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Research paper

Novel alkoxo-titanium(IV) complexes with fluorinated 2-hydroxymethylphenol derivatives as catalysts for the formation of ultra-high molecular weight polyethylene nascent reactor powders

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A B S T R A C T

A series of titanium (IV) complexes **3a–g** stabilized by fluorinated derivatives of 2-hydroxymethylphenol have been synthesized; their composition and structure have been confirmed by NMR, IR-spectroscopy and elemental analysis. The structures of compounds **3c**, **3f** and **3g** have been unambiguously established by X-ray diffraction study. The complexes in the presence of a binary cocatalysts {alkyl aluminum chloride + $MgBu_2$} catalyze ethylene polymerization to afford Ultra High Molecular Weight Polyethylene (UHMWPE). The effects of substituents in the ligands on the catalytic activity and properties of the obtained polymer – molecular weight, DSC melting behavior, and morphology of nascent reactor powders have been investigated. UHMWPE samples were processed by a solid-state uniaxial deformation into high-strength (up to 2.65 GPa) and high-modulus (over 140 GPa) oriented film tapes, which indirectly indicates a low degree of entanglements between the macromolecular chains.

1. Introduction

Ultra-high molecular weight polyethylene (UHMWPE) is a linear (non-branching) semi-crystalline polymer which can be described as a two phase composite consisting of crystalline and amorphous phases [1]. The ultra-high molecular weight of UHMWPE (1–6 10^6 Da) results in excellent mechanical properties such as high strength, resistance to aggressive media, high wear resistance, low friction coefficient (self-lubrication behavior), high toughness, very high resistance to low temperatures. As a result, UHMWPE has found successful applications in many industrial sectors [2]. On the other hand, the ultra-high molecular weight of this polymer determines its high melt viscosity and lack of fluidity which greatly hinders its processing by standard polymer processing methods, such as injection molding, ram extrusion, etc. One of the most promising approaches to the processing of UHMWPE is the production of high-modulus and high-strength tapes and films. At present, gel spinning technique with further stretching is used for this purpose. However, this technology involves the use of highly diluted polymer solutions (3–5%), whereby necessity to regenerate large volumes of high boiling solvents significantly increases the cost of the final product. An alternative is a solvent-free solid-phase monolithization of UHMWPE reactor powder with subsequent orientation extraction. This methodology, introduced by Smith et al., [3–4] was further considerably improved by Rastogi et al. [5–6].

The microstructure of UHMWPE can be considered as a matrix of heterogeneously distributed entanglements, where the disentangled regions reside in the crystalline domains and the entangled regions in the amorphous domains [7]. By reducing the entanglement density the UHMWPE nascent reactor powders can be processed in solid-state below its melting temperature, leading to the high-strength and high-modulus oriented materials. The UHMWPE reactor powders of the required quality – i.e. with reduced entanglement density of the

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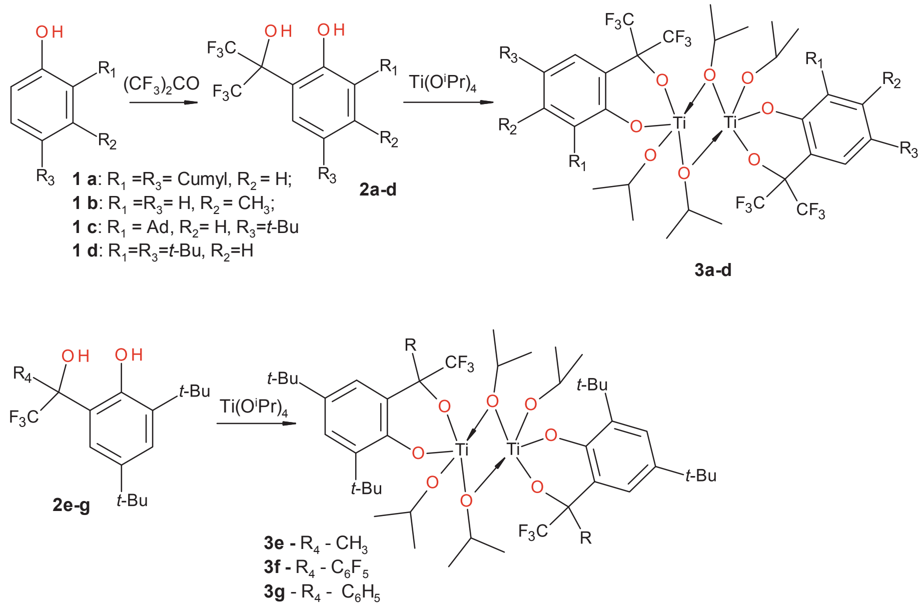

Scheme 1. Synthetic procedures for complexes **3a–g**.

molecular chains, can be obtained when homogeneous catalysts are used in diluted systems and the temperature of polymerization is kept low. Subject to these conditions, the polymer chains will begin to crystallize during the polymerization, that facilitates the formation of polymer with highly disentangled chains [5–8] (Scheme 1).

Previously, we proposed a new group of titanium complexes stabilized by 2-hydroxymethylphenol derivatives capable to catalyze the production of UHMWPE suitable for solvent-free processing into high-strength and high-modulus films and film tapes [9–12] (examples of such structures are shown in Fig. 1).

In the present work, ligands with perfluorinated substituents were used to obtain titanium complexes. Replacement of hydrogen with fluorine leads to an increase in the lipophilicity of ligand molecule and in the acidity of hydroxyl groups, and probably in Lewis acidity the central metal atom. In this case, the geometric parameters of the molecule change slightly (the van der Waals radii of the CH_3 and CF_3 groups are 1.29 A and 1.35 A, respectively). The high chemical stability of C–F bonds should be noted, which is unattainable for other halogens [13]. It is known that relatively more basic alkoxide ligands (compared to phenoxides) often act as bridging ligands in the process of complexation, which leads to the formation of highly agglomerated structures. Increasing the acidity of alcohol hydroxyl (as well as increasing the steric bulk of alkyl substituents) partially suppresses this process [14–16]. The interest in fluorinated precatalysts for olefin polymerization was also stimulated by the works of Fujita [17–20]. They showed that group 4 metal complexes stabilized by partially or fully fluorinated phenoxyimine ligands significantly outperform non-fluorinated analogs in activity and stereo-selectivity in the polymerization of propylene and higher α-olefins and in the molecular weights of the obtained polymers.

Therefore, the main purpose of present work is the synthesis of new titanium complexes stabilized by 2-hydroxymethylphenol derivatives and studying the impact of both fluorinated fragments and bulky substituent in position 6 of the ligand on the catalytic activity in ethylene polymerization and on the properties of the resulting polymers including their ability to be processed by a solid-state solvent-free method below melting temperature.

2. Experimental

2.1. Catalysts and synthetic methods

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 Clean™ Gas Filters.

NMR spectra were recorded on Bruker Avance-400 instrument. Deuterated solvents ($CDCl_3$, THF-d8) were degassed by freeze-pump-thaw vacuum cycles and stored over 3 Å molecular sieves. Chemical shifts are reported in ppm vs. $SiMe_4$ 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. Ligands **2b**, **2d** and **2c** were synthesized as described [21,22], its ^1H and ^{13}C NMR spectra were found to match the published data. Ligands **2d–f** were obtained by the interaction of 1-(3,5-di-*tert*-butyl-2-hydroxy-phenyl)-2,2,2-trifluoroethanone with the corresponding organometallic compounds [23].

