

Copolymerization of Ethylene with α -Olefins Over Supported Titanium–Magnesium Catalysts. I. Effect of Polymerization Duration on Comonomer Content and the Molecular Weight Distribution of Copolymers

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ABSTRACT: The data on the effect of polymerization duration on molecular weight (MW), molecular weight distribution (MWD), and content of α -olefin were obtained for ethylene/1-hexene copolymers produced on a supported titanium–magnesium catalyst (TMC) upon polymerization in the absence and presence of hydrogen. An increase in MW, narrowing of the MWD, and a decrease in 1-hexene content in the copolymer takes place with increasing polymerization duration. It was shown by molecular weight fractionation of copolymers obtained at different polymerization duration followed by analysis of narrow fractions to determine the butyl branching content that the decrease comonomer content in copolymers with increasing polymerization duration is accounted for by the decrease in the share of low molecular weight fractions

with an increased butyl branch content. These data, in combination with the data concerning the narrowing of the MWD of copolymers and the decrease in activity with polymerization duration allow arriving at conclusion that active sites producing low molecular weight polymer with an increased butyl branching content is predominantly deactivated with polymerization. Active sites producing high molecular weight polymer has a low ability to copolymerize ethylene with α -olefins; however, these sites show higher stability during copolymerization. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 125: 2034–2041, 2012

Key words: Ziegler-Natta polymerization; polyethylene (PE); molecular weight distribution/molar mass distribution; copolymerization

INTRODUCTION

Copolymers of ethylene and α -olefins produced over Ziegler-Natta catalysts are finding wide practical application. Various aspects of copolymerization processes over these catalysts, including analysis of kinetic parameters of copolymerization and ascertaining the relationship between catalyst composition and the molecular structure of the resulting copolymers have been studied in numerous works.^{1–12} However, many questions regarding copolymerization of ethylene and α -olefins have remained ambiguous. A number of unexpected effects were revealed for catalytic copolymerization processes; those effects have not been convincingly interpreted yet. Among them is the effect of considerable increase in activity in the case of ethylene/ α -olefins copolymerization as compared with ethylene homopolymerization.^{2–6,8,10,12} The influence

of polymerization duration (polymer yield) on copolymer composition (α -olefin content in the copolymer) at a constant ethylene/ α -olefin ratio upon polymerization over Ziegler-Natta catalysts was another unexpected result.^{6–8}

The influence of the reaction duration upon ethylene/1-butene copolymerization on the titanium–magnesium catalyst of composition $\text{TiCl}_4/\text{MgCl}_2$ was studied in Refs. 6 and 7. It was found that a small increase in MW and narrowing of the MWD, as well as a decrease in 1-butene content in the copolymer, occur with the reaction duration increasing from 5 to 40 min. The results of deconvolution of MWD curves into Flory components and deconvolution of TREF curves for ethylene/1-butene copolymers obtained at different polymerization times allow one to assume that several types of active sites differing in their copolymerization ability are present in the TMC. The authors^{6,7} believe that different types of active sites in the reactions of ethylene/ α -olefin copolymerization are formed and terminated at a different rate. High molecular weight sites, which are inefficient in ethylene/ α -olefin copolymerization and do not polymerize α -olefins, are formed at a slower rate. However, they possess a higher

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kinetic stability. Low molecular weight active sites are more efficient in ethylene/ α -olefin copolymerization and are activated in the presence of α -olefins; however, they are quickly deactivated. As a result, the copolymer with a decreased content of 1-butene is formed at long polymerization duration.

The influence of polymerization duration (10 and 60 min) upon ethylene/1-hexene copolymerization in the presence of hydrogen on two TMC modifications (catalyst $\text{MgCl}_2\text{-TiCl}_4\text{-Al(OR)}_3$ supported over SiO_2 and catalyst $\text{MgCl}_2\text{-TiCl}_4$ prepared by precipitation method) was studied in Ref. 8. With the reaction duration increasing from 10 to 60 min, the increase in MW, narrowing of the MWD, and the considerable decrease in 1-hexene content in the copolymer were observed.

A limited number of studies has been published^{13,14} containing the data on MW and the MWD of ethylene/ α -olefin copolymers produced over supported titanium–magnesium catalysts in the absence of hydrogen. The introduction of hydrogen results in a considerable decrease in MW and a slight broadening of the MWD of the resulting copolymers. However in this work polymerization duration effect was not investigated.

