Accepted Manuscript

Novel titanium (IV) complexes with 1,2-diolate ligands: Synthesis, structure and catalytic activities in ultra-high molecular weight polyethylene production

Vladislav A. Tuskaev, Svetlana Ch Gagieva, Dmitrii A. Kurmaev, Victor N. Khrustalev, Pavel V. Dorovatovskii, Elena S. Mikhaylik, Evgenii K. Golubev, Mikhail I. Buzin, Sergey V. Zubkevich, Nikolay A. Kolosov, Galina G. Nikiforova, Viktor G. Vasil'ev, Boris M. Bulychev

PII: S0022-328X(18)30712-5

DOI: 10.1016/j.jorganchem.2018.09.014

Reference: JOM 20571

To appear in: Journal of Organometallic Chemistry

Received Date: 11 August 2018

Revised Date: 17 September 2018

Accepted Date: 18 September 2018

Please cite this article as: V.A. Tuskaev, S.C. Gagieva, D.A. Kurmaev, V.N. Khrustalev, P.V. Dorovatovskii, E.S. Mikhaylik, E.K. Golubev, M.I. Buzin, S.V. Zubkevich, N.A. Kolosov, G.G. Nikiforova, V.G. Vasil'ev, B.M. Bulychev, Novel titanium (IV) complexes with 1,2-diolate ligands: Synthesis, structure and catalytic activities in ultra-high molecular weight polyethylene production, *Journal of Organometallic Chemistry* (2018), doi: https://doi.org/10.1016/j.jorganchem.2018.09.014.

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.





ACCEPTED MANUSCRIPT

Novel titanium (IV) complexes with 1,2-diolate ligands: synthesis, structure and catalytic activities in ultra-high molecular weight polyethylene production

Vladislav A. Tuskaev^{a,b}*, Svetlana Ch. Gagieva^{a,b}, Dmitrii A. Kurmaev^a, Victor N. Khrustalev^{c, d}, Pavel V. Dorovatovskii^e, Elena S. Mikhaylik^{b,e}, Evgenii K. Golubev^{b,e}, Mikhail I. Buzin^b, Sergey V. Zubkevich^a, Nikolay A. Kolosov^a, Galina G. Nikiforova^b, Viktor G. Vasil'ev^b, Boris M. Bulychev^a

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

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

^cInorganic Chemistry Department, Peoples' Friendship University of Russia, 117198 Moscow, Miklukho-Maklay St., 6, Russia

^d National Research Center "Kurchatov Institute", Moscow, Russia

^e Enikolopov Institute of Synthetic Polymer Materials, Russian Academy of Sciences,

Profsoyuznaya Str., 70, 117393 Moscow, Russian Federation

KEYWORDS Ziegler-Natta Polymerization, Titanium, OO-ligands, UHMWPE

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

ABSTRACT A series of titanium (IV) complexes **3a-f** stabilized by 1,2-diolate ligands **2 a-e** have been synthesized. Structures of complexes **3d** and **3e** have been determined by X-ray diffraction. Titanium atoms in these complexes have a distorted square-pyramidal environment. All resulting complexes are highly active in ethylene polymerization in the presence of $\{3Et_2AlCl + MgBu_2\}$ or $\{1.5Et_3Al_2Cl_3 + MgBu_2\}$ binary co-catalysts. In the latter case, higher molecular weights of UHMWPE samples (up to 7.7 10⁶) are achieved. Obtained polymers are suitable for the modern processing methods – the solvent-free solid state formation of super high-strength (over 2.0 – 2.8 GPa) and high-modulus (up to 145 GPa) oriented film tapes.

1. Introduction

Unique properties of UHMWPE make it one of the most promising modern construction materials, however, the high viscosity of its melts makes it difficult to use conventional methods (extrusion, injection molding, etc.) for its processing. In this regard, the development of new and improvement of known technologies for the production of high-strength and high-modulus UHMWPE films and tapes are of special importance. At present, this problem is mainly solved by using the gel-spinning method with subsequent orientation drawing [1]. The main disadvantage of this method is the low solubility of the polymer, which determines the need for large quantities of high-boiling solvents and the associated high costs for its regeneration. The developed method of solid-phase processing of UHMWPE reactor powders in high-strength films and tapes [2-4] certainly has a number of serious technological and economic advantages in comparison with gel spinning. However, this method can be successfully used only for processing of UHMWPE nascent reactor powders with a morphology close to that of singlecrystal mats [5].

It was established in [5-13] that the nascent reactor powders of the required quality can be obtained on single-center post-metallocene catalysts, under mild conditions of polymerization process (low concentrations of the catalysts, low temperature and pressure). In the overwhelming majority of publications, phenoxyimine complexes of titanium (IV) are used as single-center catalysts.