2.1.1. 2-(1,1,1,3,3,3-Hexafluoro-2-hydroxypropan-2-yl)-4,6-bis(1-methyl-1-phenyl–ethyl)-phenol (2a)

To a pre-dried ampule, 6.61 g (0.02 mol) of 2,4-bis(1-methyl-1-phenyl-ethyl)-phenol and 25 mL of CCl_4 were introduced under argon flow. After the solution was degassed it was cooled down to −35 °C and 5.0 g (~0.03 M) of 1,1,1,3,3,3-hexafluoroacetone was added over a period of 20 min. The ampule was sealed and incubated for 24 h at r.t. Upon completion, the ampule was frozen, unsealed and the remaining gas was removed by argon and trapped in a washing bottle. The organic phase was concentrated under reduced pressure. The crude product was purified by recrystallization from *n*-hexane to give the title compound as colorless crystals. Yield: 6.16 g (62%). Anal. Calc. for $C_{27}H_{26}F_6O_2$

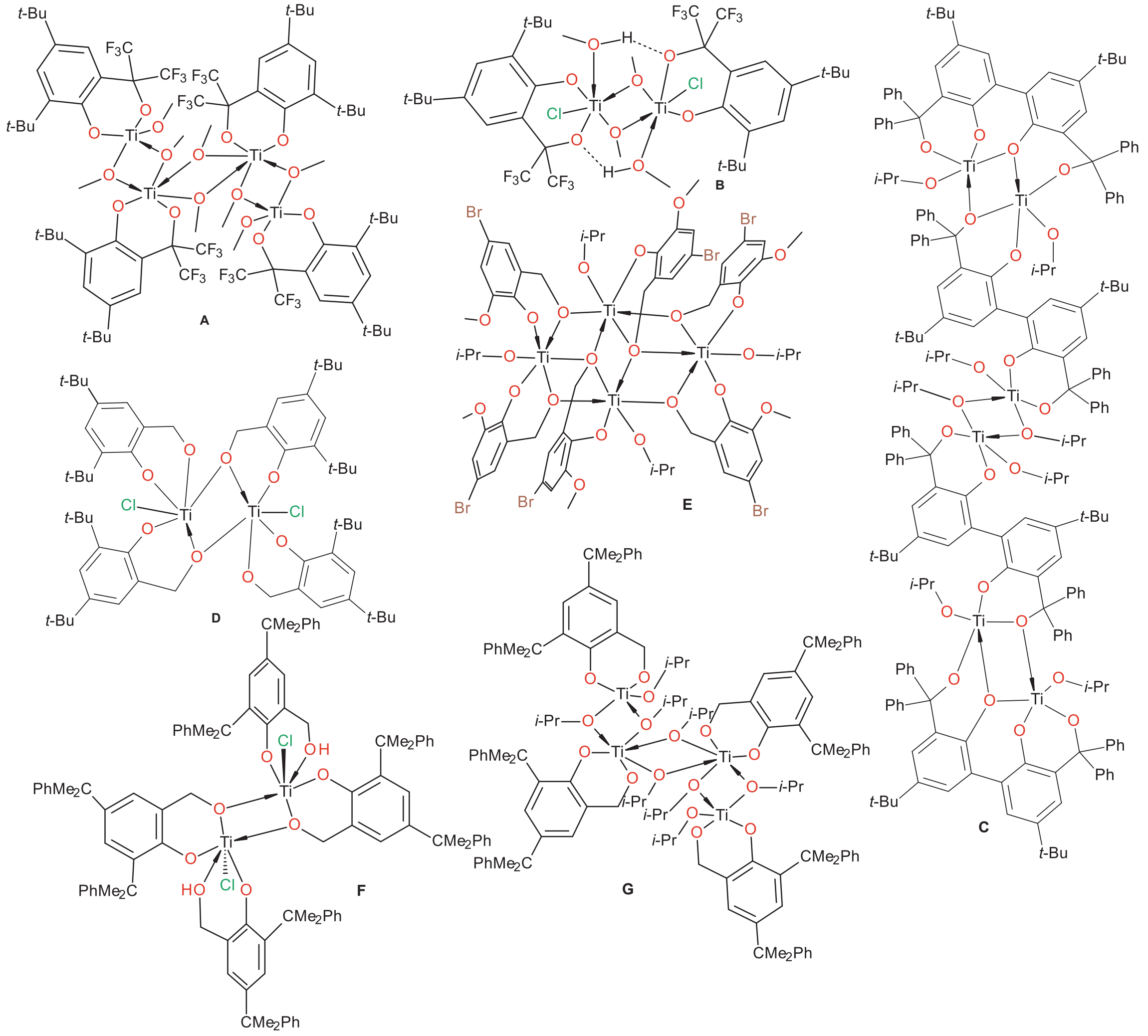

Fig. 1. Examples of Titanium(IV) complexes with 2-hydroxymethylphenole derivatives suitable for disentangled UHMWPE production.

(496.48): C, 65.32; H, 5.28; F, 22.96. Found (%): C, 65.30; H, 5.26; F, 22.94. ^{1}H NMR ($CDC1_3$, 400 MHz): $\delta = 1.62$ (s, 6H, CH_3), 1.75 (s, 6H, CH_3), 5.17 (s, 1H, OH), 7.29–7.44 (m, 12H, Ar). ^{19}F NMR (376 MHz, $CDCl_3$): δ = −75.34. ^{13}C NMR (101 MHz, $CDCl_3$): $\delta = 150.45$, 149.88, 146.54, 143.89, 136.98, 129.90, 129.16, 128.14, 128.05, 127.05, 126.65, 125.93, 125.89, 125.72, 124.28, 121.41, 116.36, 42.85, 42.21, 31.07, 30.82, 29.61. ESI-MS: *m/z* (%): 496 [M$^+$, 82.37], 481 [100], 403 [21.15], 377 [3.38].

*2.1.2. 2-(1,1,1,3,3,3-Hexafluoro-2-hydroxypropan-2-yl)-5-methylphenol (**2b**)*

This ligand was prepared as described above for **2a**, starting from a suspension of sodium m-cresolate (2.6 g, 0.02 mol) in tetrachloroethane (40 mL) and 1,1,1,3,3,3-hexafluoroacetone (5.0 g; 0.03 M). Reaction was conducted for 48 h at r.t and upon removing the unreacted gas, the organic phase was washed by diluted HCl, water and brine. The organic phase was concentrated under reduced pressure and the crude product was purified by recrystallization from *n*-hexane to give the title compound as colorless crystals. Yield: 4.49 g (82%). Calculated (%) for $C_{10}H_8F_6O_2$ (274): C, 43.81; H, 2.94; F, 41.58. Found (%): C, 43.78; H, 2.92; F, 41.56. ^{1}H NMR (400 MHz, $CDC1_3$): $\delta = 2.32$ (s, 3H, CH_3), 6.73 (s, 1H, Ar), 6.82 (d, $J = 7.7$ Hz, 1H, Ar), 7.32 (d, $J = 8.2$ Hz, 1H, Ar), 8.64 (s, 1H, OH). ^{19}F NMR (376 MHz, d-THF): δ = −75.73. ^{13}C NMR (101 MHz, d-THF): $\delta = 154.59$, 139.69, 138.58, 126.16, 126.13, 126.11, 126.09, 125.64, 125.16, 122.77, 119.90, 119.62, 119.16, 117.06, 116.27, 115.00, 109.98, 65.00, 64.78, 64.56, 64.34, 64.12, 61.01, 22.95, 22.84, 22.77, 22.64, 22.56, 22.44, 22.24, 22.04, 21.94, 18.09.

*2.1.3. 2-(1,1,1,3,3,3-Hexafluoro-2-hydroxypropan-2-yl)-4-tert-butyl-6-adamantylphenol (**2c**)*

The title compound was prepared as described above for **2a**, starting from a solution of 2-adamantyl-4-*tert*-butylphenol [24] (5.69 g, 0.02 mol) in tetrachloromethane (40 mL) and 1,1,1,3,3,3-hexafluoroacetone (5.0 g; 0.03 M). Reaction was conducted for 48 h at r.t Yield: 6.22 g (69%). Calculated (%) for $C_{23}H_{28}F_6O_2$ (438): C, 61.33; H, 6.27; F, 25.31. Found (%): C, 61.28; H, 6.23; F, 25.28. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.29$ (s, 9H, CH_3), 1.79 (s, 5H, CH), 2.14 (s, 10H, CH_2), 5.40 (s, 1H, OH), 7.80 (s, 1H, Ar), 7.36 (s, 1H, Ar). ^{19}F NMR (376 MHz, $CDCl_3$): δ = −75.13. ^{13}C NMR (101 MHz, $CDCl_3$): $\delta = 153.69$, 141.95, 137.57, 126.35, 124.17, 122.13, 121.36, 111.61, 80.80, 40.67, 40.46, 37.14, 31.27, 29.32, 29.10.

