and PP4 are indicative of the similar distribution of active sites in terms of their reactivity in the reactions determining the molecular weight of these polymers.

Ethylene Polymerization

As shown in Ref. [16], some catalysts that are highly active in propylene polymerization (the polymerization rate of (1–2 kg PP)/(g_{cat} × h × bar)) exhibit a very low activity in ethylene polymerization (~0.1 kg PE/(g_{cat} × h × bar)). The low rate in ethylene polymerization was attributed to the specific morphology of these catalysts, which hinders efficient fragmentation of the catalyst particles during polymerization of a highly reactive monomer (ethylene). This leads to the emergence of diffusion limitations and a dramatic drop in activity toward ethylene polymerization over these catalysts. Prepolymerization with pro-

pylene (a preliminary polymerization under mild conditions) makes it possible to eliminate the diffusion limitations and abruptly increase the catalyst activity in ethylene polymerization.¹⁶ This is why the ethylene polymerization over TMC-PP catalyst was preceded by prepolymerization with propylene according to the method reported in Ref. [16] (the yield of PP = 100 g/g_{cat} at the prepolymerization stage). The contribution of PP produced over prepolymerization step to polyethylene was neglected (<3%).

Table III lists the data on catalyst activity and molecular weight characteristics of PE produced over the catalysts of different composition. The TMC-PE catalyst without the internal donor yields PE with $M_w = 230 \times 10^3$ g/mol and $M_w/M_n = 5.0$ (sample PE1). The external donor introduced to the catalyst has virtually no effect on the M_w and MWD values for the resulting PE (samples PE1 and PE2). The introduction of internal donor to the catalyst composition (TMC-PP) only slightly affects the M_w and MWD values of the produced PE (samples PE1 and PE3). However, the introduction of external donor to the TMC-PP catalyst already containing the internal donor leads to a substantial decrease in M_w of PE, the M_w/M_n remaining virtually unchanged (samples PE3 and PE4, Table III). Figure 3 displays the MWD curves for samples PE3 and PE4 produced over the TMC-PP catalyst. One can see that the introduction of the external donor to TMC-PP catalyst does not change the shape of MWD curve, but shifts it towards the low molecular weight region. The data obtained at deconvolution of MWD curves for

Table III. Molecular Weight Characteristics of PE Produced Over TMC with Different Composition (TMC-PE and TMC-PP Catalysts)

Catalyst ^a	Polymer No.	Al/PTMS	Yield (kg PE/g _{cat})	$M_n (\times 10^{-3})$	$M_w (\times 10^{-3})$	M_w/M_n
TMC-PE	PE1	-	7.7	46	230	5.0
	PE2	20	5.1	49	240	4.9
TMC-PP ^b	PE3	-	10	55	235	4.3
	PE4	20	3.1	27	130	4.8

^a TMC-PE does not contain an ID, TMC-PP contains DBPh as an ID.

^b Prepolymerization with C₃H₆ (see Experimental Part).

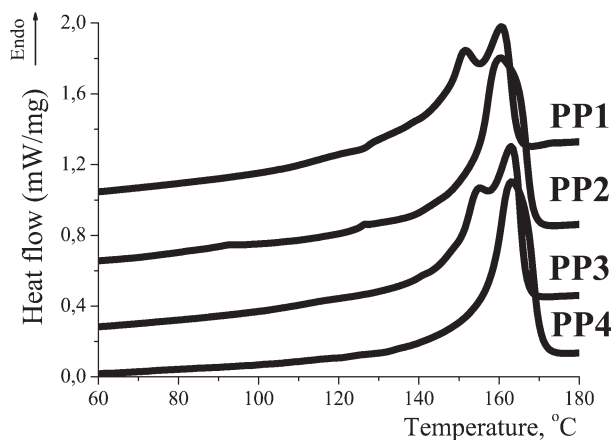


Figure 2. Comparison of second melting DSC curves for PP1 and PP2, produced over TMC-PE catalyst, and PP3 and PP4, produced over TMC-PP catalyst. Curve numbers correspond to the numbers in Table I.

samples PE3 and PE4 into individual Flory components (Table IV) indicate that these curves are well described by four Flory components. The introduction of the external donor (sample PE4) produces a substantial (two- or threefold) decrease in the molecular weight of all components and insignificant changes in the fractions of individual components.