However, in [14] we showed the possibility of using more accessible titanium (IV) diolate complexes (Compound A, Fig.1) in combination with aluminum alkyl chlorides and organomagnesium compounds; the obtained UHMWPE powder was processed into orientated film tapes with breaking strength over 2.3 GPa and elastic modulus over 150 GPa. However, the geometry of 1,4-diolate ligands leading to the formation of unstable 7-membered metallocycles, facilitated the formation of $L_3Ti_2(OiPr)_2$ complexes (Compound B, Fig.1). It could be assumed that the activation of such complexes by the organoaluminium compounds will lead to the cleavage of ligands, which inevitably leads to the appearance of a set of catalytically active sites and broadening of the MWD of polymers.

Despite the fact that 1,2-diols are able to form stable five-membered chelate rings, the catalytic activity of such titanium complexes in olefin polymerization has been studied rather poorly. The diolate complexes C and D (Fig. 1), activated with $Et_3Al_2Cl_3$, catalyzed the formation of low molecular weight PE [15]. It is known that pinacol derivatives form highly stable titanium-containing Metal-Organic Framework (structure E, Fig. 1) [16], but their ability to catalyze the polymerization of olefins has not been studied. With the increasing of steric hindrance around hydroxyl groups, it becomes possible to obtain "individual" coordination compounds (structures F and G in the crystalline state are dimers stabilized by O \rightarrow Ti bonds) [17-19].



Fig. 1. Examples of Ti (IV) diolate complexes.

The present work aims to investigate the relationship between the structures of novel 5membered diolate titanium (IV) complexes and their activity in ethylene polymerization, and mainly with their ability to catalyze the production of disentangled UHMWPE.

2. Results and discussion

2.1.Ligands and coordination compounds synthesis and structure.

It is known that the introduction of highly fluorinated fragments into the diol ligands significantly increases their acidity. A larger steric hindrance, in comparison with non-fluorinated analogs, as well as chemical inertness, in a number of cases makes it possible to increase the stability of $LTiX_2$ complexes. In the present work, we used fluorinated and non-fluorinated 1,2-diols - commercially available pinacol and perfluoropinacol. Tetraphenylethane-1,2-diol, 1,2-diphenyl-1,2-perfluorophenylethane-1,2-diol and tetrakis(pentafluorophenyl) ethane-1,2-diol have been obtained by reductive dimerization of the corresponding carbonyl compounds with zinc powder in THF/NH₄Cl aq. [20].



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

Alkoxo-titanium complexes have been obtained by the interaction of toluene solutions of ligands **2a-e** with titanium (IV) tetraisopropoxide at room temperature. The resultant complexes **3a-f** have been identified on the basis of ¹H, ¹³C and ¹⁹F NMR spectra, IR spectroscopy and elemental analysis.

The structures of the complexes **3d** and **3e** have been unambiguously established by Xray diffraction study and are shown in Fig. 2A and B respectively, along with the atomic numbering schemes. The pertinent bond lengths and angles are given in Table S1-S2.



Fig. 2. A. Molecular structure of complex **3d** (A) and **3e** (B). 50% ellipsoids, hydrogen atoms are omitted for clarity.

The both titanium complexes are the centrosymmetrical dimers and, in the crystal, occupy the special positions on the inversion centers. The dimers include the central fourmembered Ti_2O_2 -ring formed by the two μ -bridging isopropoxy (in the case of **3e**) or deprotonated pinacol (in the case of **3d**) ligands, with the Ti…Ti separation of 3.1218(12) and $3.265(2) \Box$, respectively. The geometry around each titanium atom is distorted square-pyramidal, with the basal planes consisting of the O1, O2, O4 and O4A oxygen atoms for **3e** and the O2, O2A, O3 and O4 oxygen atoms for **3d**. The metal centers are tilted from these planes in the direction of the apical oxygen atoms O3 (in the case of **3e**) and O1 (in the case of **3d**). The chelate five-membered cycles adopt the *envelope* conformations. As expected, the μ -bridging Ti—O bond distances are significantly longer than the terminal ones (Table 1).

Crystal packing of 3d and 3e is stacking along the crystallographic b and a axis, respectively (Figures S1 and S2). The molecules are arranged at van-der-Waals distances.

It is quite obvious that the dissociation of the $Ti \leftarrow O$ bond of these complexes during the activation by organoaluminum compounds will result in the formation of monomer complexes with a coordinatively unsaturated tetrahedral titanium (IV) atom and two terminal and easily substituted isopropoxy groups. This, in accordance with modern concepts of the Ziegler catalysis mechanism, is of fundamental importance for the manifestation of catalytic activity for olefin polymerization.

2.2. Catalytic properties of Ti diolate complexes.

All complexes reported herein have been tested for their ability to catalyze the ethylene polymerization. The polymerization was carried out under the same conditions such as temperature, Al/Ti ratio, solvent and ethylene pressure. The most relevant results of ethylene polymerization using pre-catalysts **3a-f** are shown in Table 1. It was observed that complexes **3a-f** in the presence of Et_2AlCl or $Et_3Al_2Cl_3$ as co-catalyst have demonstrated rather low catalytic activity and yielded only the trace amounts of the polyethylene. Introduction of dibutylmagnesium to the catalytic systems containing aluminum alkyl chlorides leads to a significant increase in activity (up to 3029 kg of PE mol⁻¹h⁻¹ atm⁻¹, run 14). The obtained results are consistent with the works [21-22], in which a mixture of AlR₂Cl/MgR₂ was proposed as universal cocatalysts for Ziegler–Natta catalytic systems.

