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Polymerization of Hexene-1 and Propylene over Supported Titanium–Magnesium Catalyst: Comparative Data on the Polymerization Kinetics and Molecular Weight Characteristics of Polymers

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Abstract: Data are presented on the great differences of the kinetics of hexene-1 and propylene polymerization over the same supported titanium–magnesium catalyst, as well as molecular weight and molecular weight distribution of the polymers produced. It is found that the composition of cocatalysts (AlEt_3 or $\text{Al}(\text{i-Bu})_3$) greatly affects the kinetics of hexene-1 polymerization and molecular weight distribution of polyhexene, contrary to data obtained at propylene polymerization. The presence of hydrogen at hexene-1 polymerization leads to a much higher increase of activity in comparison with propylene polymerization. Possible reasons for these differences are discussed on the basis of experimental results.

Keywords: hexene-1 polymerization; propylene polymerization; titanium-magnesium catalyst; molecular weight; molecular weight distribution polyhexene; polypropylene



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1. Introduction

Polyhexene (PH) is a relatively new promising polymer, which may be applied in various fields. The most well-known application is ultrahigh molecular weight polyhexene with the molecular weight higher than 10×10^6 g/mol, which is employed as drag reducing additives to reduce hydrodynamic resistance in oil pipelines [1,2]. At the same time, PH with different molecular weights necessary for other applications can be obtained by varying the polymerization conditions and the composition of catalysts used for PH production.

Catalysts of different compositions can be employed to produce polyhexene; among them are traditional Ziegler-Natta type catalysts, supported titanium-magnesium catalysts (TMC) [3–16], and homogeneous metallocene catalysts [17–20]. Kinetics of hexene-1 polymerization over Ziegler-Natta catalysts with different composition and data on the effect of catalysts' composition, and polymerization conditions on the molecular weight and molecular weight distribution of polyhexene are presented and discussed in refs. [3–20]. Modern TMC, which are commonly used for stereospecific propylene polymerization, are highly active in hexene-1 polymerization also. It was shown in ref. [16] that variation of the composition of a catalytic system and polymerization conditions makes it possible to obtain polyhexene with the molecular weight from 7×10^4 to 2×10^6 g/mol, controllable molecular weight distribution (MWD) (M_w/M_n in the region from 3.7 to 25), and different isotacticity (the content of mmmm pentads from 56 to 96%).

The analysis of literature data shows that polymerization of hexene-1 over titanium–magnesium catalysts strongly differs from the results obtained for propylene. In particular, propylene polymerization over the TMC containing dibutyl phthalate as a stereoregulating component and triethylaluminum (AlEt_3) as a cocatalyst leads to the formation of polypropylene (PP) with quite narrow MWD ($M_w/M_n = 4–6$). However, polymerization of hexene-1 over a similar TMC with the AlEt_3 cocatalyst yields polyhexene with

a broad MWD ($M_w/M_n = 15\text{--}25$) [12]. When the AlEt_3 cocatalyst is replaced by tri-isobutylaluminium (Al(i-Bu)_3), polyhexene with a narrower MWD ($M_w/M_n = 3.7\text{--}15$) is formed over the same TMC. It should be noted that data concerning the effect of the cocatalyst composition (AlEt_3 or Al(i-Bu)_3) on the polymerization kinetics of propylene and molecular weight characteristics of polypropylene are absent in the literature. We think that possible reasons of differences in the polymerization kinetics of hexene-1 and propylene and in the molecular weight characteristics of the produced polymers could be revealed by a more detailed investigation of the polymerization kinetics of these monomers and molecular weight characteristics of polyhexene and polypropylene obtained on similar samples of titanium-magnesium catalyst.

In this paper, we have presented comparative data on the polymerization kinetics of hexene-1 and propylene over the same supported TMC used for stereospecific polymerization of propylene, as well as the data on molecular weight and MWD of polyhexene and polypropylene obtained under variation of polymerization conditions and cocatalyst composition. The data were used to discuss possible reasons for the great differences in the polymerization kinetics of these monomers and in the MWD of PH and PP samples.

2. Materials and Methods

The stereospecific titanium–magnesium catalyst used in this study contains TiCl_4 supported onto MgCl_2 (2.4 wt% of Ti) and dibutyl phthalate (DBP, 12 wt%) as the internal donor; average particle size of catalyst is 20 μm .

