

The effect of the comonomer on the copolymerization of ethylene with long chain α -olefins using Ziegler–Natta catalysts supported on $\text{MgCl}_2(\text{THF})_2$

M. Białek, K. Czaja*

Institute of Chemistry, University of Opole, 45-052 Opole, Oleska 48, Poland

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Abstract

The effect of the type of the comonomer (1-pentene, 1-hexene, 1-octene, 1-decene and 1-dodecene) on the copolymerization of ethylene with α -olefin over vanadium (VOCl_3 and VCl_4) and titanium (TiCl_4) catalysts supported on $\text{MgCl}_2(\text{THF})_2$ and activated by Et_2AlCl was studied. The results show that the introduction of a longer α -olefin in the ethylene polymerization feed depresses the catalytic activity of all investigated catalysts. The catalyst activity does not depend on the type of the comonomer applied but changes with the comonomer concentration in the feed. The incorporation of α -olefin in the polymer chain was found to be dependent on the type and concentration of the comonomer in the feed as well as the type of catalyst. The incorporation of α -olefin increases with the increase of the comonomer concentration in the polymerization feed and the comonomer reactivity decreases with the increase of the size of the α -olefin chain, especially in the case of comonomers longer than octene. It should be stressed, however, that both vanadium catalysts clearly demonstrate higher activity in the copolymerization process than their titanium counterpart and also produce copolymers with higher comonomer content.

The density, crystallinity and melting temperature of the copolymers decrease with increase of the amount of the comonomer incorporated, but the type of the comonomer does not have a strong influence on these properties. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Copolymers of ethylene with other α -olefins are important products with favourable properties in comparison to homopolyethylene. Therefore, there has been a continuing interest in these polymers. Introduction of an α -olefin comonomer to the polyethylene chain changes the structure, and consequently the properties of the polymer product obtained. This effect is dependent on the type of catalytic system used, polymerization conditions as well as the comonomer type that is introduced [1]. It is known that longer comonomers such as 1-hexene change the polyethylene properties such as density, melting point and crystallinity more effectively than smaller units such as propene at the same concentration.

Earlier we found that two vanadium-based catalysts supported on complex magnesium chloride, $\text{MgCl}_2(\text{THF})_2/\text{VOCl}_3/\text{Et}_2\text{AlCl}$ and $\text{MgCl}_2(\text{THF})_2/\text{VCl}_4/\text{Et}_2\text{AlCl}$, offer high activity and stability in ethylene polymerization [2,3].

Therefore, it has been of interest to us to study the investigated catalytic systems supported on Mg–THF complex in the copolymerization of ethylene with other α -olefins. First, the catalytic properties of these two vanadium systems and, for comparison, their titanium counterpart based on TiCl_4 in the copolymerization of ethylene with 1-hexene were studied [4]. It was found that vanadium catalysts gave higher activity than the titanium one and also show a better incorporation of 1-hexene to the polymer chain for the same comonomer concentration in the feed. These positive results encouraged us to extend our study using other α -olefins. 1-Pentene, 1-hexene, 1-octene, 1-decene and 1-dodecene were used as comonomers.

2. Experimental

All the operations were always carried out in dry and oxygen-free argon.

2.1. Materials

Ethylene (Petrochemia SA Płock, Poland) and pure argon

* Corresponding author. Tel.: + 48-77-454-5841; fax: + 48-77-441-0740.

E-mail address: czaja@uni.opole.pl (K. Czaja).

