

Homo-polymerization of α -Olefins and Co-polymerization of Higher α -Olefins with Ethylene in the Presence of $\text{CpTiCl}_2(\text{OC}_6\text{H}_4\text{X}-p)/\text{MAO}$ Catalysts ($\text{X} = \text{CH}_3, \text{Cl}$)

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Abstract: Cyclopentadienyl-titanium complexes containing $-\text{OC}_6\text{H}_4\text{X}$ ligands ($\text{X} = \text{Cl}, \text{CH}_3$) activated with methylaluminoxane (MAO) were used in the homo-polymerization of ethylene, propylene, 1-butene, 1-pentene, 1-butene, and 1-hexene, and also in co-polymerization of ethylene with the α -olefins mentioned. The $-\text{X}$ substituents exhibit different electron donor-acceptor properties, which is described by Hammett's factor (σ). The chlorine atom is electron acceptor, while the methyl group is electron donor. These catalysts allow the preparation of polyethylene in a good yield. Propylene in the presence of the catalysts mentioned dimerizes and oligomerizes to trimers and tetramers at 25°C under normal pressure. If the propylene pressure was increased to 7 atmospheres, $\text{CpTiCl}_2(\text{OC}_6\text{H}_4\text{CH}_3)/\text{MAO}$ catalyst at 25°C gave mixtures with different contents of propylene dimers, trimers and tetramers. At 70°C we obtained only propylene trimer. Using the catalysts with a $-\text{OC}_6\text{H}_4\text{Cl}$ ligand we obtained atactic polymers with M_w 182,000 g/mol (at 25°C) and 100,000 g/mol (at 70°C). The superior activity of the $\text{CpTiCl}_2(\text{OC}_6\text{H}_4\text{Cl})/\text{MAO}$ catalyst used in polymerization of propylene prompted us to check its activity in polymerization of higher α -olefins (1-butene, 1-pentene, 1-hexene) and in co-polymerization of these olefins with ethylene. However, when homo-polymerization was carried out in the presence of this catalyst no polymers were obtained. Gas chromatography analysis revealed the presence of dimers. The activity of the $\text{CpTiCl}_2(\text{OC}_6\text{H}_4\text{Cl})/\text{MAO}$ catalyst in the co-polymerization of ethylene with higher α -

olefins is limited by the length of the co-monomer carbon chain. Hence, the highest catalyst activities were observed in co-polymerization of ethylene with propylene (here a lower pressure of the reagents and shorter reaction time were applied to obtain catalytic activity similar to that for other co-monomers). For other co-monomers the activity of the catalyst decreases as follows: propylene >1-butene > 1-pentene >> 1-hexene. In the case of co-polymerization of ethylene with propylene, besides an increase in catalytic activity, an increase in the average molecular weight M_w of the polymer was observed. Other co-monomers used in this study caused a decrease of molecular weight. A significant increase in molecular weight distribution (M_w/M_n) evidences a great variety of polymer chains formed during the reaction.

Keywords: Hemititanocene, ethylene, propylene, 1-butene, 1-pentene, 1-hexene, co-polymerization of ethylene

Introduction

The polymerization of α -olefins in the presence of homogenous catalysts based on transition metal complexes of is one of the most interesting issues in the catalysis, organic chemistry and chemistry of polymers. Apart from typical metallocene catalysts active in polymerization of α -olefins, with constrained geometry (*ansa*-metallocenes), the complexes of the CpM(L)Cl₂ type (*hemi*-metallocenes) were investigated (Cp - cyclopentadienyl; M - Ti, Zr; L - OAr, halogen, alkyl) [1-12]. The synthesised and investigated earlier by us CpTiCl₂(OC₆H₄X-*p*) complexes activated by methylaluminoxane (MAO) belong to this group of catalysts [13, 14]. The catalysts of CpTiCl₂(OC₆H₄X-*p*) type are commonly used in syndiotactic polymerization of styrene.

In our previous investigations on polymerization of styrene we used CpTiCl₂(OC₆H₄X-*p*) catalysts activated with MAO, where X = -Cl, -H, -CH₃. We found that the substituents -X of the phenoxy ligand affect the yield of this reaction. In our previous article [15] it has been reported that the content of titanium ions in various oxidation states depends on the electron donor-acceptor properties of the substituent X (Table 1). As can be seen from Table 1, the content of Ti(III) in the solution decreases, and the content of Ti(IV) rises with the electron acceptor properties of X substituents. The Ti(II) content did not exceed 15% in any sample studied.

