Accepted Manuscript

Novel titanium (IV) diolate complexes: Synthesis, structure and catalytic activities in ultra-high molecular weight polyethylene production

Svetlana Ch Gagieva, Vladislav A. Tuskaev, Ivan V. Fedyanin, Mikhail I. Buzin, Viktor G. Vasil'ev, Galina G. Nikiforova, Egor S. Afanas'ev, Sergey V. Zubkevich, Dmitrii A. Kurmaev, Nikolay A. Kolosov, Elena S. Mikhaylik, Evgenii K. Golubev, Alexandr I. Sizov, Boris M. Bulychev

PII: S0022-328X(16)30530-7

DOI: 10.1016/j.jorganchem.2016.11.026

Reference: JOM 19711

To appear in: Journal of Organometallic Chemistry

Received Date: 23 October 2016

Revised Date: 16 November 2016

Accepted Date: 17 November 2016

Please cite this article as: S.C. Gagieva, V.A. Tuskaev, I.V. Fedyanin, M.I. Buzin, V.G. Vasil'ev, G.G. Nikiforova, E.S. Afanas'ev, S.V. Zubkevich, D.A. Kurmaev, N.A. Kolosov, E.S. Mikhaylik, E.K. Golubev, A.I. Sizov, B.M. Bulychev, Novel titanium (IV) diolate complexes: Synthesis, structure and catalytic activities in ultra-high molecular weight polyethylene production, *Journal of Organometallic Chemistry* (2016), doi: 10.1016/j.jorganchem.2016.11.026.

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.





Novel titanium (IV) diolate complexes: synthesis, structure and catalytic activities in ultra-high molecular weight polyethylene production

Svetlana Ch. Gagieva^a, Vladislav A. Tuskaev^{a,b*}, Ivan V. Fedyanin^b, Mikhail I. Buzin^b, Viktor G. Vasil'ev^b, Galina G. Nikiforova^b, Egor S. Afanas'ev^b, Sergey V. Zubkevich^a, Dmitrii A. Kurmaev^a, Nikolay A. Kolosov^a, Elena S. Mikhaylik^{b,c}, Evgenii K. Golubev^{b,c}, Alexandr I. Sizov^a, Boris M. Bulychev^a

^a Department of Chemistry, M. V. Lomonosov Moscow State University,1 Leninskie Gory, 119992 Moscow, Russian Federation

^b A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,28 ul. Vavilova, 119991 Moscow, Russian Federation

^c Enikolopov Institute of Synthetic Polymer Materials, Russian Academy of Sciences, Profsoyuznaya Str., 70; 117393 Moscow, Russia

KEYWORDS Ziegler-Natta polymerization; ultra-high molecular weight polyethylene; titanium; non-metallocene; diolate ligands

Corresponding Author *E-mail: tuskaev@yandex.ru.

ABSTRACT

In this work we describe synthesis of new chloride and alkoxo-titanium (IV) complexes 3-7 with diol 0,0-type ligands from readily available and scalable precursors. Structure of complex 6 was established by X-ray diffraction. Titanium atom adopts a tetrahedral geometry formed by three oxygen atoms of ligands and one oxygen atom of isopropoxo group. The resulting complexes 3-6 are moderately or highly active in ethylene polymerization in the presence of $\{3Et_2AlCl + Bu_2Mg\}$ binary co-catalyst. Obtained polymers are linear polyethylene of ultrahigh molecular weight (3.7-8.8 10^6 g/mole) with a broad molecular weight distribution. Polymers are suitable for the modern methods of polymer processing - the solventless solid state formation of super high-strength (breaking strength over 2.3 GPa) and high-modulus (elastic modulus over 150 GPa) oriented films and film tapes.

1. Introduction

The application of single-site homogeneous catalysts with well-defined structure opens wide possibilities to regulate not only molecular weight, but the morphology of the obtained polymers. Successful examples of non-metallocene catalysts used for the synthesis of UHMWPE with desired morphology are shown in the review [1]. The least researched olefin polymerization catalysts are based on the group 4 metal complexes with di- and polyol ligands. A few examples of such catalysts are mentioned in [2] (Fig.1, structures A-B)]. Published research [3-7] were also dedicated to the investigation of the catalytic activity of dichloride Ti complexes with TADDOLs (Fig.1, structure C).



Fig. 1. Examples of Ti (IV) diolate olefin polymerization catalysts.

The above mentioned research has established that TADDOL systems with group 4 metals are catalytically active in the polymerization or co-polymerization of ethylene, propylene and other higher olefins, only in presence of MgCl₂ which is a byproduct of the complex synthesis or a product of components interaction in a binary activator $\{MgBu_2+3AlEt_2Cl\}$ [8-9.].

It was established that despite the moderate catalytic polymerization activity, the system has a number of advantages when compared to the better studied titanium phenoxyimine complexes. Among those benefits are their ability to demonstrate catalytic properties at low Ti/Al ratios, as well as system capacity to withstand the deactivation due to C=N bond reduction by non-transition organometallic compounds are among those benefits.