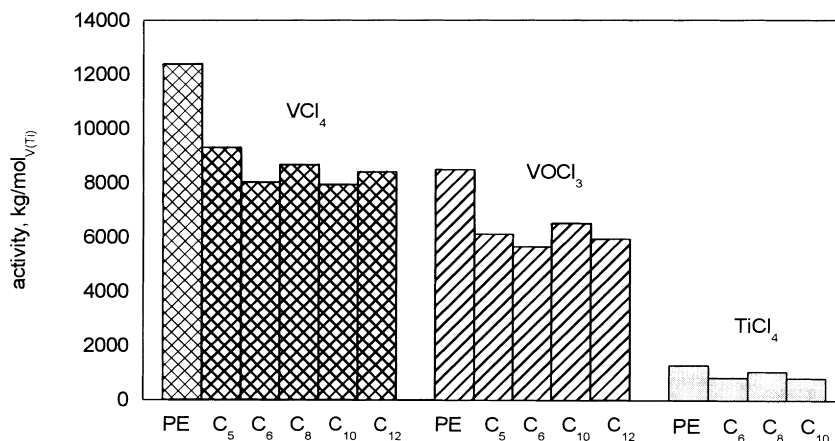


Fig. 1. Effect of the type of comonomer on the activity in ethylene/ α -olefin copolymerization using $\text{MgCl}_2(\text{THF})_2$ /transition metal compound/ Et_2AlCl as a catalytic system; α -olefin concentration: 0.57×10^{-2} – 8.6×10^{-2} mol/dm³.

(Praxair, Poland) were used after having been passed through a column of sodium metal supported on Al_2O_3 . Pure-grade hexane (Petrochemia SA Płock, Poland) was refined with sulphuric acid, dried by refluxing in argon over sodium metal and stored over 4 Å molecular sieves. 1-Pentene, 1-hexene, 1-octene, 1-decene and 1-dodecene (Aldrich) were stored over 4 Å molecular sieves and used without further purification. VOCl_3 , VCl_4 (Aldrich) and Et_2AlCl (Fluka), TiCl_4 (Merck) were used without further purification. $\text{MgCl}_2(\text{THF})_2$ was prepared by the Institute of Chemistry, University of Wrocław (Poland), and was used as received.

2.2. Catalyst preparation

The supported vanadium or titanium magnesium catalyst precursors were prepared by ball-milling of 5 g solid $\text{MgCl}_2(\text{THF})_2$ with VOCl_3 , VCl_4 or TiCl_4 (molar ratio $\text{Mg}:\text{V}(\text{Ti}) = 10$) in a glass mill (capacity: 250 cm³; with 35 balls of 1 cm diameter) in a slurry (70 cm³ hexane) at room temperature for 24 h.

2.3. Copolymerization

The copolymerization reactions were carried out in a 1 dm³ reactor equipped with a mechanical stirrer. The reactor was filled with hexane (0.7 dm³) and required amounts of Et_2AlCl and the catalyst precursors: $\text{MgCl}_2(\text{THF})_2/\text{VOCl}_3$, $\text{MgCl}_2(\text{THF})_2/\text{VCl}_4$ or $\text{MgCl}_2(\text{THF})_2/\text{TiCl}_4$. Among the catalysts mentioned above only the titanium catalyst was aged for 15 min. Next, α -olefin was charged into the reactor and the copolymerization was initiated by the introduction of ethylene. The monomer pressure was kept constant during the polymerization by continuous addition of ethylene. The reaction was stopped through addition of acidic methanol solution; the polymer was subsequently filtered off, washed with methanol and dried. The copolymerization conditions were (values in brackets for copolymerization over the titanium catalyst):

$[\text{VOCl}_3] = 1.5 \times 10^{-5}$ or 1×10^{-5} mol/dm³; $[\text{VCl}_4] = 1 \times 10^{-5}$ mol/dm³; $[\text{TiCl}_4] = 4.5 \times 10^{-5}$ mol/dm³; $[\text{Al}] = 25 \times 10^{-3}$, (30×10^{-3} mol/dm³); $p_{\text{Et}} = 0.5$ MPa; $T = 35$ (50°C); $t = 60$ min.

2.4. Characterization of the polymers

Copolymer compositions were determined by the modified IR method [5] using a Philips PU 9800 FT-IR spectrometer. The samples were used in the form of polymer powder pills with KBr.