Table 1.

Luiyiene i orymenzation by complexes 3a-u	Ethylene Pol	ymerization	by comp	lexes 3a-d "
--	--------------	-------------	---------	---------------------

Run	Comp- lex	Cocatalyst, Al/Mg	A ^b	Bulk density, g/cm ³	M _v , 10 ⁶	T _m ^c °C	Deg.of Crystal ^d %
1	3 a	Et ₂ A1Cl/ MgBu ₂ 300/100	2629	0.035	1.58	139/136	67.5/48.9
2	3 a	Et ₃ Al ₂ Cl ₃ /MgBu ₂ 300/100	2057	0.056	7.73	142/136	78.5/49.7
3	3b	Et ₂ AlCl/MgBu ₂ 300/100	2457	0.035	1.08	136/132	65.0/51.6

ACCEPTED MANUSCRIPT							
4	3b	Et ₃ Al ₂ Cl ₃ /MgBu ₂ 300/100	2800	0.076	4.86	140/133	78.1/49.3
5	3c	Et ₂ AlCl/ MgBu ₂ 300/100	2629	0.040	1.34	137/135	78.6/64.6
6	3c	Et ₃ Al ₂ Cl ₃ / MgBu ₂ 300/100	2314	0.064	4.67	140/135	76.5/44.7
7	3d	Et ₂ AlCl/ MgBu ₂ 300/100	2629	0.046	2.42	138/134	64.1/44.9
8	3d	Et ₃ Al ₂ Cl ₃ /MgBu ₂ 300/100	2514	0.051	5.63	141/135	76.3/46.6
9	3e	Et ₂ AlCl/ MgBu ₂ 300/100	1829	0.031	2.94	139/136	75.3/48.2
10	3e	Et ₃ Al ₂ Cl ₃ /MgBu ₂ 300/100	1829	0.042	5.18	141/136	74.7/41.9
11 ^e	3e	Et ₂ AlCl/ MgBu ₂ 300/100	2029	0.066	1.31	138/134	67.2/52.3
12 ^e	3e	Et ₃ Al ₂ Cl ₃ /MgBu ₂ 300/100	2114	0.084	3.20	140/135	68.7/45.0
13	3f	Et ₂ AlCl/ MgBu ₂ 300/100	2286	0.035	2.92	139/135	72.5/45.9
14	3f	$Et_{3}Al_{2}Cl_{3}/\\MgBu_{2}300/100$	3029	0.060	6.71	142/136	75.4/46.6
15	Ti(O ⁱ Pr) ₄	Et ₂ AlCl/ MgBu ₂ 300/100	2914	0.049	1.66	138/133	68.4/52.8
16	Ti(O ⁱ Pr) ₄	Et ₃ Al ₂ Cl ₃ /MgBu ₂ 300/100	2971	0.053	3.34	140/135	75.1/47.2
17	Ti(O ⁱ Pr) ₄	Et ₂ AlCl/ MgBu ₂ 200/100	2571	0.059	1.59	135/130	61.4/41.1

^a Polymerizations carried out in 100 mL of toluene with 5 10⁻⁶ mol of catalyst at a constant 0.7 atm ethylene pressure for 30 min, temperature 30 °C. ^b Activity, kg of PE mol⁻¹h⁻¹ atm⁻¹.

^c Melting points were determined by DSC, the values for the first and second heating runs are given

^d. Degree of crystallinity was calculated by use of value $\Delta H_m^{100\%} = 288 \text{ J/g} [23]$; the values for the first and second heating runs are given. ^e amount of catalyst - 1 10⁻⁵ mol.

From Table 1 it is apparent that the structure of pre-catalyst, as well as the nature of organoaluminum activator, does not have a significant effect on the activity of the complexes, which, ceteris paribus, is in the range 1829-3029 kg of PE mol⁻¹h⁻¹ atm⁻¹. Unexpectedly the maximum catalytic activity in this series was shown not by systems based on dimeric complexes, capable of dissociation upon activation by aluminum and magnesium organics, but by a system based on a spiro-complex 3f with covalent Ti-O bonds. Using the example of pre-catalyst 3e it was shown that an increase in the catalyst amount from $5 \cdot 10^{-6}$ to $1 \cdot 10^{-5}$ moles is accompanied by a slight increase in activity and a marked decrease in the viscosity-average molecular weights of the polymers (runs 9 vs. 11 and 10 vs. 12).