1-Hexene polymerization was carried out in a 1 L steel reactor in heptane. Catalyst concentration was 0.04 g L^{-1} ; tri-ethylaluminum (AlEt_3) or tri-isobutylaluminium (Al(i-Bu)_3) were used as cocatalysts. Cocatalyst concentration was 5–6 mmol L^{-1} . Propyl-trimethoxysilane (PTMS) was used at polymerization as an external donor with molar ratio AlR_3/PTMS equal to 10–12. Additional data on polymerization conditions and MWD of polyhexene are presented in Tables. Activity of TMC was calculated according to the yield of the polymer, with allowance of monomer conversion during polymerization.

Propylene polymerization was performed in the 1L steel reactor in heptane at constant propylene pressure (6 bar) and hydrogen pressure (0.14 bar). AlEt_3 and Al(i-Bu)_3 was used as a cocatalyst ($[\text{AlR}_3] = 4 \text{ mmol L}^{-1}$); the catalyst concentration was 0.032 g L^{-1} . Cyclohexylmethyl-di-methoxysilane (CHMDMS) was used as an external donor.

The method of MWD determination is described in [16].

3. Results and Discussion

Our earlier study [15] revealed that in the case of hexene-1 polymerization over titanium–magnesium catalyst, the composition of cocatalyst (AlEt_3 or Al(i-Bu)_3) substantially affects the MWD of the produced polyhexene. In particular, the use of AlEt_3 as a cocatalyst leads to the formation of a polyhexene with a broader molecular weight distribution in comparison with MWD of polyhexene obtained in the presence of the Al(i-Bu)_3 cocatalyst. More detailed data on MWD of polyhexene produced with the AlEt_3 cocatalyst under variation of polymerization time and polyhexene yield in the experiments performed in the absence or presence of hydrogen are listed in Table 1. According to these data, dependences of the polymerization rate vs. polymerization duration were obtained for the experiments carried out in the presence or absence of H_2 (Figure 1).

It is seen that MWD of polyhexene narrows with an increase in polymerization time (polymer yield); however, the MWD remains quite broad ($M_w/M_n = 15$ and 10 in Exps. 3 and 6, Table 1) even at high yields of the polymer. The introduction of hydrogen into polymerization leads to the decrease of the molecular weight and significantly narrows the MWD for both cocatalysts (Tables 1 and 3).

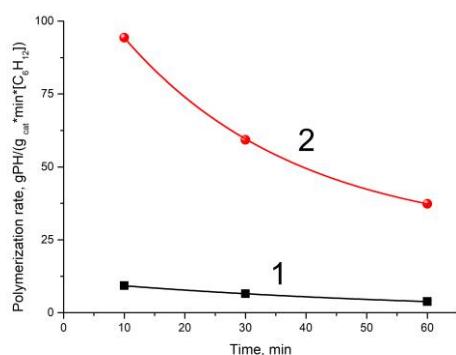


Figure 1. Dependence of hexene-1 polymerization rate on the polymerization duration with cocatalyst AlEt₃ at polymerization in the absence of hydrogen (curve 1) and in the presence of H₂ (curve 2) (see polymerization conditions in Table 1).

Table 1. Data on the effect of polymerization duration on the polymerization rate and molecular weight of polyhexene upon hexene-1 polymerization with AlEt₃ as cocatalyst.

Exp. ¹ No.	Hydrogen Presence	Polymerization Duration, min	G ³	R _p ⁴	M _n , kg/mol	M _w , kg/mol	M _w /M _n
1	—	10	0.18	9.2	22	490	22
2	—	30	0.37	6.5	27	510	19
3	—	60	0.43	3.8	32	490	15
4 ²	+	10	1.5	94	17	230	13.5
5 ²	+	30	2.4	59	16	170	11
6 ²	+	60	2.8	37	15	150	10

¹ Polymerization at 70 °C, [C₆H₁₂] = 2 M. ² H₂ pressure is 0.1 bar in Exps 4–6. ³ Polymer yield, kg PH/g cat. ⁴ g PH/(g cat. × min × mol C₆H₁₂).

It is seen that the rate of hexene-1 polymerization with the AlEt₃ is higher during the initial period of polymerization (10 min) and then decreases with time (Table 1 and Figure 1). As was noted earlier [15], hydrogen introduction into polymerization of hexene-1 leads to a sharp increase in the polymerization rate (ca. 10-fold, Table 1).

Data on the polymerization rates of propylene and hexene-1 in the case of the same titanium–magnesium catalyst and different cocatalysts (AlEt₃ and Al(i-Bu)₃), as well as the data on MWD and isotacticity of the produced polymers are listed in Tables 2 and 3. Figure 2 displays typical kinetics curves of propylene polymerization (time dependences of polymerization rate) that were obtained with AlEt₃ and Al(i-Bu)₃ cocatalysts in the presence or absence of H₂. A comparison of the results presented in Tables 2 and 3 reveals the following peculiarities of polymerization of these monomers over titanium–magnesium catalysts.