Our previous results [15, 16] and theoretical considerations [17] indicate that Ti(III) ions are responsible for syndiotactic styrene polymerization in hemititanocene catalytic systems. The theoretical considerations claimed that olefin polymerization runs also in the presence of Ti(IV) ions in these systems [17].

In this paper we present the results of our investigation on homo-polymerization of ethylene, propylene, 1-butene, 1-pentene and 1-hexene, and on co-polymerization of ethylene with α -olefins in CpTiCl₂(OC₆H₄X-*p*)/MAO catalytic system (X = -Cl, -CH₃). It was of considerable interest to find out if Ti(IV) complexes present in the mixture would be active in these reactions.

Table 1. Percentage of titanium ions in different oxidation states in the CpTiCl₂(OC₆H₄X-*p*)/MAO system as a function of Hammett's factors "σ"

Oxidation state of Ti	Substituent X (σ)		
	Cl (0,23)	H (0)	CH₃ (-0,17)
Ti (IV) %	35	25	10
Ti (III) %	55	65	75
Ti (II) %	10	10	15

Results and Discussion

Homo-polymerization of ethylene

Ethylene polymerization results are included in Table 4. The activity of the CpTiCl₂(OC₆H₄Cl-*p*)/MAO catalyst in the homo-polymerization of ethylene was 167 kg/(mol Ti*h). The polymer obtained had melting point of 129 °C. Its average molecular weight was 667 000 g/mol and molecular weight distribution 2.4.

Homo-polymerization of propylene.

On the basis of polarographic measurements made for styrene polymerization in the presence of CpTiCl₂(OC₆H₄X)/MAO catalysts [15], for the polymerization of propylene we have chosen titanium complexes in which the X substituent is -Cl or -CH₃. These substituents have different electron donor-acceptor properties, which are described by Hammett's factors (σ). The chlorine atom is an electron acceptor, while the methyl group is electron donor. Phenoxy ligand is a reference (Table 2). Propylene at 25°C under normal pressure dimerizes and oligomerizes to trimers and tetramers.

Table 2. Products of oligomerization of propylene in the presence of CpTiCl₂(OC₆H₄X)/MAO under normal pressure

Substituent	σ	Oligomers of propylene [wt%]		
		C₆	C₉	C₁₂
CH₃	-0.17	50,1	31,3	18,6
H	0	49,9	31,7	18,4
Cl	0.23	55,6	30,2	14,2

In the case of CpTiCl₂(OC₆H₄CH₃)/MAO and CpTiCl₂(OC₆H₅)/MAO catalysts the percentage of the products is similar: ~50%_{wt} of dimer, ~30%_{wt} of trimer and ~18%_{wt} of tetramer.

For CpTiCl₂(OC₆H₄Cl)/MAO catalyst the percentage of the dimer rises at the cost of the tetramer. Results obtained for polymerization of propylene under an increased pressure are shown in Table 3.

Table 3. Results of polymerization of propylene in the presence of CpTiCl₂(OC₆H₄X)/MAO catalysts under increased pressure (7 atm.).

Substituent X	σ	Weight of the product [g]		DSC [°C]		Form of the product
		25°C	70°C	25°C	70°C	
CH₃	-0.17	~3.2*	~0.6**	-	-	Fluid
H	0	2.20	1.04	95.0;118.1	106.4;128.1;203.2	Gum
Cl	0.23	1.77	3.71	163.6	~100;119.2;164.5	Gum

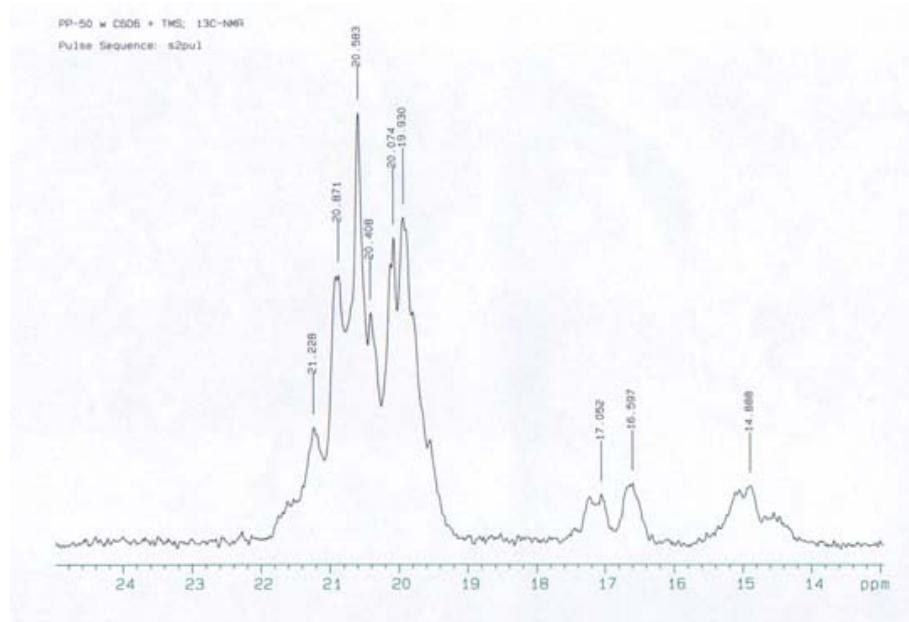
*The product was a mixture of oligomers: C₆=91.4%wt;C₉=8.1%_{wt};C₁₂=0.5%_{wt}

