

BIS-SALICYLADENIMINE FLUORINE-CONTAINING TITANIUM(+4) COMPLEXES IN POLYMERIZATION OF HIGHER α -OLEFINS

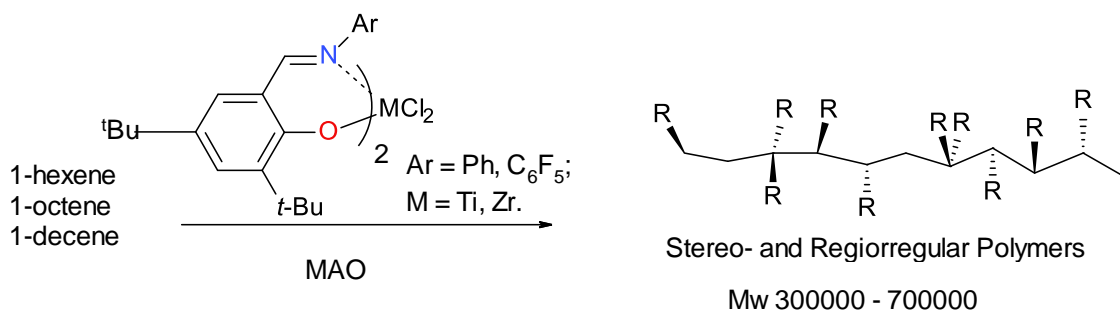
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Abstract:

The catalytic properties of post-metallocene system, based on titanium (+4) complex and zirconium (+4) complex with bis-salicylideneimine fluorine-containing ligand in the polymerization of higher olefins were studied. It was shown that the complex activation by methylalumoxane (MAO), depending upon the synthesis conditions, leads to formation of syndio- and isotactic poly- α -olefins with molecular mass from $0.01 \cdot 10^5$ to $19.98 \cdot 10^5$ and with productivity up to 2217 kg Polymer/mole Ti).

INTRODUCTION

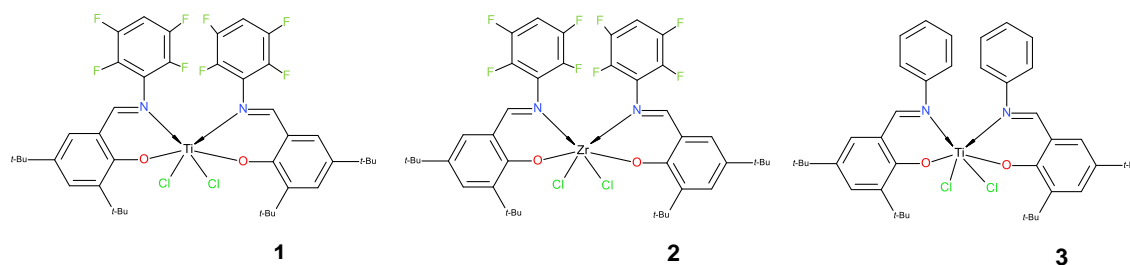
In the end of 1990th the synthesis of new highly-active catalysts for polymerization of olefins, based on group IV metal complexes with bis(phenoxyimines) and bis(pyrolylimines) ligands was reported [1,2]. Depending from the structure of pre-

catalyst, post-metallocene systems activity reached and even exceeded metallocene systems activity. Some complexes turned out to be capable of catalyzing ethylene living polymerization processes, of propylene stereo specific polymerization and even of ethylene and α -olefins with polar co-monomers copolymerization [3].

An ability to vary electronic and steric characteristics of pre-catalysts by choosing ligands with different substituents (orientation of the composition and structure of the catalyst on the synthesis of polyolefins with certain properties) is one of the most interesting properties of FI catalysts. Besides that, it was shown that some FI titanium complexes, usually with fluorine-containing substituents at ligand's imine part, when being activated by polymethylalumoxane (MAO) are capable to conduct «living» ethylene and propylene polymerization, even at high temperatures (50-70 °C) [1,4-14]. "Living polymerization" means polymer molecular mass linear dependence from the time of the process, in other words – there are same catalytic centers in the system. This fact cannot be explained only by electrophilic effect of fluorine atoms, which rises the metal center electrophilicity and leads to energy of ethylene molecule inputting degradation, as it was supposed in the studies [13-14]. Today, by the NMR-spectroscopy, neuronal diffractometry and DFT-calculations it was proven that ligand's fluorine atom cooperate with hydrogen atom in β -position of polymer chain, preventing the process of β -hydride transfer [15]. Complexes with fluorine atoms only in meta- and/or para – positions of aniline ring are also highly active, but they are not the catalysts for the «living polymerization» ($M_w/M_n=1.78-2.18$) [16-17]. The probability of the ethylene and propylene «living polymerization» is shown in [18], where binuclear fluorine-containing bis(salicylidene)imine titanium complexes were taken as an example.