Earlier,¹⁵ when studying ethylene polymerization over TMC in the absence of hydrogen, we demonstrated that the increase in MW and narrowing of the MWD of the produced polymer occur with reaction duration increasing from 2 to 60 min. It was shown that the ratio between the rate of chain transfer to cocatalyst and that of chain transfer to monomer changes; the contribution of the reaction of chain transfer to monomer increasing with polymerization duration. Taking these data into account, it is of interest to investigate the effect of polymerization duration on composition and molecular-weight characteristics of the copolymers produced by copolymerization in the absence and presence of hydrogen.

In this work, we studied the effect of the reaction duration on the yield, MW, MWD, and composition of copolymers produced upon ethylene/1-hexene copolymerization over a titanium–magnesium catalyst (TMC) in the absence and presence of hydrogen. The effect of copolymerization duration on the comonomer distribution in copolymers for different copolymerization conditions (in the presence and absence of hydrogen, and for different 1-hexene/ethylene molar ratios) was studied by preparative fractionation into narrow fractions followed by the analysis of composition of these fractions and deconvolution of MWD curves into Flory components.

EXPERIMENTAL

Catalyst TMC (2.6 wt % of Ti) was synthesized via a procedure described elsewhere¹⁶ by supporting tita-

nium tetrachloride on the support (with the average particle size of 10 μm) prepared by interaction of a solution of organomagnesium compound $\text{Mg}_3\text{Ph}_4\text{Cl}_2$ in dibutyl ether and PhCl with the mixture of PhSiCl_3 and Si(OEt)_4 .

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); triethylaluminum (AlEt_3) was used as a cocatalyst, catalyst concentration was 0.016–0.032 g/L. The agents were added in the following sequence: heptane, 1-hexene, cocatalyst, hydrogen (if used), ethylene, catalyst. Comonomer was introduced singly at the beginning of the experiment. The weighed portion of the catalyst was selected in such a manner that the copolymer yield was limited in order to prevent the changes of 1-hexene concentration over 15 wt %.

Concentrations of ethylene and hydrogen were calculated from their partial pressures with the Henry law $C = K_H P$, where C is ethylene or hydrogen concentration (mol/L), K_H is the Henry constant (mol/(L \times bar)), P is ethylene or hydrogen pressure (bar). The values of the Henry constants at 80°C are as follows: for ethylene $K_H = 0.071$ M/bar¹⁷, for hydrogen 0.011 M/bar.¹⁸

MWD measurements were made on a high-temperature Waters 150C gel permeation chromatograph combined with a Viscotek 100 differential viscometer, at 140°C in 1,2,4-trichlorobenzene at a flow rate of 1 mL/min. The polymers were analyzed using four TSK columns (GMHXL-HT, Tosoh Corp.). The instrument was calibrated using polyethylene and polystyrene standards with narrow MWD.

Deconvolution of MWD curves was performed as described in Refs. 4 and 19.

The comonomer distribution in copolymers was obtained by fractionating copolymers⁴ into narrow fractions on a PolymerChar PREP mc2 fractionation instrument. Next, we measured the MWD and comonomer content in each fraction by IR spectroscopy on a Shimadzu FTIR 8400 S spectrometer or by NMR spectroscopy^{20,21} on a Bruker MSL-400 spectrometer.

RESULTS AND DISCUSSION

It was shown earlier¹⁵ that PE with MW less than 1×10^6 g/mol is produced over the $\text{TiCl}_4/\text{MgCl}_2(\text{OR})_x/\text{AlEt}_3$ catalytic system, which makes it possible to reliably measure the MWD of the polymer by GPC. We used this catalytic system for the more detailed investigation of the effect of reaction duration on MW and MWD, as well as composition of ethylene/1-hexene copolymers produced in the absence of hydrogen.

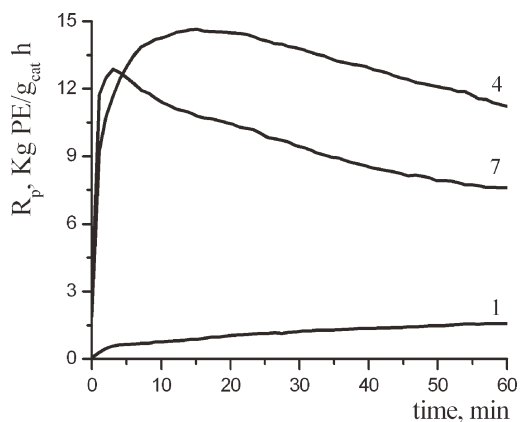


Figure 1 Kinetic curves of ethylene homopolymerization (Curve 1) and ethylene/1-hexene copolymerization over TMC: Curves 4 and 7 – copolymerization in the absence of hydrogen. Curve numbers correspond to the numbers of experiments in Table I.