**trimer:100%_{wt}; polymerization conditions: 0.01 mmol Ti, Al/Ti=300, propylene pressure 7 atm., time 1h

In the presence of CpTiCl₂(OC₆H₄CH₃)/MAO catalyst, both at 25°C and 70°C, we obtained mixtures with different content of propylene dimers, trimers and tetramers. At 70°C only propylene trimer were obtained.

In the case of the catalysts with phenoxy and chlorophenoxy ligand polymers with average molecular weight 182 000 g/mol (at 25°C) and 100 000 g/mol (at 70°C) were obtained. Both the absence of a clear signal of the melting point on the DCS curve and the gummy product formed suggest that atactic polypropylene was obtained. This was confirmed by the ¹³C NMR measurements. The spectra contain signals assigned to atactic polypropylene in the 19-22 ppm range [18] (Figure 1).

Figure 1. ¹³C NMR spectra of PP obtained



The catalyst with a phenoxy ligand was more active at 25°C than the one with a chlorophenoxy ligand. CpTiCl₂(OC₆H₄Cl)/MAO catalyst was more active at 70°C, because it is more stable at higher temperatures than other catalysts investigated [16].

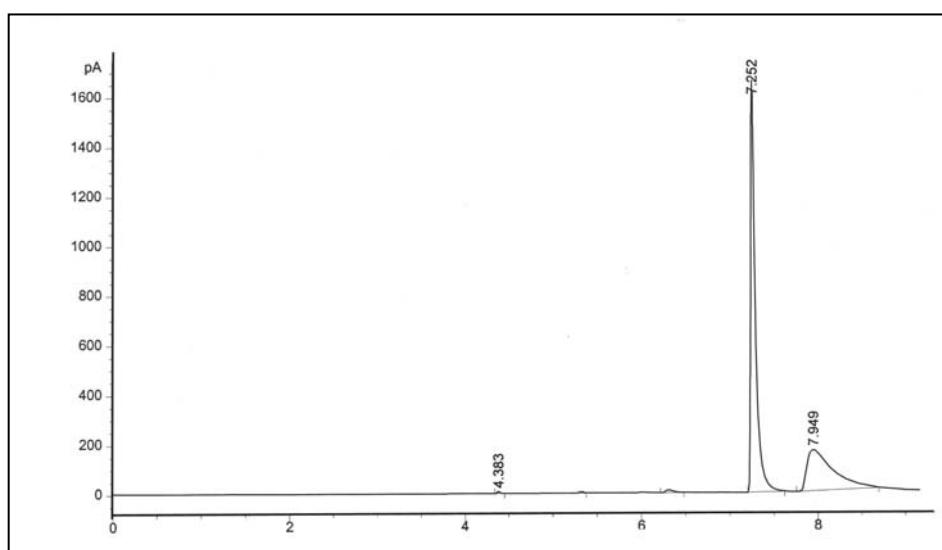
The results obtained for oligomerization of propylene under normal pressure did not show the effect of substituent X on the reaction course. Composition of the products is indicative of the significance of the reactions, which terminate the polymer chains growth. In the case of *hemi*-titanocene catalysts it is mainly the reaction of hydrogen β-elimination [19, 22]. Because the propylene concentration in the reaction mixture is low, the rate of the termination reactions was higher, compared with the rate of growth of polymer chains on the active centers.