Considering oxophilic nature of group 4 metals, we believe that the study of new catalytic systems supported by O,O-type ligands can be quite interesting. The main objective of this study is the synthesis of a TADDOL's analogues without the labile ketal moiety, capable of interaction with the organoaluminum or organomagnesium compounds. To achieve such structural alteration we have synthesized titanium(IV) complexes with diols ligands in which two diphenylmethanol fragments are connected through either benzene ring or $-(CH_2)_2$ -linker. We have also evaluated the catalytic properties of these complexes in ethylene polymerization.

2. Results and discussion

2.1. Ligands and coordination compounds synthesis and structure.

Ligands 1 and 2 were synthesized from succinic and phthalic ethers according to the literature procedures, their ¹H and ¹³C NMR spectra were found to match the published data [10-12]. Titanium chloride complexes 4 and 5 were synthesized by direct interaction of 1 and 2 with titanium dichlorodiisopropylate in dichloromethane (Scheme 1). When $Ti(O^{i}Pr)_{4}$ is used as a starting material, the products of reaction with 1 and 5 strongly depend on the ratio of the initial substances. According to these ratios we have synthesized mono- and bi-nuclear complexes 3, 6 and 7, which are conveniently characterized by ¹H and ¹³C NMR spectroscopy and elemental analysis.

The ¹H NMR spectrum of these complexes comprises of signals of ligand's protons as well as two signals of isopropoxy group protons (CH and CH₃). Thus, this compound is monomeric in CDCl₃ solution at room temperature. The spectra of **4** and **5** include the peak at 5.5-5.1 ppm indicating the presence of coordinated isopropanol molecules.

The FT-IR spectrum of complexes **3-6** has demonstrated bands at 620-590 cm⁻¹, characteristic of the Ti-O bonds, with simultaneous disappearance of the hydroxyl groups stretching frequencies in ligand. Spectra of complexes **4** - **5** also contain a narrow band at 3180 cm⁻¹ characteristic of isopropanol hydroxyl group valent vibrations.



Scheme 1. Synthesis of Ti(IV) diolate complexes 3-7.



Fig. 2. The core of the complex **6** in crystal. Ph and iPr stand for chemical groups disordered by symmetry. Bond lengths Ti1-O1 1.7883(8), Ti1-O2 1.7734(16) O1-C2 1.4182(15), C1-C2 1.5436(17), C2-C2C 1.514(3) Å, bond angles O1-Ti1-O1A 108.80(3), O1-Ti1-O2 110.14(3)°.

The structure of the complex **6** as a toluene solvate was also established by singlecrystal X-ray diffraction (Figure 2). The molecule has an approximate D_3 symmetry, and the independent part includes only Ti atom, coordinated with isopropoxo group and half of the ligand. The Ti atom adopts a tetrahedral geometry formed by three oxygen atoms of ligands and one oxygen atom of isopropoxo group. Due to disorder of phenyl and isopropyl groups imposed by symmetry, the discussion of their geometric parameters is irrelevant, but bond lengths and angles for the ordered part are within the expected values. All synthesized compounds with the exception of **7** contain either chlorine or alkoxo moieties. Such moieties are known to be a good leaving groups in exchange reactions with aluminum- or magnesium-organic compounds. Alcohol molecules leaving the Ti atom coordination sphere vacate the coordination position for the respective monomer, thus facilitating the catalysis. Overall, complexes **3-6** can be used to catalyze the polymerization reaction, while spiro-complex **7** was expected to lack such catalytic activity.

2.2. Catalytic properties of Ti diolate complexes.

Table 1 displays the ethylene polymerization activity of synthesized diolate complexes **3-6.** Similarly to TADDOL Ti complexes, currently evaluated complexes display only trace ethylene polymerization activity in presence of MAO, Et₂AlCl or Et₃Al. However, they are getting effectively activated by binary mixes like Et₂AlCl/Bu₂Mg or Et₃Al₂Cl/Bu₂Mg even with relatively low Al/Ti ratios. This observation indicates the overall similarity of currently synthesized complexes and other Ti complexes containing *O,O*-type ligands that were evaluated previously. As proposed before, this level of activity can be explained by formation of heterometalic Ti-Mg complexes [13-14] and their involvement in catalysis.

It is noteworthy that: 1) as expected, complex 7 could not be activated by any of the above mentioned cocalysts; 2) all synthesized polyethylenes were of ultra-high molecular weight (ranging from 3.7 to $8.8 \cdot 10^6$ D).

Table 1.