*2.1.4. 2-(1,1,1,3,3,3-Hexafluoro-2-hydroxypropan-2-yl)-4,6-di-tert-butylphenol (**2d**)*

The title compound was prepared as described above for **2a**, starting from a solution of 2,4-di-*tert*-butylphenol. Yield: 5.22 g (75%). Calculated (%) for $C_{17}H_{22}F_6O_2$ (372): C, 54.84; H, 5.96; F, 30.61. Found (%): C, 54.81; H, 5.93; F, 30.57. ^{1}H NMR (toluene-d_8), δ: 1.28 (s, 9H); 1.53 (s, 9H); 3.99 (br.s, 1H); 7.51 (s, 1H); 7.58 (s, 1H); 8.23 (br.s, 1H). ^{19}F NMR (376 MHz, (benzene-d_6): δ = −75.11; ^{13}C NMR (101 MHz, $CDCl_3$): $\delta = 154.55$, 141.48, 138.19, 137.32, 128.94, 128.70, 128.47, 128.03, 127.80, 127.56, 126.48, 125.20, 124.96, 124.72, 124.57, 122.25, 121.69, 111.21, 81.64, 81.34, 81.04, 35.46, 34.26, 31.24, 29.71, 20.82, 20.63, 20.44, 20.25, 20.05, 19.86, 19.67.

2.1.5. *2-(1,1,1-Trifluoro-2-hydroxy-propan-2-yl)-4,6-di-tert-butyl-6-phenol (**2e**)*

To a solution of MeMgI (10 mmol) in Et_2O, prepared from magnesium (0.29 g, 12 mmol) and MeI (0.62 mL, 10 mmol) was added dropwise an ethereal solution of 1-(2,4-di-*tert*-buthylphenyl)-2,2,2-trifluoromethylethanone-1 (1.08 g, 3.6 mmol) at 0 °C. The reaction mixture allowed to slowly warm to room temperature, stirred overnight, quenched with HCl (1 M, 5 mL) and then and the product was extracted by diethyl ether. The combined organic phase was dried over Na_2SO_4, and the solvent was removed under reduced pressure. Recrystallization of the crude product from hexane gave 0.78 g (69%) of a colorless solid. Calculated (%) for $C_{17}H_{25}F_3O_2$ (318.38): C, 64.13; H, 7.91; F, 17.90. Found: C, 64.10; H, 7.88; F, 17.84. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.28 (s, 9H), 1.42 (s, 9H), 1.90 (s, 3H), 3.29 (s, 1H) 7.04 (s, 1H), 7.44 (s, 1H), 8.66 (s, 1H). ^{19}F NMR ($CDCl_3$, 25 °C): δ = −81.24 (s). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 153.67, 140.82, 137.57, 126.95, 124.47, 122.46, 119.11, 35.22, 34.09, 31.53, 29.92, 24.11.

2.1.6. *2-[2,2,2-Trifluoro-1-hydroxy-1-pentafluorophenyl-ethyl]-4,6-di-tert-butylphenol (**2f**)*

A solution of 1.0 mL (8.1 mmol) of C_6F_5Br in 20 mL of Et_2O was cooled to 78 °C, and 3.24 mL of nBuLi (2.5 M solution in hexane, 8.1 mmol) was added dropwise. The reaction mixture was stirred at 78 °C for 30 min, and then a solution of 1-(2,4-di-*tert*-buthylphenyl)-2,2,2-trifluoromethylethanone-1 (1.1 g, 3.64 mmol) in diethyl ether was added dropwise. The resultant solution was stirred overnight at room temperature, cooled to 0 °C, and then quenched with an aqueous NH4Cl solution (50 mL) and extracted with ether. The combined organic phase was dried over Na_2SO_4, and the solvent was removed under reduced pressure. Recrystallization of the crude product from hexane gave 2.99 g (82%) of a colorless solid; mp 149–150 °C. Calculated (%) for $C_{22}H_{22}F_8O_2$ (470.0): C, 56.17; H, 4.71; F, 32.31. Found (%): C, 56.12; H, 4.69; F, 32.28. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.19 (s, 9H, CH_3), 1.25 (s, 9H, CH_3), 4.39 (s, 1H, OH), 6.68 (s, 1H, Ar), 7.12 (m, 1H, Ar). ^{19}F NMR (376 MHz, $CDCl_3$): δ = − 76.36, −137.53, −151.10, −160.88. ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.45, 142.04, 137.68, 125.44, 121.73, 80.14, 77.32, 76.68, 35.03, 34.44, 31.42, 29.83.

2.1.7. *2-[2,2,2-Trifluoro-1-hydroxy-1-phenyl–ethyl]-4,6-di-tert-butylphenol (**2g**)*

To a stirred solution of PhMgBr (25 mmol) in ether (50 mL) was added dropwise a solution of 1-(2,4-di-*tert*-buthylphenyl)-2,2,2-trifluoromethylethanone-1 (2.17 g, 7.2 mmol) in ether (25 mL) at 0 °C in 1 h. After completion of the addition, the mixture was allowed to stand at room temperature overnight. The resulting mixture was poured into an aqueous NH_4Cl solution and extracted with ether. The organic layer was removed, dried (Na_2SO_4) and evaporated under reduced pressure. Recrystallization of the crude product from hexane gave 2.21 g (81%) of a colorless solid. Calculated (%) for $C_{22}H_{27}F_3O_2$ (380.44): C, 69.46; H, 7.15; F, 14.98. Found (%): C, 69.41; H, 7.11; F, 14.67. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.29 (s, 9H, CH_3), 1.40 (s, 9H, CH_3), 3.52 (s, 1H, OH), 7.12 (t, 1H, Ar), 7.39 (m, 2H, Ar), 7.42 (s, 1H, Ar), 7.52 (m, 2H, Ar), 7.60 (s, 1H, Ar). ^{19}F NMR (376 MHz, $CDCl_3$): δ = −75.93. ^{13}C NMR (101 MHz, $CDCl_3$) δ = 152.87, 140.66, 137.66, 137.53, 129.23, 128.32, 127.42, 127.40, 126.35, 125.11, 123.50, 123.19, 123.16, 123.13, 121.77, 82.04, 81.75, 81.46, 35.24, 34.32, 31.50, 29.69.

2.1.8. *Di{2-[α,α-bis(trifluoromethyl)methanolato]-4,6-di-(1-methyl-1-phenyl-ethyl)phenolato}- di(μ-isopropoxy)di-(isopropoxo) dititanium (**3a**)*

Compound **2a** (0.496 g, 1.0 mmol) and toluene (20 mL) were placed into a Schlenk tube equipped with a magnetic stirrer under argon atmosphere, followed by the addition of $Ti(OiPr)_4$ (0.296 mL, 1.0 mmol) at 40 °C and the reaction mixture was kept at 40 °C for 12 h. The red crystals that formed were filtered off, washed with toluene, and dried *in vacuo*. Yield 0.82 g (62.0%). Calculated (%) for $C_{66}H_{76}F_{12}O_8Ti_2$ (1321.0): C, 60.01; H, 5.80; F, 17.26; Ti, 7.25. Found (%): C, 59.99; H, 5.73; F, 17.20; Ti, 7.21. ^1H NMR ($CDC1_3$): δ = 1.19 (d, 24H, CH_3), 1.58 (s, 12H, CH_3), 1.73 (s, 12H, CH_3), 4.14 (s, 4H, CH), 7.11–7.47 (m, 24H, Ar). ^{19}F NMR ($CDC1_3$): δ = −75.34. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 157.49, 150.72, 141.45, 135.03, 129.37, 129.06, 128.08, 127.91, 127.32, 126.70, 126.00, 125.88, 125.77, 125.67, 125.56, 125.28, 124.94, 124.38, 122.05, 119.26, 67.22, 42.94, 42.81, 42.68, 42.32, 31.09, 30.79, 29.65, 29.58, 24.72. FT-IR (KBr): 600, 440 cm^{-1} ν(Ti-O).