The effect of reaction duration on copolymer composition upon ethylene/1-hexene copolymerization in the absence of hydrogen

Figure 1 shows the kinetic curves of ethylene homopolymerization and ethylene/1-hexene copolymerization over TMC. It can be seen that activity of TMC in the case of ethylene/1-hexene copolymerization is considerably higher than that in the case of ethylene homopolymerization. The shape of the kinetic curve changes, as well. In the copolymerization process, the maximum activity is attained during the first 15 min of the reaction, followed by the observable decrease in activity. The increase in activity upon copolymerization over Ti-based supported catalysts as compared with that upon homopolymerization was previously noted in a number of studies.^{1-6,8}

Table I summarizes the data on the effect of the reaction duration on MW, MWD, and composition of the produced copolymers. The increase in the reaction duration from 5 to 60 min (exps. 2-4, Table I)

upon ethylene/1-hexene copolymerization results in growth of MW and narrowing of the MWD of the resulting copolymers. It should be noted that we observed earlier the similar increase in MW and narrowing of the MWD with increasing polymerization duration upon ethylene homopolymerization over the same catalyst.¹⁵ The polydispersity of copolymers produced in exps. 4 and 5 (the copolymers produced during 60 min) is close to that of the homopolymer produced during the same time (exp. 1). The lower molecular weight of copolymers (exps. 4 and 5) as compared with that of homopolymer (exp. 1) is accounted for by the participation of the comonomer in the chain transfer reaction.

The increase in copolymerization duration from 5-15 to 60 min results in a noticeable reduction of 1-hexene content in the copolymer. The similar data on variation of MW, MWD, and copolymer composition with polymerization duration were obtained in the experiments carried out at a higher concentration of 1-hexene ($C_6/C_2 = 4.6$, exps. 6 and 7, Table I).

Figure 2 shows the MWD curves of copolymers produced after different polymerization times. It can be seen that with increasing polymerization duration, the major peak shifts into the high-molecular weight region. MWD curves of PE and copolymers obtained in a 60-min polymerization differ merely by the fact that there is no shoulder in the high molecular weight region for copolymers [Figs. 2(A,B), Curves 1, 5, and 7].

When increasing the reaction duration from 5 to 60 min, 1-hexene content in the resulting copolymers decreases (the amount of incorporated 1-hexene drops from 2.5 to 1.0 mol % (Table I, exps. 2 and 4)). In the experiment 4, 1-hexene consumption during 60 min was no higher than 15%. This result can not be accounted for the decrease in 1-hexene content in exp. 4 as compared with exp. 2. We carried out an additional experiment (exp. 5, Table I), where 1-hexene concentration was maintained constant (by feeding the calculated amount of 1-hexene into the

TABLE I
Data on Effect of Polymerization Duration on the Molecular Weight and MWD of Copolymers and Content of 1-Hexene in Copolymers

Exp No. ^a	Reaction time, min	C ₆ /C ₂ ^b	Yield, kg PE/g _{cat}	$M_n \times 10^{-3}$	$M_w \times 10^{-3}$	$M_z \times 10^{-3}$	M_w/M_n	1-hexene content in copolymer, mol %
1	60	–	1.22	76	690	3700	9.1	–
2	5	2.3	1.1	14	180	1200	12.9	2.5
3	15		3.3	21	260	1400	12.4	2.1
4	60		12.5	59	540	2200	9.2	1.0
5 ^(c)	60		11.8	57	480	1800	8.4	1.2
6	15	4.6	3.2	14	230	1500	16.4	3.4
7	60		8.7	49	430	1900	8.8	2.3

^a Polymerization conditions: ethylene pressure = 2 bar, 80°C, [TEA] = 2.6 mmol/L.

^b Molar ratio of 1-hexene/ethylene upon polymerization.

^c Experiment with constant 1-hexene concentration (constant 1-hexene concentration was maintained by introducing additional 1-hexene during the reaction).

