

Copolymerization of ethylene with α -olefins over highly active supported ziegler-natta catalyst with vanadium active component

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ABSTRACT

A new highly active supported vanadium-magnesium catalyst (VMC) has been studied in α -olefin (1-butene, 1-hexene)/ ethylene copolymerization in the presence of hydrogen. Data on the effect of α -olefin/ethylene ratio in copolymerization on the content of branchings in copolymers, kinetic profile, copolymer yield, molecular weight and molecular weight distribution of copolymers have been obtained. It was found that both α -olefins are effective chain transfer agents in the ethylene- α -olefins copolymerization. The copolymerization ability of VMC is much higher than that of the well-known titanium-magnesium catalysts. It was found that the use of optimal conditions of ethylene/ α -olefin polymerization on the VMC catalyst makes it possible to obtain copolymers with a high yield (10-16 kg gcat⁻¹ cat for 2 h) and broad and bimodal MWD. Data on the branchings distribution in copolymers prepared with VMC catalyst have been obtained via fractionation of copolymers on the fractions with narrow polydispersity ($M_w/M_n \approx 2$). Quite a uniform distribution of branchings over fractions with different molecular weights was found in distinction to inhomogeneous distribution of branchings in copolymers produced over the well-known supported titanium-magnesium catalyst. **Polyolefins J (2019) 6: 117-126**

Keywords: Polyethylene (PE); supported vanadium-magnesium catalyst; molecular weight distribution; effect of comonomer; reactivity ratio.

INTRODUCTION

The supported titanium-magnesium catalyst (TMC) of Ziegler-Natta type with a titanium active center is well known in the world production of polyolefins. The polyethylene (PE) obtained using this catalyst has a narrow molecular weight distribution (MWD = 4-8) [1]. It is very important to control MWD and short chain branching (SCB) distribution for high density polyeth-

ylene (HDPE) intended for pipe applications [2, 3]. A general method to produce polyethylene with broad/bimodal MWD and SCB over titanium-magnesium catalyst is the use of tandem reactors with different polymerization conditions. The nature of the active component may exert a considerable effect on the molecular weight characteristics of PE and ethylene- α -olefin

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copolymers [1-16]. Supported vanadium-magnesium catalysts (VMC) containing vanadium chloride as the active component supported on $MgCl_2$ differ considerably from TMCs regarding the regulation of molecular structure of PE and copolymers of ethylene with α -olefin[1,7-16]. First of all, unlike TMCs, VMCs make it possible to produce PE with a broad MWD in one polymerization reactor [8-16]. However, the main problem in application of vanadium-magnesium catalysts for the production of polyethylenes with broad MWD is their deactivation in the presence of hydrogen as the polymer chain regulator.

Recently, we have developed a new modification of highly active vanadium-magnesium catalyst with the improved morphology for ethylene slurry polymerization [17]. Data on the homopolymerization of ethylene over these highly active VMCs and the properties of polyethylene produced have been presented in ref. [17]. It was shown that the indicated vanadium-magnesium catalyst (VMC, the vanadium content of 3 wt%) is highly active in ethylene homopolymerization in the presence of hydrogen. This ensures the yield of polyethylene from 9 to 15 kg gcat⁻¹ for two hours of polymerization at 80°C, $PC_2 = 9$ bar and $PH_2 = 0.3\text{--}1.0$ bar, with TIBA as a co-catalyst with controllable molecular weight. In addition, the new VMC, similar to previous modifications of vanadium-magnesium catalyst [13,16], had a very high hydrogen response and provided an effective control of PE molecular weight. The 5 vol% concentration of hydrogen in ethylene polymerization reactor makes it possible to obtain polymers with the molecular weights required for extrusion PE grades ($M_w = (250\text{--}350) \times 10^3$ g mol⁻¹) [17]. The produced PEs have broader bimodal molecular weight distributions ($M_w/M_n = 15.0\text{--}33.0$) [16, 17].

It is known that polymers with broad MWD can be used to produce pipes and high-strength films by extrusion. In the industrial production, physicomechanical properties of extrusion polyethylene grades are always improved by the addition of comonomers (for example, 1-butene or 1-hexene) during ethylene polymerization. Therewith, it is very important to control the comonomer distribution in the produced polymer.

This paper presents new kinetic data on the α -olefin/ethylene copolymerization over new highly active vanadium–magnesium catalysts and the molecular struc-

ture of copolymers produced with different α -olefins (1-hexene or 1-butene). The comonomer reactivity ratios of α -olefin/ethylene copolymerization (r_1) have been calculated. The effect of comonomer and its concentration on the homogeneity of ethylene-1-butene and ethylene-1-hexene copolymers produced with vanadium-magnesium catalysts was elucidated.

EXPERIMENTAL

Catalyst preparation

A supported vanadium-magnesium catalyst (VMC) was prepared by deposition of VCl_4 on highly dispersed $MgCl_2$, which was synthesized according to ref. [17], at room temperature, reacting for 1 h (V/Mg molar ratio = 0.065, 60°C), followed by washing with heptane. The catalyst contains 3.0 wt% of vanadium, 15.7 wt% of magnesium and 1.1 wt% of aluminum.