2.1.9. *Di{2-[α,α-bis(trifluoromethyl)methanolato]-5-methylphenolato}di(μ-isopropoxo)di-(isopropoxy) dititanium (**3b**)*

This complex was prepared as described above for **3a**, starting from a solution of ligand **2b** (0. 274 g, 1.0 mmol) in toluene (10 mL) and Ti $(OPr^i)_4$ (0.29 mL, 1.0 mmol). Reaction was conducted for 48 h at 50 °C and workup afforded **3b** as a red–orange powder. Yield 0.72 g (82.2%). Calculated (%) for $C_{32}H_{40}F_{12}O_8Ti_2$ (876.4): C, 43.86; H, 4.60; F, 26.01; Ti, 10.92. Found (%): C, 43.75; H, 4.57; F, 25.96; Ti, 10.87. ^1H NMR (THF- *d8*): δ = 1.08 (s, 12H, CH_3), 1.12 (s, 12H, CH_3), 2.26 (s, 6H, CH_3), 3.70 (m, 4H, CH), 6.70 (m, 4H, Ar), 7.31 (d, 2H, Ar). ^{19}F NMR ($CDC1_3$): δ = −76.23. ^{13}C NMR (101 MHz, d-THF): δ = 154.59, 139.69, 138.58, 126.16, 126.13, 126.11, 126.09, 125.64, 125.16, 122.77, 119.90, 119.62, 119.16, 117.06, 116.27, 115.00, 109.98, 77.68, 61.01, 18.09. δ FT-IR (KBr): 601, 533 cm^{-1} ν(Ti-O).

2.1.10. *Di{2-[α,α-bis(trifluoromethyl)methanolato]-4-tert-buthyl-6-(1-adamantyl)phenolato}di(μ-isopropoxy)di-(isopropoxo) dititanium (**3c**)*

This complex was prepared as described above for **3a**, starting from a solution of ligand **2c** (0.438 g, 1.0 mmol) in toluene (15 mL) and Ti $(OPr^i)_4$ (0.29 mL, 1.0 mmol). Reaction was conducted for 24 h at 40 °C and workup afforded **3c** as an orange powder, yield 0.97 g (78.9%). Calculated (%) for $C_{58}H_{80}F_{12}O_8Ti_2$ (1228.96): C, 56.68; H, 6.56; F, 18.55; Ti, 7.79. Found (%): C, 56.61; H, 6.50; F, 18.51; Ti, 7.74. ^1H NMR (400 MHz, $CDC1_3$): δ = 1.21–1.31 (m, 54H), 2.12–2.25 (s, 18H), 4.15 (s, 4H, CH), 7.38 (s, 2H, Ar), 7.47 (s, 2H, Ar). ^{19}F NMR ($CDC1_3$): δ = -74.94. ^{13}C NMR (101 MHz, $CDCl_3$): δ = ^{13}C NMR (101 MHz, $CDCl_3$): δ = 155.92, 147.35, 138.04, 132.90, 125.65, 123.78, 122.46, 121.74, 121.36, 34.61, 29.58, 24.82, 18.05. FT-IR (KBr): 600, 473 cm^{-1} ν(Ti-O).

2.1.11. *Di{2-[α,α-bis(trifluoromethyl)methanolato]-4,6-di-tert-buthylphenolato}di(μ-isopropoxy)di-(isopropoxo) dititanium (**3d**)*

This complex was prepared as described above for **3a**, starting from a solution of ligand **2d** (0.438 g, 1.0 mmol) in toluene (20 mL) and Ti $(OPr^i)_4$ (0.29 mL, 1.0 mmol). Reaction was conducted for 24 h at 40 °C and workup afforded **3d** as a red powder. The crystals that formed were filtered off, washed with hexane, and dried *in vacuo*. Yield 0.83 g (77.3%). Calculated (%) for $C_{46}H_{72}F_{12}O_8Ti_2$ (1074.5): C, 51.50; H, 6.39; F, 21.25. Found (%): C, 51.45; H, 6.31; F, 21.18. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.32 (s, 18H, CH_3), 1.45 (s, 18H, CH_3), 1.47 (s, 24H, $CH(C\underline{H}_3)_2)$), 4.84 (m, 4H, $C\underline{H}(CH_3)_2$), 7.43 (s, 2H Ar-H), 7.59 (s, 2H Ar-H). ^{19}F NMR (C_6D_6): δ = −80.28. ^{13}C NMR (101 MHz, C_6D_6) δ 158.47, 143.19, 136.29, 128.04, 125.43, 122.90, 119.38, 35.70, 34.45, 34.38, 31.45, 30.65, 29.73, 24.48, 1.17.

2.1.12. *Di{2-[α-trifluoromethyl-α-methyl-methanolato]-4,6-di-tert-buthyl-phenolato}di(μ-isopropoxy) di-(isopropoxo) dititanium (**3e**)*

This complex was prepared as described above for **3a**, starting from a solution of ligand **2e** (0.438 g, 1.0 mmol) in toluene (10 mL) and Ti $(OPr^i)_4$ (0.29 mL, 1.0 mmol). Reaction was conducted for 24 h at 40 °C and workup afforded **3e** as a dark red powder. The crystals that formed were filtered off, washed with hexane, and dried *in vacuo*. Yield 0.85 g (91.3%). Calculated (%) for $C_{46}H_{74}F_6O_8Ti_2$ (964.8): C, 57.26; H, 7.73;

F, 11.81; Ti, 9.92. Found (%): C, 57.19; H, 7.69; F, 11.78; Ti, 9.83. ^{1}H NMR (400 MHz, $CDC1_3$): δ = 1.47–1.53 (m, 42H, CH_3), 1.69 (s, 18H, CH_3), 1.74 (s, 6H, CH_3), 3.62 (m, 4H, CH), 7.13 (d, 4.2 Hz, 2H, Ar), 7.34 (d, 4.2 Hz, 2H, Ar). ^{19}F NMR ($CDC1_3$): δ = −80.33. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 134.88, 125.70, 123.87, 123.33, 35.46, 35.33, 34.30, 34.21, 31.55, 30.74, 30.50, 30.45. FT-IR (KBr): 611, 594 cm^{-1} ν(Ti-O).

2.1.13. *Di{2-[α-trifluoromethyl-α-pentafluorophenyl-methanolato]-4,6-di-tert-buthyl-phenolato}di(μ-isopropoxo)di-(isopropoxy) dititanium (3f)*

This complex was prepared as described above for **3a**, starting from a solution of ligand **2f** (0. 470 g, 1.0 mmol) in toluene (10 mL) and Ti $(OPr^i)_4$ (0.29 mL, 1.0 mmol). Reaction was conducted for 48 h at 40 °C and workup afforded **3f** as a red powder. The crystals that formed were filtered off, washed with hexane, and dried *in vacuo*. Yield 0.79 g (62.3%). Calculated (%) for $C_{56}H_{68}F_{16}O_8Ti_2$ (1268.8): C, 53.01; H, 5.40; F, 23.96; Ti, 7.54. Found (%): C, 52.96; H, 5.32; F, 523.88; Ti, 7.51. ^{1}H NMR (400 MHz, $CDC1_3$): δ = 1.19 (s, 12, CH_3), 1.21 (s, 18, CH_3), 1.22 (s, 18, CH_3), 1.24 (s, 12H, CH_3), 4.13 (s, 4H, CH), 7.28 (d, J = 2.5 Hz, 2H, Ar), 7.42 (d, J = 2.7 Hz, 2H, Ar). ^{19}F NMR ($CDC1_3$): δ = −76.36, −137.54, −151.54, −161.26. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 141.81, 141.58, 135.15, 134.95, 129.01, 128.20, 126.70, 125.00, 124.71, 124.61, 124.42, 123.78, 123.51, 123.13, 122.27, 83.51, 35.41, 35.26, 35.17, 34.32, 34.18, 34.13, 31.45, 31.36, 31.33, 30.60, 30.55, 30.11, 30.08, 29.99, 29.89, 29.70, 25.06, 24.09, 23.94. δ 155.92, 147.35, 138.04, 132.90, 125.65, 123.78, 122.46, 121.74, 121.36, 34.61, 29.58, 24.82, 18.05. FT-IR (KBr): 605, 437 cm^{-1} ν(Ti-O).