Ethylene Polymerization by complexes 6-9^{*a*}

Run	Com- plex	[Ti], mol	Co- catalyst, Al/Mg	m _(pol) , g	A ^b	Bulk density, g/cm ³	MW, 10 ⁶ D	Deg.of Crystal ^d %	T _m ^b	σ, MPa/ ε, %
1.	3	2 10-6	Et ₂ AlCl/ Bu ₂ Mg 300/100	0.4	570	0.07	n.d.	n.d.	n.d.	
2.	3	2 10-6	$\begin{array}{c} Et_{3}Al_{2}Cl_{3} / \\ Bu_{2}Mg \\ 300 / 100 \end{array}$	traces	-	n.d.	n.d.	n.d.	n.d.	
3.	4	5 10 ⁻⁶	Et ₂ AlCl / Bu ₂ Mg 300/100	4.65	2660	0.06	5.36	76	142	1596/ 2.0
4.	4	5 10 ⁻⁶	$\begin{array}{c} Et_{3}Al_{2}Cl_{3} \\ Bu_{2}Mg \\ 300 / 100 \end{array}$	3.2	1830	0.09	3.71	81	141	1265/ 2.9
5.	5	5 10 ⁻⁶	Et ₂ AlCl / Bu ₂ Mg 300/100	0.5	286	0.09	6.14	77	145	

		-	ACCI	EPTED	MANI	JSCRIP	Т			1
6.	5	5 10 ⁻⁶	Et ₃ Al ₂ Cl ₃ / Bu ₂ Mg 300/100	traces	-	0.08	n.d.	n.d.	n.d.	2258/ 2.1
7.	6	1 10-6	Et ₂ AlCl / Bu ₂ Mg 150/50	0.75	540	0.07	n.d.	n.d.	n.d.	
8.	6	1 10-6	Et ₂ AlCl / Bu ₂ Mg 300/50	3.65	2600	0.07	4.06	80	144	2258/ 2.1
9.	6	1 10-6	Et ₂ AlCl / Bu ₂ Mg 450/50	2.90	2070	0.05	4.45	76	143	1770/ 1.5
10.	6	1 10-6	Et ₂ AlCl / Bu ₂ Mg 600/50	3.48	2480	0.07	8.78	80	143	2210/ 1.9
11.	6	1 10-6	Et ₂ AlCl / Bu ₂ Mg 900/50	2.50	1780	0.06	5.57	75	142	1985/ 1.9
12.	6	5 10-6	Et ₂ AlCl / Bu ₂ Mg 300/100	3.5	2490	0.095	4.62	77	140	1960/ 3.1
13.	6	5 10 ⁻⁶	Et ₃ Al ₂ Cl ₃ / Bu ₂ Mg 300/100	6.2	4380	0.12	7.26	78	141	1548/ 2.7

^a Polymerization conditions: ethylene pressure = 0.7 atm., toluene = 50 ml, incubation time 30 min, temperature 30°C; ^b Activity, kg of PE mol Ti⁻¹ atm⁻¹ h⁻¹; ^c Melting temperatures determined by DSC at first heating of PE samples; ^d Degree of crystallinity of UHMWPE samples was calculated by use of value $\Delta H_m^{100\%} = 288$ J/g. [15].

As evident from the table 1, the dimeric alkoxo-complex **3** has displayed a mediocre catalytic properties even when activated with Et_2AlCl/Bu_2Mg . Hence it was excluded from further evaluations. The monomeric dichloride complex **4**, when activated with Et_2AlCl/Bu_2Mg at molar ratio of 300/100 has demonstrated good activity. However, substitution of Et_2AlCl for $Et_3Al_2Cl_3$, while maintaining the same Ti:Al:Mg ratio resulted in a decrease in activity from 2660 to 1830 kg/mol Ti h atm.

Change of the linker type that connects diphenylcarbinol fragments notably altered the catalytic system properties. Thus catalytic system with complex **5** despite the similarities to complex **4** has demonstrated the catalytic properties that were worse than for system **6** in ethylene polymerization reaction. Also, as in the cases of **3** and **4**, the activity has decreased dramatically in presence of $Et_3Al_2Cl_3/Bu_2Mg$ activator mixture.

Catalytic system containing complex **6** has demonstrated low catalytic activity with $Al/Mg \le 150$. However the increase of organoaluminum component in the system while maintaining the Bu₂Mg concentration (Ti/Mg = 50) results in the superior catalytic activity for this compound (2600 kg/mole Ti h atm at Ti/Al ratio of 1/300). Further increase of the ratio leads to gradual decrease of activity. The molecular weight of produced polymer (8.78 · 10⁶ D) reaches its peak at Ti/Al = 1/600 (Table 1, Fig 3). The greatest breaking strength (2600 MPa) was achieved with the Ti/Al ratio of 1/300 and had an MW = 4.06 · 10⁶ D. Once the Ti/Al ratio reaches 1/900, both MW and breaking strength decrease (Fig. 3). These observations suggest the lack of correlation between the MW of the synthesized polymer (as well as its melting temperature and degree of crystallinity) and its breaking strength. Potentially, it can be explained by lack of sufficient statistics for obtained samples as well as by the differences in MW distribution of synthesized polymers.

The increase of Bu_2Mg amount in binary activator (runs 8 and 12, Table 1) has little impact on the system catalytic activity, or the molecular weight of the resulting polymer. At the same time the breaking strength of the polymer sample decreases slightly (Table 1). As above, it can be also explained by insufficient statistical validity of the results or alteration of molecular weight distribution.



Fig. 3. Catalytic activity of complex **6** (1), molecular weight of resulting polymer (2) and tensile strength (3) as a function of catalytic system Ti/Al ratio.

