

# Effect of phenoxy ligands on catalytic properties of titanium half-sandwich complexes/MAO systems

D. Jamanek, K. Niciński, R. Kazimierczuk, T. Woźniewski, Z. Wieczorek, W. Skupiński\*

*Industrial Chemistry Research Institute, Rydygiera 8, 01-793 Warszawa, Poland*

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## Abstract

A study on the effect of phenoxy ligands of an donor or acceptor character in titanium half-sandwich catalytic systems of a general formula  $LTiCl_2(OC_6H_4X-p)/MAO$  (where L is cyclopentadienyl, indenyl or pentamethylcyclopentadienyl;  $X=NO_2, Cl, H, CH_3, t-C_4H_9, OCH_3$ ; MAO: methylalumoxane) on their activity and selectivity in the reactions of polymerization of olefins and styrene and of their co-polymerization, showed that the effect of coordination of the polymerization centers by the phenyl rings substituted with donor groups is involved here. The effect resulted in the formation of polymers of a lower molecular weight and was crucial to the composition of the products obtained: polymer or oligomer, co-polymer or homopolymer mixture.

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## 1. Introduction

Monocyclopentadienyl complexes of titanium have for long been the research object of increased interest. They may be represented by a general formula:  $LTiY_3$ , where L = a ligand containing a cyclopentadienyl grouping: cyclopentadienyl, indenyl, fluorenyl, alkyl derivatives of cyclopentadienyl rings, while Y is any monoanionic ligand, e.g. halogen, OR,  $OC_6H_4X$ ,  $O(O=C)$  anions, etc. The anionic character of ligands Y allows for their being easily exchanged, while in the syntheses of these complexes just any ligand containing cyclopentadienyl grouping capable of yielding an anion is suitable [1].

Accordingly, the chemistry of these compounds is considerable. Indeed, it has been advanced lately, when the complexes upon activation with methylalumoxane were found to provide the catalysts which are virtually the only effective catalysts of syndiotactic polymerization of styrene [2,3].

Aside from this reaction the catalysts exhibit an activity in stereoregular 1,4-*cis*-polymerization of dienes and in their copolymerization [4]. These are also active in polymerization of olefins, co-polymerization of ethylene with higher olefins or with styrene [5–7].

By activating titanium half-sandwich complexes with methylalumoxane a mixture of titanium[IV], titanium[III] and titanium[II] complexes is produced in the reaction, the composition of which depends on ligands L and Y and on the activation conditions [8].

Intensive researches effort on these systems by both experimental and calculative techniques allowed to assign to the titanium[IV] complexes the activity in the reactions of polymerization of olefins and co-polymerization of ethylene with styrene; to the titanium[III] complexes the activity in the reactions of syndiotactic styrene polymerization and of 1,4-*cis*-polymerization of dienes [9–11]. The titanium[II] complexes, when complexed with aromatic compounds, were shown to exhibit an activity in the olefin oligomerization reactions, e.g. in ethylene trimerization [12].

This paper reviews the effect of selected phenoxy ligands of an acceptor or donor character on the activity of the  $LTiCl_2(OC_6H_4X-p)/MAO$  catalytic system in the olefin polymerization, ethylene with styrene co-polymerization, and syndiotactic styrene polymerization reactions.

## 2. Experimental

All the operations were conducted under anhydrous (molecular sieves 3A) and oxygen-free ( $Cu/SiO_2$ ) argon, by the Schlenk method. Solvents: toluene, hexane and methylene chloride were purified by standard methods.

\* Corresponding author. Tel.: +48 22 568 2183; fax: +48 22 568 2184.  
E-mail address: [wincenty.skupinski@ichp.pl](mailto:wincenty.skupinski@ichp.pl) (W. Skupiński).

Ethylene, propylene (PKN Orlen) and 1-butene (Aldrich, pure) were purified by passing through molecular sieves 4A.

1-Pentene, 1-hexene (Aldrich, pure) were distilled over CaH<sub>2</sub> directly before use.

Styrene (FCh Dwory) was passed through activated alumina (to remove the stabilizer) and distilled from over CaH<sub>2</sub> directly before use.