The usage of phenoxyimines catalysts in homopolymerization of higher olefins with MAO as co-catalyst is much less studied [19]. This research shows the results of polymerization investigation of higher α -olefins (hexene-1, oktene-1 and decene -1) on post-metallocene complexes, shown in the Scheme 1.

Scheme 1



The catalyst activity of catalyst systems with complexes (pre-catalysts) **1-3** was studied in α -olefins mass at 25°C using the commercial MAO as an activator. The Co-catalyst/pre-catalyst molar ratio was varied between 100-1000 mole/mole at stable pre-catalysts concentration $2.3 \cdot 10^{-6}$ mole/l. Relatively low-level system activity at 25°C showed the necessity for long polymerization time (10 days). The main results are shown in the Table 1.

Table 1. Catalyst activity **1-3** in α -olefins polymerization (C_6 – hexene-1, C_8 – oktene-1, C_{10} – decene-1) in mass (monomer volume – 9 ml, $[Ti] = 2.3 \cdot 10^{-6}$ mole/l, co-catalyst – MAO, temperature 25°C), polymerization time -10 days.

№№	Pre-catalyst	Mono-mer	Al/Ti	Yield, g	A, kg polymer/mole Ti	M_w , 10^5	M_n , 10^4	M_w/M_n
1	1	C_6	100	0.4	182.6	8.72	4.13	21.1
2	1	C_6	250	5.1	2217.4	5.90	5.71	10.3
3	1	C_6	500	5.0	2173.9	6.19	4.58	13.3
4	1	C_6	750	4.5	1956.5	8.17	3.71	22.1
5	1	C_6	1000	4.6	2000.0	19.98	1.41	141.9
6	2	C_6	1200	2.2	349.2	0.09	0.12	7.9
7	2	C_6	1500	2.2	349.2	0.01	0.09	1.4
8	3	C_6	250	2.5	929.6	1.19	2.21	5.4
9	3	C_6	500	0.9	314.8	0.99	2.16	4.6
10	3	C_6	750	0.3	118.5	1.28	2.06	6.2

11	3	C ₆	1000	0.1	37.0	3.31	1.62	20.4
12	1	C ₈	100	0.6	265.2	5.81	4.28	13.6
13	1	C ₈	250	1.5	652.2	5.72	6.47	8.8
14	1	C ₈	500	2.0	856.5	5.83	6.52	8.9
15	1	C ₈	750	1.8	795.7	5.49	6.24	8.8
16	1	C ₈	1000	1.8	782.6	5.10	5.09	9.9
17	2	C ₈	560	1.9	293.6	0.02	0.11	1.4
18	2	C ₈	1200	6.5	663.3	0.02	0.13	1.5
19	2	C ₈	1500	6.5	1000.0	0.02	1.29	1.5
20	2	C ₈	2000	4.0	634.9	0.02	0.12	1.6
21	1	C ₁₀	100	0.6	239.1	4.11	2.61	15.8
22	1	C ₁₀	250	1.2	521.7	5.31	6.53	8.1
23	1	C ₁₀	500	1.7	734.8	4.63	4.92	9.7
24	1	C ₁₀	750	1.2	500.0	5.31	5.81	9.1
25	1	C ₁₀	1000	1.4	595.6	5.09	3.89	13.0
26	3	C ₁₀	250	0.6	237.0	0.01	0.01	7.9
27	3	C ₁₀	500	2.0	722.2	0.06	0.09	6.5
28	3	C ₁₀	750	2.1	777.8	0.04	0.08	4.9
29	3	C ₁₀	1000	2.2	814.8	0.09	0.09	9.3
30	3*	C ₆	500	0.3	120.0	0.55	1.91	2.9

* MAO was added to catalyst, than held for a week and after this, hexene-1 was added.