It is evident from the results (Table 1) that catalytic systems based on complex 6 and others based on complexes 3-5 notably differ in their catalytic activity, activation conditions

and resulting polymer molecular weight. Unlike in case of **4** and **5**, in **6** Et₂AlCl substitution for Et₃Al₂Cl₃ result in nearly doubling of the catalytic activity of the system (from 2490 to 4380 kg/mole Ti h atm), along with the increase in the molecular weight of the resulting polyethylene (from $4.42 \cdot 10^6$ to $7.26 \cdot 10^6$ D). Previously, such impact of the cocatalyst substitution was observed in Ni-based systems with alpha-diimine ligands [16].

In reality, structurally related soluble titanium complexes, bearing alkoxo ligands, in most cases produced polyethylene with an average molecular weight, e.g. [17-18, 2]. Moreover, the main products of ethylene transformation on titanium catalysts with phenolic ligands (without additional donor atoms) are low molecular weight oligomers [19-21]. Obviously, the fact of UHMWPE formation, considered in this manuscript, is determined not only by the structure of the pre-catalyst but also by an activator nature. The introduction of organomagnesium compounds into the catalytic system creates principal possibility of heterogenization of the titanium(IV) complexes on the surface of magnesium chloride formed in the reaction { $Bu_2Mg + 2Et_2AlCl = 2MgCl_2 + 2Et_2AlBu$ }. On the other hand, the formation of bimetallic titaniummagnesium intermediates that probably determine the ultra-high molecular weight of the resulting polyethylene also is not excluded. The theoretical possibility of such structures formation was implicitly confirmed by DFT calculations [13-14]. In these papers it is assumed that the presence of Al-Mg binary activator changes the composition and structure of the active site (as compared with a conventional cationic) and, accordingly, the polymerization mechanism, but the exact mechanism of the chain transfer reduction rate remains unclear.

2.3. Thermal and mechanical properties of synthesized UHMWPE

According to DSC, all synthesized polymers have high melting temperatures (140-145°C) and degrees of crystallinity (75-80%, Table 1). Typical TGA and DTA curves for one of the synthesized polymer sample (Run 13, Table 1) are presented in Figure 4. The curves for other samples varied insignificantly from the presented on Fig.4.



Fig. 4. TGA (1) and DTA (2) curves for UHMWPE sample (Run 13, Table 1) at a heating rate 10°C/min in air.

It is evident from Fig. 4 DTA curve that endothermic effect corresponding sample melting (~141 °C) is followed by the exothermic peak with maximum at 220 °C. We expect this effect to be related to the development of low temperature thermo-oxidative processes in the surface layers of the polymer. TGA curve displays a notable increase in the sample weight (up to 3%). According to DSC, this exothermal effect for reactor (nascent) powder was 620 J/g. Upon compaction at 139 °C it decreases to 400 J/g which is consistent with a decrease of oxygen accessible area.

All UHMWPE samples behaved similarly under the thermomechanical analysis (TMA) conditions. A typical TMA curve is presented in Figure 5; this particular curve was determined from the analysis of the powder obtained in experiment 13 (The curves for other experimental samples are presented in the Supplementary Information).



Fig. 5. TMA curve for UHMWPE (run 13, table 1) at a heating rate 5°C/min and a force of 1N in air.

As evident from the plot, the first area of deformation (~50%) corresponds to the melting range of the polymer. According to the literature, the UHMWPE doesn't flow while melting [22], hence this deformation might be related not to real flow of the polymer, but rather to thermo-compacting caused by melting of polymer crystal areas and pseudo-monolythization. Second area of deformation (~8%) is observed in the range of low temperature oxidation processes where it is feasible to observe a certain polymer softening that result in the plateau on TMA curve, resembling those characteristic for the superelasticity. It should be mentioned that the peroxides formed during this process not only destroy the structure, but can also to create a number of cross-links in PE macromolecules. As a result, we observe another plateau that stretches to the temperatures of complete UHMWPE destruction, when sample deformation reaches 100%.

TMA data were used for the selection of conditions for solvent free formation of oriented tape from the reactor UHMWPE powders. The tapes were prepared by making monolithic samples of the UHMWPE reactor powder at a pressure and shear deformation at an elevated temperature below polymer melting point. Then subsequent orientation drawing of monolithic tapes was conducted to a maximum achievable draw ratio (see experimental

section). The biggest among others draw ratio values (up to 32) was reached with the polymers obtained in the runs 8-11 (complex **6**-based catalyst).

The samples from the experiments 8 and 10 has demonstrated the highest elastic modulus as well as breaking strength at optimal breaking elongation values (Table 1, Fig. 6). The tapes produced from these UHMWPE powders display abrupt character of rupture indicating the homogeneity of the samples. The identical values of elongation at break and modulus of elasticity for a set of samples with the same draw ratio prepared with the polymer synthesized in the runs 8 and 10 confirm the high quality of the obtained nascent reactor powders.



Fig. 6. Stress-elongation curves for UHMWPE orientated tapes.