For all studied catalyst precursors, the replacement of Et₂AlCl with Et₃Al₂Cl₃ leads to a significant increase in the molecular weight of the polymer (Table 1, Figure 3). A similar trend was observed for titanium complexes stabilized with 1,4-diol ligands [14].



Fig. 3. Molecular weight of the obtained UHMWPE samples versus the nature of activators.

The production of low molecular weight PE (639-1036 g mol⁻¹) on 1,2-diolate titanium complexes activated with $Et_3Al_2Cl_3$ [15] clearly indicates a significant rate of chain transfer process on the organoaluminum compounds. Obviously, the introduction of the organomagnesium compound in the catalyst system significantly retards the process. The observed increase in the molecular weight of PE with the use of $Et_3Al_2Cl_3$ instead of Et_2AlCl is difficult to explain solely by the nature of the organoaluminum compounds. Thus, for example, the molecular weight of PE synthesized on Cp_2TiCl_2/Et_2AlCl was 15-30% higher than the values obtained using the $Cp_2TiCl_2/Et_3Al_2Cl_3$ system [24]. It is more likely that the reason for such a significant increase in the molecular weight of UHMWPE is in the composition of the interaction products of the binary activator { $Et_3Al_2Cl_3 + Bu_2Mg$ }, which, for example, can be formed by reactions 1-2:

$$3Et_{2}AlCl + Bu_{2}Mg = MgCl_{2} + 2AlEt_{2}Bu + AlEt_{2}Cl$$

$$1$$

$$3Et_{3}Al_{2}Cl_{3} + 2Bu_{2}Mg = 2MgCl_{2} + 2AlEt_{2}Bu + AlEtBu_{2} + Et_{2}AlCl + 2EtAlCl_{2} + \dots$$

$$2$$

The above equations are conditional and do not have full experimental confirmation. They do not take into account the differences in the reactivity of alkyl aluminum chlorides, possible symmetrization processes, exchange reactions, etc., but the established fact of the magnesium chloride formation when combining the activator components indicates a significant increase in the content of aluminum alkyl chlorides of various nature in the reaction media and, accordingly, the formation of a set of active sites. Apart from increasing the molecular weight, a replacement of Et_2AlCl with $Et_3Al_2Cl_3$ leads to a marked increase in the crystallinity degree and melting temperature of UHMWPE samples at the first heating. During the second heating run, these values are leveled, which indirectly indicates a high degree of disentanglement of nascent reactor powders.

2.1. Mechanical properties of synthesized UHMWPE

The processing of reactor powders of UHMWPE obtained on complexes **3a-f** into high-modulus oriented films was carried out by preparing monolithic samples under pressure and shear deformation at an elevated temperature below polymer melting point with subsequent uniaxial drawing [5]. Criteria for the quality of the resulting oriented film tapes were: homogeneity of the resulting filament along the width and homogeneity of the samples masses within one multiplicity at one length. For comparison, the mechanical properties of film tapes drawn from the UHMWPE reactor powder obtained on the Ti(OiPr)₄/Et₃Al₂Cl₃ (run 16) are given in the table 2. As can be seen, the maximum drawing ratio in this case did not exceed 20 at rather mediocre mechanical characteristics of the filaments.

Table 2.

Run ^a	Catalytic system ^b	Draw ratio	σ, GPa	E, GPa	ε, ^e %
2	3a/ Et ₃ Al ₂ Cl ₃ /MgBu ₂	24	2.56	135	2.88
1	3b/ Et ₃ Al ₂ Cl ₃ /MgBu ₂	40	2.73	140	2.30
4		44	2.72	140	2.48
6	3c/ Et ₃ Al ₂ Cl ₃ /MgBu ₂	36	2.82	145	2.46
8	3d/ Et ₃ Al ₂ Cl ₃ /MgBu ₂	36	2.74	130	2.55
9	3e/ Et ₂ AlCl/MgBu ₂	20	2.09	75	3.28
10	3e/ Et ₃ Al ₂ Cl ₃ /MgBu ₂	32	2.72	140	2.37
13	3f/ Et ₂ AlCl/MgBu ₂	36	2.47	120	2.71
14	3f / Et ₃ Al ₂ Cl ₃ /MgBu ₂	28	2.41	105	2.27
16	Ti(O ⁱ Pr) ₄ /Et ₃ Al ₂ Cl ₃ /MgBu ₂	20	1.99	105	2.12

Mechanical properties of UHMWPE oriented film tapes

^a Numbering corresponds to Table 1.

^b Molar ratio [Ti]:[Ål]:[Mg] = 1:300:100.

Most of the reactor powders produced on catalytic systems with Et_2AlCl proved to be unsuitable for solid-phase processing, with the exception of the powders synthesized on complexes **3e** and **3f** stabilized by perfluoropinacol (Table 2, runs 9 and 13).

Practically all of the rector powders synthesized using $Et_3Al_2Cl_2$ have been successfully processed into high-strength, high-modulus materials. Reactor powders obtained in the present work allowed to achieve maximal drawing ratios (up to 44), among the samples obtained on titanium complexes with OO-type ligands [14, 25-26].