A rise in the propylene pressure to 7 atm. made the effect of the X substituents (their electron donor-acceptor properties) on the reaction course evident. Such a conclusion can be drawn on the basis of the reaction yield and the form of the products obtained. CpTiCl₂(OC₆H₄CH₃)/MAO catalyst with an electron donor substituent in the phenoxy ligand has low activity in the reaction described. CpTiCl₂(OC₆H₅)/MAO reference catalyst and CpTiCl₂(OC₆H₄Cl)/MAO catalyst, with an electron acceptor substituent, gave products in good yield. A superior activity of CpTiCl₂(OC₆H₄Cl)/MAO catalyst in polymerization of propylene prompted us to check its activity in polymerization of higher α-olefins (1-butene, 1-pentene, 1-hexene) and in co-polymerization of these olefins with ethylene.

Homo-polymerization of 1-butene, 1-pentene and 1-hexene

According to the literature [8], the solid products of the reaction should be obtained after extraction with chloroform and removal of the substrate (1-pentene or 1-hexene) residues from the mixture under vacuum. However, when homo-polymerization was carried out in the presence of CpTiCl₂(OC₆H₄Cl-*p*)/MAO no polymers were obtained. Analysis of the chloroform solutions by means of gas chromatography revealed the presence of dimers. (Figure 2)

Figure 2. A chromatogram of a chloroform solution containing products of 1-butene polymerization. (Catalyst CpTiCl₂(OC₆H₄Cl-*p*)/MAO 4.383 1-butene; 7.252 chloroform; 7.949 dimers of 1-butene)



Co-polymerization of ethylene with higher α -olefins

The results obtained for co-polymerization of ethylene with α -olefins: propylene, 1-butene, 1-pentene and 1-hexene are presented in Table 4.

In the case of co-polymerization of ethylene with propylene the activity of the catalyst rised to 506 kg/(mol Ti*h). Melting point of the copolymer (127°C) was close to the melting point of polyethylene obtained. The molecular weight of the copolymer was raised to 758 000 g/mol and molecular weight distribution to 5.1 in comparison with polyethylene.

Table 4. Conditions of the reaction, catalyst activity, DSC signals, average molecular weight and molecular weight distribution of copolymers obtained with $\text{CpTiCl}_2(\text{OC}_6\text{H}_4\text{Cl}-p)/\text{MAO}$ catalyst.

Sample	Ethylene Pressure [atm.]	Time [min.]	Mass of the product [g]	Activity [kg/(mol Ti*h)]	DSC I [$^{\circ}\text{C}$]	DSC II [$^{\circ}\text{C}$]	Mw/1000 [g/mol]	Mn/1000 [g/mol]	M_w/M_n
PE	5	30	1.67	167	133	129	667	279	2.4
Pp-1	4	15	2.53	506	133	127	758	146	5.1
B-1	5	30	8.69	869	114, 125	104	319	122	2.6
P-2	3	30	0.35	35	Very wide signal with max. temp. 119	Wide signal two max. temp. 102 and 116	234	69	3.3
P-4	5	10	0.37	111	108	100 and 115	272	75	3.6
P-5	5	20	0.32	48	112	100 and 118	408	84	4.8
P-1	5	30	6.33	633	109, 138	105	301	86	3.5
P-3	8	30	8.07	807	122	121	283	60	4.7
H-2	5	30	0.77	77	112, 135	113	245	45	5.5
H-3	8	30	0.63	63	Wide, tattered signal from 100 to 163	122	258	103	2.5

PE – ethylene homo-polymerization, Pp – co-polymerization of ethylene with propylene, B - co-polymerization of ethylene with 1-butene, P - co-polymerization of ethylene with 1-pentene, H - co-polymerization of ethylene with 1-hexene

In co-polymerization of ethylene with 1-butene the catalyst activity reached 869 kg/(mol Ti*h). On the DSC thermogram obtained during the first heating of the sample two signals with maximums at 114 and 125°C are visible. During the second heating the only one signal with a maximum at 104°C was recorded. The average molecular weight of the copolymer decreased to 319,000 g/mol, in comparison with PE homopolymer. The molecular weight distribution (2.6) was approximately equal to that obtained for PE.

The activity of the $\text{CpTiCl}_2(\text{OC}_6\text{H}_4\text{Cl}-p)/\text{MAO}$ catalyst in co-polymerization of ethylene with 1-pentene changes from 35 to 807 kg/(mol Ti*h) according to the reaction parameters. As the pressure of ethylene is higher, the higher activity of the catalyst is observed. On the thermographic curves recorded for the products of the co-polymerization conducted under ethylene pressure of 3 atm. for 30 minutes, and also for products of the reaction carried out under pressure of 5 atm. of ethylene for 10 and 20 minutes, signals with maximums at 100 and 116°C are observed. For the samples obtained under ethylene pressure of 5 and 8 atm, for the reaction time of 30 minutes, melting points 105 and 121°C are noticed, respectively (single signals). The molecular weights of polymers are heightening, according to reaction parameters, from 234,000 g/mol to 408,000 g/mol. The molecular weight distribution of the copolymers of ethylene with 1-pentene is also higher than the one for the copolymers of the ethylene with 1-butene described earlier (in this case the values are in the range of 3.3 - 4.8).