3. Conclusion

Indeed, considered catalytic systems, containing titanium alkoxide complexes, organomagnesium and chlorine-containing organoaluminum compounds, occupy an intermediate position between the "pure" non –metallocene systems and Ziegler-Natta catalysts with internal donors. However, the differences between considered systems and classical Ziegler catalysts become apparent when the morphology of the resulting PE is compared. The results of scanning electron microscopy on the nascent powders of commercially available UHMWPE [23] and polymer samples, obtained on complex 6, are shown in Figure S35. It is easy to see that that the latter samples have a more "porous" structure. The high porosity of the nascent reactor powders defines the unique low bulk density (0.05-0.12 g/cm3) and also facilitates compression of the powder below its melting temperature.

Overall, the described catalytic system, based on complex **6** with binary activator, results in a high yield of desired polymer and allows to control molecular weight of the product and its morphology. This system also allows optimizing polymer powder properties and achieving high values for mechanical properties of orientated materials obtained by a solid state processing.

4. Experimental section

All manipulations were performed under argon by using standard Schlenk techniques. Toluene, hexane, diethyl ether and THF were distilled from Na/benzophenone prior to use. Water contents of these solvents were periodically tested by Karl-Fischer coulometry with a Methrom 756 KF apparatus. Argon and ethylene of special-purity grade were dried by purging through a Super CleanTM Gas Filters.

Diethylaluminumcloride, aluminium sesquichloride, di-*n*-butylmagnesium (Aldrich) were used as 1.0 M solution in heptane. Dichloro-bis(isopropoxy)titanium was synthesized as described in [24]. Ligands - [2-[hydroxy(diphenyl)methyl]phenyl]-diphenyl-methanol and 1,1,4,4-tetraphenylbutane-1,4-diol were synthesized by interaction of corresponding dicarboxylic acid esters with phenylmagnesium bromide; their ¹H and ¹³C NMR spectra were found to match the published data [10-12].

NMR spectra were recorded by Bruker WP-600 and Bruker AMX-400 instruments. Air-sensitive NMR spectra were taken in J. Young tubes with Teflon valve plugs. IR spectra were recorded on a Magna-IR 750 spectrophotometer. Elemental analysis was performed by the microanalytical laboratory at A. N. Nesmeyanov Institute of Organoelement Compounds.

The thermogravimetric analysis was performed on a NETZSCHSTA-Jupiter449 C instrument. Measurements were carried out under argon flow (100 mL/min) with the temperature ranging from 40 to 300° C. The rate of heating was 5° C/min.

[2-[Hydroxy(diphenyl)methyl]phenyl]-diphenyl-methanol (Ligand 1). To bromobenzene (1.74 g, 10 mmol) dissolved in diethyl ether at -78°C butyl lithium was slowly added with syringe (8.80 ml, 22 mmol). A solution of dimethyl succinate (0.41 g, 2.5 mmol) in diethyl ether was added after 4 hours of stirring. The reaction mixture was further stirred at room temperature for 10 hours, and then was washed with a saturated solution of NH₄Cl, the solvent was evaporated, and the product was recrystallized from methanol. Yield 3.17 g (72%), m.p. 112 °C, Found (%): C, 86.80; H, 5.84. $C_{32}H_{26}O_2$. Calculated (%): C, 86.85; H, 5.92. ¹H NMR, δ : (400 MHz, CDCl₃, d, J/Hz) δ : 7.62-7.44 (m, 20 H, Ar), 4.40 (s, 2H, OH), 3.20 (s, 4H, CH₂). **1,1,4,4-Tetraphenylbutane-1,4-diol** (Ligand **2**). To bromobenzene (1.74 g, 10 mmol) dissolved in diethyl ether at -78°C butyl lithium was slowly added with syringe (8.80 ml, 22 mmol). Diethyl ether solution of succinic acid (0.30 g, 2.5 mmol) was added after 4 hours of stirring. The reaction mixture was further stirred at room temperature for 10 hours, and then was washed with a saturated solution of NH₄Cl, the solvent was evaporated, and the product was recrystallized from methanol. Yield 2.96 g (75%), m.p. 106 °C (lit. 104-105°C)., Found (%): C, 85.21; H, 6.60. C₂₈H₂₆O₂. Calculated (%): C, 85.25; H, 6.64. MW =394,52 ¹H NMR, δ : 7.98 (d, 2 H, *J* = 7.5 Hz); 7.83 (d, 2 H, *J* = 7.3 Hz); 7.39 (t, 2 H, *J* = 7.3 Hz, J = 7.5 Hz); 6.85 (s, 2 H.); 5.18 (br.m, 4 H); 4.98, 4.85 (both d, 2 H each, *J* \approx 3 Hz); 1.36 (d, 12 H, *J* = 5.8 Hz); 1.28, 1.23 (both d, 6 H each, *J* = 6.8 Hz). (s, 2 H, CH); 1.57 (s, 6 H, Me).