Polymerization

Polymerization of ethylene or ethylene– α -olefin (1-butene or 1-hexene) slurry was carried out in a 1 L stainless steel reactor. The reactor was equipped with an external heating jacket and an internal cooling coil to maintain the polymerization temperature. It was also equipped with a magnetic coupled stirrer with variable stirring speed. A pressure sensor was used to keep the polymerization pressure by a controlling ethylene valve; also, a temperature sensor was used to keep the polymerization temperature by controlling heat and cool water valve. The polymerization conditions were as follows: heptane was used as a solvent (0.25 L); polymerization temperature was 80°C; ethylene or ethylene-1-butene mixture (2–8 vol% of 1-butene) polymerization pressure was 4–9 bar; in some experiments hydrogen or 1-hexene was charged into the reactor at the beginning of the polymerization; TIBA (triisobutyl-aluminum) was used as a co-catalyst (4.8 mmol L⁻¹). The reaction time was 15–120 min.

Measurements

The vanadium, aluminum and magnesium concentrations in the catalyst were determined by ES-ICP (Optima 5300DV spectrometer). MWD measurements were carried out using a high-temperature gel perme-

ation chromatography (GPC) PL 220 system equipped with RI and DV detectors in 1,2,4-trichlorobenzene at a flow rate of $1 \text{ mL}\cdot\text{min}^{-1}$ at 160°C . The polymers were analyzed using a set of Olexis columns. The instrument was calibrated using polyethylene and polystyrene standards with narrow MWD.

Polymer separation into fractions with narrow MWD was performed using a Polymer Char PREP mc 2 fractionation station. A sample (1 g) was dissolved in a definite volume of xylene for 2 h. A calculated amount of 2-(2-butoxyethoxy)-ethanol was then added to the polymer solution to cause partial precipitation of the polymer.

The total volume of the liquid (xylene and 2-(2-butoxyethoxy)-ethanol) was always 180 mL. A hot polymer solution was filtered into a collecting flask. The precipitated polymer was dissolved in a new portion of xylene. The hot polymer solution was filtered into a precipitation-dissolution procedure was repeated to obtain 5-6 fractions with narrow MWD. The last fraction was washed with pure xylene. The comonomer content in copolymers and fractions was determined by infrared spectroscopy (IRS) and ^{13}C nuclear magnetic resonance (NMR), as described earlier [18,19]. Melting temperature and crystallinity of the polymer were determined by means of differential scanning calorimetry (DSC) using NETSCH DSC 204 F1 equipment, according to ASTM D 3418-82 procedure. The melting point and enthalpy (ΔH) were measured using the second melting data.

RESULTS AND DISCUSSION

Effect of α -olefin and polymerization time on the properties of ethylene-1-hexene and ethylene-1-butene copolymers produced with VMCs

Table 1 and Figure 1 present data on copolymerization

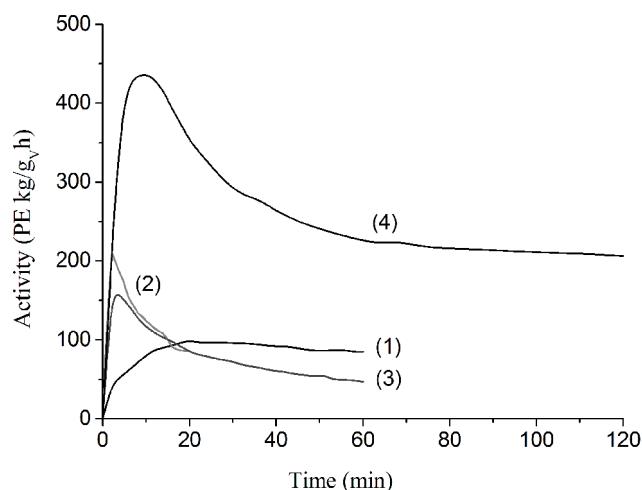


Figure 1. Kinetic curves of ethylene homopolymerization (curve 1) and ethylene/1-hexene copolymerization under different polymerization conditions (curves 2-4) over VMC with $\text{Al}(\text{i-Bu})_3$ as a co-catalyst (the number of curves corresponds to runs indicated in Table 1).

of ethylene with 1-hexene (the molar ratio $[\text{C}_6]/[\text{C}_2] = 0.29$ in heptane) over the VMC upon variation of polymerization time (runs 2 and 3). Runs of copolymerization ethylene with 1-hexene are compared with the runs of ethylene homopolymerization on VMC (Table 1, run 1; Figure 1, curve 1). Figure 1 shows the kinetic curves of ethylene homopolymerization (curve 1) and ethylene/1-hexene copolymerization (curves 2, 3) over the VMC in the presence of hydrogen.

One can see that the rate of ethylene/1-hexene copolymerization at the beginning of reaction is higher than that of ethylene homopolymerization (compare runs 1 and 2, 3). A higher ethylene/ α -olefin copolymerization rate as compared to that of ethylene homopolymerization was observed upon copolymerization with α -olefins of different composition over metallocene and post-metallocene catalysts [20-28], titanium-magnesium and different modifications of vanadium-magnesium catalysts [16,28-35]. Activity of the VMC in ethylene homopolymerization in-

Table 1. Effect of α -olefin and polymerization duration on the ethylene- α -olefin copolymer properties.