In co-polymerization of ethylene with 1-hexene the catalyst investigated has low activity. A value of 77 kg/(mol Ti*h) is the lowest in comparison with the activity calculated for co-polymerization of ethylene with 1-butene or 1-pentene. It is also lower than the value calculated for homo-polymerization of ethylene. When the pressure of ethylene is raised from 5 to 8 atm. the activity of $\text{CpTiCl}_2(\text{OC}_6\text{H}_4\text{Cl}-p)/\text{MAO}$ catalyst lowers to 63 kg/(mol Ti*h). The copolymers obtained have melting points of 113 and 122°C, respectively. The molecular weight of the copolymer obtained under ethylene pressure of 5 atm. is 245 000 g/mol, and its molecular weight distribution 5,5. The molecular weight of ethylene/1-hexene copolymer obtained under 8 atm. of ethylene is 258,000 g/mol, and molecular weight distribution – 2.5.

On the basis of the data presented in Table 4 and described above we can tell that the presence of such co-monomers as propylene, 1-butene and 1-pentene increases the yield of the reaction in comparison with homo-polymerization of ethylene.

The fact of an increase in the catalyst activity in co-polymerization of ethylene with propylene has already been known. It was observed for $[\text{C}_2\text{H}_4(\text{Ind})_2]\text{ZrCl}_2$ catalyst and other metallocenes [20]. The analysis of the sequences of the mers in the chains of the polymers obtained in the presence of catalyst mentioned above do not manifest any changes in reaction mechanism of the reaction. The presence of the co-monomer in the reaction mixture increases electron density in the region of the active center, and in consequence changes the rate of the olefin insertion to the metal ion [21]. In the same way we can explain the increasing activity of $\text{CpTiCl}_2(\text{OC}_6\text{H}_4\text{Cl}-p)/\text{MAO}$ catalyst in co-polymerization of ethylene with propylene, 1-butene and 1-pentene.

In the presence of 1-hexene the catalytic activity of $\text{CpTiCl}_2(\text{OC}_6\text{H}_4\text{Cl}-p)/\text{MAO}$ system decreases in comparison with homo-polymerization of ethylene, and also as compared with the co-polymerization of ethylene with the monomers mentioned above. This is probably due to the influence of the length of carbon chain in 1-hexene. The 1-hexene molecule presents a too big steric hindrance around the active center, which is the Ti(III) ion bonded with cyclopentadienyl ligand [22], to make bonding of another ethylene or 1-hexene molecule possible and in consequence inhibits the polymer chain growth.

The activity of the catalyst investigated here is limited by the length of the carbon chain in the α -olefin molecule, which reacts with ethylene. Hence, higher catalyst activities were observed in co-polymerization of ethylene with propylene (in this case a lower pressure of the reagents and shorter

reaction time were applied to obtain a catalytic activity similar to that for other co-monomers). The activity of the catalyst for the reaction investigated for co-monomers used decreases as follows: propylene > 1-butene > 1-pentene >> 1-hexene.

In the case of co-polymerization of ethylene with propylene, besides an increase of catalytic activity, an increase in the average molecular weight M_w of the polymer is observed. Other co-monomers used cause a decrease in molecular weight. A significant increase in molecular weight distribution (M_w/M_n) evidences a great variety of polymer chains to be formed during the reaction.

Ethylene-propylene copolymers are obtained in industry on a large or commercial scale and are used as rubbers. A copolymer obtained here, which has a molecular weight higher than PE homopolymer and melting point at 127°C near the one calculated for PE, should have better mechanical properties.

Copolymers of ethylene with higher α -olefins, such as: 1-butene, 1-hexene, 1-octene are industrially made and are known as PE-LD (*Linear Low Density Polyethylene*) polymers. They are used mainly to produce packages [23]. The longer the branch chains are, the better the stretch resistance of the copolymer is and the thinner leafs can be obtained. In this respect the most interesting copolymers of those investigated here will be the copolymers of ethylene with 1-pentene (considering the reaction yield). Therefore we paid more attention to this particular copolymer and we investigated whether the reaction parameters (time and ethylene pressure) change its molecular weight M_w and melting point.

For shorter reaction times - 10, 20 min. - we expected homogenous copolymer with a greater participation of 1-pentene, but the product we obtained gives two signals on the DSC thermographic curve. It suggests the presence of two different crystalline phases in homogenous polymer fraction (only one signal on M_w chromatogram). The reaction conducted for 30 minutes yielded homogenous copolymers with a lower molecular weight. When the ethylene pressure was heightened from 5 to 8 atm. the copolymers obtained had higher melting points, hence, a higher content of ethylene. Presence of two signals on the thermogram and a higher molecular weight distribution suggest that during the initiation of the reaction different active centers are formed.

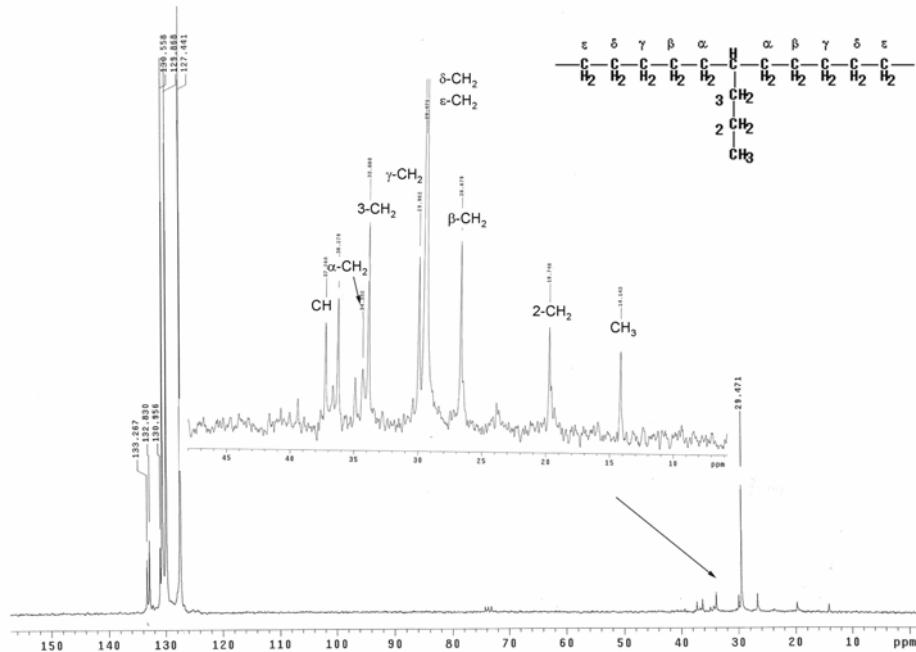
The differences in melting points indicate that the products obtained are copolymers. Melting point for polyethylene is 129°C. It is lower for ethylene-propylene copolymer to 127°C. Such a small difference in T_m can be explained by similarity of the structure of carbon chains in homo- and co-polymer. The longer branch chain of the built-in α -olefin and the higher co-monomer content, both the smaller crystallinity of copolymer and the lower melting point. The lowest melting points were recorded for ethylene-butene and ethylene-hexene copolymers. Their values are 104 and 100°C, respectively, which suggest a high content of 1-butene and 1-pentene in the copolymers obtained.

Co-polymerization of ethylene with 1-hexene yielded products of T_m 113 and 122°C. We expected copolymer with lower melting point in comparison with T_m of the products of ethylene/1-butene and ethylene/1-pentene co-polymerization. An increase of melting point and a low yield of the reaction suggest a low content of 1-hexene in the copolymer.

Despite a difficulty with dissolving samples, we managed to record the 1H NMR and ^{13}C NMR spectra for the samples obtained to check if the reaction products are real copolymers and not only a physical mixture of homopolymers. Exemplary spectra, recorded for the product of the reaction of ethylene with 1-pentene, are reported in Figure 2. There, signals from several carbon atoms in polymer

chain are presented. Taking into consideration the analysis of the spectra we can say that the product obtained is a copolymer, which is confirmed by a signal at 37,260 ppm from the -CH- group characteristic of the bond between the pentene and ethylene units [21].

Figure 2. ^{13}C -NMR spectra recorded for ethlene/1-pentene copolymer obtained in the presence of $\text{CpTiCl}_2(\text{OC}_6\text{H}_4\text{Cl}-p)/\text{MAO}$ catalyst.



Conclusions

Our study on the reaction of polymerization of propylene showed that the electron donor-acceptor properties of the substituent -X in $\text{CpTiCl}_2(\text{OC}_6\text{H}_4\text{X})$ complexes have an effect on the yield and selectivity of the reaction. Catalyst $\text{CpTiCl}_2(\text{OC}_6\text{H}_4\text{CH}_3)$ with an electron-donor substituent, a methyl group, gave only propylene oligomers. The $\text{CpTiCl}_2(\text{OC}_6\text{H}_4\text{Cl})$ catalyst exhibits high activity in this reaction which allows one to obtain atactic polypropylene in a good yield.

Unfortunately, the $\text{CpTiCl}_2(\text{OC}_6\text{H}_4\text{X})/\text{MAO}$ catalyst was inactive in the polymerization reaction of higher α -olefins: 1-butene, 1-pentene and 1-hexene. During the reaction only dimers of the mentioned olefins were obtained. These results are quite different from those obtained by Nomura [6] for $\text{Cp}'\text{TiCl}_2(\text{O}-2,6-i\text{Pr}_2\text{C}_6\text{H}_3)/\text{MAO}$ catalysts (where $\text{Cp}' = \text{Cp}, t\text{BuC}_5\text{H}_4, 1,3-\text{Me}_2\text{C}_5\text{H}_3, 1,3-t\text{Bu}_2\text{C}_5\text{H}_3, \text{C}_5\text{Me}_5$) and $\text{Cp}^*\text{TiCl}_2(\text{OAr})/\text{MAO}$ ($\text{OAr} = 2,6-i\text{Pr}_2\text{C}_6\text{H}_3, 2,4,6-\text{Me}_3\text{C}_6\text{H}_2, 2,6-\text{Me}_2\text{C}_6\text{H}_3, 2-t\text{Bu}-4,6-\text{Me}_2\text{C}_6\text{H}_2, 4-\text{MeC}_6\text{H}_4$). In the presence of the catalysts mentioned above polyhexene in yields in the range of 26 - 728 kg polymer/(mol Ti*h) were obtained, along with polymers of 1-octene and 1-decene.

He claimed that both electronic and steric factors of the substituents on cyclopentadienyl group play an essential role in the catalytic activity of these complexes. $\text{CpTiCl}_2(2,6-i\text{Pr}_2\text{C}_6\text{H}_3)$ catalyst, with a structure essentially the same to the catalyst investigated in our study, also showed high activity in polymerization of 1-hexene and 1-octene. It results that not only electron donor-acceptor properties of the substituent at phenoxy ligand, but also their position have the effect on the yield and selectivity of the reaction.

Taking into consideration the activity of the catalyst and DSC data we can say that for the CpTiCl₂(OC₆H₄Cl-*p*)/MAO catalyst the most promising results are obtained in the case of co-polymerization of ethylene with 1-butene and 1-pentene.

In the case of co-polymerization of ethylene with 1-hexene, the key role is played by steric hindrances caused by the long 1-hexene chain. In this reaction more efficient are the catalysts with substituents on cyclopentadienyl group. They probably minimise rotations of the molecule bonded to the active site.

Experimental

General

Solvent – toluene (PKN Orlen) was dried over Na/K alloy and distilled just before the reaction was started. Ethylene, propylene (PKN Orlen) and 1-butene (Aldrich) were dried before the start of the reaction on the column filled with 4 Å type molecular sieves. 1-Pentene (95% Aldrich) and 1-hexene (97% Aldrich) were distilled over CaH₂ before the reaction. Methylaluminoxane (MAO) – EURECEN AL 5100/10T (Crompton GmbH) as 10% solution in toluene was used to activate CpTiCl₂(OC₆H₄Cl-*p*) complex. CpTiCl₂(OC₆H₄Cl-*p*) complex was synthesized according to the method described previously [10]. Each operation was performed under an argon atmosphere using Schlenk technique. The gas was free of water and oxygen. DSC spectra were recorded for samples of co-polymers obtained using a Perkin-Elmer DSC 7 thermograph. The temperature was changed from 40 to 260 °C, and next the sample was cooled and heated again. The ¹H-NMR and ¹³C-NMR analyses were performed on samples of co-polymers dissolved in deuterated 1,1,2,2-tetrachloroethane using a Varian 200 apparatus. The molecular weight was determined using a high-temperature WATERS 150-CV gel permeation chromatograph, with 1,2,4-trichlorobenzene as a solvent (135 °C).

Homo-polymerization of ethylene

The homo-polymerization of ethylene was conducted in a pressure reactor (250 mL) at 40°C. The reactants: toluene (125 mL), 10% MAO solution (5 mL) and a toluene solution of the titanium complex (0.5 mL, containing 0.02 mmol Ti) were added to the reactor in the ethylene stream. Then the reactor was closed and the ethylene pressure was raised to 5 atm. Methanol was added to the reactor after 1 hour to complete polymerization. The final product was separated and dried to a constant weight under vacuum.