LTiCl<sub>2</sub>(OC<sub>6</sub>H<sub>4</sub>X-*p*) complexes were prepared by the procedures described in the available literature [13–16].

### 2.1. Polymerization and co-polymerization of olefins and styrene

Polymerization and co-polymerization reactions were carried out in solvents or in the bulk under atmospheric pressure allowing, if needed, to pass the gaseous substrates through a reaction mixture placed in glass reaction vessels or, when the reactions were conducted under pressure, in a 600-ml autoclave equipped with a stirrer, a thermocouple, a heating jacket and valves.

For olefin polymerization, into the reactor were added, in this order: methylalumoxane solvent (a 10% toluene solution, Crompton), the olefin, and the catalyst solution. For styrene polymerization styrene was added first into the reaction vessel, then MAO, and last the catalyst. In the event of co-polymerization the reactants were added in the following order: solvent, MAO, the olefin (styrene), ethylene. The amounts of the individual reactants taken and the reaction conditions are reported in tables and in the footnotes under the tables.

The reactions were brought to completion by adding ethanol. When polymers were produced, they were precipitated using a 2% ethanolic HCl.

The solid products were filtered off and dried to a constant weight at suitable temperatures, if needed, under a reduced pressure (oil pump).

Molecular weights of the products were determined by gel-permeation chromatography using a Waters 150-CV instrument.

<sup>13</sup>C NMR spectra were recorded with a Varian 200 instrument.

Thermal transitions and melting points were determined by DSC technique using a Perkin-Elmer model DCS 7 apparatus.

The liquid products were determined by GLC technique using a Hewlett-Packard HP 6890 instrument.

## 3. Results

The ethylene polymerization reaction was carried out at either an atmospheric or elevated pressures. In either case a solid polymer was obtained. Yields and average molecular weights  $M_w$ , of the polyethylenes obtained are reviewed in Table 1.

Irrespective of substituents X in the phenoxy rings in the catalytic systems studied, during ethylene polymerization at atmospheric pressure the products were obtained in the same yields, which appears to be due to the reaction running in the diffusion range.

If the catalytic systems examined do not differ in activity, the molecular weight of the polyethylenes obtained is diverse. For

Table 1

Ethylene polymerization in the presence of the CpTiCl<sub>2</sub>(OC<sub>6</sub>H<sub>4</sub>X-*p*)/MAO catalytic system, where X = NO<sub>2</sub>, Cl, H, CH<sub>3</sub>, *t*-C<sub>4</sub>H<sub>9</sub>, OCH<sub>3</sub> under atmospheric pressure

X	Yield (g)	M.p. (°C)	$M_w/10^4$ (g/mol)
NO <sub>2</sub>	0.10	136	18.1
Cl	0.10	137	14.1
H	0.14	130	13.8
CH <sub>3</sub>	0.11	132	6.6
<i>t</i> -C <sub>4</sub> H <sub>9</sub>	0.09	127	9.2
OCH <sub>3</sub>	0.10	131	7.3
Cl <sup>a</sup>	1.67	133	667

0.02 mmol Ti; Ti:Al (Al in MAO) = 1:300; 20 °C, 2 h, 50 ml toluene, ethylene bubbled through the reaction mixture: 3 dm<sup>3</sup> l/h, activity ~5 kgPE/mol Ti h.

<sup>a</sup> 5 at ethylene, 250 ml toluene, 40 °C, 0.5 h, activity 167 kgPE/mol Ti h.

the systems containing substituents X = NO<sub>2</sub>, Cl or H, i.e. substituents of an acceptor character [14] polymers were obtained of an  $M_w$  larger than 100 000 g/mol, the value being the greater, the stronger acceptor effect of the phenoxy ligand.

If the character of the effect of the X substituent is the donor one (CH<sub>3</sub>, *t*-C<sub>4</sub>H<sub>9</sub> and OCH<sub>3</sub> substituents) [14],  $M_w$  of the polyethylenes obtained is smaller than 100 000 g/mol.

An increased ethylene concentration in the reaction mixture, i.e. when polymerization reaction was carried out under a pressure of 5 at, caused the yields and molecular weights of the polyethylene to rise to the values equalled 667 000 g/mol, typical of this type of the catalysts [6].