COMPARISON OF KINETIC PARAMETERS IN THE ETHYLENE AND PROPYLENE POLYMERIZATION OVER TMCs OF DIFFERENT COMPOSITION

Effect of Catalyst Composition on the Molecular Weight Characteristics of Polymers in Ethylene and Propylene Polymerization

Now let us consider the data concerning the effect of the internal and the external donor on polymerization degree of PE and PP produced over the catalysts of different composition. The data in Tables I and III show that the introduction of the internal donor into the composition of TMCs (comparison of the TMC-PE and TMC-PP catalysts) slightly increases the M_w value in the case of propylene polymerization (PP1 and PP3 samples, Table I) and slightly affects it in the case of ethylene polymerization (PE1 and PE3 samples, Table III). The effect of the external donor on the molecular weight of polymer depends on the catalyst composition. If catalyst does not comprise an internal donor, the introduction of the external donor increases the molecular weight in the case of propylene polymerization (PP1 and PP2 samples, Table I), but has virtually no effect on the molecular weight in the case of ethylene polymerization (PE1 and PE2 samples, Table III). In the case of TMC-PP catalyst comprising the internal donor, the introduction of the external donor has different effects on the molecular weight of PE and PP. During propylene polymerization over this catalyst, the introduction of ED increases molecular weight of the polymer (samples PP3 and PP4, Table I). Deconvolution of MWD curves into Flory components for these polymers (Table II) shows that individual components of the polymers have close molecular weights and the average molecular weight of PP4 increases due to an increase in the fraction of high-molecular weight components III and IV as compared to sample PP3. In the case of ethylene polymerization over TMC-PP

catalyst, the introduction of ED noticeably decreases the polymer molecular weight (samples PE3 and PE4, Table III). Deconvolution of MWD curves for these polymers indicates that this effect is caused by a decrease in molecular weights of all components by a factor of 2–2.5 (Table IV).

Effect of Catalyst Composition on the Kinetic Parameters in Ethylene and Propylene Polymerization

Table V lists the data on the polymerization degree (P_n and P_w) values of PP samples that do not contain the APP fraction soluble in heptane during polymerization as well as the data on PE samples. One can see that ethylene and propylene polymerization over the catalysts of different composition gives rise to polymers with close values of P_w/P_n (4.4–5.1). Deconvolution of MWD curves into Flory components shows that MWD curves are described by four Flory components in all cases (Tables II, IV). This suggests that ethylene and propylene polymerization over the tested catalysts involves a similar set of active sites (four types of active sites) differing in their reactivity toward the reactions of polymer chain propagation and transfer with hydrogen, which determine under the given conditions the molecular weight of resulting polymers.

Comparative data on the catalyst activity in ethylene and propylene polymerization related to a similar concentration of the monomer (1 mol/L) and data on the polymerization degrees of PE and PP produced over the catalysts of different composition are listed in Table V. As seen from this Table, activity of the catalysts strongly depends on their composition; however, in all cases, the rate of ethylene polymerization substantially exceeds the rate of propylene polymerization for the catalysts of identical composition. For TMC-PE and TMC-PP catalysts, this ratio ranges from 7 to 9. This value qualitatively corresponds to the ratio of rate constants for chain propagation reactions in polymerization of ethylene (1.2×10^4 L/(mol s)) and propylene ($(0.5\text{--}2.5) \times 10^3$ L/(mol s)) known from the literature.^{16–19} This ratio may indicate that close numbers of active sites are involved in ethylene and propylene polymerization over similar catalysts. The only exception is the TMC-PE + ED catalyst for which this ratio is 18.