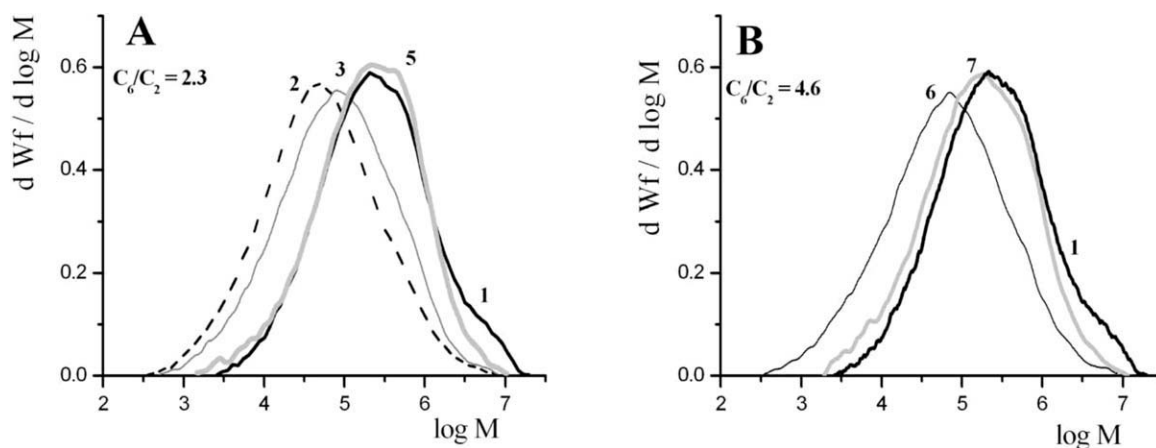


Figure 2 MWD curves of ethylene/1-hexene copolymers produced at different polymerization duration in the absence of hydrogen (curve 1 – homopolymer). (A) Curves 2, 3, 5: copolymerization at $C_6/C_2 = 2.3$ (molar); (B) Curves 6, 7: copolymerization at $C_6/C_2 = 4.6$ (molar). Curve numbers correspond to the experiment numbers in Table I.

reaction mixture). The increase in MW, narrowing of the MWD, and the lower 1-hexene content (as compared with the copolymers produced during 5–15 min) was also observed for the copolymer produced upon constant 1-hexene concentration during 60 min (exp. 5, Table I).

The results of deconvolution of the MWD curves of copolymers produced at different polymerization times into Flory components are summarized in Table II. The MWD curves of the copolymers produced after 60 min (exps. 5 and 7, Table II) can be well described using five Flory components. Meanwhile, six Flory components are required to provide correct deconvolution of MWD curves of copolymers obtained after 15 min (exps. 3 and 6, Table II). When copolymerization duration is increased from 15 to 60 min, in both cases with C_6/C_2 ratios being 2.3 (exps. 3 and 5, Table II) and 4.6 (exps. 6 and 7, Table II), the low molecular weight component I disappeared, the

contribution of Components II and III decreases, and the contribution of high molecular weight Components IV and VI grows. It follows from these results that the share of active sites producing low molecular weight polymer is reduced and the share of ASs producing high molecular weight polymer is increased with increasing polymerization duration.

Copolymers produced at different polymerization times were separated into narrow fractions on the basis of their molecular weights, followed by the analysis of composition of these fractions by GPC, as well as IR and ^{13}C -NMR spectroscopy. Figure 3(A) shows the resulting data on comonomer distribution in copolymers produced at a C_6/C_2 ratio = 2.3 after 15- and 60-min polymerization. Figure 3(B) represents these data for copolymers produced at different polymerization times at a C_6/C_2 ratio = 4.6. In both cases, copolymers produced after a short polymerization time are characterized by an increased content of low

TABLE II
Results of Deconvolution of MWD Curves into Flory Components For Copolymers Obtained at Different Polymerization Duration

C ₆ /C ₂ ^a	2.3				4.6			
	15		60		15		60	
Reaction time, min	15		60		15		60	
Exp No (Table I)	3		5		6		7	
Flory component	%	$M_w \times 10^{-3}$	%	$M_w \times 10^{-3}$	%	$M_w \times 10^{-3}$	%	$M_w \times 10^{-3}$
I	6.2	5.2			6.8	3.7		
II	15.9	19	4.3	12	14.7	14	5.5	11
III	25.9	60	14.3	50	26.2	45	17.7	45
IV	26.4	160	29.7	140	27.3	130	32.3	140
V	20.6	510	38.5	490	18.8	430	34.2	500
VI	4.9	1700	12.7	1600	5.9	1500	10.2	1800
Sum ^b								
$M_w \times 10^{-3}$	250		420		220		410	
M_w/M_n	12		7.6		15		8.6	

^a Molar ratio of 1-hexene/ethylene upon polymerization.

^b MWD of the sum of Flory components.

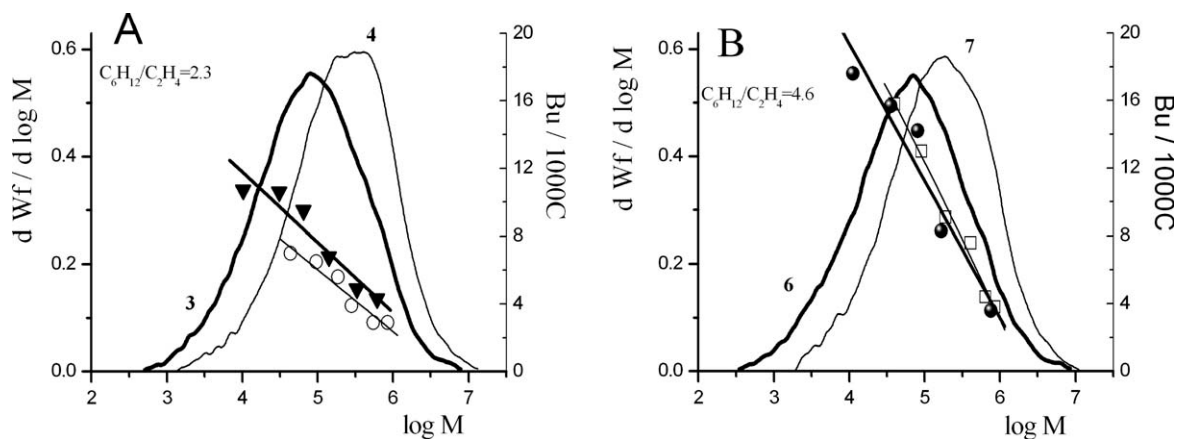


Figure 3 MWD curves and SCB profiles for copolymers produced at different polymerization duration and different ratios C₆/C₂: A: C₆/C₂=2.3, ▼-exp. 3 ($\tau_p = 15$ min), ○-exp. 4 ($\tau_p = 60$ min); B: C₆/C₂=4.6, ●-exp. 6 ($\tau_p = 15$ min), □-exp. 7 ($\tau_p = 60$ min). Numbers correspond to the experiment numbers in Table I.

molecular weight fraction (Flory Components I and II in Table II, exps. 3 and 6), which is equal to 22.1 and 21.5%. Therefore, these copolymers have the broadened MWD ($M_w/M_n = 12.4$ and 16.4, Table I, exps. 3 and 6). Copolymers produced after a long polymerization duration (60 min) have a considerably lower content of low molecular weight fraction II (4.3 and 5.5%, Table II, exps. 5 and 7) and a more narrow MWD ($M_w/M_n = 8.4$ and 8.8). As can be seen from the data given in Figure 3, low molecular weight fractions contain a considerably larger amount of butyl branches as compared with that in high molecular weight fractions. With provision for the increased content of low molecular weight fractions in copolymers produced at short polymerization duration (15 min), these results can be used to interpret the considerably higher 1-hexene content (by a factor of 1.5–2) in copolymers produced at short polymerization duration (5–15 min) as compared with those produced at a longer polymerization duration (60 min).

Figure 4(A) shows the MWD curves and the data on branching content in narrow fractions for the copoly-

mers produced at different 1-hexene concentrations at polymerization for 15 min. It can be seen that it was mainly active sites producing low molecular weight polymer that responded to the twofold increase in 1-hexene concentration (branching content in fraction I increased by a factor of 1.7). The branching content in the high molecular weight part remained virtually the same. The similar data were also obtained for copolymers produced at different concentrations of 1-hexene in 60-min polymerization [Fig. 4(B)]. An increase in 1-hexene concentration results in a small decrease in MW and a slight narrowing of the MWD. “Low molecular weight” active sites are also the ones that predominantly respond to the twofold increase in 1-hexene concentration (branching content in fraction I increases by a factor of 2.5).

Thus, the data obtained show that the content of butyl branches in copolymers decreases with increasing polymerization duration due to the decrease in the fraction of low molecular weight polymer containing an increased number of butyl branches (Table II and Fig. 3). These results can be

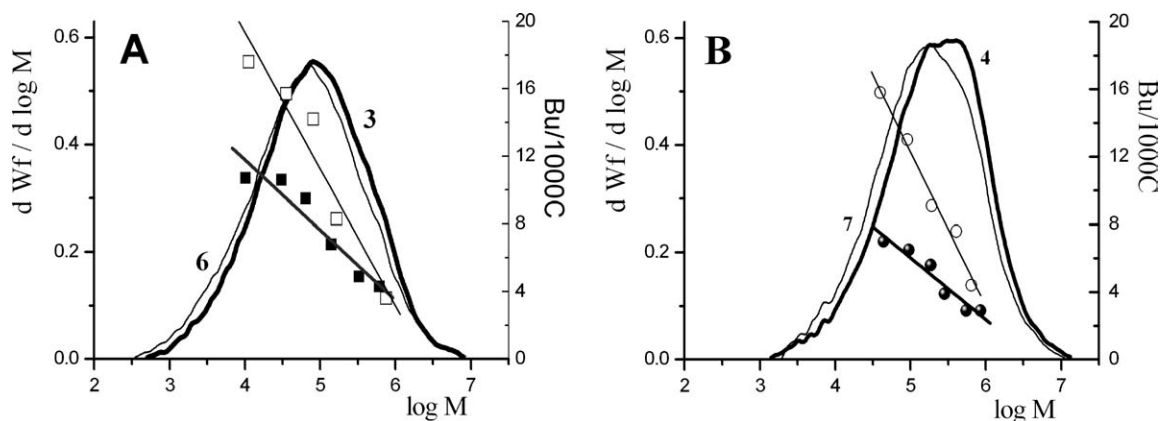


Figure 4 MWD curves and SCB profiles for copolymers produced at different 1-hexene concentration: A: $\tau_p = 15$ min, ■-exp. 3 (C₆/C₂=2.3), □-exp. 6 (C₆/C₂=4.6); B: $\tau_p = 60$ min, ●-exp. 4 (C₆/C₂=2.3), ○-exp. 7 (C₆/C₂=4.6). Numbers correspond to the experiment numbers in Table I.

TABLE III
Effect of Polymerization Duration on the Molecular Weight, MWD, and Composition of Copolymers upon Polymerization in Presence of Hydrogen

Exp No	Reaction time, min	Yield, kg PE/g _{cat}	$M_n \times 10^{-3}$	$M_w \times 10^{-3}$	$M_z \times 10^{-3}$	M_w/M_n	1-hexene content in copolymer, mol %
1 ^a	60	1.22	76	690	3700	9.1	–
2 ^b	60	0.9	35	200	600	5.7	–
3 ^c	7	1.9	16	100	380	6.3	2.5
4 ^c	10	2.2	24	110	370	4.6	2.1
5 ^c	60	4.5	39	180	570	4.6	1.3

^a Ethylene homopolymerization: ethylene pressure = 2 bar, 80°C, [TEA] = 2.6 mmol/L.

^b Ethylene homopolymerization: ethylene pressure = 2 bar, hydrogen pressure = 0.25 bar, 80°C, [TEA] = 2.6 mmol/L.

^c Ethylene/1-hexene copolymerization at molar ratio C₆/C₂ = 2.3; ethylene pressure = 2 bar, hydrogen pressure = 0.25 bar, 80°C, [TEA] = 2.6 mmol/L.

accounted for by the fact that the amount and share of active sites producing the low molecular weight polymer with an increased content of butyl branching decreases with increasing copolymerization duration due to deactivation of these sites. The deactivation of the sites results in the reduction of the catalytic activity with polymerization duration (Fig. 1) and in the increase in molecular weight and narrowing of the MWD of the copolymer (Table I).

The effect of reaction duration on copolymer composition upon ethylene/1-hexene copolymerization in the presence of hydrogen

The introduction of hydrogen leads to the decrease in yield, the considerable decrease in MW, and narrowing of the MWD of the resulting PE (exps. 1 and 2, Table III). Figure 5 shows the kinetic curves of ethylene homopolymerization (Curve 2) and ethylene/1-hexene copolymerization (Curve 5) in the presence of hydrogen. As can be seen, upon ethylene homopolymerization in the presence of hydrogen (Curve 2, Fig. 5), as well as without it (Curve 1, Fig. 1), there has been a little change in activity with reaction duration. The introduction of 1-hexene

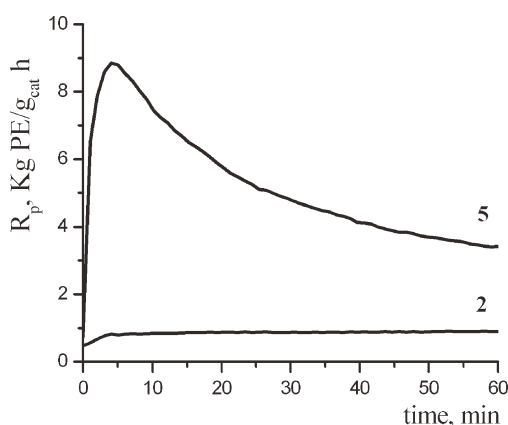


Figure 5 Kinetic curves of ethylene homopolymerization and ethylene/1-hexene copolymerization in the presence of hydrogen (exps. 1, 4, Table III).