Likewise, the propylene, 1-butene, 1-pentene and 1-hexene polymerization reactions were conducted under atmospheric pressure with the catalytic systems studied. The results obtained are presented in Table 2.

If ethylene was polymerized under normal pressure in the presence of the catalytic systems studied, higher olefins only oligomerized at atmospheric pressure: propylene only to dimers, trimers and tetramers, higher olefins only to dimers. For propylene oligomers, the dimers account for 50%, whereas the trimer content is ca. 30%. The properties of X substituents have no effect on the composition or on the yield of the oligomers.

More methylenic groups in the olefin chain make a gradual decline in the yield of products.

Table 2

The propylene, 1-butene, 1-pentene and 1-hexene polymerization in the presence of the CpTiCl<sub>2</sub>(OC<sub>6</sub>H<sub>4</sub>X-*p*)/MAO catalytic system (where X = Cl, H, CH<sub>3</sub>) under atmospheric pressure

X	Olefin	Yield (g)	Oligomers		
			Dimer (%)	Trimer (%)	Tetramer (%)
CH <sub>3</sub>	Propylene	0.23	50	31	19
H	Propylene	0.21	50	32	18
Cl	Propylene	0.24	56	30	14
Cl	1-Butene	0.1	100		
Cl	1-Pentene	0.06	100		
Cl	1-Hexene	0.04	100		

0.01 mmol Ti, Al/Ti = 300, 50 ml toluene, propylene and 1-butene pressure bubbled through the reaction mixture: 3 dm<sup>3</sup> l/h; 5 ml of 1-pentene and 1-hexene, 20 °C, 1 h.

Table 3

Propylene polymerization in the presence of the CpTiCl<sub>3</sub>(OC<sub>6</sub>H<sub>4</sub>X-*p*)/MAO catalytic system (where X = Cl, H, CH<sub>3</sub>) at 25 and 70 °C under pressure 7 atm

X	Olefin	Yield (g)		GLC/DSC (°C)		Product
		25 °C	70 °C	25 °C	70 °C	
CH <sub>3</sub>	Propylene	3.28	0.6	Dimer 91%, trimer 8%, tetramer 1%	Trimer 100%	Liquid
H	Propylene	2.20	1.04	95, 118 <sup>a</sup>	106, 128, 203 <sup>a</sup>	aPP <sup>b</sup>
Cl	Propylene	1.77	3.71	163 <sup>a</sup>	100, 119, 164 <sup>a</sup>	aPP <sup>b</sup>

0.01 mmol Ti, Al/Ti = 300, toluene 50 ml propylene pressure 7 atm, time 1 h.

<sup>a</sup> Signals of the propylene oligomers occluded in aPP.<sup>b</sup> Determined by <sup>13</sup>C NMR.

Table 4

Ethylene–styrene co-polymerization in the presence of CpTiCl<sub>3</sub>(OC<sub>6</sub>H<sub>4</sub>X-*p*)/MAO catalytic system (where X = Cl, OCH<sub>3</sub>) under atmospheric pressure

Substituent X	Time (min)	Yield (g)	THF-soluble fraction (%)	DSC (°C)
Cl	0	1.7	0	256
Cl	60	0.9	17	254 <sup>a</sup> (110)
OCH <sub>3</sub>	0	2.8	0	258
OCH <sub>3</sub>	60	1.3	27	235 <sup>a</sup>

0.01 mmol Ti, Al/Ti = 300, 10 ml (0.095 mol) styrene, ethylene bubbled through the reaction mixture: 3 dm<sup>3</sup> l/h, toluene 10 ml, 25 °C.<sup>a</sup> Of THF soluble fraction.

While for 1-pentene and 1-hexene the pressure has no effect, as the reactants are liquid under conditions of the reactions, for propylene a higher pressure in the reaction system should be expected to rise the concentration of this monomer. This may enhance the chain propagation rate. To verify this assumption, propylene polymerization was conducted in the presence of the catalytic systems studied under pressure of 7 atm, at two temperatures: 20 and 70 °C. The results obtained are reviewed in Table 3.