Table 2. Data on the propylene polymerization over TMC with AlEt₃ or Al(i-Bu)₃ cocatalysts.

Exp. No.	Cocatalyst	P _{H2} , Bar	G ¹	R _p ²	II ³	M _n , kg/mol	P _n ⁴	M _w , kg/mol	M _w /M _n
1		—	7.8	3100	—	—	—	—	—
2	AlEt ₃	0.16	14.5	5800	97	81	1900	320	4.0
3		0.5	13.7	5400	—	35	800	140	4.0
4		—	6.3	2600	—	—	—	—	—
5	Al(i-Bu) ₃	0.16	14.4	5700	88	75	1800	300	4.0
6		0.5	11.1	4300	—	20	500	110	5.4

Polymerization at 70 °C, [C₃H₆]—2 mol/L, [AlR₃]—4 mol/L, AlR₃/ED = 20, polymerization duration—1 h.

¹ Polymer yield, kg PP/g cat. ² Polymerization rate, mol C₃H₆/(mol Ti × min × mol C₃H₆). ³ Isotacticity of PP, %. ⁴ Polymerization degree.

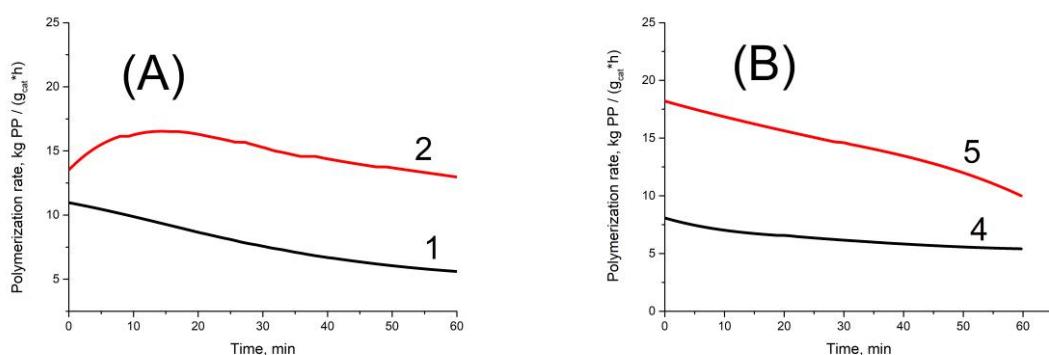


Figure 2. Kinetic curves of propylene polymerization over TMC with AlEt_3 (A) and $\text{Al}(\text{i-Bu})_3$ (B) as cocatalysts at polymerization in the absence of hydrogen (curves 1 and 4) and in the presence of hydrogen (curves 2 and 5). Numbers of curves correspond to numbers in Table 2.

Table 3. Data on the hexene-1 polymerization over TMC with different cocatalysts.

Exp. No.	Cocatalyst	P_{H_2} , Bar	τ_p ¹ , min	G ²	R_p ³	II ⁴	M_n , kg/mol	P_n ⁵	M_w , kg/mol	M_w/M_n
1	AlEt_3	—	60	0.2	80	—	20	400	350	17.5
2		0.2	10	1.2	2800	95	12	200	170	14.0
3	$\text{Al}(\text{i-Bu})_3$	—	60	1.0	380	—	600	7140	2500	4.2
4		0.5	10	2.0	4800	96.5	37	440	185	5.0

Polymerization at 70°C , $[\text{C}_6\text{H}_{12}] = 1 \text{ mol/L}$, $[\text{AlR}_3] = 6 \text{ mmol/L}$, $\text{AlR}_3/\text{ED} = 10$. ¹ Polymerization duration, min. ² PH yield, kg/g cat. ³ Polymerization rate, mol $\text{C}_6\text{H}_{12}/(\text{mol Ti} \times \text{min} \times \text{mol C}_6\text{H}_{12})$. ⁴ Content of [mmmm] pentad. ⁵ Degree of polymerization.