No	PC_2H_4 , bar	PH_2 , bar	α -olefin	$[\text{Co}]/[\text{C}_2]$, (mol) (heptane)	Pol. time, min	Yield, kg $\text{g}^{-1}_{\text{cat}}$	Activity, $\text{kg g}^{-1}_{\text{cat}} \text{h}^{-1}$	$M_w \cdot 10^3$, g mol^{-1}	$(\text{CH}_3)/1000^\circ\text{C}$	$[\text{C}_\alpha]$ in polymer, mol%	T_m , $^\circ\text{C}$	X %
1	4	0.2	-	-	60	2.6	0.8	500	1.6	-	137.4	52
2	4	0.2	C_6	0.29	20	1.3	1.0	230	5.5	0.78	130.4	45
3	4	0.2	C_6	0.29	60	2.4	0.6	250	4.6	0.60	131.8	48
4	9	0.5	C_6	0.25	120	15.9	0.9	330	3.5	0.38	135.0	49
5 ^(a)	8	0.4	C_4	0.12	20	3.2	1.2	270	3.8	0.44	133.5	46
6 ^(a)	8	0.4	C_4	0.12	60	7.1	0.9	230	5.1	0.62	133.0	46

Polymerization conditions: heptanes (250 mL), 80°C , TIBA as co-catalyst (4.8 mmol L⁻¹). (a)[C₄] in the C₄/C₂ mixture = 2.4 mol%

creased during first 20 min and then became stable while high initial activity in ethylene/1-hexene copolymerization gradually decreased (Figure 1). After 60 min of polymerization over the VMC, the rates of homo- and co-polymerization became almost close, as can be seen on Figure 1. Total yield of polymers are close (Table 1) due to different activity in the beginning of reactions in ethylene homopolymerization and ethylene/1-hexene copolymerization.

According to the data obtained, ca. 10 wt% of 1-hexene is incorporated into the polymer chain after 20 minutes of reaction. This is accompanied by the formation of branched polymer ($5.5 \text{ CH}_3/1000 \text{ C}$) having a lower melting point and a smaller crystallinity as compared to homopolymer (Table 1, runs 1 and 2). As seen in Table 1, ethylene homopolymer produced in run 1 contained 1.6 CH_3 -groups on 1000 C . According to the earlier obtained data [17, 18], methyl branches can form due to isomerization of the polymer chain during ethylene polymerization on VMC in the presence of hydrogen (the number of such branches increases with the hydrogen concentration). Taking into account the methyl branches of the homopolymer, we have counted the content of butyl branching in a copolymer produced upon ethylene copolymerization with 1-hexene in the presence of hydrogen (runs 2-4).

When polymerization time is increased from 20 to 60 minutes, a ca. 10% conversion of 1-hexene to polymer is retained (Table 1, run 2 and 3). In the process, the amount of branches (the content of comonomer) decreases, whereas crystallinity and melting point of the polyethylene product obtained over the VMC (Table 1, runs 2 and 3) increase.

According to the literature, in polymerization on TMC the comonomer content decreases at a longer polymerization time [31, 32]. It means that the efficient insertion of 1-hexene into the polymer chain occurs only at the beginning of the reaction, when the polymer layer may form on the catalyst particles with a high fraction of amorphous regions. As density of the polymer layer around catalyst particles increases during polymerization, the diffusion limitation for 1-hexene may increase, thus hindering its insertion into the polymer chain and decreasing the probability of transfer of the polymer chain with this comonomer.

One can see in Table 1 that the introduction of

1-hexene into polymerization medium at $[\text{C}_6]/[\text{C}_2] = 0.29$ molar (in heptane) also decreases by a factor of ~2 the molecular weight (M_w) of copolymer relative to M_w of homopolymer (Table 1, compare runs 1 and 2, 3). It was demonstrated earlier [28-30] that upon ethylene/1-hexene copolymerization over a supported titanium-magnesium catalyst 1-hexene is an effective chain transfer agent and the molecular weight of the polymer decreases in its presence. According to the data presented in Table 1, 1-hexene is an effective chain transfer agent also upon ethylene-1-hexene copolymerization over the VMC in the presence of hydrogen.

The use of optimal conditions of ethylene polymerization in the presence of 1-hexene and hydrogen on the VMC (Table 1, run 4) makes it possible to obtain copolymer with a high yield ($15.9 \text{ kg gcat}^{-1}$). The produced copolymer has broad bimodal molecular weight distributions (Table 1, Figure 2, $M_w/M_n = 14$) and characterized by optimal particle size for slurry polymerization process (~250 microns), narrow particle size distribution ($\text{SPAN} = 0.68$) and high bulk density (390 g/L). Data on activity of the VMC and characteristics of polymer samples produced over VMC during the ethylene-1-butene polymerization with different polymerization times are shown in Table 1 (runs 5 and 6) and Figure 3. The kinetic curves of ethylene-1-butene copolymerization in the presence of hydrogen (Figure 3) resemble the kinetic curves of ethylene-1-hexene copolymerization (Figure 1): the maximum rate of the