Under an increased pressure the catalytic system in which a phenoxy donor ligand X = CH<sub>3</sub>, is present, at 25 °C afforded primarily propylene dimers (90%), while at 70 °C the product was exclusively trimers.

If the phenoxy ligands were of acceptor character (X = H or Cl) the propylene polymerization product was atactic polypropylene irrespective of the reaction temperature.

Titanium half-sandwich catalysts are also active in the ethylene–styrene co-polymerization reactions. In this study the catalytic systems used in this reaction contained phenoxy ligands with Cl or OCH<sub>3</sub> substituents. Results of the reaction carried out at an atmospheric pressure are presented in Table 4.

The reactions were carried out by bubbling ethylene through a mixture containing the catalytic system and styrene dissolved

Table 5

Ethylene–styrene co-polymerization in the presence of CpTiCl<sub>3</sub>(OC<sub>6</sub>H<sub>4</sub>Cl-*p*)/MAO catalytic system under elevated pressure of ethylene

pC <sub>2</sub> = (atm)	Time (min)	Activity (kg/mol Ti h)	THF sol. fr. (%)	M.p. DSC <sup>a</sup> (°C)	M <sub>w</sub> /10 <sup>4a</sup> (g/mol)	MWD <sup>a</sup>	Structure <sup>a</sup>
4	40	243	73	63	19 (1.2)	2.2 (1.2)	ESE, ESESE, PE, PS
8	20	906	58	71	9 (0.5)	1.7 (1.7)	ESE, PE, PS

0.02 mmol Ti; Al/Ti = 300, styrene: 60 ml (0.55 mol), toluene: 150 ml.

<sup>a</sup> Of the THF-soluble fraction.

in toluene. The yields of products were invariably lower than in co-polymerization than homopolymerization reactions.

The solid product obtained was extracted with THF to isolate the copolymer fraction [6]. In the case of the catalytic system comprising a chlorophenoxy ligand the fraction obtained melted just two degrees lower than the homopolymer. This indicates the presence of a greater number of structural errors in the chain of the syndiotactic polystyrene (sPS) obtained as compared with the homopolymerization sPS [15].

Those structural errors occur in greater number in the product made in the case of the reaction catalyzed by the system comprising a methoxyphenoxy ligand.

When the co-polymerization reactions were carried out under increased ethylene pressure only a mixture of the ethylene and styrene homopolymers was obtained in the case of this system.

Under this condition, for the system with a chlorophenoxy ligand a typical high ethylene–styrene copolymer was obtained which melted below 100 °C [5–7] cf. Table 5.

The product yield, its composition: mer sequence, molecular weights, melting points depend on the conditions of the co-polymerization reaction: ethylene pressure and the reaction time.

An effect of the phenoxy ligands of the catalytic systems under study manifests itself also on the yield of the syndiotactic polystyrenes obtained and on their average molecular weights M<sub>w</sub> (cf. Table 6).

The catalytic systems studied showed a typical of this catalyst type differences in activity and the values of average molecular weights depending on the cyclopentadienyl ligand [3]. Both their activity and the M<sub>w</sub> of the polymers obtained decrease in the following order: Cp\* > Ind. > Cp.

Irrespective of the kind of cyclopentadienyl ligands L and the activities displayed by the catalytic systems studied, when the phenoxy ligand has a methoxy group, in each case sPS was obtained in a higher yield and with a relatively lower average molecular weight, than if the X substituent was chlorine.

Table 6

Syndiotactic styrene polymerization in the presence of  $\text{LTiCl}_2(\text{OC}_6\text{H}_4\text{X-}p)/\text{MAO}$  catalytic system ( $\text{X} = \text{Cl}, \text{OCH}_3$ )

Ligand L	Substituent X	Styrene:Al:Ti, mol:mol:mol	Yield (Tonne) % (sPS/Ti)	$M_w/10^3$ , g/mol
Cp	Cl	8000:300:1	22.4 (1760)	116
Cp	OCH <sub>3</sub>	8000:300:1	34.2 (2720)	61
Ind	Cl	6000:300:1	52.4 (3120)	410
Ind	OCH <sub>3</sub>	6000:300:1	69.6 (4200)	97
Cp*	Cl	15000:500:1	25.59 (3900)	550
Cp*	OCH <sub>3</sub>	15000:500:1	36.7 (5550)	84

0.01 mmol Ti, Al/Ti = 300, styrene: 60 ml (0.55) mol, 1 h, 50 °C (bulk polymerization).