Homo-polymerization of propylene

Polymerization under normal pressure of propylene.

The polymerization reaction was carried out in a 15 mL glass reactor connected to a vacuum-argon line. MAO solution (3 mL) was added to the reactor first and then the contents were saturated with propylene. The toluene solution of the catalyst (2 mL, 0.01 mmol Ti) was subsequently added while still passing propylene through the mixture. The reactions were conducted at 25°C. Methanol was

added to the reactor after 1h to complete polymerization. The toluene layer was separated and analyzed with an Agilent Technologies 6890 gas chromatograph equipped with a FID detector.

Polymerization of propylene under increased pressure (7 atm.)

The homo-polymerization of propylene was conducted in a 250-mL pressure reactor at temperatures of 25 and 70 °C. The reactants: toluene (125 mL), 10% MAO solution (3 mL) and toluene solution of the titanium complex (2 mL, containing 0.01 mmol Ti) were added to the reactor in the propylene stream. Subsequently, the reactor was closed and the propylene pressure was raised to 7 atm. Methanol was added to the reactor after 1 hour to complete polymerization. The final product was separated and dried to a constant weight under vacuum. When the polymer was not observed, toluene solution was analysed with the gas chromatograph.

Homo-polymerization of 1-butene, 1-pentene and 1-hexene

The homo-polymerization reaction was carried out in 15-mL glass reactors, which were connected to a vacuum-argon line. A sequence of the reactants added to the reactor was as follows: 1-pentene or 1-hexene (5 mL), MAO solution (2.5 mL) and the solution of the titanium complex in toluene (2.5 mL, 0.01 mmol Ti). In the case of 1-butene homo-polymerization, MAO and the titanium complex solutions were added to the reactor first, and subsequently 1-butene was allowed to pass through the mixture. The reactions were conducted at 25 °C. Methanol was added to the reactor after 1h to complete polymerization. The reaction products were extracted with CHCl₃. The chloroform solution was washed with a 5% aqueous solution of HCl. The chloroform layer was separated and dried over Na₂SO₄. Chloroform solutions obtained in homo-polymerization of 1-butene, 1-pentene and 1-hexene were analyzed with gas an Agilent Technologies 6890 chromatograph equipped with a FID detector.

Ethylene/propylene co-polymerization

The reaction of co-polymerization of ethylene with propylene was conducted in a 250-mL pressure reactor at 40°C. The reactants were added to the reactor in ethylene stream: toluene (100 mL), 10% MAO solution (5 mL) and toluene solution of the titanium complex (0.5 mL, containing 0.02 mmol Ti). Upon addition of the reactants the reactor was closed and the pressure of ethylene was raised to 4 atm. When the pressure in the reactor dropped to 3 atm. propylene was added twice to result in a pressure rise of one atmosphere. Every subsequent pressure drop occurring in the reactor was compensated for by ethylene. Methanol was added to the reactor after 15 minutes to complete co-polymerization. The final product was separated and dried to a constant weight under vacuum.

Ethylene/1-butene co-polymerization

The co-polymerization of ethylene with 1-butene was conducted in a 250-mL pressure reactor at 40 °C. The reactants: toluene (100 mL), 10% MAO solution (5 mL) and toluene solution of titanium complex (0.5 mL, containing 0.02 mmol Ti) were added into the reactor in the ethylene stream. Upon

addition of all the reactants mentioned above, the mixture was being saturated with 1-butene for 5 minutes. The 1-butene pressure was around 1 atm. (0.16 mol of 1-butene was introduced into the reaction mixture). Next, the ethylene pressure was increased. The reaction was running for 30 minutes. Subsequently, methanol was added to the reactor to complete the co-polymerization reaction. The final product was separated and dried under vacuum to a constant weight.

Ethylene/1-pentene and ethylene/1-hexene co-polymerization

The co-polymerization of 1-pentene or 1-hexene with ethylene was carried out in a 250-mL pressure reactor at 40 °C. The reactants: toluene (100 mL), 1-pentene or 1-hexene (10 mL), 10% MAO solution (5 mL) and toluene solution of titanium complex (0.5 mL, containing 0.02 mmol Ti) were added to the reactor were added into the reactor in the ethylene stream. Upon addition of all reactants the ethylene pressure was raised to 3, 5 or 8 atm. After 30 minutes methanol was added to the reactor to complete co-polymerization. The final product was separated and dried to a constant weight.

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