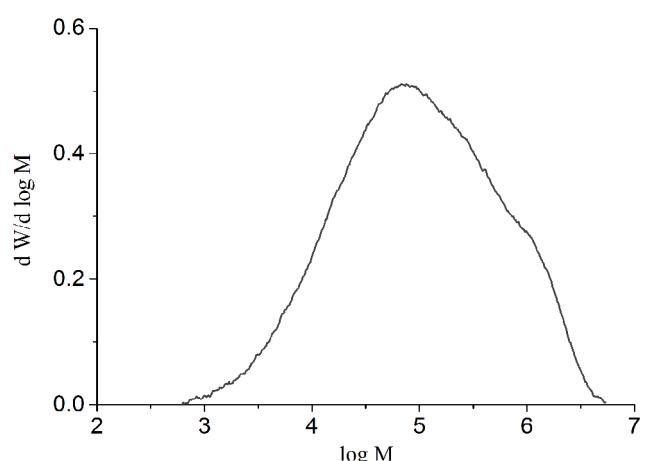


Figure 2. Molecular-weight distribution of PEH copolymer obtained with VMC in ethylene-1-hexene copolymerization in the presence of hydrogen (run 4 in Table 1, polydispersity $(M_w/M_n) = 14$).

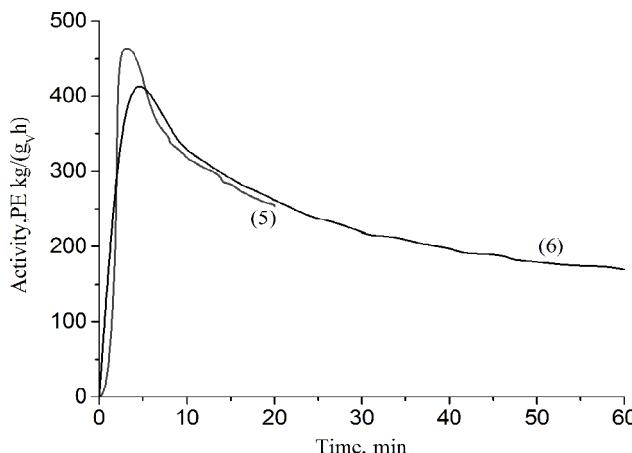


Figure 3. Kinetic curves of ethylene/1-butene copolymerization over VMC at different polymerization times (the number of curves corresponds to runs indicated in Table 1).

reaction is reached in the initial period of polymerization for 5 min with a subsequent decrease in the polymerization rate. However, similar to copolymerization in the presence of 1-hexene (Table 1, run 4), a longer time of C_2/C_4 copolymerization on the VMC would allow reaching the required high yields of the polymer. The use of 1-butene instead of 1-hexene at lower molar ratios of comonomer to ethylene (0.12 instead of 0.29) under similar polymerization conditions (H_2/C_2) makes it possible to produce ethylene-1-butene copolymers with similar α -olefin content and molecular weight (compare data of runs 3 and 6 in Table 1). These data indicate that, 1-butene insertion into the polymer chain is more efficient than that of 1-hexene. In distinction to ethylene-1-hexene copolymers (PEH), the amount of branching in ethylene-1-butene copolymers (PEB) (the content of $CH_3/1000 C$) does not decrease with increasing the polymerization time (Table 1, runs 5, 6). Ethylene-1-butene copolymers, as seen in Figure 4, have a broad bimodal MWD ($M_w/M_n = 9.2-9.6$).

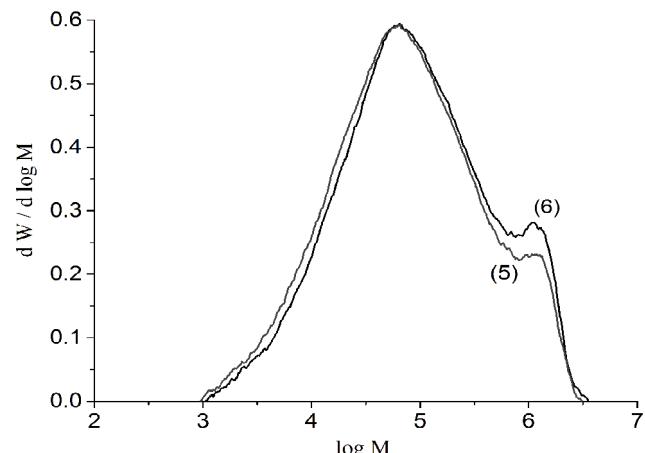


Figure 4. Molecular-weight distribution of PEB copolymers produced with VMC in the ethylene-1-butene copolymerization (runs 5 and 6 in Table 1, polydispersity (M_w/M_n) equal to 9.6 and 9.2, respectively).

Effect of Ca/C_2 molar ratio on characteristics of copolymers produced with vanadium-magnesium catalysts

Tables 2 and 3 and Figure 5 illustrate the effect of the monomer concentration on the kinetic curves of α -olefin/ethylene polymerization and characteristics of ethylene-1-butene and ethylene-1-hexene copolymers produced with vanadium-magnesium catalysts. An increase in the concentration of 1-butene in the gas mixture is accompanied also by changes in the shape of kinetic curves (Figure 5). The acceleration period of copolymerization reaction decreases with increasing the concentration of 1-butene: from 12 min for 1-butene concentration of 2.2 mol% to 6 min for 1-butene concentration of 4-6 mol%. However, the effect of 1-butene concentration on the polymer yield for 1 hour is virtually absent.

As seen in Table 2, adding of 1-butene (2.2 mol%) during the ethylene polymerization in the presence of hydrogen decreases the molecular weight of the polymer from $450 \cdot 10^3$ (run 1, ethylene homopolymer, $1.7 CH_3/1000 C$) to $330 \cdot 10^3$ (run 2, PEB) g mol⁻¹. So, 1-butene concentration in the gas mixture has a significant effect on the molecular weight of the polymer.