2.1.14. *Di{2-[α-trifluoromethyl-α-phenyl-methanolato]-4,6-di-tert-buthyl-phenolato}di(μ-isopropoxy)di-(isopropoxo) dititanium (3g)*

This complex was prepared as described above for **3a**, starting from a solution of ligand **2 g** (0.380 g, 1.0 mmol) in toluene (20 mL) and Ti $(OPr^i)_4$ (0.29 mL, 1.0 mmol). Reaction was conducted for 24 h at 40 °C and workup afforded **3g** as a dark red powder. The crystals that formed were filtered off, washed with toluene, and dried *in vacuo*. Yield 0.93 g (85.4%). Calculated (%) for $C_{56}H_{78}F_6O_8Ti_2$ (1088.9): C, 61.77; H, 7.22; F, 10.47; Ti, 8.79. Found (%): C, 61.73; H, 7.15; F, 10.38; Ti, 8.72. ^{1}H NMR (400 MHz, d-THF): δ = 1.14 (d, 18H, CH_3), 1.26 (s, 18H, CH_3), 1.46 (s, 12H, CH_3), 4.54 (s, 4H, CH), 7.26 (m, 10H, Ar), 7.49 (d, 4H, Ar). ^{19}F NMR (d-THF): δ = −74.44. ^{13}C NMR (101 MHz, d-THF): δ = 158.24, 143.58, 139.00, 135.07, 127.54, 127.32, 127.27, 126.46, 124.67, 123.26, 123.23, 122.68, 87.06, 86.78, 77.12, 75.85, 67.07, 66.94, 66.85, 66.72, 66.63, 66.50, 66.28, 66.06, 62.77, 35.02, 33.90, 31.05, 29.74, 25.99, 25.42, 25.03, 24.88, 24.75, 24.68, 24.55, 24.48, 24.35, 24.15, 23.95. FT-IR (KBr): 623, 461 cm^{-1} ν(Ti-O).

2.2. *X-ray crystal structure determination*

The single-crystal X-ray diffraction data for **3c**, **3f** and **3g** 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. In total, 480–720 frames were collected with an oscillation range of 1.0° in the φ scanning mode using two different orientations for each crystal. The semiempirical correction for absorption was applied using the *Scala* program [25]. The data were indexed and integrated using the utility ***iMOSFLM*** from the CCP4 software suite [26]. For details, see Table S1. 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. The independent part of the unit cell of **3f** contained a toluene solvate molecule, which was disordered over two positions around the inversion center. The hydrogen atoms 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 [27].

Crystallographic data for **3c**, **3f**·$CH_3C_6H_5$ and **3g** have been deposited with the Cambridge Crystallographic Data Center, CCDC 1914946 (**3c**), CCDC 1902082 (**3f**), and CCDC 1914947 (**3g**). The supplementary crystallographic data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

2.3. *Polymerization of ethylene*

The ethylene polymerization was performed in a 450-mL reactor (Parr Instrument Co.) equipped with a magnetic stirrer and inlets for loading components of catalytic systems and ethylene at a total ethylene and toluene vapors pressure of 1.7 atm. Toluene (100 mL) and the necessary amount of a co-catalyst (Et_2AlCl/Bu_2Mg or $Et_3Al_2Cl_3/Bu_2Mg$) 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 by addition of 20 mL of isopropanol to the reactor. The polymer was filtered off placed in a beaker and stirred with 10% HCl/isopropanol mixture for 30 min at elevated temperature. Then the polymer was filtered off and washed several times with water/isopropanol mixture and dried under vacuum at 70 °C until a constant weight was achieved.

2.4. *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); [η] = 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 from the synthesized polymers were evaluated using the oriented tapes obtained by a solid state processing of UHMWPE nascent reactor powders. The monolithic tapes uniform over the entire length (100 μm 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.

3. Results and discussion

3.1. *Ligands and coordination compounds synthesis and structure*

Ligands **2a–d** were synthesized by uncatalyzed C-alkylation of phenols **1a–d** with hexafluoroacetone according to the general procedure suggested in [28]. Ligands **2e–g** were obtained by the interaction of 1-(3,5-di-*tert*-butyl-2-hydroxy-phenyl)-2,2,2-trifluoroethanone with the corresponding organometallic compounds [23]. The synthesis and crystal structure of the complex **3d** has been previously described in [29].

Reactions of the diprotio ligands **2a-g** with $Ti(OPr^i)_4$ proceeded in toluene solution at 40–50 °C, via isopropanol elimination, to afford the corresponding alkoxo-titanium(IV) complexes **3a–g**. All compounds were isolated in 62–93% yields as red, air-sensitive powders, which are almost insoluble in pentane, moderately soluble in aromatic hydrocarbons, and soluble in dichloromethane and THF. The compositions and structures of complexes **3a–g** were confirmed by IR, ^{1}H and ^{13}C

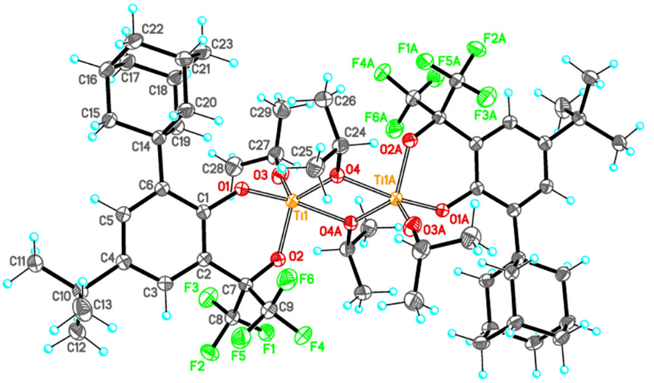

Fig. 2. General view of molecule **3c** in crystal in thermal ellipsoid representation (p = 50%).

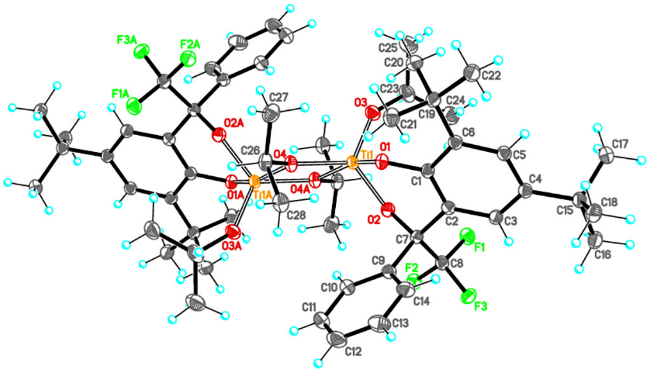

Fig. 4. General view of molecule **3g** in crystal in thermal ellipsoid representation (p = 50%).

NMR spectroscopies as well as by elemental analysis. The integration of the NMR signals confirmed the presence of two isopropoxy groups per ligand unit in the reaction product. Isopropanol, liberated during the interaction of the ligand and $Ti(OPr^i)_4$ was not coordinated with titanium, as it takes place for complexes of the composition $LTiCl_2{*}2^iPrOH$ [29].

However, these data do not preclude aggregation of monomeric units in order to increase coordination number.

The structures of the products **3c**, **3f** and **3g** were unambiguously established by X-ray diffraction study and are shown in Figs. 2–4 along with the atomic numbering scheme. Experimental data for the X-ray diffraction studies of compounds and selected bond lengths and angles are given in Tables S1 and S2. Crystals suitable for X-ray diffraction studies were obtained from concentrated solution of complexes in toluene.