Bis{[2-[(diphenyl)methyl]phenyl-methanolato]-diphenyl- methanolato]} di(μisopropoxy)di(isopropoxy)-dititanium (3)

 $Di\{2-[\alpha,\alpha-bis(trifluoromethyl)methanolato]-4,6-di-tert-$

butylphenolato}di(µ-isopropoxy)di(isopropoxy)dititanium,

To a solution of ligand (1) (0.442 g, 1.0 mmol) in 10 ml of methylene chloride, Ti(OiPr)₄ (0.299 ml, 1.0 mmol) was added with stirring at 40 °C. After a reaction time of 7 h, the mixture was dried in vacuo completely to remove any volatile materials. The residue was crystallized from toluene:pentane (1:3) mixture. White precipitate was filtered out and washed with 2 ml of hexane. Yield 0.43 g (71%). Calculated (%) for $C_{76}H_{76}O_8Ti_2$: C, 75.24; H, 6.31; Ti, 7.89. Found (%): C, 75.01; H, 6.08; Ti, 7.68. ¹H NMR (400 MHz, CDCl₃, d, J/Hz) δ : 7.75-7.37 (m, 48 H, Ar), 4.06-4.04 (m, 2H, CH), 1.29 (s, 12H), 1.23(s, 12H). ¹³C NMR (101 MHz, CDCl₃) δ : 139.09, 137.11, 131.32, 129.88, 128.41, 127.46, 126.96, 124.99, 76.71, 76.21, 64.39, 26.54, 25.36, 1.02. FT-IR (KBr), v, cm⁻¹: 636, 557 (Ti-O).

[2-[(diphenyl)methyl]phenyl-methanolato]-diphenyl-methanolato]-dichloro-di(isopropanol) Titanium (4)

To a solution of ligand (1) (0.442 g, 1.0 mmol) in 10 ml of methylene chloride, $TiCl_2(OiPr)_2$ (0.12 g, 0.5 mmol) in 2 ml of methylene chloride was added and left unstirred for 12 h at room temperature. White precipitate was filtered out and washed with 4 ml of toluene. The yield was 0.52 g (76%). Calculated (%) for $C_{38}H_{40}$ Cl₂O₄Ti: C, 67.17; H, 5.93; Cl, 10.44; Ti, 7.04. Found (%): C, 67.02; H, 5.86; Cl, 10.27; Ti, 7.53. ¹H NMR (400 MHz, CDCl₃) δ : 7.74-7.34 (m, 24 H, Ar), 5.07 (br-s, 2H, OH), 1.39 (s, 12H). ¹³C NMR (101 MHz, CDCl₃) δ 139.09, 137.11, 131.33, 129.88, 128.41, 127.46, 126.96, 124.99, 77.33, 77.01, 76.69, 25.37. FT-IR (KBr): 3180 cm⁻¹ v(OH), 1632 cm⁻¹ δ (OH), 636, 590 cm⁻¹ v(Ti-O).

[1,1,4,4-Tetraphenylbutane-1,4-diolate-O,O]-dichloro-di(isopropanol) Titanium (5)

To a solution of ligand (**2**) (0.394 g, 1.0 mmol) in 10 ml of toluene, $TiCl_2(OiPr)_2$ (0.12 g, 0.5 mmol) in 2 ml of toluene was added and left unstirred for 6 h at room temperature. White precipitate was filtered out and washed with 3 ml of toluene. The yield was 0.39 g (62%). Calculated (%) for $C_{34}H_{40}Cl_2O_4Ti$: C, 64.67; H, 6.38; Cl, 11.23; Ti, 7.58. Found (%): C, 64.47; H, 6.25; Cl, 11.19; Ti, 7.53. ¹H NMR (400 MHz, CDCl₃) δ : 7.46-7.28 (m, 20 H, Ar), 5.51(s, 2H, OH), 4.07 (br-s, 4H, CH₂), 1.22 (s, 12H). ¹³C NMR (101 MHz, CDCl₃) δ 170.88, 170.35, 146.71, 143.26, 134.00, 128.34, 128.18, 126.84, 126.04, 95.41, 78.23, 64.14, 35.95, 35.65, 29.70, 25.35. FT-IR (KBr): 3182 cm⁻¹ v(OH), 1632 cm⁻¹ δ (OH), 620, 593 cm⁻¹ v(Ti-O).

Tris[1,1,4,4-Tetraphenylbutane-1,4-diolate-O,O]-bis-(isopropoxy) Titanium (6)

To a solution of ligand (**2**) (0.394 g, 1.0 mmol) in 10 ml of toluene, Ti(OiPr)₄ (0.299 ml, 1.0 mmol) in 2 ml of toluene was added and left unstirred for 6 h at room temperature. White precipitate was filtered out and washed with 3 ml of pentane. The yield was 0.32 g (69%). Calculated (%) for C₉₀H₈₆O₈Ti₂: C, 77.69; H, 6.23; Ti, 6.88. Found (%): C, 77.54; H, 6.17; Ti, 6.59. ¹H NMR (400 MHz, CDCl₃), δ : 7.75-7.35 (m, 20 H, Ar), 4.56-4.51, (m, 12H, CH₂), 4.07-4.03 (m, 2H, CH), 1.25 (s, 12H). ¹³C NMR (101 MHz, CDCl₃), δ : 139.11, 137.13, 131.34, 129.90, 128.43, 127.48, 126.97, 125.01, 64.36, 26.57, 25.38. FT-IR (KBr): 626, 597 cm⁻¹ v(Ti-O).