As it is shown in the Table 1, when increasing the molecular ratio Al/Ti from 250 to 1000 while using complex **1** we can observe small activity decline from 2217.4 to 2000 kg polymer/mole Ti and at the same time the significant raise not only weight-average polyhexene molecular mass up to $2 \cdot 10^6$, but also molecular-mass distribution figures up to 121. At the same time, in case of application in the system of zirconium complex (+4) (**2**) of same composition, the raise of molecular ratio Al/Ti significantly decreases activity, molecular mass and molecular-mass distribution. Molecular-mass distribution

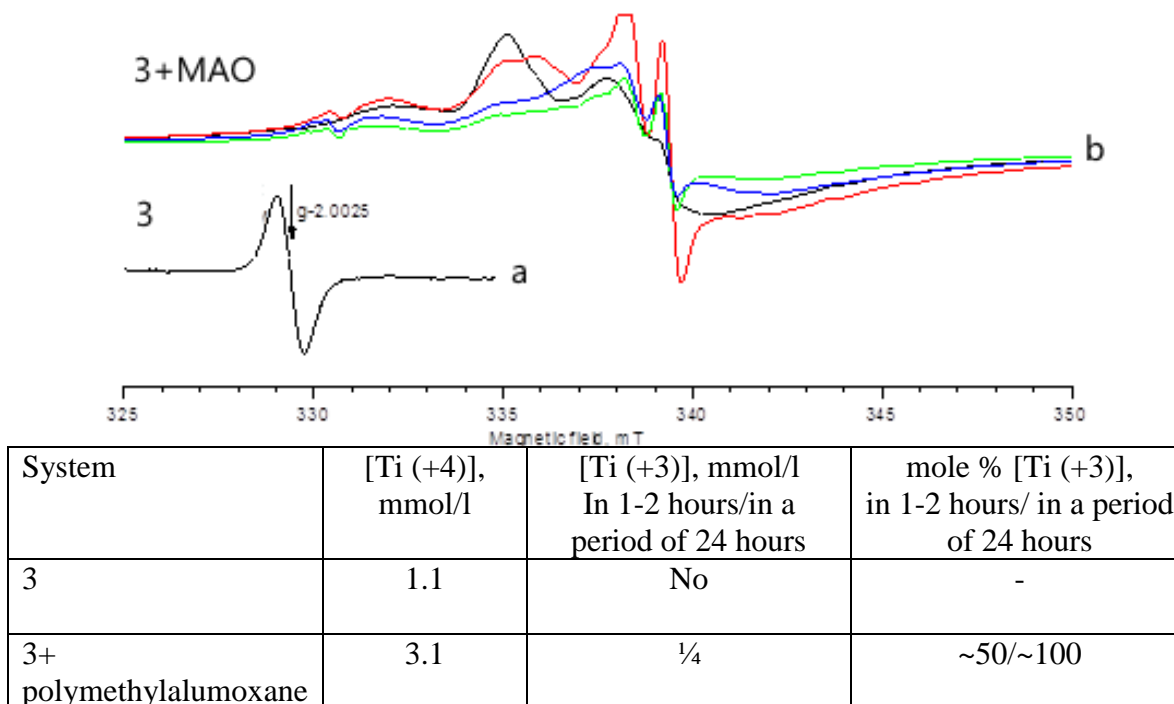
decreases up to 1.4, what means that the systems becomes single-centered (with one type of active center).

The catalyst system, which was formed on pre-catalyst **3**, where there is no fluorine atom in ligand, shows its own properties. In this case ratio increase Al/Ti from 250 to 1000 immediately leads to activity decrease up to the most minimum for this system value – 37 kg Polyhexene/mole Ti, although the molecular-mass distribution variety in this case is much lower, than we can observe on the system **1**.

High molecular mass distribution of polymers, obtained on the systems with pre-catalysts **1** and **3**, shows that the polymers are multicentred. There are several reasons for it starting with the differences in the metal nature and properties of its compounds (for example: titanium atom (+4) which is easily reducible under the influence of organoaluminium compositions and zirconium atom (+4) which is proof against this influence) and finishing with the activator's - commercial MAO properties, which contains from 30 to 40 mole % accompanied trimethylaluminium (TMA), and the ways of system's formation. Actually, if after mixing pre-catalyst **1** with the commercial MAO and the mixture is allowed to stand for several days, and then hexane-1 is added to the solution, than we find out that the system's activity has decreased nearly in 18 times (compare ex.3 in standart execution with the results of ex. 30, Table 1). The molecular mass also decreases by ten times.