In polymerization of propylene, the activity of TMC (polymerization rate) is close for AlEt_3 and $\text{Al}(\text{i-Bu})_3$ cocatalysts at polymerization in the absence or presence of H_2 (compare Exps. 1 and 2, 4 and 5 in Table 2). At the same time, in polymerization of hexene-1 with the AlEt_3 as a cocatalyst, the catalyst activity is much lower compared to the $\text{Al}(\text{i-Bu})_3$ cocatalyst, especially at polymerization in the absence of H_2 (Exps. 1 and 3 in Table 3). However, in the presence of H_2 the catalyst activity at polymerization of hexene-1 sharply increases by a factor of 12–32 (Table 3) and approaches the activity of the same catalyst in polymerization of propylene (compare Exps. 2, 3, 5, 6 in Table 2 with Exps. 2 and 4 in Table 3). In the case of propene polymerization, activity of the catalyst increases upon hydrogen introduction only by a factor of 1.5–2. Thus, the effect of the catalyst activity growth due to hydrogen introduction at polymerization of hexene-1 is much more pronounced than in the case of propylene polymerization. In refs. [21] it was shown that the increase of TMC activity during propene polymerization in the presence of H_2 is associated with reactivation of temporarily inactive, so called “dormant” sites, which are formed due to 2,1-addition of propylene to the propagating polymer chain. Our data on a more abrupt increase of the TMC activity after hydrogen introduction at polymerization of hexene-1 testify that the fraction of dormant sites formed during polymerization of hexene-1 in the absence of hydrogen is much greater as compared to polymerization of propylene. In this case, the reactivity of propylene and hexene-1 in the polymer chain propagation reaction should be estimated from the data on the catalyst activity obtained at polymerization in the presence of H_2 (in the absence of dormant sites). Data obtained under the indicated conditions using the $\text{Al}(\text{i-Bu})_3$ cocatalyst (Exps. 5, 6 in Table 2 and Exp. 4 in Table 3) demonstrate close reactivities of these monomers in the polymer chain propagation reaction.

In the case of propylene polymerization, the cocatalyst type affects isotacticity of polypropylene; the application of $\text{Al}(\text{i-Bu})_3$ as a cocatalyst significantly decreases isotacticity of polypropylene (Table 2, Exps. 2 and 5). At the same time, at polymerization of hexene-1,

isotacticity of polyhexene-1 does not depend on the composition of cocatalyst (Table 3, Exps. 2 and 4).

Polypropylene samples produced in the presence of H_2 with $AlEt_3$ or $Al(i-Bu)_3$ cocatalysts have close molecular weights (Table 2, Exps. 2 and 5). These polymers also have close polydispersity values ($M_w/M_n = 4.0–5.4$). Data on the MWD of polyhexene (Table 3) greatly differ from the data obtained for polypropylene. Polyhexene produced in the absence of hydrogen with the $AlEt_3$ cocatalyst has a much lower molecular weight and a very broad MWD ($M_w/M_n = 17.4$) compared to PH produced with the $Al(i-Bu)_3$ cocatalyst (Table 3, Exps. 1 and 3). The introduction of H_2 leads to a sharp decrease in the molecular weight of polyhexene and to some narrowing of MWD in the case of $AlEt_3$ cocatalyst; nevertheless, the M_w/M_n values for PH produced with the $AlEt_3$ cocatalyst remain much higher than the values for PH produced with $Al(i-Bu)_3$ cocatalyst (Table 3, compare Exps. 1 and 2 with Exps. 3 and 4).

Reactivities of propylene and hexene-1 in the chain transfer reactions can be compared using the polymerization degree (P_n) data for polypropylene and polyhexene obtained under close conditions in the presence of hydrogen. In the case of propylene and hexene polymerization with the $AlEt_3$ cocatalyst at a low hydrogen content, the polymerization degree of PH is much lower than that of PP (200 and 1900, respectively) (Exp. 2 in Table 2 and Exp. 2 in Table 3). However, in polymerization with the $Al(i-Bu)_3$ cocatalyst, the polymerization degree of PP and PH are close (500 and 440) (Exp. 6 in Table 2 and Exp. 4 in Table 3). Presumably, these results may be caused by a great contribution of the chain transfer reaction, with $AlEt_3$ at a low hydrogen content to polymerization degree of polyhexene in comparison with propylene polymerization. At the same time, during polymerization of propylene and hexene with the $Al(i-Bu)_3$ cocatalyst at an increased hydrogen content, the contribution of the chain transfer reaction with cocatalyst to the polymerization degree is insignificant. For the indicated polymerization conditions, polymerization degree is determined by the rate constant ratio for chain propagation and polymer chain transfer with H_2 . Data on the close polymerization degree of PP and PH obtained for such polymerization conditions indicate that the ratios of these rate constants for polymerization of propylene and hexene-1 over TMC are also close.