Bis[1,1,4,4-Tetraphenylbutane-1,4-diolate-O,O]-titanium (7)

To a solution of ligand (2) (0.394 g, 1.0 mmol) in 10 ml of toluene, Ti(OiPr)₄ (0.149 ml, 0.5 mmol) in 2 ml of toluene was added and left unstirred for 12 h at room temperature. White precipitate was filtered out and washed with 3 ml of pentane. The yield was 0.29 g (70%). Calculated (%) for $C_{56}H_{48}O_4$ Ti: C, 80.76; H, 5.81; Ti, 5.75. Found (%): C, 77.54; H, 6.17; Ti, 6.59. ¹H NMR (400 MHz, d-THF) δ : 7.42-7.31 (m, 40 H, Ar), 3.58 (br-s, 8H, CH₂). FT-IR (KBr): 616, 597 cm⁻¹ v(Ti-O).

X-ray crystal structure determination. X-ray diffraction data for **6** was collected on a Bruker APEX DUO diffractometer (λ (CuK α) = 1.54178 Å, ω -scans, 2 θ <145.29°). Colorless crystals of C₉₀H₈₆O₈Ti₂, 2(C₇H₈) at 120(2) K are trigonal, space group R-3c, a = 15.6009(7), c = 62.163(3) Å, V = 13102.7(13) Å³, Z = 6 (Z' =0.5), d_{calc} = 1.198 g cm⁻³. Intensities of 2903 independent reflections (R_{int} = 0.0375) out of 59199 collected were used in structure solution and refinement. The structure was solved by direct methods and refined by the full-matrix least-squares technique against F² in the anisotropic approximation. The positions of hydrogen atoms were calculated. Hydrogen atoms were refined in riding model with $U_{iso}(H)$ equal to 1.5 $U_{eq}(C)$ and 1.2 $U_{eq}(C)$ of the connected methyl and other carbon atoms. As the structure is highly disordered by symmetry, some constraints were applied to coordinates and anisotropic displacement parameters of the disordered atoms. Phenyl rings were refined in a rigid-body model. The contribution to the diffraction of the highly disordered solvating toluene molecules was accounted with SQUEEZE method implemented in PLATON prigram [25]. The refinement converged to $R_1 = 0.0350$ (calculated for 2624 observed reflections with $I>2\sigma(I)$), w $R_2 = 0.1027$ and GOF = 1.029. All calculations were performed with SHELX software package [26]. Atomic coordinates, bond lengths and angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Center (CCDC), reference 1509955. Copies of the data can be obtained can be obtained free of charge via <u>http://www.ccdc.cam.ac.uk/data request/cif</u>, or by emailing <u>data request@ccdc.cam.ac.uk</u>, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223-336033.

Polymerization of ethylene

The ethylene polymerization was performed in a 100-ml reactor (Parr Instrument Co.) equipped with a magnetic stirrer and inlets for loading components of catalytic systems and ethylene at a total pressure of ethylene and toluene vapours of 0.7 atm. Toluene (50 ml) and the necessary amount of a co-catalyst (Et₂AlCl/Bu₂Mg or Et₃Al₂Cl₃/Bu₂Mg) were loaded in the reactor. The reactor was heated to a specified temperature, and the reaction mixture was saturated with ethylene. Polymerization was started by the addition of pre-catalyst to the reaction mixture. The pressure of ethylene was maintained constant during polymerization. Polymerization was stopped through the addition of 10% HCl solution in ethanol to the reactor. The polymer was filtered off, washed several times with water-ethanol mixture, and dried under vacuum at 50-60 °C until a constant weight was achieved.

Polymer Evaluation Methods.

TGA and DTA measurements were done by a "Derivatograph-C" (MOM, Hungary) at a heating rate 10°C/min in air. DSC was performed by a differential scanning calorimeter DSC-822e (Mettler-Toledo, Switzerland) at a heating rate 10°C/min in air. TMA was carried out by TMA Q400 (TA Instruments, USA) on powder samples at a heating rate 5 °C/min and a share stress 1N in air.

Viscosity-average molecular weight of synthesized UHMWPE samples was calculated with the Mark-Houwink equation: $MW = 5.37 \cdot 10^4 [\eta]^{1.37}$ [22], where: MW = viscosity-

average molecular weight (g/mol); $[\eta]$ = intrinsic viscosity in decalin at 135°C (dl/g); $[\eta]$ = ($2\eta_{sp} - 2ln\eta_r$)^{1/2}/0.056 (η_{sp} - specific viscosity decalin at 135°C; η_r - relative viscosity in decalin at 135°C; $\eta_r = \eta_{sp} + 1$.

The mechanical characteristics of the oriented materials prepared with the synthesized polymers were evaluated on the oriented tapes obtained by a solid state processing of UHMWPE nascent reactor powders. The uniform over the entire length monolithic tapes (100 microns in thickness and 10 mm in width) were formed at a pressure and shear deformation below the polymer melting point (124-126 °C). The tapes were subjected to uniaxial drawing while using a Spinline Daca equipment. The drawing temperature was set 4 °C below the polymer melting point. The mechanical characteristics of the tapes were measured with a Hounsfield H1KS machine at the gauge length of the tested samples 120 mm with 2 mm/min initial deformation rate. The reported values were the average of at least 8 samples.