As can be seen from Table 2, the best mechanical characteristics were demonstrated by films obtained on complexes with fluorinated ligands. Among the complexes **3a-c** stabilized by the ligands with aromatic substituents, the maximum strength characteristics -2.82 GPa was obtained on an "asymmetric" pre-catalyst **3c** (elastic modulus 145 GPa at draw ratio = 36, run 6). For the pre-catalysts **3d-f** with aliphatic ligands, the positive effect of the presence of fluorine manifests itself to a lesser degree. Interestingly, the mechanical characteristics of the film from UHMWPE obtained on the spiro-complex **3f** activated with Et₂AlCl surpassed the analog obtained from **3f**/Et₃Al₂Cl₂. The maximum achievable drawing ratio of the film from the UHMWPE powder obtained on Ti(OiPr)₄/Et₃Al₂Cl₂ system did not exceed 20. The mechanical characteristics of this film are also very mediocre.

It is well known [27] that drawability of UHMWPE highly depends on its supramolecular structure. To examine the morphologies of these powders, SEM observations have been made (Figure 4). All of these micrographs are of the same magnification for comparative purposes. As can be seen from the scanning electron micrographs at low magnification, the polymer particles have the irregular shape and porous structure, that determines the low bulk density (0.031-0.084 g/cm³) of the obtained samples.







Fig. 4. Scanning electron micrographs of a series of nascent reactor powders, prepared on 3a/Et₂AlCl (A-B), 3a/Et₃Al₂Cl₃ (C-D), 3c/Et₂AlCl (E-F), 3c/Et₃Al₂Cl₃ (J-H).

The high magnification micrographs clearly show that all catalytic systems, regardless of the nature of the organoaluminum activator, were found to produce polymers with nodular type microstructures. The main morphological difference between UHMWPE powders obtained on **3a-e** /Et₃Al₂Cl₃, and samples obtained on **3a-e**/Et₂AlCl, and unsuitable for orientational drawing is the irregular shape of microparticles - nodes. It is known that polymeric powders having irregular, spongy particles compacted better than those consisting of spherical, dense particles [28].

In general, the morphology of the polymers obtained using various activators (Et₂AlCl or $Et_3Al_2Cl_3$) differs insignificantly. Obviously, in this case, the factors determining the possibility of solid-phase processing are significantly higher values of Mv and crystallinity of the polymers obtained with $Et_3Al_2Cl_3$.

3. Conclusion

- In summary, a series of titanium (IV) complexes bearing 1,2-diolate ligands have been synthesized in high yields. Structures of complexes **3d-e** have been established by X-ray diffraction.
- All complexes in the presence of a binary co-catalysts $\{3Et_2AlCl + Bu_2Mg\}$ or $\{1.5Et_3Al_2Cl_3 + Bu_2Mg\}$ exhibited moderate to high activities towards ethylene polymerization (1829-3029 kg of PE mol⁻¹h⁻¹ atm⁻¹).
- It should be noted that the spiro-complex **3f** unexpectedly showed high catalytic activity, despite its activation, in our opinion, is more difficult compared with the complexes having the composition LTi(OiPr)₂.
- All investigated pre-catalysts produced ultra-high-molecular-weight polyethylene (viscosity-average molecular weights were in the range 1.1-7.7 10⁶).
- The complexes activated with $Et_3Al_2Cl_3$ produce polymers with significantly higher values of Mv, crystallinity and melting point on first heating run. This may be due to differences in the composition of the reaction products { $3Et_2AlCl + Bu_2Mg$ } or { $1.5Et_3Al_2Cl_3 + Bu_2Mg$ }.
- All UHMWPE reactor powders obtained with Et₃Al₂Cl₃ were processed into oriented films with a strength of 2.0 2.8 GPa and an elasticity coefficient up to 145 GPa.
- The best mechanical properties were exhibited by films obtained on complexes with polyfluorinated ligands;
- The properties of the produced films, and especially the drawing ratios, are superior to materials previously obtained on titanium complexes with 1,4-diol ligands.

4. Experimental section

All manipulations with air-sensitive materials were performed with rigorous exclusion of oxygen and moisture in oven-dried Schlenk glassware on a dual manifold Schlenk line, interfaced to a high-vacuum line. Argon and ethylene of special-purity grade (Linde gas) were dried by purging through a Super CleanTM Gas Filters.

NMR spectra were recorded on Bruker AMX-400 instrument. Deuterated solvents (CDCl₃, THF-d8) were degassed by freeze-pump-thaw vacuum cycles and stored over 3 Å

molecular sieves. Chemical shifts are reported in ppm vs. SiMe₄ and were determined by reference to the residual solvent peaks. All coupling constants are given in Hertz. 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.