Data presented in Tables 2 and 3 show the essential differences in the MWD of polypropylene and polyhexene are observed only at polymerization with cocatalyst $AlEt_3$. This cocatalyst is the efficient agent of the chain transfer reaction in the case of ethylene, propylene, and hexene-1 polymerization in the absence of hydrogen. In case of ethylene polymerization over TMC it was proposed in [22] that $AlEt_3$ is able to form temporarily inactive (“dormant”) sites due to the reversible adsorption on active sites (AS). This reaction proceeds additionally to the decrease of molecular weight of polyhexene and broadening of MWD [22]. Probably the contribution of this reaction increases at polymerization of hexene-1 compared to ethylene and propylene polymerization due to the elevated concentration of $AlEt_3$ on the catalyst surface. This phenomenon may be caused by the formation of a homogeneous reaction medium (a polyhexene solution in heptane) in distinction to a heterogeneous medium that appears when solid polypropylene particles are formed as a suspension in a heptane medium.

Earlier in our paper [15], we have presented data concerning the effect of reaction temperature on the polymerization rate of hexene-1 over TMC with cocatalysts $AlEt_3$ and $Al(i-Bu)_3$ in the presence or absence of H_2 at polymerization. We have found in most cases that the polymerization rate decreases when the reaction temperature is increased from 30 °C up to 70 °C. Due to this unusual effect of decreasing polymerization rate with elevation of the reaction temperature, the calculated effective activation energies for polymerization rate (E_{eff}) have anomalous negative values. The most pronounced effect on the temperature dependence of hexene-1 polymerization rate and the calculated values of E_{eff} was exerted by the composition of cocatalyst and the presence of H_2 during polymerization (Table 4).

Table 4. Data on the influence of reaction temperature on the rate of hexene-1 polymerization and values of effective activation energy (E_{eff}) upon polymerization over TMC with different cocatalysts in the presence and absence of hydrogen.

Cocatalyst	Exp. No.	T, °C	H ₂	R _p ¹	E _{eff} ² , kJ/mol
AlEt ₃	1	30	-	9.6	-21
	2	50	-	7.6	
	3	70	-	3.3	
Al(i-Bu) ₃	4	30	-	66	-2.2
	5	50	-	78	
	6	70	-	59	
Al(i-Bu) ₃	7	30	+	120	20
	8	50	+	230	
	9	70	+	300	

Polymerization at [C₆H₁₂]—1 mol/L, polymerization duration 60 min in Exps. 1–3 and 30 min in Exps. 4–6 and 10 min in Exps. 7–9. ¹ g PH/(g cat. × min × mol C₆H₁₂). ² Effective activation energy.

Data concerning the effect of reaction temperature on the polymerization rate of hexene-1 greatly differ from the results obtained for propylene polymerization over the same titanium–magnesium catalyst with AlEt₃ as a cocatalyst (Table 5).

Table 5. Data on the influence of reaction temperature on the rate of propylene polymerization and values of effective activation energy (E_{eff}) upon propylene polymerization over TMC with AlEt₃ cocatalyst in the presence and absence of H₂.

Exp. No.	T, °C	H ₂	R _p ¹	E _{eff} , kJ/mol
1	30	+	27	45.2
2	50	+	70	
3	70	+	220	
4	30	-	27	31.7
5	50	-	63	
6	70	-	117	

Polymerization with cocatalyst AlEt₃, polymerization duration 30 min. ¹ Polymerization rate, g PP/(g cat. × min × mol C₃H₆).

One can see that in the case of propylene, the polymerization rate substantially increases with elevation of the reaction temperature. The E_{eff} values (32–45 kJ/mol) calculated from these data are in the region known for polymerization of propylene over TMC. The indicated values strongly differ from the anomalous negative values of E_{eff} (−2.2 and −21 J/mol) calculated for polymerization of hexene-1 with AlEt₃ or Al(i-Bu)₃ cocatalyst in the absence of H₂ (Table 4, Exps. 1–3 and Exps. 4–6). The “normal” positive value of E_{eff} (20 kJ/mol, Exps. 7–8 in Table 4) was obtained only for polymerization with the Al(i-Bu)₃ cocatalyst in the presence of H₂.

The data on the decreasing of hexene-1 polymerization rate with an increase of polymerization temperature (Table 4, Exps. 1–3 and 4 and 6) may be related to a decrease in the number of AS that occurs at elevation of polymerization temperature under the indicated conditions. The appearance of this effect is determined by the composition of cocatalyst (AlEt₃) and the absence of hydrogen at polymerization.