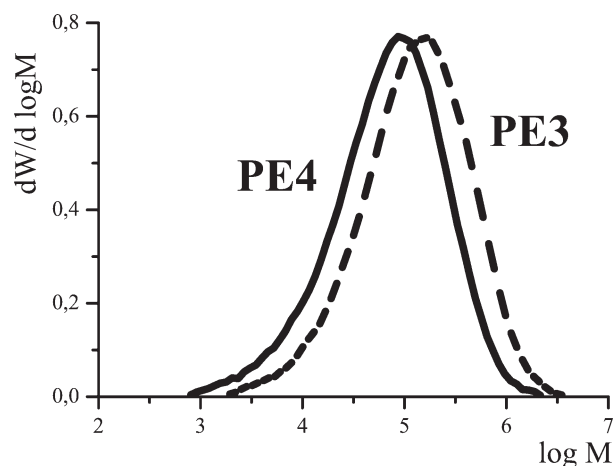


Figure 3. MWD curves of PE produced over TMC-PP without ED (curve 3) and with ED (curve 4). Curve numbers correspond to the numbers in Table III.

Table IV. Results of Deconvolution of MWD Curves Into Flory Components for PE Produced Over TMC-PP Catalyst Without and with External Donor

ED Flory component	− PE3 ^a		+ PE4 ^a	
	%	$M_w (\times 10^{-3})$	%	$M_w (\times 10^{-3})$
I	8.1	23	6.0	8.2
II	33.8	84	22.5	34
III	40.0	230	47.1	100
IV	17.7	580	23.8	290
Total polymer ^b	$M_w (\times 10^{-3})$	220		122
	M_w/M_n	4.0		4.4

^aCurve numbers correspond to the numbers in Table III.

^bData for the sum of Flory components.

Hydrogen is known to be the most efficient chain transfer agent in polymerization of olefins over ZN catalysts. Rate constants of chain transfer reactions, in particular chain transfer with hydrogen, are usually calculated from data on the effect of transfer agent concentration on the polymerization degree of propylene.

According to Ref. [13] the degree of polymerization (P_n) is determined by the ratio between polymer chain propagation rate (V_p) and the sum of transfer reaction rates (ΣV_{tr}):

$$\frac{1}{P_n} = \frac{\sum V_{tr}}{V_p} \quad (1)$$

The effect of the hydrogen on polymerization degree of the polymer is described by the following equation:

$$\frac{1}{P_n} - \frac{1}{P_{n0}} = \frac{k_{tr}^H C_H^n}{k_p C_M} \quad (2)$$

where P_{n0} polymerization degree of the polymer produced under polymerization in the absence of hydrogen; k_{tr}^H is the rate constant of chain transfer reaction with hydrogen; C_M and C_H are the concentrations of monomer and hydrogen, respectively; n rate order of chain transfer reaction with hydrogen.

Ethylene polymerization over TMC-PE catalyst performed under the conditions of this article but in the absence of hydrogen gives rise to PE with the average viscosity molecular weight $M_w = 1.8 \times 10^6$ g/mol.²⁰ The introduction of hydrogen (25 vol% in the reactor gas phase) sharply decreases the molecular weight to $M_w = 230 \times 10^3$ g/mol (Table III, sample PE1). Thus, under the conditions of ethylene polymerization used in this article, the reaction of chain transfer with hydrogen dominates over other chain transfer reactions, and expression (2) can be written in a simplified form as:

$$\frac{1}{P_n} \approx \frac{k_{tr}^H C_H}{k_p C_M} \quad (3)$$

where $n = 1$ for ethylene polymerization.^{11,20}

In the case of propylene polymerization, the difference between values of polymerization degree for PP samples obtained via polymerization without hydrogen and P_n values for PP obtained via polymerization with hydrogen is not so big (e.g., for PP4 value $P_{n0} = 2300$ in comparison with $P_n = 1160$). So, in this case of propylene polymerization it is not correct to use this simplified method (eq. (3)) for calculation of k_{tr}^H/k_p values.