Toluene was distilled over Na/benzophenone ketyl and the water content was periodically controlled by Karl-Fischer coulometry by using a Methrom 756 KF apparatus. Diethylaluminum chloride, ethylaluminum sesquichloride and di-n-butylmagnesium (Aldrich) were used as 1.0 M solution in heptane. Decafluorobenzophenone and perfluoropinacol were obtained from SIA "P&M-Invest" Ltd., Moscow

4.1. Ligands 3a-c were obtained using general procedure [20].

Zn powder (4 mmol, 0.26 g) and carbonyl compound (2 mmol) were slurried in 3 cm³ saturated aqueous NH_4Cl and 5 cm³ THF. The mixture was stirred at room temperature. The temperature rose, and the Zn powder had disappeared. The solvents were evaporated to dryness, and the product was extracted with diethyl ether. The etheral layer was separated and evaporated to dryness to afford the pure pinacol.

4.2. (1,1,2,2-Tetraphenylethane-1,2-diyloxy)bis(isopropoxy)titanium (3a)

Compound **3a** (3.66 g, 10 mmol) and toluene (20 mL) were placed into a Schlenk tube equipped with a magnetic stirrer under argon atmosphere, followed by the addition of Ti(OiPr)₄ (3.0 ml, 10 mmol) at r.t. The resulting suspension was heated until all solids dissolved. After 10 h at r. t. the formed crystals were collected by filtration and dried in vacuo. Yield 8.7 g (65.7 %). Calculated (%) for $C_{65}H_{72}O_8Ti_2$ (1076): C, 72.49; H, 6.74; Ti, 8.89. Found (%): C, 72.41; H, 6.68; Ti, 8.83. ¹H NMR (CDC1₃): δ = 1.22-1.24 (d, J = 6.1 Hz, 24 H, CH₃), 4.04 (m, 4H, CH), 6.80-7.34 (m, 40H, Ar). ¹³C NMR (101 MHz, CDCl₃) δ 144.25, 132.83, 132.44, 131.81, 130.29, 130.07, 129.66, 129.21, 128.91, 128.64, 128.37, 128.28, 127.24, 127.12, 126.90, 126.72, 126.55, 126.20, 125.78, 125.50, 83.04, 80.50, 64.51, 25.86, 25.73, 25.58, 25.30, 22.90. FT-IR (KBr): 662, 554 cm⁻¹ v(Ti-O).

Using this general procedure, the following compound have been isolated:

4.3. (1,1,2,2-tetrakis(pentafluorophenyl)-ethane-1,2-diyloxy)bis(isopropoxy)titanium (3b) Yield 54.9 %. Calculated (%) for $C_{65}H_{32}F_{40}O_8Ti_2(1760)$: C, 43.45; H, 1.80; Ti, 5.33. Found (%): C, 43.38; H, 1.72; Ti, 5.26. ¹H NMR (CDC1₃): δ =1.26-1.27 (d, J = 6.1 Hz, 24 H, CH₃), 4.51 (m, 4H, CH). ¹⁹F NMR (300 MHz, CDCl₃) δ 140.78, 148.43, 160.22. FT-IR (KBr): 623, 552 cm⁻¹ v(Ti-O). **4.4. 1,2-bis(pentafluorophenyl)-1,2-diphenylethane-1,2-diyloxy)bis(isopropoxy)titanium** (**3c)** Yield 42.9 %. Calculated (%) for $C_{65}H_{52}F_{20}O_8Ti_2(1436)$: C, 54.34; H, 3.65; Ti, 6.66. Found (%): C, 54.27; H, 3.58; Ti, 6.49. ¹H NMR (CDC1₃): $\delta = 1.77$ (m, 24 H, CH₃), 3.65 (m, 4H, CH), 7.13-7.27 (m, 20H, Ar). FT-IR (KBr): 613, 552 cm⁻¹ v(Ti-O).

4.5. (2,3-dimethyl-butane-2,3-diyloxy)bis(isopropoxy)titanium (3d). Yield 61.5 %. Calculated (%) for $C_{25}H_{56} O_8Ti_2$ (580): C, 51.73; H, 9.72; Ti, 16.49. Found (%): C, 51.68; H, 9.69; Ti, 16.45. ¹H NMR (CDC1₃): δ =1.13-1.16 (m, 48 H, CH₃), 3.93 (m, 4H, CH). FT-IR (KBr): 613, 552 cm⁻¹ v(Ti-O).

4.6. (1,1,1,4,4,4-hexafluoro-2,3-bis(trifluoromethyl)-butane-2,3-diyloxy)-bis(isopropoxy)titanium (3e). Yield 62.9 %. Calculated (%) for $C_{25}H_{56}F_{24}O_8Ti_2$ (1012): C, 29.66; H, 3.19; Ti, 9.46. Found (%): C, 29.51; H, 3.11; Ti, 9.39. ¹H NMR (CDC1₃): δ =1.23-1.29 (m, 24 H, CH₃), 4.43 (m, 2H, CH), 4.81 (m, 2H, CH). ¹⁹F NMR (300 MHz, CDCl₃) δ 71.19, 71.53. FT-IR (KBr): 666, 575 cm⁻¹ v(Ti-O).