According to this data we can assume that titanium atom (+4) in complex **1** in case of long-time treatment by TMA and MAO recovers to titanium atom (+3) . With titanium (+3) the catalyst system that has different from the system with titanium (+4) composition and activity is formed. This assumption circumstantially confirms experimental data concerning the polymerization of ethylene based on the commercial MAO and on so called «dry» MAO (TMA was distilled off almost completely from MAO by vacuumizing for a long time). We showed that the presence of trimethylaluminium in co-catalyst leads to system's activity decrease and to the massive reduction of polymer molecular mass in comparison with the catalyst system that was activated by «dry» MAO. This fact can be explained by more efficient transmission of the growing polymer chain on the organoaluminium composition in the first case [20].

The titanium (+3) formation is proved by electronic paramagnetic resonance spectra of complexes solutions, which were held with the commercial MAO during several days (pic. 2, TEMPO as a standart). In two hours the number of paramagnetic compounds, containing Ti(+3) ($g=1.968$) atoms became 2 mole %, in a period of 24 hour - 50%, in two days – 100% («b» spectra).



Pic. 3. electronic paramagnetic resonance researches of the catalyst **3** (curve a) and catalyst **3** in the presence of polymethylalumoxane (curve b)

According to ^{13}C NMR spectroscopy, microstructure of polyhexene obtained corresponds to the iso- and syndiotactic polymer structure [21]. Content of isotactic pentads *mmmm*, found as a ratio of to integral apex intensity of 35.21 ppm peak to integral intensity of all pentad field (33.5-35.4 ppm) is approximate 12-23 %.

Therefore, titanium (+4) complexes' catalyst properties with bis-salicyladenimine fluorine-containing ligand in the polymerization of higher olefins were studied. It was shown that the complex activation by methylalumoxane (MAO), depending upon the synthesis conditions, leads to formation of syndio- and isotactic poly- α -olefins with

molecular mass from $0.01 \cdot 10^5$ to $19.98 \cdot 10^5$ and with productivity up to 2217 kg Polymer/mole Ti).

Assumption was made that the titanium atom (+4) in complex **1** if being treated by organoaluminium compounds (TMA and MAO) for a long time – reduced to titanium (+3), at the same time the catalyst system, which operates the process is formed.

Experimental

Complexes' synthesis was held under an argon atmosphere. Tetrahydrofuran, dichloromethane, toluene, isopropanol, hexane and ethyl acetate reagent grade were extra purified according to the methodology, described in literature [22]. TiCl_4 , purchased from Fluka, was extra distilled in the argon atmosphere. 1-3 complexes were obtained according to the methodology, described in the literature [23].

NMR spectra of ligands solutions in CDCl_3 were recorded on "Bruker WP-500" and "Bruker AMX-400", IR spectra - on "Magna-IR 750". Elemental analysis was held on "Carlo Erba-1106" and "Carlo Erba-1108".

The polymerization reaction

Polymerization of the higher olefins was held in M-Braun under dry argon atmosphere, was polymerized in mass in glass retort without mixing. Catalysts' activity was calculated according to the polymer's yield/mol Ti.

Analysis of polymers

Microstructure of polymers was examined by ^{13}C NMR spectroscopy. ^{13}C NMR spectra of 10% polymers' solutions in the mixture (1,2,4-trichlorobenzene +deuterated benzene) were recorded on "Bruker AVANCE III 400" (frequency 100.613 MHz) at 120°C . Signals attribution was based on the data, described in the literature [24, 25]. From the ^{13}C NMR spectra of polymer samples the content of steric pentads was found. Gel-chromatograms of polymer samples were obtained on «Agilent 1200» (evaporative detector in light diffusion) using Styragel HMW6E columns in toluene at 25°C . The average MM was calculated according to the general calibration curve using relative to polystyrene (PS) standards.

The analysis was performed at 130 °C using 1,2,4-trichlorobenzene as a solvent. Average molecular weights were determined from the universal calibration dependence relative to polystyrene standards.

This work was financially supported by RFBR (grant № 17-03-00234).