All complexes have dimeric structure consisting of two five-coordinated mononuclear fragments shared the central four-membered $Ti–(\mu\text{-}OPr^i)_2–Ti$ cycle, and, in the crystal, occupy a special position on the inversion center, i.e., the intrinsic symmetry of the complexes is C_i ($\bar{1}$) and their mononuclear fragments are equivalent. The μ-isopropoxo ligands are asymmetrically bridging [1.8983(11) and 2.1276(11) Å (**3c**), 1.9378(17) and 2.0845(18) Å (**3f**), 1.9370(9) and 2.0945(9) Å (**3g**), Table S2] between the titanium atoms, so the four-membered cycles represent a rhombus with the non-bonding Ti⋯Ti separation. The coordination geometry around the titanium atoms can be described as a distorted trigonal-bipyramidal, with the aryloxy and μ-isopropoxy ligands being in the axial positions. Hence, each bridging μ-isopropoxy group is apical with respect to one titanium atom and equatorial with respect to the other titanium atom. The ancillary ligands are bidentate and form the six-membered chelate rings to the metal atoms. The chelate rings are non-planar and adopt a *boat* conformation, with the O1 oxygen and C7 carbon atoms deviating by 0.195(2) and 0.151(2) Å (**3c**), 0.232(2) and 0.343(3) Å (**3f**), 0.438(1) and 0.510(2) Å (**3g**), respectively, from the mean plane passed through the other atoms of the ring. Interestingly, the Ti1–O1 and Ti1–O2 distances are very close to each other (Table S2), regardless the different types of the oxygen atoms – axial aryloxy-O1 and equatorial alkoxy-O2. As expected, the Ti1–O3 distance of the terminal isopropoxy ligand is significantly shorter than those of the both bridging isopropoxy and bidentate chelating ligands.

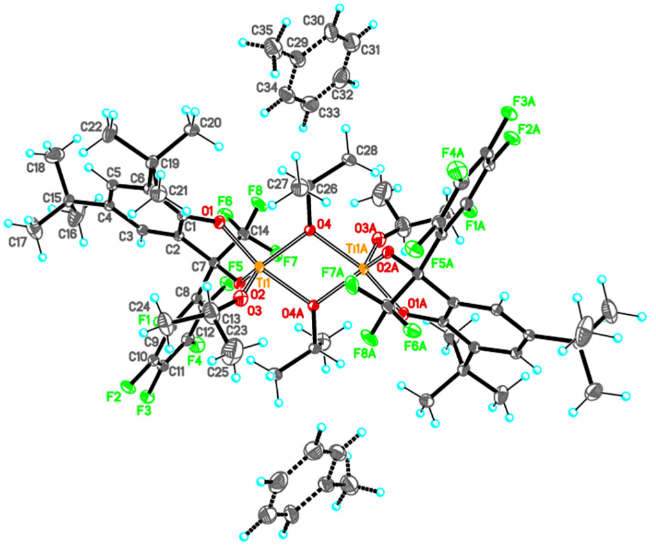

Fig. 3. General view of molecule $\mathbf{3f}{\cdot}CH_3C_6H_5$ in crystal in thermal ellipsoid representation (p = 50%).

Crystal packing of **3c**, **3f** and **3g** is stacking along the crystallographic ***b***, ***c*** and ***c*** axis, respectively (Figs. S41–43). The molecules of **3c** and **3g** are arranged at van-der-Waals distances, whereas the molecules of **3f** are linked within the stacks by weak non-valent F1⋯F2 ($1 - x$, $1 - y$, $1 - z$) [2.839(3) Å] interactions.

It is known that titanium alkoxides have a high tendency to increase their coordination numbers. In the absence of an external Lewis base the coordination number is increased by aggregation to larger units via alkoxo bridges. It is known that the degree of association depends on the steric bulk of the alkoxo ligands, for example, the titanium atoms in the tetramer $[Ti(OR)_4]_4$ (R = Me, Et) reach their optimal coordination number of 6 by formation of two μ3-OEt and four μ2-OEt ligands [30], while bulkier $Ti(OCH_2{}^tBu)_4$ exists in the dimeric form with five-coordinate titanium [31]. It is interesting, that in our case, even a ligand **2b** that does not contain bulky substituents in the *ortho*-position to the phenolic hydroxyl, also forms centrosymmetric dimer. However, the use of 2-hydroxyphenole derivatives without substituents on benzylic carbon atom, results in more complicated coordination compounds (for example, complexes **D**, **E**, **F** and **G** (Fig. 1); their crystal structures are described in [10,12]).

3.2. Catalytic properties of Ti(IV) complexes

Catalytic properties of compounds **3a–g** in ethylene polymerization are summarized in Table 1. To activate pre-catalysts, a binary activator $\{3Et_2AlCl + Bu_2Mg\}$, proposed by Kissin et al. [32–33] or $\{3Et_3Al_2Cl_3 + Bu_2Mg\}$, were used.

The maximum catalytic activity in this series − 2660 kg PE mol $(Ti)^{-1}\,h^{-1}\,atm^{-1}$, were demonstrated by complexes **3c** and **3d**, activated by the binary cocatalyst $\{1.5\ Et_3Al_2Cl_3 + MgBu_2\}$. In most cases (for complexes **3a**, **3c**, **3d** and **3e**) the use of $Et_3Al_2Cl_3$ allows to achieve higher activity (Table 1, Fig. 5A). According to T. Fujita classification [20], most of these pre-catalysts can be classified as highly active.

Complexes stabilized by ligands containing bis-(trifluoromethyl)-

Table 1
Ethylene Polymerization by complexes **3a–f.**[a]

Run	Complex	Cocatalyst, [Al]/[Mg]	A[b]	Bulk density, g/cm^3	M$_v$, 10^6 D	Deg. of crystal[d] %	T$_m$[c] °C
1	**3a**	Et_2AlCl/Bu_2Mg 300/100	1580	0.049	3.1	74.7/49.2	141/137
2	**3a**	$Et_3Al_2Cl_3/Bu_2Mg$ 300/100	2090	0.060	2.8	69.4/47.1	139/132
3	**3b**	Et_2AlCl/Bu_2Mg 300/100	2540	0.039	1.8	73.8/50.9	140/133
4	**3b**	$Et_3Al_2Cl_3/Bu_2Mg$ 300/100	2345	0.060	2.1	69.1/48.2	140/135
5	**3c**	Et_2AlCl/Bu_2Mg 300/100	2340	0.044	1.0	70.3/57.8	138/134
6	**3c**	$Et_3Al_2Cl_3/Bu_2Mg$ 300/100	2660	0.095	2.9	67.7/48.2	140/133
7	**3d**	Et_2AlCl/Bu_2Mg 300/100	2290	0.046	1.6	59.72/40.9	139.1/136.4
8	**3d**	$Et_3Al_2Cl_3/Bu_2Mg$ 300/100	2660	0.072	3.6	75.45/43.2	140.6/134.8
9	**3e**	Et_2AlCl/Bu_2Mg 300/100	1490	0.054	2.2	75.8/49.5	140/136
10	**3e**	$Et_3Al_2Cl_3/Bu_2Mg$ 300/100	1543	0.071	2.2	69.8/39.9	140/135
11	**3f**	Et_2AlCl/Bu_2Mg 300/100	743	0.031	2.4	75.0/50.6	139/136
12	**3g**	Et_2AlCl/Bu_2Mg 300/100	1060	0.053	1.8	80.4/52.1	138/136
13	**3g**	$Et_3Al_2Cl_3/Bu_2Mg$ 300/100	540	0.06	2.7	76.0/45.0	143/137
14[e]	**Ti(O^{i}Pr)$_4$**	$Et_2AlCl/MgBu_2$ 300/100	2914	0.049	1.66	68.4/52.8	138/133
15[e]	**Ti(O^{i}Pr)$_4$**	$Et_3Al_2Cl_3/MgBu_2$ 300/100[e]	2971	0.053	3.34	75.1/47.2	140/135

[a] Polymerizations were carried out in 100 mL of toluene with $5 \cdot 10^{-6}$ mol of precatalyst at a constant 0.7 atm excessive ethylene pressure for 30 min, temperature 30 °C.

[b] Activity, kg of PE·mol^{-1} h^{-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 J/g; the values for the first and second heating runs are given.