The heat of fusion (ΔH_f) and melting temperature (T_m) were measured on the samples which had been previously melted and recrystallized with the use of a TA Instruments 2010 DSC calorimeter at a heating rate of 5 K/min. From ΔH_f , the percent crystallinity $X_c = \Delta H_f \times (100/290)$ was calculated [6].

The density of the copolymers was measured according to the Polish Standard PN-92/C-89035.

3. Results and discussion

3.1. Catalyst activity

The negative effect [7,8] of the presence of higher α -olefin on the activity of the catalysts in the copolymerization of ethylene with higher α -olefins or the lack of this effect [9–11] is known from earlier reports. The effect of activation caused by higher α -olefin, particularly for low concentrations of this comonomer, on the yield of ethylene polymerization on both typical heterogeneous Ziegler–Natta catalysts and metallocene catalysts was observed [7,9–24]. Our results on ethylene polymerization as well as ethylene/ α -olefin copolymerization over vanadium and titanium catalysts are shown in Fig. 1. As can be seen, the introduction of the comonomer in the polymerization feed depresses the catalyst activity.

Nevertheless, the activity of the catalysts depends on the

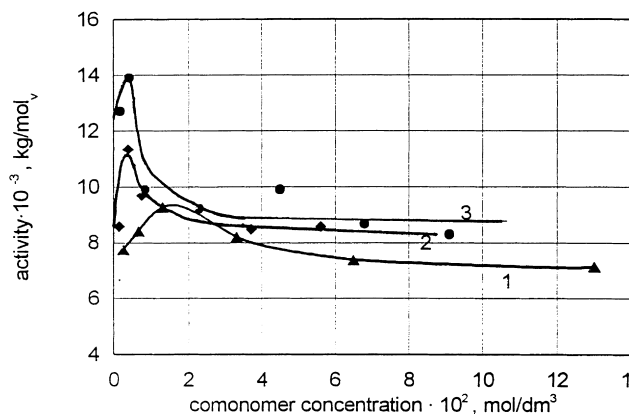


Fig. 2. Effect of comonomer concentration on the activity in ethylene/ α -olefin copolymerization. (1) $\text{MgCl}_2(\text{THF})_2/\text{VCl}_4/\text{Et}_2\text{AlCl}$, 1-pentene; (2) $\text{MgCl}_2(\text{THF})_2/\text{VOCl}_3/\text{Et}_2\text{AlCl}$, 1-decene; (3) $\text{MgCl}_2(\text{THF})_2/\text{VOCl}_3/\text{Et}_2\text{AlCl}$, 1-octene.

comonomer concentration in the polymerization feed. The catalytic activities obtained for vanadium-based catalysts in ethylene/1-pentene, ethylene/1-octene and ethylene/1-decene copolymerizations are presented in Fig. 2. These results show that a small quantity of comonomers in the

polymerization feed results in some increase of the catalytic activity. Further increase of the comonomer concentration leads to reduction of this activity and then it shows a tendency to remain constant. The same effect was observed in the copolymerizations of ethylene with α -olefins catalysed by other catalytic systems [8,18,25].

The results presented in Fig. 1 and also in Fig. 2 indicate that there is no significant effect of the length of the comonomer chain on the catalyst activity as it was observed in other studies [26].

It should be stressed that, independently of the comonomer type and concentration, both vanadium catalysts clearly demonstrate higher activity in comparison to their titanium counterpart as it was confirmed earlier for the polymerization of ethylene [2].

3.2. Ethylene/ α -olefin copolymers

To study the effect of the catalyst system on the comonomers reactivity it is necessary to know the structure of the copolymerization products. The composition of ethylene/ α -olefin copolymers is usually determined by IR or ^{13}C NMR spectroscopic methods [27,28]. Unfortunately, because of the low solubility of the copolymers obtained our attempts

Table 1

α -Olefin content in the copolymers obtained with vanadium and titanium catalysts supported on $\text{MgCl}_2(\text{THF})_2$ (M_E and M_M are, respectively, the concentrations of ethylene and α -olefin in the polymerization feed, and m_M is the content of α -olefin in the copolymer)

Catalyst	Comonomer	M_E (mol/dm ³)	M_M ($\times 10^2$ mol/dm ³)	m_E (mol%)
$\text{MgCl}_2(\text{THF})_2/\text{VOCl}_3/\text{Et}_2\text{AlCl}$	1-Pentene	0.4880	0.65	0.286
			1.30	0.387
			3.25	0.429
			6.47	0.511
			12.85	0.838
	1-Decene		0.75	0.195
			1.89	0.237
			3.75	0.253
			5.60	0.284
	1-Dodecene		0.64	0.169
			1.60	0.189
			4.77	0.216
$\text{MgCl}_2(\text{THF})_2/\text{VCl}_4/\text{Et}_2\text{AlCl}$	1-Pentene	0.4880	1.30	0.333
			3.25	0.384
			12.85	0.784
			0.91	0.161
			2.27	0.195
	1-Octene		4.52	0.339
			6.75	0.394
			8.97	0.474
			1.89	0.183
	1-Decene		5.60	0.218
			7.44	0.227
			1.60	0.176
1-Dodecene	4.77	0.198		
	$\text{MgCl}_2(\text{THF})_2/\text{TiCl}_4/\text{Et}_2\text{AlCl}$	0.3865	8.97	0.390
			34.44	0.649
7.44			0.315	
1-Decene	0.3865	28.55	0.354	

Table 2
The reactivity ratio, r_E , obtained for ethylene/ α -olefin copolymerization

α -Olefin	Precatalyst		
	MgCl ₂ (THF) ₂ /VOCl ₃	MgCl ₂ (THF) ₂ /VCl ₄	MgCl ₂ (THF) ₂ /TiCl ₄
1-Pentene	48.7	50.8	–
1-Octene	–	50.6	252.5
1-Decene	120.7	203.9	1400.5
1-Dodecene	232.0	295.3	–

to get ¹³C NMR spectra were unsuccessful. These data indicate, however, that copolymerization products obtained on the catalysts supported on MgCl₂(THF)₂ have very high molecular weight, similar to the ethylene homopolymers synthesized on the same systems. Because of this, the composition of copolymers was measured only by the modified IR method [5], using the A_{1379}/A_{1368} absorbance ratios, which were obtained by the separation of analytical bands. Comparison of the percentage of the comonomer incorporated in the copolymer and the comonomer content in the feed for all the investigated catalysts is shown in Table 1. The results indicate that the content of the comonomer in the product increases with the increase of its concentration in the feed for all the investigated comonomers and catalysts. It should be stressed, however, that the intensity of this increase is dependent on the comonomer as well as the catalyst type.

The results of the determination of the copolymer compositions (Table 1) show that for all the investigated cases, copolymers were synthesized with very low comonomer content. This means that ethylene exhibits much higher activity compared to that of the comonomer. In such cases the known copolymer composition equation used in the Fineman–Ross method can be replaced with the following

simplified one [29,30]:

$$\frac{m_M}{m_E} = \frac{1}{r_E} \times \frac{M_M}{M_E} \quad (1)$$

where M_E and M_M are, respectively, the contents of ethylene and α -olefin comonomer in the polymerization feed, m_E and m_M are, respectively, the mole fractions of ethylene and the comonomer incorporated in the copolymer chain, and r_E is the reactivity ratio of ethylene.

On the basis of the results obtained the ethylene reactivity ratios were calculated. The results presented in Table 2 indicate that the comonomer reactivity values depend on the type of comonomer as well as the catalytic system used. It was confirmed that the comonomers ability to copolymerize decreases with the increase in the number of their carbon atoms in the molecule (r_E value increases), especially in the case of comonomers longer than octene. The steric hindrance of higher comonomers is probably the reason for these observations because they make the insertion of a big molecule to an active metal–carbon bond of catalytic complex difficult.

It was also confirmed that the r_E values depend on the type of catalytic system used and they are clearly smaller for both vanadium catalysts than for the titanium catalyst.

Table 3
Effect of 1-pentene and 1-decene incorporation on the properties of copolymers obtained (ethylene/1-pentene and ethylene/1-decene, respectively) with the vanadium catalytic system MgCl₂(THF)₂/VOCl₃/Et₂AlCl

Type of comonomer	Comonomer concentration $M_M (\times 10^2 \text{ mol/dm}^3)$	Comonomer content in the copolymer m_M (mol%)	Melting temperature (°C)	Degree of crystallinity (%)	Density (g/dm ³)
1-Pentene	0.0	0.0	144.00	64.8	955.7
	0.26	0.286	142.75	54.5	951.7
	1.3	0.387	141.68	56.3	940.3
	3.2	0.429	142.37	55.4	–
	6.5	0.511	141.08	49.0	–
	9.7	0.527	140.52	46.6	–
	13.0	0.838	136.50	43.1	–
1-Decene	0.0	0.0	144.00	64.8	955.7
	0.75	0.195	142.65	58.6	935.2
	1.8	0.237	143.08	63.0	929.5
	5.6	0.284	142.63	57.7	919.5
	7.5	–	134.33	43.3	–

Table 4
Effect of the type of comonomer on the properties of ethylene/ α -olefin copolymers obtained with vanadium catalysts

Comonomer	Comonomer concentration M_M ($\times 10^{-2}$ mol/dm ³)	Comonomer content in the copolymer m_M (mol%)	Degree of crystallinity (%)	Melting temperature (°C)
MgCl ₂ (THF) ₂ /VOCl ₃ /Et ₂ AlCl				
–	0.0	0.0	64.8	144.0
1-Pentene	0.65	0.286	54.5	142.75
1-Octene	9.1	0.265	52.7	143.27
1-Decene	5.6	0.284	57.7	142.63
MgCl ₂ (THF) ₂ /VCl ₄ /Et ₂ AlCl				
–	0.0	0.0	62.4	144.52
1-Pentene	1.3	0.333	52.3	141.90
1-Hexene	1.14	0.323	52.2	143.62
1-Octene	4.52	0.339	52.5	142.45

These results indicate that the vanadium catalysts preferentially incorporate comonomers into the polyethylene chain. Thus, vanadium catalysts are not only more active in the ethylene polymerization and copolymerization than their titanium counterpart but also produce copolymers with higher comonomer content.

3.3. Properties of the copolymers

Table 3 presents the influence of the 1-pentene and 1-decene concentration in the feed on the properties of the copolymers produced (ethylene/1-pentene and ethylene-1-decene, respectively). As expected, the melting point and the crystallinity decrease with the increase of the amount of comonomer in the polymerization feed and with the increase of its content in the copolymer. We can also observe that the density of these copolymers decreases with the increase of the amount of the comonomer incorporated.

We also studied, by DSC, the melting and crystallization behaviour of ethylene copolymers with different α -olefins. The results are shown in Table 4. As can be seen, the melting point and crystallinity of all copolymers are smaller in comparison to the values obtained for homopolyethylene but we do not observe a strong influence of the comonomer type (from 1-pentene to 1-dodecene) at similar mole fractions of α -olefins on these properties. It seems that the elongated branch does not influence the melting point and crystallinity of the copolymers obtained.

4. Conclusions

Vanadium catalysts are much more effective in the copolymerization of ethylene with longer olefins than the corresponding titanium system. The reactivity of all the studied comonomers in the copolymerization with ethylene was found to be clearly higher in the presence of both vanadium catalysts. These catalysts are not only more active in the ethylene polymerization and copolymerization but also produce copolymers with the highest comonomer content

(higher r_E value). Therefore, when using vanadium systems, a smaller amount of comonomers is necessary to obtain copolymers with the desired composition and properties.

Acknowledgements

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