4.7. Bis-(1,1,1,4,4,4-hexafluoro-2,3-bis(trifluoromethyl)-butane-2,3-diyloxy) titanium (**3f).** Yield 48.3 %. Calculated (%) for $C_{12}F_{24}O_4Ti$ [•] C_3H_8O (772): C, 23.34; H, 1.04; Ti, 6.20. Found (%): C, 23.27; H, 0.91; Ti, 6.17. ¹H NMR (CDC1₃): $\delta = 1.35$ (b-c, 6 H, CH₃), 4.80 (m, 1H, CH). ¹⁹F NMR (300 MHz, CDCl₃) δ 70.73, 71.53. FT-IR (KBr): 666, 575 cm⁻¹ v(Ti-O).

4.8. X-ray crystal structure determination.

The single-crystal X-ray diffraction data for 3e and 3d were collected on the 'Belok' beamline of the Kurchatov Synchrotron Radiation Source (National Research Center 'Kurchatov Institute', Moscow, Russian Federation) using a Rayonix SX165 CCD detector at $\lambda = 0.80246$ Å. A total of 720 images for two different orientations in the case of each crystal were collected using an oscillation range of 1.0° and φ scanning mode. The data were indexed and integrated using the utility iMOSFLM from the CCP4 program suite [29] and then scaled and corrected for absorption using the Scala program [30]. For details, see Table 2. The structures were determined by direct methods and refined by full-matrix least square technique on F^2 in anisotropic approximation for non-hydrogen atoms. In the crystal of 2, two different isomers are arranged in the same positions with the occupancies of 0.75:0.25. The hydrogen atoms in 3e and **3d** were placed in calculated positions and refined within the riding model with fixed isotropic displacement parameters $[U_{iso}(H) = 1.5U_{eq}(C)$ for the methyl groups and $1.2U_{eq}(C)$ for the other groups]. All calculations were carried out using the SHELXTL program suite [31]. Crystallographic data for **3e** and **3d** have been deposited with the Cambridge Crystallographic Data Center, CCDC 1855966 and CCDC 1855965. The supplementary crystallographic data can be obtained free of charge from the Cambridge Crystallographic Data Centre via

4.9. Polymerization of ethylene

The ethylene polymerization was performed in a 300-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 (100 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.

4.10. Polymer evaluation methods

DSC was performed by a differential scanning calorimeter DSC-822e (Mettler-Toledo, Switzerland) at a heating rate 10 °C/min in air.

Viscosity-average molecular weight of synthesized UHMWPE samples was calculated with the Mark-Houwink equation: $Mv = 5.37 \cdot 10^4 [\eta]^{1.37} [1]$, where: Mv = viscosity-average molecular weight (g/mol); $[\eta] =$ intrinsic viscosity in decalin at 135°C (dl/g); $[\eta] = (2\eta_{sp} - 2ln\eta_r)^{1/2}/0.056 (\eta_{sp} - specific viscosity decalin at 135°C; <math>\eta_r$ - 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 mm 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). Synchrotron radiation-based single-crystal X-ray diffraction measurements were performed at the unique scientific facility Kurchatov Synchrotron Radiation Source supported by the Ministry of Education and Science of the Russian Federation (project code RFMEFI61917X0007) and the RUDN University Program "5-100".

References

- M. S. Kurtz, Ultra-high molecular weight polyethylene in total joint replacement, in: The Uhmwpe Handbook, Elsevier Inc., 2004.
- [2] Smith P., Chanzy H.D., B.R. Rotzinger Polymer Commun. 26 (1985) 258.
- [3] Smith P., Chanzy H.D., Rotzinger B.R. J. Mater. Sci. 22 (1987) 523.
- [4] Smith P., Chanzy H.D., Rotzinger B.R. Polymer 30 (1989) 1814.
- [5] Ozerin A.N., Ivanchev S.S., Chvalun S.N., Aulov V.A., Ivancheva N.I., Bakeev N.F., Catalyst. Polym. Sci. 54 (2012), 950-954, https://doi.org/10.1134/S0965545X12100033.
- [6] Rastogi S., Lippits D.R., Peters G.W.M., Graf R., Yao Y.F., Spiess H.W. Nature Mater. 4 (2005) 635-647.
- [7] Rastogi S., Yao Y., Lippits D. R., Hohne G. W. H., Graf R., Spiess H. W., Lemstra P. J. Macromol. Rapid Commun. 30 (2009) 826.
- [8] Taleli S., Duchatu R., Rastogi S., Kaschta J., Peters G. W. M., Lemstra P.J., Macromolecules 43 (2010) 2780.
- [9] Balzano L., Rastogi S., Peters G., Macromolecules 44 (2011) 2926.
- [10] Pandey A., Champouret Y., Rastogi S., Macromolecules, 44 (2011) 4952.
- [11] Rastogi S., Yao Y., Ronca S., Bos J., van der Eem J., Macromolecules 44 (2011) 5558.
- [12] Ronca S., Romano D., Forte G., Andablo-Reyes E., Rastogi S., Advances in Polymer Technology 31 (2012), 193.
- [13] Ronca S., Forte G., Tjaden H., Rastogi S. Ind. Eng. Chem. Res. 54 (2015) 7373–7381, DOI: 10.1021/acs.iecr.5b01469.
- [14] Gagieva S. Ch., Tuskaev V. A., Fedyanin I. V., Buzin M. I., Vasil'ev V. G., Nikiforova G. G., Afanas'ev E. S., Zubkevich S. V., Kurmaev D. A., Kolosov N. A., Mikhaylik E. S., Golubev E. K., Sizov A. I., Bulychev B. M. J. Organomet. Chem. 828 (2017) 89-95, <u>http://dx.doi.org/10.1016/j.jorganchem.2016.11.026</u>.
- [15] Mehta A., Tembe G., Parikh P. and Mehta G. Polym. Int. 63 (2014) 206–13, <u>https://doi.org/10.1002/pi.4484</u>.
- [16] Chuck C. J., Davidson M. G., Jones M. D., Kociok-Köhn G., Lunn M. D., and Wu S.
 Inorg. Chem. 45 (2006) 6595–6597, DOI: 10.1021/ic060969+.