Acknowledgments

This work was financially supported by the Russian Science Foundation (Project No 16-13-10502).

References

- [1] M.C. Baier, M.A. Zuideveld and S. Mecking, Angew. Chem. Int. Ed. 53 (2014) 9722– 9744.
- [2] A. Mehta, G. Tembe, P. Parikh and G. Mehta, Polym. Int. 63 (2014) 206–213.
- [3] Y.N. Belokon', S.Ch. Gagieva, T.A. Sukhova, A.B. Dmitriev, K.A. Lyssenko, N.M. Bravaya, B.M. Bulychev, D. Seebach, Russ. Chem. Bull. 54 (2005) 2348-2353.
- [4] L.A. Rishina, N.M. Galashina, S.Ch. Gagieva, V.A. Tuskaev, B.M. Bulychev, Y.N. Belokon', Polymer Sci. Series A 50 (2008) 110-118.
- [5] S.Ch. Gagieva, V.A. Tuskaev, O.V. Smirnova, S.S. Galibeev, B.M. Bulychev, N.M. Bravaya, Polymer Sci. Series B 53 (2011) 299-306.
- [6] L.A. Rishina, N.M. Galashina, S.Ch. Gagieva, V.A. Tuskaev, Y.V. Kissin, Polymer Sci. Series B 53 (2011) 42-51.
- [7] V.A. Tuskaev, S.Ch. Gagieva, V.I. Maleev, A.O. Borissova, M.V. Solov'ev, Z.A. Starikova, B.M. Bulychev, Polymer 54 (2013) 4455-4462.

- [8] Y.V. Kissin, T.E. Nowlin, R.I.Mink, A.J. Brandolini, Macromolecules 33 (2000) 4599-4601.
- [9] Y.V. Kissin, R.I. Mink, A.J. Brandolini, T.E. Nowlin, J. Polym. Sci. Part A Polym. Chem. 47 (2009) 3271-3285.
- [10] R.K. Haynes, M.K.S. Probert, I.D. Wilmot, Aust. J. Chem. 31 (1978) 1737 1746.
- [11] M.C. Kloetzel, J. Am. Chem. Soc. 62 (1940) 3405–3410.
- [12] I. Tatsushi, Y. Ryo, K. Seiji, Chem. Eur. J. 18 (2012) 10802 10807.
- [13] L.Y. Ustynyuk, B.M. Bulychev, Mendeleev Commun. 26 (2016) 45-48.
- [14] L.Y. Ustynyuk, B.M. Bulychev, J Organomet Chem. 793 (2015) 160-170.
- [15] B. Wunderlich, C.M. Cormier, J. Polym. Sci., Part A-2: Polym. Phys. 5 (1967) 987-988.
- [16] V.A. Tuskaev, S.Ch. Gagieva, D.A. Kurmaev, T.M. Zvukova, I.V. Fedyanin, B.M. Bulychev, Inorg. Chim. Acta 442 (2016) 167–171.
- [17] N. R. de S. Basso, P. P. Greco, C. L.P. Carone, P. R. Livotto, L.M.T. Simplicio, Z. N. da Rocha, G. B. Galland, J. H.Z. dos Santos, J. Mol. Cat. A: Chem. 267 (2007) 129–136.
- [18] J. A. Suttil, D. S. McGuinness, M. Pichler, M. G. Gardiner, D. H. Morgan and S. J. Evans, Dalton Trans., 2012, 41, 6625-6633.
- [19] J.B. Cazaux, P. Braunstein, L. Magna, L. Saussine and H. Olivier-Bourbigou. Eur. J. Inorg. Chem. 20 (2009) 2942–2950.
- [20] F. Grasset, J.-B. Cazaux, L. Magna, P. Braunstein and H. Oliver-Bourbigou, Dalton Trans. 41 (2012) 10396-10404.
- [21] J. A. Suttil, D. S. McGuinness, M. Pichler, M. G. Gardiner, D. H. Morgan and S. J. Evans, Dalton Trans. J. Chem. Soc., Dalton Trans. 41 (2012) 6625–6633.
- [22] The UHMWPE handbook: ultra-high molecular weight polyethylene in total joint replacement / Steven M. Kurtz., 2004, Elsevier Academic Press.
- [23] K. Liu, S. Ronca, E. Andablo-Reyes, G. Forte, and S. Rastogi, Macromolecules 48 (2015) 131–139.
- [24] K. Mikami, M. Terada, T. Nakai, J. Am. Chem. Soc. 112 (1990) 3949-3954.
- [25] A.L. Spek, Acta Crystallogr. C71 (2015) 9-18.
- [26] G.M. Sheldrick, Acta Crystallogr. A64 (2008) 112–122.

Novel titanium complexes bearing diol-type $[O, O]^2$ ligands were synthesized. Complexes activated by Et₂AlCl+Bu₂Mg produced ultra-high molecular weight polyethylene. Polymers are suitable for the solventless formation of high-modulus oriented films.