Table V. Comparative Data on the Polymerization Rate and Polymerization Degree (P_n and P_w) of PP and PE and Constants of Chain Transfer Reaction with Hydrogen at Ethylene Polymerization^a

Catalyst	Monomer	R_p^b (kg polymer/ $g_{Ti} \times h \times C_{Cz}$)	P_n	P_w	P_w/P_n	k_{tr}^H/k_p
TMC-PE	Propylene (PP1) ^c	110	750	3400	4.5	–
	Ethylene (PE1)	920	1640	8400	5.1	0.016
TMC-PE + ED	Propylene (PP2) ^c	30	1000	5000	5.0	–
	Ethylene (PE2)	560	1750	8570	4.9	0.015
TMC-PP	Propylene (PP3) ^c	240	855	3800	4.5	–
	Ethylene (PE3)	2150	1930	8500	4.4	0.013
TMC-PP+ED	Propylene (PP4) ^c	340	1160	5520	4.8	–
	Ethylene (PE4)	2150	950	4800	5.1	0.027

^a $[Cz]/[H_2] = 1400$ for propylene polymerization and $[Cz]/[H_2] = 26$ for ethylene polymerization

^b R_p maximum polymerization rate

^cData for PP powder which does not contain fraction soluble in polymerization heptane (70°C).

Table V lists the k_{tr}^H/k_p values calculated by equation (3) for ethylene polymerization over the catalysts of different composition. In the case of ethylene polymerization over TMC-PE, TMC-PE + ED and TMC-PP k_{tr}^H/k_p value is independent of the catalyst composition ($k_{tr}^H/k_p = 0.013\text{--}0.016$). In the case of TMC-PP + ED catalyst k_{tr}^H/k_p value increases to 0.027. The literature¹¹ provides the k_{tr}^H/k_p values calculated for polymerization of ethylene from the data on the effect of hydrogen concentration on the polymerization degree of polymer for the TMC. The k_{tr}^H/k_p ratio is 0.008 for ethylene polymerization over this catalyst (this value is close to our data for TMC-PE, TMC-PE+ED).

CONCLUSIONS

1. The activity of catalysts in ethylene and propylene polymerization strongly depends on their composition. However, in all cases, the polymerization rate related to a similar concentration of monomer for catalysts of identical composition is much higher for ethylene polymerization as compared to that for propylene polymerization. On the qualitative level, the rate ratio corresponds to the ratio between the rate constants for chain propagation reactions in ethylene and propylene polymerization.
2. Ethylene and propylene polymerization over the catalysts of different composition produces polymers with $M_w/M_n = 4.4\text{--}7.5$. According to deconvolution of MWD curves into Flory components, these catalysts contain four types of active sites differing in terms of their reactivity in polymer chain propagation and transfer reactions in ethylene and propylene polymerization.
3. The introduction of the internal donor to the catalyst composition increases the molecular weight of polymers in propylene polymerization, but exerts no significant effect on the polymer M_w in ethylene polymerization. The M_w/M_n value decreases for propylene polymerization and does not change in the case of ethylene polymerization.
4. The effect of external donor introduced to catalytic system on the polymer molecular weight depends on catalyst composition. In the case of a catalyst without internal donor, the introduction of external donor affects both the PP and PE molecular weights. In the case of catalyst with the internal donor, the introduction of the external donor increases the molecular weight of PP and substantially decreases that of PE. Deconvolution of MWD curves into Flory components shows that PP molecular weight increases due to increasing the contribution of high molecular weight components to the average molecular weight without any noticeable changes in molecular weight of individual components. In the case of ethylene polymerization, PE molecular weight decreases due to a considerable (2–2.5-fold) decrease in molecular weight of all individual Flory components.
5. A simplified method was proposed for calculating the ratio between the rate constants for polymer chain transfer with hydrogen (k_{tr}^H) and chain propagation (k_p) from the data on polymerization degree of the polymer produced under con-

ditions when chain transfer with hydrogen dominates over other chain transfer reactions. This method was used to calculate the k_{tr}^H/k_p values for ethylene polymerization over the catalysts of different composition.

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