- [17] Al-Qaisi F., Streng E., Tsarev A., Nieger M., Repo T. Eur. J. Inorg. Chem. 32 (2015) 5363-5367, https://doi.org/10.1002/ejic.201500760.
- [18] Mahrwald R., Ziemer B., Ram M. J. Pract. Chem. 338 (1996) 583-585, DOI: 10.1002/prac.199633801110.
- [19] Marsh R. E., Space group P1: an update. Acta Cryst. B61 (2005) 359, https://doi.org/10.1107/S0108768105009651.
- [20] Hekmatshoar R., Yavari I., Beheshtiha Y. S., and Heravi M. M. Monatshefte fur Chemie 132 (2001) 689-691.
- [21] Kissin Y.V., Nowlin T.E., Mink R.I., Brandolini A.J., Macromolecules 33 (2000) 4599.
- [22] Kissin Y.V., Mink R.I., Brandolini A. J., Nowlin T. E., J. Polym. Sci. Part A Polym. Chem. 47 (2009) 3271-3285.
- [23] Wunderlich B., Cormier C.M., J. Polym. Sci., Part A 2 Polym. Phys. 5 (1967) 987-988.
- [24] Acosta Y. K. R., Céspedes R. I. N., Velázquez M. G. N., Elizondo J. D., Enríquez-Medrano F., López L. A. V., Aguiñaga M. E. R., Caballero H. S. and de León R. D. J. Mex. Chem. Soc. 58 (2014) 119-125.
- [25] Gagieva S. Ch., Tuskaev V.A., Fedyanin I.V., Sizov A.I., Mikhaylik E.S., Golubev E.K., Bulychev B.M. Polyhedron 122 (2017) 179, https://doi.org/10.1016/j.poly.2016.11.007.
- [26] Tuskaev V. A., Gagieva S. Ch., Kurmaev D.A., Zubkevich S. V., Kolosov N. A., Golubev E. K., Nikiforova G. G., Khrustalev V. N., Bulychev B. M. J. Organomet. Chem. 867 (2018) 266-272, <u>https://doi.org/10.1016/j.jorganchem.2017.12.027.</u>
- [27] Michler G. H., Seydewitz V., Buschnakowski M., Myasnikowa L. P., Ivan'kova E.
 M., Marikhin V. A., Boiko Y. M., Goerlitz S. J. Appl. Polym. Sci. 118 (2010) 866– 875, https://doi.org/10.1002/app.32346.
- [28] Scheirs J., Bigger S.W., Delatycki O. J. Mater. Sci. 26 (1991) 3171, https://doi.org/10.1007/BF01124659.
- [29] Battye T. G. G., Kontogiannis L., Johnson O., Powell H. R., Leslie A. G. W., Acta Cryst. D67 (2011) 271-281.
- [30] Evans P. R. Acta Cryst. D62 (2006) 72-82.
- [31] Sheldrick G. M., Acta Cryst. C71 (2015) 3-8.

ACCEPTED MANUSCRIPT

Highlights

Novel titanium complexes bearing 1,2-diolate ligands were synthesized and fully characterized.

Complexes in the presence of $\{Et_2AlCl+Bu_2Mg\}$ produced high molecular weight polyethylene

The replacement of Et_2AlCl with $Et_3Al_2Cl_3$ leads to a significant increase in Mv (up to 7.7 10^6) and the crystallinity of UHMWPE samples.

Polymers are suitable for the solvent-free formation of high-strength (up 2.8 GPa) and highmodulus (up to 145 GPa) oriented film tapes.