References

1. Small, B. L.; Brookhart, M. *J. Am. Chem. Soc.* **1998**, *120*, 7143.
2. Britovsek, G. J. P.; Gibson, V. C.; Kimberley, B. S.; Maddox, P. J.; McTavish, S. J.; Solan, G. A.; White, A. J. P.; Williams, D. J. *Chem. Commun.* **1998**, 849.
3. S. Matsui, Y. Tohi, M. Mitani, J. Saito, H. Makio, H. Tanaka, T. Fujita. *Chem. Lett.* **1999**, 1065.
4. Bianchini, C.; Giambastiani, G.; Rios, G. I.; Mantovani, G.; Meli, A.; Segarra, A. M. *Coord. Chem. Rev.* **2006**, *250*, 1391.
5. Stoufer, R. C.; Busch, D. H. *J. Am. Chem. Soc.* **1956**, *78*, 6016.
6. Lions, F.; Martin, K. V. *J. Am. Chem. Soc.* **1957**, *79*, 2733.
7. Johnson, L. K.; Killian, C. M.; Arthur, S. D.; Feldman, J.; PCT Int. Appl. WO9623010, 1996; *Chem. Abstr.* **1996**, *125*, 222773.
8. P.G. Cozzi, C. Floriani, A Chiesi-Villa, C. Rizzoli. *Inorg. Chem.* **1995**, *34*, 29.
9. P.G. Cozzi, E. Gallo, C. Floriani, A Chiesi-Villa, C. Rizzoli. *Organometallics*, **1995**, *14*, 4994.
10. Laine, T. V.; Klinga, M.; Maaninen, A.; Aitola, E.; Leskela, M. *Acta Chem. Scand.* **1999**, *53*, 968-973.
11. L.K.Floriany, C.M. Killian, *J. Am. Chem. Soc.*, **1995**, *117*, 6414.
12. S. Matsui, Y. Tohi, M. Mitani, J. Saito, H. Makio, H. Tanaka, T. Fujita. *Chem. Lett.* **1999**, 1065.
13. S. Matsui, M. Mitani, J. Saito, Y. Tohi, H. Makio, H. Tanaka, T. Fujita. *Chem. Lett.* **1999**, 1163.
14. J. Saito, M. Onda, S. Matsui, M. Mitani, R. Furuyama, H. Tanaka, T. T. Fujita, *Macromol. Rapid Commun.*, **2002**, *23*, 1118.

15. Chan M. C. W., Weak Attractive Ligand–Polymer and Related Interactions in Catalysis and Reactivity: Impact, Applications, and Modeling, *Chemistry – An Asian Journal*, 2008, 3, 18–27, DOI: 10.1002/asia.200700226.; Bryliakov K. P., Talsi E. P. *Coord. Chem. Rev.*, 2012, 256, 2994– 3007.
16. H. Makio, T. Fujita. *Macromol. Symp.* **2004**, 213, 221.
17. United States Patent, 5 698 487, Sacchetti , et al. **1997**.
18. S.C. Gagieva, T.A. Sukhova, D.B. Savinov, N.M. Bravaya, Y.N. Belokon, B.M. Bulychev. *Russian Chemical Bulletin*, **2004**, 53, 12, 2763-2767.
19. Makio H., Terao H., Iwashita A., and Fujita T.. *Chem. Rev.*, **2011**, 111, 2363–2449, [dx.doi.org/10.1021/cr100294r](https://doi.org/10.1021/cr100294r)
20. N.M. Bravaya, E.E. Faingol'D, A.N. Panin, E.O. Perepelitsina, S.Ch. Gagieva, V.A. Tuskaev, B.M. Bulychev. *Polymer Science - Series B*, **2010**, 52, 11, 629-636.
21. S.Ch. Gagieva, V.A. Tuskaev, B.M. Bulychev, O.V. Smirnova, S.S. Galibeev, N.M. Bravaya. *Polymer Science - Series B*, **2011**, 53, 5-6, 299.
22. *Organikum*. T.2, M.: Mir, 1992, 472 s.
23. S.Ch. Gagieva, T.A. Sukhova, D.V. Savinov, V.A. Optov, N.M. Bravaya, Yu N. Belokon', B.M. Bulychev. *Russian Chemical Bulletin*, **2003**, 52, 8, 1693-1697.
24. T. Asakura, M. Demura, Y. Nishiyama. *Macromolecules*, **1991**, 24, 9, 2334.
25. X. Zhao, G. Odian, A.Rossi. *J. Polym. Sci., Polym. Chem.*, **2000**, 38, 3802.

Supplement:

