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Ethylene homopolymerization and copolymerization with 1-hexene and 1-octene catalyzed by titanium(IV) dichloride TADDOLate complex activated with MAO

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Abstract

The synthesis and olefin polymerization behavior of a new TADDOL-based Ti(IV) complex, (4R,5R)-2,2-dimethyl-α,α,α′,α′-tetrakis[bis-(3,5-trifluoromethyl)phenyl]-1,3-dioxolane-4,5-dimethanolato-titanium(IV) dichloride, are described. Upon activation with MAO, this complex polymerized ethylene, producing ultra-high molecular weight linear polyethylene (UHMWPE) with activities up to 4500 kg mol (Ti)$^{-1}$ [C$_2$H$_4$]$^{-1}$ h^{-1} atm^{-1} and molecular weights up to 3.25×10^6. The optimal temperature for UHMWPE synthesis was 50 °C. This complex is also capable of copolymerizing ethylene with 1-hexene and 1-octene, giving high molecular weight copolymers with α-olefin incorporation up to 7.8%. The copolymers, obtained with a different ratio of comonomers, are statistical, according to the analysis of the ^{13}C NMR spectra. The reaction parameters that influenced the copolymerization behavior, such as comonomer concentration, reaction temperature and [Al]/[Ti] molar ratio, are examined in detail. Furthermore, high catalytic activities up to 12,531 kg mol(Ti)$^{-1}$ [C$_2$H$_4$]$^{-1}$ h^{-1} atm^{-1} were observed in copolymerization of ethylene and 1-hexene or 1-octene with the **2**/MAO catalytic system. The obtained copolymers possess high molecular weights ($M_w = 1.4 \times 10^6$—ethylene/1-hexene and 1.86×10^6—ethylene/1-octene) with broad MWD ($M_w/M_n = 3.04$–8.23) and high comonomer incorporation degrees (up to 6.2 mol% of 1-hexene and 7.8 mol% of 1-octene). Depending on the synthesis conditions, it is possible to form both a statistical copolymer and a block copolymer.

Keywords Titanium · OO-ligands · TADDOL · Polymerization · Ethylene/α-olefin copolymer


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Introduction

Polyolefins account for more than 50% in weight of the produced polymers and remain at the top of the global production of synthetic polymers [1]. The ever-growing demand for new synthetic polymer materials is driving the development of new catalytic systems. Among a myriad of post-metallocene catalysts created in recent decades [2–6], complexes in which the ligand environment is formed exclusively from alkoxo-oxygen atoms are extremely rare. (Examples of such structures are shown in Fig. 1.)

Probably this is due to the low catalytic activity of such systems upon their activation by the conventional for non-metallocene cocatalysts (alkylaluminoxanes, alkylaluminum or alkylaluminum chlorides). For example, the diolate complex **B** (Fig. 1), activated with $Et_3Al_2Cl_3$, catalyzed the formation of low molecular weight PE with productivity not exceeding 30.4 kg PE g(Ti)$^{-1}$ h^{-1} [7].

However, when using mixtures of alkylaluminum chlorides and organomagnesium compounds proposed by Kissin et al. [8, 9], quite effective catalytic systems are formed. We have successfully used titanium dichloride and alkoxide complexes with 1,4- and 1,2-diolate ligands (complexes **B–E**) to produce disentangled UHMWPE [10, 11]. Based on the assumption that higher catalytic activity can be expected from complexes with a less stable 7-membered chelate ring, we used the tetraaryl-1,3-dioxolane-4,5-dimethanols (TADDOL) derivative as ligands. TADDOLs, containing two adjacent diarylhydroxymethyl groups in a trans relationship on a 1,3-dioxolane ring, were introduced by Seebach et al. [12, 13] and found wide application in asymmetric synthesis both as ligands and as organocatalysts [14]. We have previously shown that (TADDOL)TiCl$_2$ complexes effectively catalyze the polymerization
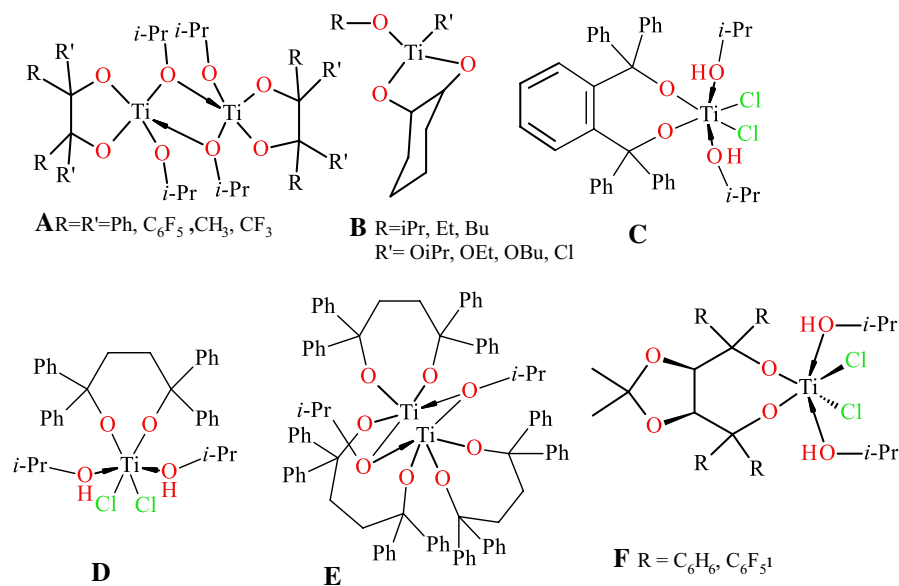
Fig. 1 Examples of titanium(IV) complexes with diolate ligands active in ethylene polymerization

of ethylene and propylene with the formation of high molecular weight polymers [15–19]. The maximum catalytic activity in ethylene polymerization with titanium TADDOLates (compounds **F**, Fig. 1) with a binary cocatalyst was shown by a complex containing perfluorophenyl fragments [19].

The aim of the present work is to verify the hypothesis that an increase in the acidity of the TADDOL's hydroxy groups will increase the catalytic activity of the corresponding complexes, as is the case for 1,2-diolate complexes [11]. In this work, we use the TADDOL ligand with four strong electron-withdrawing CF_3 substituents in phenyl fragments, because introduction of fluorine into the ligands was expected to increase the Lewis acidity of the catalyst complex [20, 21]. For a reliable analysis of the effect of substituents on catalytic activity, we used MAO as the cocatalyst. The obtained catalytic system exhibits relatively low activity that avoids limitations due to mass transport [22]. We previously showed that structurally close complexes (compounds **F**, Fig. 1), activated by MAO, form only trace amounts of polymer [19].

Experimental

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 and were determined by reference to the residual solvent peaks. All coupling constants are given in hertz. Air-sensitive NMR spectra were recorded 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.

Hexane was distilled over Na/benzophenone, and the water content was periodically controlled by Karl Fischer coulometry by using a Metrohm 756 KF apparatus. Methylaluminoxane (Sigma-Aldrich) was used as 7 wt% solution in toluene. Diisopropyl 2,3-*O*-isopropylidene-L-tartrate was synthesized according to the previously described procedure [23].

(4*R*,5*R*)-2,2-Dimethyl-α,α,α´,α´-tetrakis[bis-(3,5-trifluoromethyl)phenyl]-1,3-dioxolane-4,5-dimethanol (1)

The synthesis was carried out under argon. A solution of *n*-butyllithium (2.68 mL, 6.69 mmol) was added at −78 °C to a solution of 3,5-bis-trifluoromethyl-phenyl bromide (1.30 g, 4.46 mmol).

The reaction mixture was heated to room temperature and kept at ∼20 °C for 4 h. Then, the reaction mixture was cooled to −78 °C and a solution of

diisopropyl 2,3-O-isopropylidene-L-tartrate (0.274 g, 1.00 mmol) in diethyl ether (30 mL) was added dropwise. After warming to room temperature, the reaction mixture was refluxed for 24 h and neutralized with a saturated solution of NH₄Cl. The organic layer was separated, the solvent was evaporated, and the residue was recrystallized from hexane. Yield 1.19 g (13%), m.p. 192 °C (dec.), $[\alpha]_D = +187.3$ (c 0.5, CHCl₃). Found (%): C, 46.30; H, 2.16, F, 45.09. C₃₉H₂₂F₂₄O₄ (1010). Calculated (%): C, 46.35; H, 2.19, F, 45.12. ¹H NMR (d-THF), δ: 8.04 (s, 6 H, Ar); 7.91 (s, 2 H, Ar); 7.90 (s, 4 H, Ar); 4.58 (s, 2 H, CH); 2.56 (s, 2 OH, CH); 1.04 (s, 6 H). ¹⁹F NMR (d-THF), δ: −65.58. ¹³C NMR, δ: 23.92, 24.18, 26.03, 65.97, 66.19, 76.73, 81.17, 110.76, 121.98, 122.09, 124.69, 127.69, 128.62, 130.40, 130.73, 130.88, 131.06, 131.21, 131.39, 131.54, 145.04, 147.32. FT-IR (KBr): 652, 570 cm⁻¹ ν(Ti–O).