Table 2. Effect of 1-butene concentration on the characteristics of ethylene-1-butene copolymers.

No	[C_4H_8] in gas phase, mol%	[C_4H_8]/[C_2] (heptane), mol mol ⁻¹	Yield, kg g _{cat} ⁻¹	$M_w \cdot 10^3$, g mol ⁻¹	M_w/M_n	(CH_3)/1000 C	(C_2H_5)/1000C	[C_4H_8], mol%	T ₂ , °C	X, %	r ₁ ^(a)
1	0	0	4.0	450	-	1.7	0	0	137.4	53	
2	2.2	0.20	5.2	330	16	7.2	6.5	1.3	129.7	43	
3	3.8	0.35	5.4	280	13	11.0	9.3	1.9	127.4	38	
4	5.8	0.53	5.6	200	11	16.5	14.8	3.0	126.2	37	18.0

Polymerization conditions: heptane (250 mL), $P(C_2+C_4) = 6$ bar, $PH_2 = 0.3$ bar, 80°C, TIBA as a co-catalyst (4.8 mmol L⁻¹), for 1 h.

(a) comonomer reactivity ratio

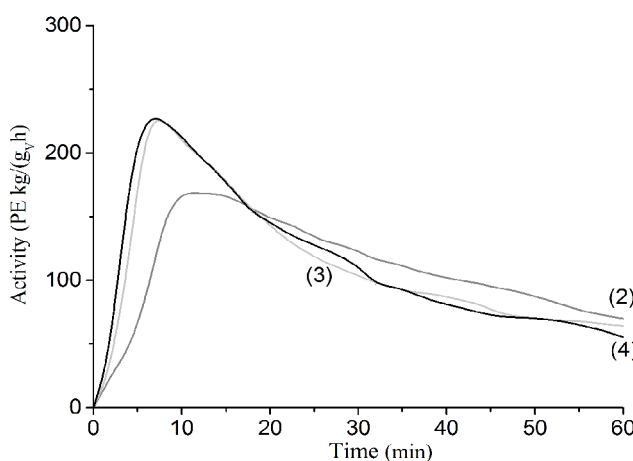


Figure 5. Kinetic curves of ethylene-1-butene copolymerization with different C_4/C_2 molar ratios over the VMC. Polymerization conditions are indicated in Table 2.

tene, similar to 1-hexene, is an effective chain transfer agent upon ethylene-1-butene copolymerization over the VMC in the presence of hydrogen. Therewith, as the concentration of 1-butene in the reaction mixture increases from ca. 2 to 6 mol%, molecular weight of the polymer continues to decrease from $330 \cdot 10^3$ to $200 \cdot 10^3$ g mol⁻¹, the amount of branches increases from 7.2 to 16.5 CH₃/1000 C and, accordingly, the polymer melting point and crystallinity decrease. For the most branched polymer obtained at the 1-butene concentration of ca. 6 mol%, T_m is equal to 126°C, and X to 37 % (Table 2, run 4).

The known simplified copolymerization equation [10] (1), which interrelates the concentration of comonomer (α -olefin) in the reaction medium and its content in the copolymer, was used to estimate the comonomer reactivity ratio (r_1) at copolymerization of 1-butene with ethylene over VMC catalyst. The contribution of methyl branches formed in C_4/C_2 copolymer during polymerization over VMC in the presence of hydrogen was taken into account. Data presented in Table 2 were used for calculation of the r₁ value.

$$(\alpha\text{-olefin}/C_2H_4) \text{ (polymer)} = 1/r_1 ([\alpha\text{-olefin}]/[C_2H_4] \text{ (heptane)}) \quad (1)$$

The r₁ value is 18.0 for ethylene-1-butene copolymerization with VMC in the presence of hydrogen. The copolymerization ability of 1-hexene with ethylene on VMC in the presence of hydrogen for a shorter polymerization time was also estimated. No more than 15 g of copolymer was produced in order to obtain 1-hexene conversion not higher than 15-20 % (to maintain a constant concentration of 1-hexene in the reaction medium).

The PEH samples produced at different C_6/C_2 ratios had different amount of branches (the content of comonomer) and thermophysical characteristics (melting point and crystallinity). Data that were used to calculate the comonomer reactivity ratio r₁ are listed in Table 3. The r₁ value is 36.0 for copolymerization of ethylene with 1-hexene over VMC.

According to the data obtained, the efficiency of 1-hexene insertion into the polymer chain (r₁=36) is approximately two times lower as compared to 1-butene (r₁ = 18). Close data on comparative copolymerization ability of 1-butene and 1-hexene were obtained earlier for the previous modifications of VMC [10] in C_4/C_2 and C_6/C_2 copolymerization at 70°C (r₁=12 and 25, respectively, copolymerization without hydrogen). Data obtained in our work and previous work [10] indicate the higher copolymerizing ability of vanadium-magnesium catalysts in comparison with titanium-magnesium catalysts.

Data on the branching distribution in ethylene-1-butene and ethylene-1-hexene copolymers produced with vanadium-magnesium catalysts

Copolymers with different content of 1-butene (Table 2, runs 2-4) and 1-hexene (Table 3, runs 1-3), which were produced in $C\alpha/C_2$ copolymerization in the pres-

Table 3. Effect of 1-hexene concentration on the characteristics of ethylene-1-hexene copolymers.