We suppose that the decrease of the number of AS and, correspondingly, the decrease of polymerization rate of hexene-1 with elevation of the reaction temperature at polymerization with AlEt₃ cocatalyst may be associated with the state of reaction medium. In this case, polymerization proceeds in a homogeneous medium with the formation of a polyhexene solution in heptane. At such state of the reaction medium, the concentration of AlEt₃ on the catalyst surface corresponds to its concentration in the polyhexene solution, in distinction to propylene polymerization, when a layer of semicrystalline polymer is

formed on the catalyst surface and the concentration of AlEt_3 on the catalyst surface is much lower than its concentration in the heptane solution. The high AlEt_3 concentration on the catalyst surface at polymerization of hexene-1 may decrease the number of AS at elevation of polymerization temperature due to the reduction of a part of Ti^{3+} ions in active sites to the inactive Ti^{2+} sites.

The revealed substantial effect of hydrogen on the dependence of hexene-1 polymerization rate of the reaction temperature (Table 4, Exps. 4–6 and 7–9) may be related to the known phenomenon consisting in the formation of “dormant” sites at polymerization of α -olefins over TMC in the absence of H_2 and the possibility of their reactivation in the presence of H_2 [21]. The dormant sites are formed at polymerization of α -olefins in the absence of hydrogen as a result of 2,1-addition of α -olefin to the propagating polymer chain. These sites are reactivated upon interaction with hydrogen, thus enhancing the activity at polymerization of propylene and hexene-1 in the presence of H_2 . As was noted above, in the case of hexene-1 polymerization, the fraction of dormant sites formed in the absence of hydrogen and, accordingly, the enhancement of activity after hydrogen introduction are much higher than in the case of propylene polymerization. Presumably, the fraction of dormant sites formed in the absence of hydrogen depends on the polymerization temperature and increases with its elevation. This occurs because the reaction of α -olefin 2,1-addition to the propagating chain has a higher activation energy compared to the normal 1,2-addition; so, the fraction of dormant sites in the absence of H_2 increases with the elevation of polymerization temperature. The effect of hydrogen on the catalyst activity at different temperatures of hexene-1 polymerization and, accordingly, on the estimated E_{eff} values manifests itself most clearly in experiments with the Al(i-Bu)_3 cocatalyst (Table 4). It is seen that at polymerization in the absence of hydrogen (Exps. 4–6) the activity weakly decreases when the polymerization temperature is increased from 30 °C to 70 °C ($E_{\text{eff}} = -2.2 \text{ kJ/mol}$). At the same time, during polymerization in the presence of hydrogen (Exps. 7–9, Table 4) the activity noticeably increases with the elevation of polymerization temperature from 30 °C to 70 °C ($E_{\text{eff}} = 20 \text{ kJ/mol}$).

Thus, at polymerization of hexene-1 over TMC the composition of cocatalyst and the presence of H_2 strongly affect the dependence of polymerization rate on the reaction temperature and determine the possibility of a substantial decrease in the number of active sites with an increasing polymerization temperature from 30 °C up to 70 °C. This fact leads, firstly, to the appearance of anomalous negative values of the apparent activation energy of polymerization and, secondly, to a pronounced difference in the calculated E_{eff} values for different compositions of the catalytic system and reaction medium. In particular, according to the data of Table 4, the calculated values of E_{eff} vary from –21 to 20 kJ/mol.

4. Conclusions

Data are obtained on the great differences of the kinetics of hexene-1 and propylene polymerization over the TMC as well as the molecular weight and molecular weight distribution of polymers produced. It is found that the composition of cocatalysts (AlEt_3 or Al(i-Bu)_3) greatly affects the molecular weight and MWD of polyhexene, contrary to polypropylene. Polyhexene produced with AlEt_3 cocatalyst has a lower molecular weight and broader MWD ($M_w/M_n = 10–22$) in comparison with polyhexene produced with Al(i-Bu)_3 cocatalyst ($M_w/M_n = 4–5$). Polypropylene produced with both AlEt_3 and Al(i-Bu)_3 cocatalysts has a similar MWD ($M_w/M_n = 4–5.5$). In the case of propylene polymerization, the activity of TMC is similar with AlEt_3 and Al(i-Bu)_3 cocatalysts, but in the case of hexene-1, the polymerization activity is much higher with Al(i-Bu)_3 cocatalyst in comparison with AlEt_3 cocatalyst.