[e] According to the results [35].

carbinol fragment (**3a–d**) showed the greatest activity. Comparing the activity of complexes **3d–g** (having the same substituents in the aromatic fragment), it can be noted that replacing one of the trifluoromethyl groups with a methyl, phenyl or perfluorophenyl group (**3e–g**) is accompanied by a significant decrease in activity (Table 1, Fig. 5A).

The size of the substituent in the *ortho*-position to the phenolic hydroxyl practically does not affect the productivity of catalytic systems (complex **3b** with no bulky hydrocarbon substituent in the 6th position, was one of the most active), but the absence of shielding of the metal center leads to a decrease in the molecular weight of the polymer. A similar trend is typical for most non-metallocene catalysts with phenol-containing ligands - the presence of bulky substituents in the *ortho*-position to phenolic hydroxyl generally increases the molecular weight of the polymer [17–20] due to increase of the propagation rate constant. To our surprise, the molecular weight of the polymer obtained on the adamantyl-containing complex **3c** activated with Et_2AlCl was unexpectedly low (1.02 10^6 D). It is obvious that in the considered series of pre-catalysts both the absence of steric shielding of the phenolic hydroxyl and the presence of rigid cyclic substituents with a large steric volume (e.g., adamantyl) is accompanied by a decrease in the molecular weight of the polymer.

In some cases, the replacement of Et_2AlCl with $Et_3Al_2Cl_3$ leads to a significant increase in the molecular weight of the polymer (Table 1, Fig. 5B). A similar trend was observed for titanium complexes stabilized with 1,4- and 1,2-diolate ligands [34,35].

The melting point and degree of crystallinity are typical for UHMWPE [1,36] and are in the range of 139–143 °C and 68–75% respectively (Table 1).

It is well known [36,37] that drawability of UHMWPE highly depends on its supramolecular structure. To examine the morphologies of these powders, SEM observations have been made (Fig. 6). 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, which determines the low bulk density (0.031–0.095 g/cm^3) of the obtained samples.

At high magnification most samples, regardless of the nature of the organoaluminum activator, have nodular type microstructures (eg, polymer prepared on **3a**/Et_2AlCl + Bu_2Mg, Fig. 6, top). However, in some cases (polymer prepared on **3f**/$Et_3Al_2Cl_3/Bu_2Mg$, Fig. 6, bottom) there are no zones with a dense packing of spherical particles on the surface; the particles look fused and connected by a large number of fibrils, forming a “cobweb” structure.

The processing of reactor powders of UHMWPE obtained with complexes **3a–g** 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 [8]. 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.

To reveal the role of the ancillary ligands, we previously conducted a series of ethylene polymerizations using {$Ti(OPr^i)_4/3Et_2AlCl/Bu_2Mg$} and {$Ti(OPr^i)_4/1.5Et_3Al_2Cl_3/Bu_2Mg$} catalytic systems [35]. All the conditions of the polymerization process – time and temperature,

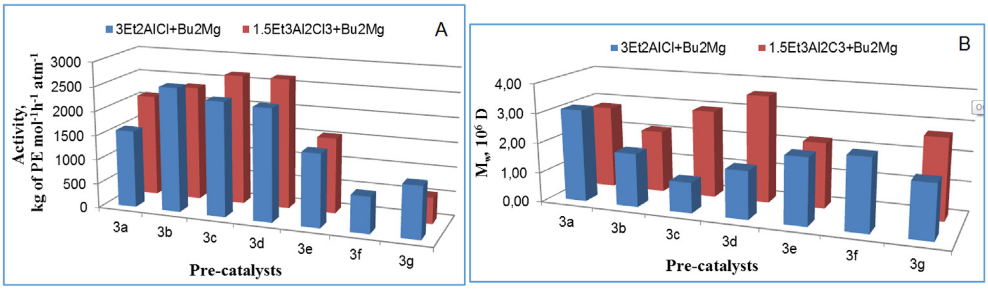

Fig. 5. Activities of the catalytic systems (A) and molecular weight of the obtained UHMWPE samples (B) versus the composition of catalytic system.

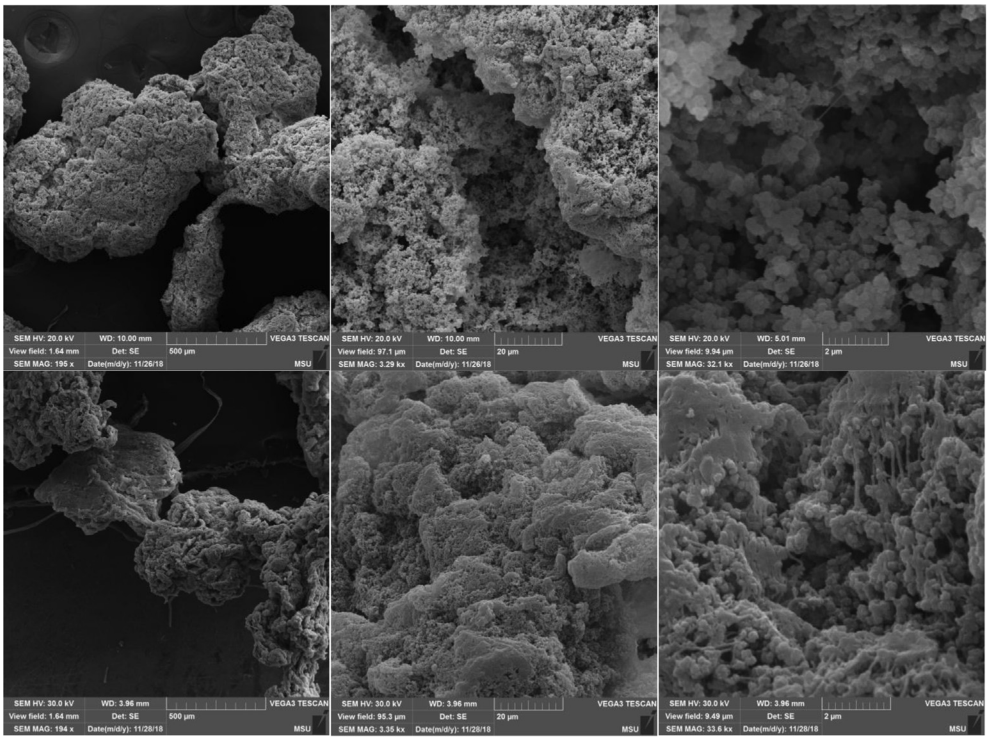

Fig. 6. Scanning electron micrographs of a series of nascent reactor powders, prepared on **3a**/Et_2AlCl + Bu_2Mg (top) and **3f**/$Et_3Al_2Cl_3$/Bu_2Mg (bottom).

Table 2
Mechanical properties of UHMWPE oriented film tapes.

Entry[a]	Catalytic system	Draw ratio	σ, GPa	E, GPa	ε, %
1	**3a**/Et_2AlCl/Bu_2Mg	44	2.65	127	2.56
2	**3a**/$Et_3Al_2Cl_3/Bu_2Mg$	24	2.00	121	2.35
3	**3b**/Et_2AlCl/Bu_2Mg	32	2.15	141	2.14
4	**3b**/$Et_3Al_2Cl_3/Bu_2Mg$	28	2.25	115	2.58
6	**3c**/$Et_3Al_2Cl_3/Bu_2Mg$	24	1.83	118	1.96
8	**3d**/$Et_3Al_2Cl_3/Bu_2Mg$	24	2.34	85	3.09
9	**3e**/Et_2AlCl/Bu_2Mg	40	2.54	143	2.23
10	**3e**/$Et_3Al_2Cl_3/Bu_2Mg$	28	2.37	113	2.67
11	**3f**/Et_2AlCl/Bu_2Mg	28	2.18	105	2.75
12	**3g**/Et_2AlCl/Bu_2Mg	20	2.10	86	3.00
15	**$Ti(O^iPr)_4$**/$Et_3Al_2Cl_3/MgBu_2$	20	1.99	105	2.12

[a] Numbering corresponds to Table 1.

ethylene pressure, molar ratios Ti/Al/Mg were identical. According to the results of the experiments, the model systems showed high activity ~2.9 10^3 kg of PE mol^{-1} h^{-1} atm^{-1} regardless of the composition of the activator (Table 1, runs 14–15). Differences are manifested in the properties of the polymer – the use of $Et_3Al_2Cl_3$ instead of Et_2AlCl results in obtaining UHMWPE with a significantly higher molecular weight ($3.3{\cdot}10^6$ and $1.7{\cdot}10^6$, respectively). The oriented film tapes, obtained from these UHMWPE powders, are characterized by low values of average tensile modulus (~105 GPa, Table 2, runs 14–15).