Table 7

Composition of the  $\text{CpTiCl}_2(\text{OC}_6\text{H}_4\text{X-}p)/\text{MAO}$ 

Titanium ion	Substituent X					
	NO <sub>2</sub>	Cl	H	CH <sub>3</sub>	<i>i</i> -C <sub>4</sub> H <sub>9</sub>	OCH <sub>3</sub>
$\sigma$	1.24	0.23	0	-0.17	-0.20	-0.27
Ti[IV]	65	35	25	10	15	0
Ti[III]	20	55	65	75	75	80
Ti[II]	15	10	10	15	10	20
sPS	12.3	22.4	36.6	35.6	36.6	38.2

Percentage concentration of Ti[IV], Ti[III] and Ti[II] ions and percentage yield of syndiotactic polystyrene [16].

#### 4. Discussion

From the study on the  $\text{CpTiCl}_2(\text{OC}_6\text{H}_4\text{Y-}p)/\text{MAO}$  catalytic system, where  $\text{Y} = \text{NO}_2, \text{Cl}, \text{H}, \text{CH}_3, t\text{-C}_4\text{H}_9$  or  $\text{OCH}_3$ , it was found that in the system the Ti[IV], Ti[III] and Ti[II] ions occur. While the number of the Ti[III] complexes is proportional to the donor effects of the phenoxy ligand, the number of the Ti[IV] complexes is inversely proportional to these effects. Also, the yield of the syndiotactic polystyrene obtained in the presence of these systems exhibits a proportionality to the donor effects of the X substituent (Table 7) [16].

As mentioned earlier, the titanium[IV] complexes in these systems should be assigned an activity in the olefin polymerization reactions. Hence, the catalytic systems containing acceptor phenoxy ligands should afford polyethylene in higher yields in the polymerization reaction in the presence of the systems under study. A diffusive character of the course of this reaction under atmospheric pressure hindered in demonstrating this activity.

The same polyethylene yield found to be independent of the phenoxy ligand kind suggests that in this range the same number of active centers participate in the reaction and that they are of the same activity. In other words, the active complexes center should not possess the phenoxy ligands that would differentiate the catalysts activity. However, the values of the molecular weights of the polymers made contradict this assumption, as they are different.

Should the value of the molecular weights here depend on the number of the polymerization centers formed in the systems under study (the more of the centers are), the lower should be the molecular weights of the polymer at a constant ethylene concentration in the reaction medium. This relationship should be expected for the catalytic systems containing acceptor phenoxy

ligands. They contain more Ti[IV] complexes responsible for olefin polymerization [9–11]. However, the results obtained fail to corroborate this assumption.

Studies on polymerization of olefins and of styrene in the presence of cyclopentadienyl titanium complexes, where an additional coordination of titanium ions is likely to take place by the aryl ligands, showed that the polymers obtained are of relatively lower molecular weights. The aryl ligands are linked to the cyclopentadienyl ring or by some aromatic compounds of donor properties added to the reaction mixtures (e.g. mesitylene).

Here, the formation of a complex with the aryl ring competes with the olefin coordination in the chain propagation process. This on the one hand impairs chain growth and on the other hand it facilitates chain termination process. As a result, the polymer chain is detached from the catalytic center relatively earlier to provide polymers of a lower molecular weight. The effect is more visible, when the donor properties of the aryl ligand are more pronounced [12,17–19].

It may therefore be justifiably supposed that it is this effect that is responsible for the results obtained. Beside, it occurs only if the phenoxy ligands are of an donor character. Although in the majority of the catalytic systems described in literature, where this effect is involved the catalysts, are the titanium complexes where titanium ions are coordinated with aryl substituents linked with methylene-bridge to the cyclopentadienyl ligands.

The effect occurs also if other molecules present in the system have such a substituent, e.g. in the co-catalyst molecule. In either case the aromatic rings coordinate the titanium ions at the polymerization centers [20].