results in a considerable increase in catalytic activity. The maximum activity was attained after 5 min and then noticeably reduced with the reaction duration (Curve 5, Fig. 5). A more significant decrease in activity is observed in the presence of hydrogen as compared with the hydrogen-free experiment (Curve 4, Fig. 1; Curve 5, Fig. 5).

Table III lists the data on the effect of polymerization duration on yield, MW, MWD, and 1-hexene content for the copolymers produced in the presence of hydrogen. As can be seen, an increase in MW, narrowing of the MWD of the resulting polymers, and a decrease in 1-hexene content in the copolymers are observed with increasing copolymerization duration. We demonstrated earlier¹⁵ that in case of ethylene homopolymerization in the presence of hydrogen over the same catalyst, reaction duration has no effect on MW and MWD of the resulting PE. Thus, the observed effects (the increase in MW and narrowing of the MWD) with reaction duration in the presence of hydrogen are typical only of copolymerization processes.

Figure 6 shows the MWD curves of the copolymers produced in the presence of hydrogen at different

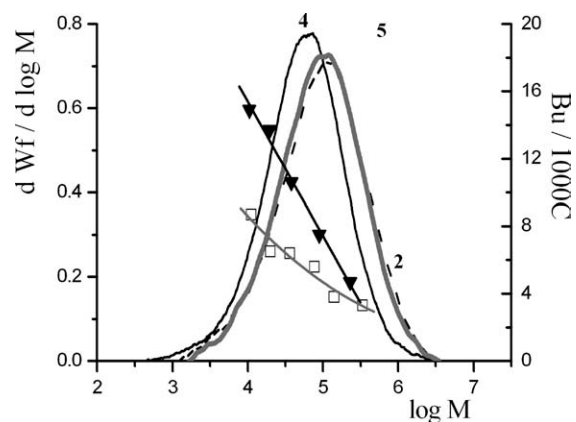


Figure 6 MWD curves for PE (Curve 2) and MWD and SCB distribution curves of copolymers (Curves 4 and 5) produced at different polymerization duration in the presence of hydrogen (▼ - τ_p = 15 min, □ - τ_p = 60 min). Numbers correspond to the experiment numbers in Table III.

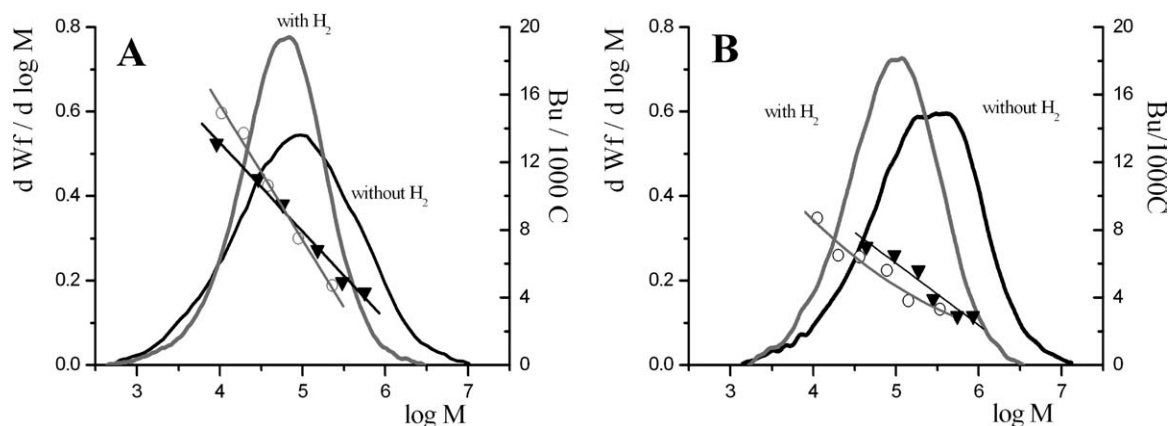


Figure 7 MWD curves and SCB distribution upon copolymerization without H_2 and with H_2 : A: $\tau_p = 10\text{--}15$ min, \blacktriangledown - copolymerization without H_2 (exp. 3, Table I, $M_w/M_n = 12.4$), \circ - copolymerization with H_2 (exp. 4, Table III, $M_w/M_n = 4.6$); B: $\tau_p = 60$ min, \blacktriangledown - copolymerization without H_2 (exp. 4, Table I, $M_w/M_n = 9.2$), \circ - copolymerization with H_2 (exp. 5, Table III, $M_w/M_n = 4.6$).