Table 2 shows the mechanical characteristics of film tapes prepared from reactor powders obtained in runs 1–4, 6 and 8–12 (Table 1). Unfortunately, not all compacted films turned out to be suitable for orientational drawing – samples 5, 7 and 9 (Table 1) could not be converted to tapes by this method. The morphology of these reactor powders is characterized by the presence of "melted" spherical particles forming a stretched fibrillar grid. The polymer obtained in run 5, was not tested due to the low molecular weight. Stress-strain curves of UHMWPE orientated film tapes are shown in Fig. 7.

The maximum value of tensile strength (2.65 GPa), with an average tensile modulus (127 GPa) and the highest value of the drawing ratio (44) in this series was observed for UHMWPE, obtained on pre-catalyst **3a,** activated by Et_2AlCl/Bu_2Mg. UHMWPE powders synthesized with complexes **3a**, **3b** and **3e** activated by Et_2AlCl, allowed to achieve larger values of drawing ratio compared with samples synthesized using $Et_3Al_2Cl_3$. The obtained results suggest that the volume of substituents in the benzylic position of the ligand has a more significant effect on the mechanical properties of oriented films than the substituent in the *ortho*-position to the phenolic hydroxyl. The films produced from powders obtained with the pre-catalyst **3e** (containing a methyl group instead of trifluoromethyl) have the greatest value of Young's modulus in this series – 143 GPa. Replacing one of the trifluoromethyl groups with bulkier phenyl or perfluorophenyl groups negatively affects the mechanical parameters of oriented films (entries 11–12).

A single-stage character of film rupture is observed in a number of cases, indicating uniformity of the samples. Close values of elongations and elastic modulus for a series of samples with the same drawing ratio confirm the high quality of UHMWPE reactor powder,

Comparing these results with those previously obtained, it can be stated that this group of pre-catalysts showed the best results in a series of titanium complexes stabilized by 2-hydroxymethylphenol derivatives. Thus, tetrameric Ti-methoxo complex **A**, as well as dimeric Ti-chloro(methoxo) complex **B** (Fig. 1) with the same ancillary ligand as in complex **3d**, are very effective catalysts for UHMWPE production, however, oriented materials obtained from these polymers are characterized by rather low values of breaking strength (~1.5 GPa) and elastic modulus (60 GPa) [10]. UHMWPE samples obtained on hexanuclear complex **C** were processed into oriented films with tensile strength values in the range 1.9–2.5 GPa, but the values of elastic modulus did not exceed 105 GPa [11].

The oriented films obtained with pre-catalyst without substituents in the benzylic position (complexes **D, E, F** and **G** (Fig. 1) are inferior to the best samples obtained in the present work and have tensile strength in the range 1.9–2.1 GPa and elastic modulus 90–110 GPa. Among them, the most interesting is the dichlorotitanium complex **F**, combining high activity (2740 kg of PE mol^{-1} h^{-1} atm^{-1}) and good mechanical characteristics of the oriented films (tensile strength

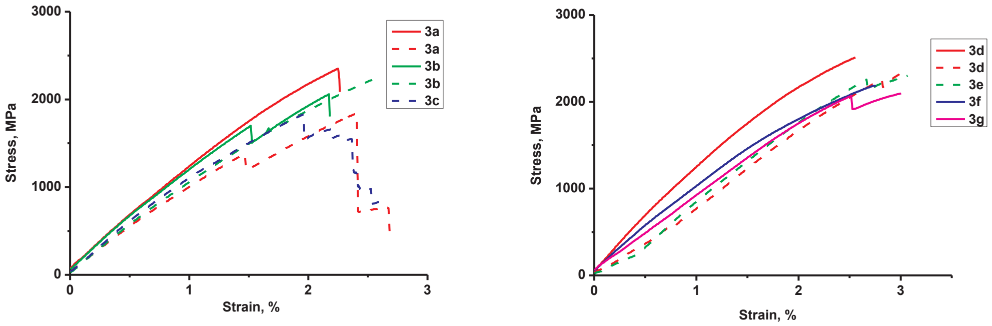

Fig. 7. Stress-elongation curves for UHMWPE orientated tapes (the samples obtained on catalytic systems with Et_2AlCl are indicated by the solid lines and with $Et_3Al_2Cl_3$ – by dotted lines).

– 2.4 GPa, elongation – 2.67%). Unlike all previously considered structures, complex **F** contains free hydroxymethyl groups. In the future, we plan to investigate in more detail the effect of this structural fragment on the activity of catalytic systems and the properties of the obtained polymers.

The present publication is a part of the screening program of a large group of transition metals coordination compounds, aimed at identifying the most promising pre-catalysts for the synthesis of disentangled UHMWPE. At this stage of research, achieving the maximum values of mechanical characteristics was not our goal, since optimization of the synthesis of UHMWPE reactor nascent powder and its solid-phase processing (eg, multistage drawing [38] or orientational drawing in the zone-drawing regime [39]) allows to significantly improve the mechanical properties of oriented materials. For example, the value of the module for UHMWE films manufactured by a similar technology by Teijin Aramid under the trade name Endumax®, is 170 GPa; and conventional UHMWPE yarn, obtained by gel spinning are characterized by the module values of 113 GPa [40].

We have previously shown that the catalysts formed upon activation of titanium complexes with OO-type ligands by a mixture of alkylaluminum chlorides and dibutylmagnesium are not single-site. In cases where the molecular weight of the polymer was not too high, which allowed applying GPC, the values of Mw/Mn were in the range 2.5–11.5 [23]. The multisite nature of such catalytic systems was also noted by Kissin et al. who proposed combinations of AlR_2Cl/MgR_2 as cocatalysts for Ziegler–Natta, Metallocene, and Post-Metallocene Catalysts [33]. On the other hand, it is known that in order to improve the processability of UHMWPE, its mixtures with low molecular weight polyethylene are used [41–43]. The main method for obtaining such blends is mixing the melts of the components in the extruder, which is rather difficult process due to significant differences in the viscosity of components. It is likely that a broad molecular weight distribution of UHMWPE samples obtained on titanium complexes activated by combinations of $AlR_2Cl/MgBu_2$ facilitates the solid-phase processing.

4. Conclusion

In summary, a series of titanium (IV) complexes bearing fluorinated 2-hydroxymethylphenol ligands have been synthesized. Structures of complexes **3c, 3f** and **3g** 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 (540–2660 kg of PE $mol^{-1} h^{-1} atm^{-1}$).

It was shown that the most active pre-catalysts contain bis-(trifluoromethyl)-carbinol fragment. Replacing one of the trifluoromethyl groups with a methyl, phenyl or perfluorophenyl group (**3e-g**) is accompanied by a significant decrease in activity.

The size of the substituent in the *ortho*-position to the phenolic hydroxyl practically does not affect the productivity of catalytic systems but the absence of a substitute significantly reduces the molecular weight of the resulting polymer.

Viscosity-average molecular weights of obtained polymer samples were in the range $1.02–3.1 \cdot 10^6$ Da. The UHMWPE nascent reactor powders were processed by a solvent-free method into high-strength (up to 2.65 GPa) and high-modulus (over 140 GPa) oriented film tapes.

To obtain disentangled UHMWPE suitable for solution-free processing, it is preferable to activate pre-catalysts with mixtures Et_2AlCl and Bu_2Mg (despite the fact that using of $Et_3Al_2Cl_3$ allows to obtain polymers with a higher yields and higher molecular weights).

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.ica.2019.119159.

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