No	[C ₆ H ₁₂]/[C ₂ H ₄] (heptane)	H ₂ /C ₂ ratio (vol) in gas phase	Yield, kg/g _{cat} ⁻¹ h ⁻¹	M _w · 10 ³ , g mol ⁻¹	M _w /M _n	(CH ₃)/1000 C	(C ₄ H ₈)/1000 C	[C ₆ H ₁₂], mol%	T ₂ , °C	X, %	r ₁ ^(a)
1	0	0.050	6.0	450	-	1.7	0	0	137.4	51	
2 ^(b)	0.36	0.056	18.1	230	33.0	7.3	5.6	1.1	129.5	46	
3	0.53	0.067	7.4	210	17.5	9.6	7.9	1.6	128.5	44	
4	1.1	0.050	6.6	140	13.0	15.0	13.3	2.7	112.6/124.9	35	36.0

Polymerization conditions: heptane (250 mL), 80°C, PC₂H₄ = 6 bar, TIBA as a co-catalyst (4.8 mmol L⁻¹), for 10-20 min.

(a) comonomer reactivity ratio

(b) ethylene pressure of 9 bar

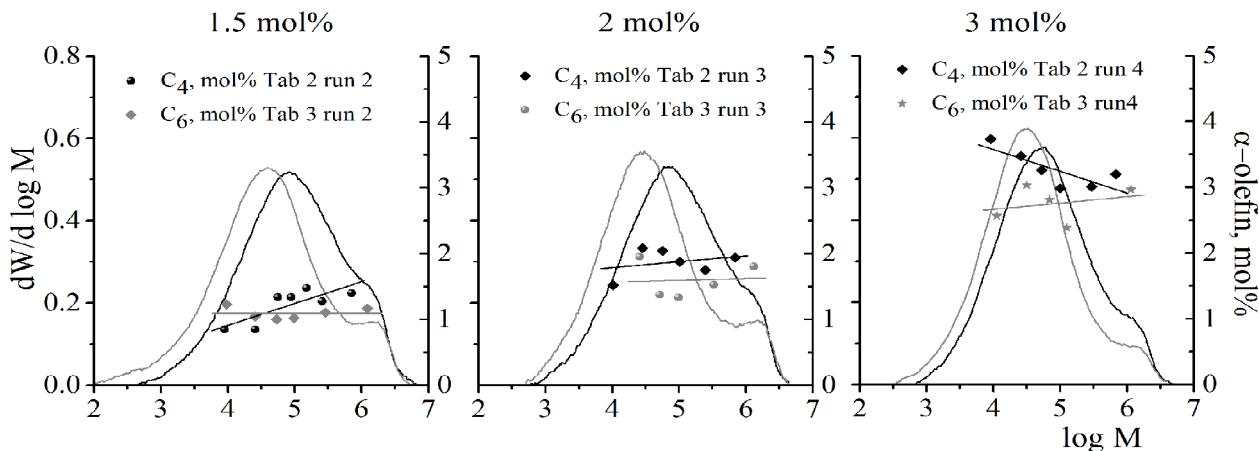


Figure 6. Effect of comonomer (1-butene or 1-hexene) in ethylene copolymers with 1-butene and 1-hexene having different contents of comonomer, which were produced over VMC, on its distribution between fractions with different molecular weights.

ence of hydrogen over VMC, were divided according to molecular weight into 5-6 fractions with $M_w/M_n \leq 2$. Comonomer content in the total copolymers and individual fractions with different molecular weights was determined by IR and ^{13}C NMR (for low-molecular fractions).

Data on the distribution of 1-butene (ethyl groups) and 1-hexene (butyl groups) in copolymers are displayed on Figure 6. One can see that at ca. 1.0 mol% content of comonomer in the polymer, a very uniform distribution of 1-hexene over the fractions with different molecular weights is observed for the PEH copolymer. For the PEB copolymer, the concentration of 1-butene increases from low-molecular fractions to high-molecular ones. It should be noted that such distribution of branching is preferable for commercial polyethylene polymers obtained on TMC by the polymerization scheme with two-tandem reactors.

An increase in comonomer content in the copolymers produced over VMC to ca. 2 mol% leads to such a uniform distribution of comonomer in PEH and PEB for all fractions of the copolymer. In contrast to copolymers produced over VMC catalyst, for the copolymer produced over TMC there is a heavy concentration of branching in the lowest MW (amounts of butyl branching in the first and last fractions differ approximately five-fold) [32,35]. TCM produces polymers with a narrower MWD but it contains highly heterogeneous centers regarding comonomer reactivity ratios [35].

For the comonomer content of ca. 3 mol%, the distribution of butyl branches is retained in the case of

PEH but somewhat changes for PEB: low-molecular fractions become more saturated with ethyl branches

CONCLUSIONS

The new highly active supported vanadium-magnesium catalyst has been studied in α -olefin (1-butene, 1-hexene)/ethylene copolymerization. It was found that the introduction of comonomer (1-butene, 1-hexene) at a molar ratio 0.2-0.5 in ethylene polymerization over VMC in the presence of hydrogen leads to the unstable kinetic curve: high polymerization rate at the beginning of reaction gradually decreases. The use of optimal conditions of ethylene/ α -olefin polymerization in the presence of hydrogen on the VMC makes it possible to obtain the branching copolymer with a high yield (ca. 16 kg g_{cat}⁻¹ for 2 h).