The addition of hydrogen at hexene-1 polymerization leads to the great increase of activity (10–32 times), but in the case of propylene polymerization, activity increases only 1.5–2 times. These results show that the fraction of “dormant” sites formed at hexene-1 polymerization in the absence of H_2 is much higher in comparison with propylene

polymerization. Note that the activity of TMC with Al(i-Bu)₃ cocatalyst in the presence of H₂ is close to the activity of this catalyst at propylene polymerization in the presence of H₂.

In the case of hexene-1 polymerization, we have found the unusual effect of the decrease of polymerization rate at increase of polymerization temperature from 30 °C up to 70 °C. Due to this effect, the activation energies calculated for polymerization rate (E_{eff}) have anomalous negative values within the range from −2.2 kJ/mol to −21 kJ/mol. These values depend on the composition of the cocatalyst and the presence of H₂; the maximal negative value (−21 kJ/mol) is observed for polymerization with AlEt₃ cocatalyst in the absence of hydrogen. Note that in the case of propylene polymerization with TEA cocatalyst we have found the usual E_{eff} values (32–45 kJ/mol). So, two main factors—the composition of the cocatalyst and the presence of H₂ leads to differences in the kinetics of hexene-1 and propylene polymerization and molecular mass characteristics of polymers.

The strong effect of cocatalyst AlEt₃ on the activity, molecular weight, and MWD of polyhexene may be caused by the formation of a homogeneous reaction medium (solution of polyhexene in heptane), in distinction of a heterogeneous medium when solid polypropylene particles are formed as a slurry in heptane. In this case, the concentration of AlEt₃ on the surface of the catalyst is much higher at hexene-1 polymerization in comparison with one at propylene polymerization. High AlEt₃ concentration on the surface of a catalyst leads to a decrease in the number of active sites (activity of catalyst), especially at high temperatures (70 °C) and an increase in the rate of chain transfer reaction with AlEt₃.

In the case of hexene-1 polymerization in the absence of H₂ activity is much lower in comparison with propylene polymerization because a higher fraction of “dormant” sites formed at hexene-1 polymerization in comparison with propylene polymerization. The addition of H₂ leads to the reactivation of “dormant” sites and an increase of activity in 10–30 times at hexene-1 polymerization. In this case, activity of TMC with Al(i-Bu)₃ cocatalyst in the presence of H₂ is close at hexene-1 and propylene polymerization.

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References

- Wang, Y.; Yu, B.; Zakin, J.L.; Shi, H. Review on drag reduction and its heat transfer by additives. *Adv. Mechan. Eng.* **2011**, *3*, 478749. [[CrossRef](#)]
- Huang, Z.; Chen, Z.; Li, Q.; Zhu, R.; Jing, S.; Zhou, Y.; Ma, Y.; Wang, N.; Chang, W. Experimental Research on the Drag Reduction Mechanism of Natural Gas Drag Reduction Agent and Its Industrial Field Test. *Ind. Eng. Chem. Res.* **2014**, *53*, 12494–12501. [[CrossRef](#)]
- Tu, C.F.; Biesenberger, J.A.; Stivala, S.S. Psychochemical Studies of Polyhexene-1. Polymerization Kinetics. *Macromolecules* **1970**, *3*, 206–214. [[CrossRef](#)]
- Kothandaraman, H.; Devi, M.S. Kinetics of polymerization of 1-octene with the catalyst systems VO(acac)²–AlEt₃ (or AlEt₂Br). *Eur. Polym. J.* **1996**, *32*, 651–659. [[CrossRef](#)]
- Chien, J.C.W.; Gong, B.M. Hexene-1 polymerization by homogeneous zirconocene and heterogeneous-supported TiCl₃ catalysts. *J. Polym. Sci. Polym. Chem.* **1993**, *31*, 1747–1754. [[CrossRef](#)]
- Saxena, P.K. Polymerization of 1-hexene using supported magnesium/titanium catalyst: Effect of cocatalyst. *Eur. Polym. J.* **1999**, *35*, 1313–1317. [[CrossRef](#)]
- Vasilenko, I.V.; Kostjuk, S.V. The influence of cocatalysts on 1-hexene polymerization with various supported magnesium-titanium catalysts. *Polym. Bull.* **2006**, *57*, 129–138. [[CrossRef](#)]

