**Electronic supplementary information**

**titanium(4+) complexes with tetraaryldioxolane  
ligands as the catalysts for the synthesis of  
ultra-high-molecular-weight polyethylene**

M. D. Evseeva,\**a* D. Saracheno,*b* L. Chuang,*b* S. Ch. Gagieva,*a,b* A. O. Vikhrov,*b*V. A. Tuskaev,*a,b* V. S. Bogdanov,*b* and B. M. Bulychev*b*

a Chemistry Department, Lomonosov Moscow State University,  
Leninskie Gory 1, str. 3, Moscow, 119991 Russia

*b Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,  
ul. Vavilova 28, str. 1, Moscow, 119334 Russia*

**Experimental section**

The target complexes were synthesized under an argon atmosphere using the standard Schlenk technique. NaH and TiCl4 were purchased from Aldrich. Tetrahydrofuran, toluene, dichloromethane, chloroform, isopropanol, hexane, and ethyl acetate of reagent grade were additionally purified according to the standard methods [S1]. The water content in the solvents was periodically monitored using the Karl Fischer coulometric method on a Methrom 756 KF instrument. Argon and ethylene of special purity grade were additionally dried by passing through Super Clean ™ gas filters. The NMR spectra were recorded on Bruker WP-300 and Bruker AMX-400 spectrometers. The IR spectra were recorded on a Magna-IR 750 spectrometer. The elemental analyses were performed on Carlo Erba-1106 and Carlo Erba-1108 instruments. The NMR and IR spectroscopic studies, as well as elemental analyses were carried out at INEOS RAS.

**Ethylene polymerization**

The polymerization was carried out in a 150 mL steel reactor (Parr Company). Before the experiment, the reactor was evacuated at a temperature of about 90 °C for 40 min, then it was filled with purified argon. A solvent (toluene) and the precatalyst with a titanium content of  
5·10–6 mol were introduced. The total volume of the solvent did not exceed 100 mL. The resulting slurry was stirred, and ethylene was fed to the reactor under a pressure of 1.7 atm for 30 min upon vigorous stirring (600 rpm) at a temperature of 30 °C, which was maintained with a thermostat. After the experiment completion, the reaction mixture was cooled. Then 20 mL of ethanol and 20 mL of 1M HCl were added to deactivate the unreacted organoaluminum compounds. The resulting polymer was filtered off and treated with a mixture of 200 mL of alcohol and 20 mL of 1M HCl for 30–40 min at 60 °C upon stirring. After that, the suspension was left at room temperature for 2 days, the precipitate obtained was filtered off, washed with distilled water and alcohol, and dried under vacuum at 70 °C for 3–4 h.

**Polymer characterization methods**

DSC studies were performed on a DSC-822e differential scanning calorimeter (Mettler-Toledo, Switzerland) at a heating rate of 10 °C min–1 in an argon atmosphere.

The viscosity-average molecular weights (MWs) of the resulting UHMWPE samples were calculated using the Mark–Houwink equation: *M*v = 5.37⸱104 [η]1.37, where *M*v is the viscosity-average MW (g·mol–1); [η] is the intrinsic viscosity in decalin at 135 °C (dL·g–1); and [η] = (2ηsp − 2lnηr)1/2/0.056 (ηsp, specific viscosity in decalin at 135 °C; ηr, relative viscosity in decalin at 135 °C; ηr = ηsp + 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 the nascent UHMWPE reactor powders [1]. 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 stretching 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 of 120 mm with 100 mm/min initial deformation rate. The reported values were the average of at least 8 samples.

**Compounds 1–4** were obtained by the published procedures [S2–S4].

**Synthesis of the complexes**

The titanium(IV) complexes were synthesized according to the following method.

**[(4*R*,5*R*)-2,2-Dimethyl-a,a,a,a-tetraphenyl-1,3-dioxolane-4,5-dimethanolato-*O*,*O*] titanium(IV)** **dichloride 5.** Sodium hydride (0.05 g, 1.0 mmol) and TiCl4 (0.06 ml, 0.5 mmol) were sequentially added to a solution of TADDOL **1** (0.233 g, 0.5 mmol) in 10 mL of toluene upon stirring at room temperature. In 5 h, the reaction mixture was filtered and evaporated under vacuum to remove all volatiles. The residue obtained was dissolved in 5 mL of a toluene–hexane mixture (1:2). The resulting precipitate was filtered off and washed with 2 mL of toluene to give the target product as a crystalline substance. Yield: 0.18 g (62%). Anal. Calcd for C31H28Cl2O4Ti (583.32): C, 63.83; H, 4.84; O, 10.97; Cl, 12.16; Ti, 8.21. Found: C, 63.80; H, 4.81; Cl, 12.13; Ti, 8.17%. 1H NMR (CDCl3): 1.58 (s, 6H), 3.35 (s, 2H), 7.38–7.47 (m, 20H).

**Compounds 6–8** were obtained in an analogous manner.

**[(4*R*,5*R*)-2,2-Dimethyl-a,a,a,a-tetrapentafluorphenyl-1,3-dioxolane-4,5-dimethanolato-*O*,*O*] titanium(IV) dichloride 6.** Crystalline substance. Yield: 0.33 g (69%). Anal. Calcd for C31H8Cl2F20O4Ti (943.13): C, 39.48; H, 0.85; O, 6.79; Cl, 7.52; F 40.29; Ti, 5.08. Found: C, 39.45; H, 0.81; Cl, 7.47; Ti, 5.06%. 1H NMR (CDCl3): 1.12 (s, 6H), 4.14 (s, 2H).

**[(4*R*,5*R*)-2,2-Dimethyl-a,a,a,a-tetra-1-naphtyl-1,3-dioxolane-4,5-dimethanolato-*O*,*O*] titanium(IV) dichloride 7.** Crystalline substance. Yield: 0.21 g (54%). Anal. Calcd for C47H36Cl2O4Ti (783.56): C, 72.04; H, 4.63; O, 8.17; Cl, 9.05; Ti, 6.11. Found: C, 72.00; H, 4.58; Cl, 9.01; Ti, 6.07%. 1H NMR (CDCl3): 1.33 (s, 6H), 3.14 (s, 2H), 7.30–7.56 (m, 28H, Ar).

**[(4*R*,5*R*)-2,2-Dimethyl-a,a,a,a-tetra-2-naphtyl-1,3-dioxolane-4,5-dimethanolato-*O*,*O*] titanium(IV) dichloride 8.** Crystalline substance. Yield: 0.27 g (69%). Anal. Calcd for C47H36Cl2O4Ti (783.56): C, 72.04; H, 4.63; O, 8.17; Cl, 9.05; Ti, 6.11. Found: C, 71.97; H, 4.60; Cl, 8.97; Ti, 6.05%. 1H NMR (CDCl3): 1.33 (s, 6H), 3.14 (s, 2H), 7.46-7.60 (m, 12H, Ar), 7.78–7.95 (m, 16H, Ar).

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