The effect of copolymerization time over VMC on the insertion of α -olefin into the copolymer was studied. It was found that in the case of 1-hexene, comonomer content in the copolymer depends on polymerization time: it decreases at a longer polymerization time. Unlike ethylene-1-hexene copolymers (PEH), the degree of branching (the content of CH₃/1000C) for ethylene-1-butene copolymers (PEB) does not decrease with increasing the polymerization time. A constant feeding of the C₂/C₄ gas mixture makes it possible to obtain PEB with a close composition in each polymerization time point.

Adding of 1-butene or 1-hexene in the ethylene polymerization over the VMC in hydrogen presence leads to

a decrease in molecular weight of the copolymer in comparison with ethylene homopolymer. So, α -olefins are effective chain transfer agents in the ethylene- α -olefins copolymerization.

The use of 1-butene instead of 1-hexene at close C₂/C₆ molar ratios and similar polymerization conditions increases the degree of branching and decreases the polymer melting point. It was found that efficiency of 1-hexene insertion into the polymer chain is approximately two times lower as compared to 1-butene: co-monomer reactivity ratios (r_1) are equal to 36 and 18 (80°C) for 1-hexene and 1-butene, respectively. The copolymerization ability of the new modification of VMC (VC) is on a level with the earlier developed vanadium-containing catalyst and strongly exceeds that of TMC [10].

It was found that the VMC produces copolymers that, similar to ethylene homopolymers have broad and bimodal MWD. Data on the branchings distribution in copolymers prepared with VMC were obtained via fractionation of copolymers into the fractions with narrow polydispersity ($M_w/M_n \approx 2$). Quite a uniform distribution of branchings over fractions with different molecular weights was found, in contrast to inhomogeneous distribution of branchings in copolymers produced over the well-known supported TMC [32, 35].

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REFERENCES

- Umberto Z, Giuliano C (1983) Control of molecular-weight distribution in polyolefins synthesized with Ziegler-Natta catalytic systems. *Adv Polym Sci* 51: 101-153
- Shan CLP, Soares JBP, Pendilis A (2002) Mechanical properties of ethylene/1-hexene copolymers with tailored short chain branching distributions. *Polymer* 43: 767-773
- Frank PA, Ludwig LB, Hans-Frieder E, Joachim B (2001) Bimodal polyethylene. Interplay of catalyst and process. *Macromol Symp* 163: 135-143
- Matta A, Zeng Y, Taniiki T, Terano M (2012) Vanadium-modified Philips catalyst with high branching ability for ethylene polymerization. *Macromol React Eng* 6: 346-350
- Comito RJ, Wu Zh, Zhang G, Lawrence III JA, Korzyński MD, Kehl JA, Miller JT, Dinča M (2018) Stabilized vanadium catalyst for olefin polymerization by site isolation in a metal-organic framework. *Angew Chem Int Ed* 57: 8135-8139
- Lorber C (2009) [ONNO]-type amine bis(phenolate)-based vanadium catalyst for ethylene homo- and copolymerization. *Pure Appl Chem* 81: 1205-1215
- Mikenas TB, Zakharov VA (1984) Polymerization of ethylene in the presence of the supported catalysts containing chloride of vanadium and chloride of magnesium. *Vysokomol Soedin Ser B* (in Russian) 26: 483-485
- Karol FG, Cann KJ, Wagner BE (1988) Development with high-activity titanium, vanadium and chromium catalyst in ethylene polymerization, in *Transition Metals and Organometallics as Catalysts for Olefin Polymerization*, ed. W. Kaminsky and H. Sinn, Springer-Verlag, Berlin
- Spitz R, Patin M, Robert P, Masson P, Dupuy J (1994) The control of molecule weight distribution in Ziegler-Natta catalysis, in *Catalyst Design for Tailor-made Polyolefins*, Kanazawa, Japan
- Zakharov VA, Echevskaya LG (1997) Kinetics of the copolymerization of ethylene with α -olefins initiated by supported titanium-magnesium and vanadium-magnesium catalyst. *Polym Sci B (Engl. Transl.)* 39: 291-294
- Mikenas TB, Zakharov VA, Echevskaya LG, Matsko MA (2001) Ethylene polymerization with supported vanadium-magnesium catalyst: hydrogen effect. *Macromol Chem Phys* 202:

475-481

12. Zakharov VA, Makhtarulin SI, Sergeev S A, Mikenas T B, Nikitin V E, Echevskaya L G, Khmelinskaya AD (1995) Method of producing a deposited catalyst for the polymerization of ethylene and copolymerization of ethylene with α -olefins, WO Patent, WO 1995/03516
13. Zakharov VA, Echevskaya LG, Mikenas TB (1991) Studying of reaction of transfer of a polymeric chain with hydrogen at polymerization of ethylene over titanium-magnesium and vanadium-magnesium catalysts. *Vysokomol Soedin Ser B* (in Russian) 33: 102-104
14. Czaja K, Bialek M (2001) Effect of hydrogen on the ethylene polymerization process over Ziegler-Natta catalysts supported on $MgCl_2(THF)_2$. II. Studies of the chain-transfer reaction. *J Appl Polym Sci* 79: 356-360
15. Matsko MA, Bukatov GD, Mikenas TB, Zakharov VA (2001) Ethylene polymerization with supported vanadium-magnesium catalyst: Number of active centers and propagation rate constant. *Macromol Chem Phys* 202: 475-481
16. Echevskaya LG, Matsko MA, Mikenas T B, Zakharov VA (2006) Molecular mass characteristics of polyethylene produced with supported vanadium-magnesium catalysts. *Polymer Int* 55: 165-170
17. Wang D, Zhao Z, Mikenas TB, Xiaomei Lang, Echevskaya LG, Zhao C, Matsko M A, Wu W (2012) A new high-performance Ziegler-Natta catalyst with vanadium active component supported on highly-dispersed $MgCl_2$ for producing polyethylene with broad/bimodal molecular weight distribution. *Polym Chem* 3: 2377-2382
18. Echevskaya LG, Zakharov V A, Golovin AV, Mikenas TB (1999) Molecular structure of polyethylene produced with supported vanadium-magnesium catalyst. *Macromol Chem Phys* 200: 1434-1438
19. Randall JC (1977) Polymer Sequence determination. Academic, New York
20. Seppala JV, Koivumaki J (1993) Observations on the rate enhancement effect with magnesium chloride/titanium tetrachloride and dicyclopentadienylzirconium dichloride (Cp_2ZrCl_2) catalyst systems upon 1-hexene addition. *Macromolecules* 26: 5535-5538
21. Cruz VL, Munoz-Escalante A, Martinez-Salazar J (1998) A theoretical study of the comonomer effect in the ethylene polymerization with zirconocene catalytic systems. *J Polym Sci A Polym Chem* 36: 1157-1167
22. Jungling S, Koltzenburg S, Multhaup R (1997) Propene homo- and copolymerization using homogeneous and supported metallocene catalysts based on $Me_2Si(2-Me-Benz[e]Ind)ZrCl_2$. *J Polym Sci Polym Chem* 35: 1-8
23. Awudza JAM, Tait P J T (2008) The “comonomer effect” in ethylene/ α -olefin copolymerization using homogeneous and silica-supported Cp_2ZrCl_2/MAO catalyst systems: Some insights from the kinetics of polymerization, active center studies, and polymerization temperature. *J Polym Sci. Polym Chem* 46: 267-277
24. Kravchenko R, Waymouth RM (1998) Ethylene-propylene copolymerization with 2-arylidene zirconocenes. *Macromolecules* 31: 1-6
25. Tang L-M, Li Y-G, Ye W-P, Li Y-S (2006) Ethylene-propylene copolymerization with bis(β -enaminoketonato) titanium complexes activated with modified methylaluminoxane. *J Polym Sci Polym Chem* 44: 5846-5854
26. Tang L-M, Hu T, Li P, Li Y-S (2005) Ethylene/ α -olefin copolymerization with bis(β -enaminoketonato) titanium complexes activated with modified methylaluminoxane. *J Polym Sci Polym Chem* 43: 6323-6330
27. Gibson VC, Spitzmesser SK (2003) Advances in non-metallocene olefin polymerization catalysis. *Chem Rev* 103: 283-316
28. Coates GW, Hustad PD, Reinartz S (2002) Catalysts for the living insertion polymerization of alkenes: access to new polyolefin architectures using Ziegler-Natta chemistry. *Angew Chem Int Ed* 41: 2236-2257
29. Zakharov VA, Echevskaya LG, Mikenas TB, Matsko MA, Tregubov AA, Vanina MP, Nikolaeva MI (2008) Supported Ziegler-Natta catalysts for ethylene slurry polymerization and control of molecular weight distribution of

- polyethylene. Chinese J Polym Sci 26: 553-560
30. Matsko MA, Echevskaya LG, Zakharov VA, Nikolaeva MI, Mikenas TB, Vanina MP (2009) Study of multi-site nature of supported Ziegler-Natta catalysts in ethylene-hexene-1 copolymerization. Macromol Symp 282: 157-166
31. Garoff T, Mannonen L, Vaananen M, Eriksson V, Kallio K, Waldvogel P (2010) Chemical composition distribution study in ethylene/1-hexene copolymerization to produce LLDPE material using $MgCl_2$ - $TiCl_4$ -based Ziegler-Natta catalysts. J Appl Polym Sci 115: 826-836
32. Nikolaeva MI, Matsko MA, Mikenas TB, Echevskaya LG, Zakharov VA (2012) 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. J Appl Polym Sci 125: 2034-2041
33. Nikolaeva MI, Matsko MA, Mikenas TB, Echevskaya LG, Zakharov VA (2012) Copolymerization of ethylene with α -olefins over supported titanium-magnesium catalysts. II. Comonomer as a chain transfer agent. J Appl Polym Sci 125, 2042-2049
34. Echevskaya LG, Zakharov VA (1996) Microtacticity of copolymers. Vysokomol Soedin Ser A 38: 959-963
35. Matsko MA, Echevskaya LG, Vanina MP, Nikolaeva MI, Mikenas TB, Zakharov VA (2012) Study of the compositional heterogeneity of ethylene/1-hexene copolymers produced over supported catalysts of different composition. J Appl Polym Sci 126: 2017-2023