polymerization times. As can be seen, the MWD curve shifts into the high molecular weight region with increasing polymerization duration. The MWD curves of PE and copolymers produced in 60-min polymerization almost coincide. Figure 6 also contains the data on the comonomer distribution in copolymers produced at $C6/C2$ ratios = 2.3 in polymerization for 15- and 60-min, respectively. As can be seen from the data presented in Figure 6, a decrease in content of butyl branching in low molecular weight fractions occurs with increasing polymerization duration; the content of branching in high molecular weight fractions not changing considerably.

The introduction of hydrogen results in a decrease in MW and a considerable narrowing of the MWD of the resulting copolymers. MWD narrowing of the copolymers obtained in the presence of hydrogen is mainly accounted for by the decreased contribution of the high molecular weight polymer. However, hydrogen has no effect on composition of the resulting copolymers: those produced both in the absence and presence of hydrogen have similar composition at similar polymerization duration (compare exps. 2, 3, and 4 in Table I; exps. 3, 4, and 5 in Table III).

Figure 7 shows the comparative data on the MWD and comonomer content in narrow fractions for the copolymers produced at the equal $C6/C2$ ratio in the absence of hydrogen (exps. 3 and 4, Table I) and in the presence of hydrogen (exps. 4 and 5, Table III) at different polymerization times. It can be seen from the data for $\tau_p = 10\text{--}15$ min [Fig. 7(A)] that low molecular weight fractions in both cases contain 13–14 butyl branches, whereas high molecular weight fractions contain 4–5 butyl branches. The data for $\tau_p = 60$ min [Fig. 7(B)] show that in both cases low and high molecular weight fractions contain 6–7 and 3–4 butyl branches, respectively. Based on these data, a conclusion can be drawn that hydrogen has almost no effect

on the character of comonomer distribution in copolymers. Moreover, the introduction of hydrogen results in the disappearance of active sites that produce high molecular weight polymer and poorly incorporate 1-hexene. Still, in general, copolymer composition in the presence of hydrogen remains invariant as compared with the copolymers produced in the absence of hydrogen (compare exps. 2, 3, and 4 in Table I and exps. 3, 4, and 5 in Table III).

CONCLUSIONS

The data on the polymerization duration effect on MW and MWD of copolymers and on the comonomer content in ethylene/1-hexene copolymers produced on a supported titanium–magnesium catalyst upon polymerization in the absence and in the presence of hydrogen were obtained in this work. The data obtained show that MW increases, MWD decreases, and the content of butyl branching in copolymers decreases with increasing polymerization duration (Table I). It was shown by molecular weight fractionation of copolymers obtained at different polymerization duration followed by analysis of narrow fractions to determine the butyl branching content that the decrease comonomer content in copolymers with increasing polymerization duration is accounted for by the decrease in the share of low molecular weight fractions with an increased butyl branches content (Fig. 3). The results of deconvolution of the MWD curve of copolymers into Flory components (Table II) show that the share of active sites producing low molecular weight polymer (Component I and II) with increased content of butyl branches decreases with increasing polymerization duration. The deactivation of these sites results in the decrease in the catalyst activity with polymerization duration (Fig. 1) and the increase in molecular

weight and narrowing of the MWD of copolymers (Tables I and II). As a result, molecular weight of the polymer increases and 1-hexene content in copolymers decreases.

An increase in MW, narrowing of the MWD of the resulting polymers, and a decrease in 1-hexene content in the copolymers are observed with increasing copolymerization duration upon polymerization in the presence of hydrogen. The decrease in comonomer content with polymerization duration upon copolymerization in the presence of hydrogen takes place due to the decrease in content of butyl branching in the low molecular weight fractions (Fig. 6). Also, hydrogen by itself deactivates a part of active sites producing high molecular weight polymer, as well. The introduction of hydrogen leads to the decrease in MW and narrowing of the MWD in resulting copolymer (Fig. 7). This effect impedes the analysis of the experimental data obtained in the presence of hydrogen and makes the conclusions less evident as compared with the results and conclusions obtained for copolymerization in the absence of hydrogen.

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