Studies on the mechanism of formation of catalytic species in  $\text{LTiY}_3/\text{MAO}$  systems, active in olefin polymerization, indicate that the Y ligands are present in the products of  $\text{LiTiY}_3$  alkylation with MAO.  $\text{LTiMe}_2\text{Y}$ , new MAO containing Y ligands and active catalytic cations  $\text{CpTiMeY}^+$  as a product of  $\text{LTiMe}_2\text{Y}$  decomposition with subsequent interaction with MAO, are these products [7,15].

Thus in the catalytic systems of our interest the donor phenoxy ligands with X substituents as the Y ligands, may also coordinate the titanium cations at polymerization centers, irrespective of whether linked to the new MAO or to titanium ions in the complexes.

The fact that in the propylene polymerization some mixtures of oligomers are obtained and in the 1-butene, 1-pentene and 1-hexene polymerization only dimers are formed is indicative of that the steric hindrance due to individual olefins hamper chain propagation, thereby providing conditions for chain termination.

The effect noted is characteristic of the phenoxy-ligand titanium half-sandwich catalysts. This is a result of a relatively small Ti–O–C angle (of the phenoxy ring), as found from X-ray evidence [6].

As for propylene polymerization, when its concentration in the reaction system was increased by a higher pressure, the chain propagation became much more manifest. The effect of coordination of polymerization centers by donor phenoxy ligands, however, (for the cresol-ligand catalysts) allowed to obtain mostly dimers at 25 °C and exclusively trimers at 75 °C. This is evidence that an increased temperature in the systems studied accelerates more the chain propagation than chain termination process.

When the effect is not involved, which is the case of phenoxy and chlorophenoxy ligands, atactic polypropylene is formed.

Formation of syndiotactic polystyrenes with a variable number of “errors” in the chain when styrene was copolymerized with ethylene under normal pressure, is probably also caused by the catalytic centers coordination effect, mentioned above. It prevents high-molecular-weight oligomers forming, and allows ethylene molecules and alternatively small-size oligomers to co-polymerize with styrene to afford a high styrene–ethylene copolymer, as it was described by Pellecchia et al. [21].

As for the methoxyphenoxy-ligand catalytic system, a higher ethylene concentration in the reaction mixture by its increased pressure yields a physical mixture of homopolymers, for chlorophenoxy-ligands under these conditions, a typical high-ethylene ethylene–styrene copolymer was obtained (Table 6).

This difference in selectivity seems to be a result of variable rate of polymerization of styrene and ethylene in the presence of the catalytic systems studied. For the methoxyphenoxy-ligand systems they exhibit relatively higher styrene polymerization rate (Table 7), which is more rapidly homopolymerized than used up in a slower co-polymerization reaction.

For the chlorophenoxy-ligand systems, which make styrene to polymerize at a lower rate, the mer may take part in being embedded into the rapidly growing polyethylene chains.

In the case of styrene homopolymerization in the presence of the catalytic systems under study the difference in yield and in the value of the molecular weights of the syndiotactic polystyrene may be due to the following reasons. A higher yield and lower molecular weights of sPS if obtained in the presence of methoxyphenoxy ligand systems is most likely due to a greater number of the polymerization centers (Ti[III] ions, Table 7) in the reaction system.

However, the molecular weights of the polymers obtained in the presence of this catalytic system are much lower than the

molecular weights of the polymers obtained with the chlorophenoxy ligand system and lower than it could be expected only on the grounds of the difference in the quantity of Ti[III] ions in both systems. This indicates the effect of coordination of polymerization centers by methoxyphenoxy ligands to occurs in styrene polymerization in the presence of the catalytic systems used.

## 5. Conclusion

Auxiliary phenoxy ligands of donor character in the titanium half-sandwich complex/MAO systems, can act as additional donor ligands in titanium active catalytic centers resulting in increasing the rate of termination step in olefin and styrene polymerization.

Auxiliary phenoxy ligands of acceptor character in the titanium half-sandwich complex/MAO systems, enhances the rate of propagation steps in olefin and styrene polymerization processes resulting in high-molecular weight ethylene and propylene polymers and enable ethylene–high olefin and ethylene–styrene copolymers formation.

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