8. Zhang, L.T.; Fan, Z.Q.; Fu, Z.S. Dependence of the distribution of active centers on monomer in supported Ziegler-Natta catalysts. *Chin. J. Polym. Sci.* **2008**, *26*, 605–610. [[CrossRef](#)]
9. Kaur, S.; Naik, D.G.; Singh, H.R.; Patil, A.V.; Kothari, V.K.; Gupta, V.K. Poly(1-octene) synthesis using high performance supported titanium catalysts. *J. Appl. Polym. Sci.* **2010**, *115*, 229–236. [[CrossRef](#)]
10. Fan, Z.; Zhang, L.; Xia, S.; Fu, Z. Effects of ethylene as comonomer on the active center distribution of 1-hexene polymerization with MgCl₂-supported Ziegler–Natta catalysts. *J. Mol. Catal. A Chem.* **2011**, *351*, 93–99. [[CrossRef](#)]
11. Rishina, L.A.; Lalayan, S.S.; Galashina, N.M.; Perepelitsina, E.O.; Medintseva, T.I.; Kissin, Y.V. Polymerization of linear higher α -olefins with a modified Ziegler catalyst. *Polym. Sci. B* **2014**, *56*, 25–30. [[CrossRef](#)]
12. Ahmadjo, S. Preparation of ultra high molecular weight amorphous poly(1-hexene) by a Ziegler–Natta catalyst. *Polym. Adv. Technol.* **2016**, *27*, 1523–1529. [[CrossRef](#)]
13. Ivchenko, P.V.; Nifant'ev, I.E.; Tavtorkin, A.N. Polyolefin drag reducing agents (review). *Pet. Chem.* **2016**, *56*, 775–787. [[CrossRef](#)]
14. Yang, P.J.; Fu, Z.S.; Fan, Z.Q. 1-Hexene polymerization with supported Ziegler-Natta catalyst: Correlation between catalyst particle fragmentation and active center distribution. *Mol. Catal.* **2018**, *447*, 13–20. [[CrossRef](#)]
15. Echevskaya, L.; Matsko, M.; Nikolaeva, M.; Zakharov, V. 1-Hexene Polymerization over Supported Titanium-Magnesium Catalyst: The Effect of Composition of the Catalytic System and Polymerization Conditions on Temperature Dependence of the Polymerization Rate. *Macromol. React. Eng.* **2018**, *12*, 1700045. [[CrossRef](#)]
16. Echevskaya, L.; Matsko, M.; Nikolaeva, M.; Zakharov, V. Regulation of Molecular Weight Characteristics and Microtacticity of Polyhexene Produced over Highly Active Supported Titanium–Magnesium Catalysts. *Macromol. React. Eng.* **2018**, *12*, 1700064. [[CrossRef](#)]
17. Subramanyam, J.; Rajamohan, P.R.; Sivaram, S. A study of the structure of poly(hexene-1) prepared by nickel(α -diimine)/MAO catalyst using high resolution NMR spectroscopy. *Polymer* **2004**, *45*, 4063–4076. [[CrossRef](#)]
18. Hofman, M.; Nomura, K. 1-Hexene polymerization by Cp^{*}TiX₂(O-2,6-iPr₂C₆H₃) [X: Cl, Me] in the presence of MAO- and MMAO-modified carbonaceous supports. *J. Mol. Catal. A Chem.* **2010**, *319*, 85–91. [[CrossRef](#)]
19. Segal, S.; Goldberg, I.; Kol, M. Zirconium and Titanium Diamine Bis(phenolate) Catalysts for α -Olefin Polymerization: From Atactic Oligo(1-hexene) to Ultrahigh-Molecular-Weight Isotactic Poly(1-hexene). *Organometallics* **2005**, *24*, 200–202. [[CrossRef](#)]
20. Haas, I.; Dietel, T.; Press, K.; Kol, M.; Kempe, R. Aminopyridinate–FI Hybrids, Their Hafnium and Titanium Complexes, and Their Application in the Living Polymerization of 1-Hexene. *Chem. Eur. J.* **2013**, *19*, 14254–14262. [[CrossRef](#)]
21. Chadwick, I.C.; Miedema, A.; Sudmeijer, O. Hydrogen activation in propene polymerization with MgCl₂-supported Ziegler-Natta catalysts: The effect of the external donor. *Macromol. Chem. Phys.* **1994**, *195*, 167–172. [[CrossRef](#)]
22. Nikolaeva, M.I.; Mikenas, T.B.; Matsko, M.A.; Echevskaya, L.G.; Zakharov, V.A. Ethylene Polymerization over Supported Titanium-Magnesium Catalysts: Effect of Polymerization Parameters on the Molecular Weight Distribution of Polyethylene. *J. Appl. Polym. Sci.* **2011**, *122*, 3092–3101. [[CrossRef](#)]

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