(4R,5R)-2,2-dimethyl-α,α,α´,α´-tetrakis[bis-(3,5-trifluoromethyl) phenyl]-1,3-dioxolane-4,5-dimethanolato titanium(IV) dichloride (complexes 2)

A 2.5 M solution of butyllithium in hexane (0.17 mL, 0.42 mmol) was added dropwise with stirring under argon to a cooled (−78 °C) solution of ligand **1** (0.20 mL, 0.20 mmol) in toluene (10 mL). The temperature of the reaction mixture was slowly brought to ambient temperature; the mixture was stirred for 4 h and cooled to −78 °C. A solution of TiCl₄ (0.024 mL, 0.20 mol) was added, and the mixture was again warmed to ambient temperature. After 3 h, the reaction mixture was filtered, the solvent was evaporated, and the product was recrystallized from toluene. Yield 0.16 g (64%), m.p. 249 °C (dec.), $[\alpha]_D = +97.9$ (c 0.5, CHCl₃). Found (%): C, 43.26; H, 2. 82, Cl, 5.64, Ti, 3.80. C₃₉H₂₀Cl₂F₂₄O₄Ti.2C₃H₈OH (1246.10). Calculated (%): C, 43.33; H, 2. 91, Cl, 5.68, Ti, 3.84. ¹H NMR (d-THF), δ: 8.15–8.06 (m, 12 H, Ar); 4.85 (s, 2 H, CH); 3.86 (s, 2 H, CH); 1.10 (s, 12 H), 0.69 (s, 6 H). ¹⁹F NMR (d-THF), δ: −63.67. ¹³C NMR, δ: 23.92, 24.12, 24.32, 24.52, 26.26, 62.03, 65.58, 66.27, 80.95, 88.94, 112.36, 121.75, 121.98, 122.09, 122.15, 124.30, 124.96, 127.30, 127.33, 127.57, 129.37, 130.01, 130.34, 130.65, 131.00, 131.06, 131.40, 131.72, 132.05, 145.63, 150.63.

Ethylene polymerization and copolymerization were carried out in hexane in a 0.5 L stainless steel reactor equipped with a mechanical stirrer. The reactor was kept under vacuum for 1 h at 90 °C before each experiment and then cooled to 20 °C, filled with dry argon and hexane, the cocatalyst (MAO), and in the case of copolymerization, the desired comonomers were introduced into it. The reactor was heated to a specified temperature, and the reaction mixture was saturated with ethylene. After saturation of the solvent with ethylene, polymerization was started by breaking the sealed glass ampule with pre-catalyst inside the reactor. The P_E was kept constant throughout each run; the ethylene loss was compensated for by introducing additional gas from a high-pressure vessel. After a prescribed time, the ethylene gas feed was stopped, and 10% HCl solution in ethanol was added to terminate the polymerization reaction. The polymer was isolated by filtration, washed with ethanol and dried at 60 °C for 12 h in a vacuum oven.

Preparation of block copolymer of ethylene and 1-octene

The preparation of polyoctene-b-poly(ethylene-*co*-1-octene) block copolymer was attempted by a sequential addition polymerization procedure. To prepare a polyoctene segment, to the stainless steel reactor prepared as described in the previous section, the cocatalyst MAO (1.04 mL of 2.7% solution in toluene, Aldrich) and the 1-octene (80 mL) were introduced. The reactor was heated to 50 °C, and the polymerization of 1-octene was started by breaking the sealed glass ampule with pre-catalyst inside the reactor. After 1 h, a sample of the reaction mass was taken for analysis and the solvent (100 mL of hexane) was introduced of the reaction and the entire solution was saturated with ethylene to produce a poly(ethylene-*co*-1-octene) segment. The P_E was kept constant throughout each run; the ethylene loss was compensated for by introducing additional gas from a high-pressure vessel. After a prescribed time, the ethylene gas feed was stopped, and 10% HCl solution in ethanol was added to terminate the polymerization reaction. The polymer was isolated by filtration, washed with ethanol and dried at 60 °C for 12 h in a vacuum oven.

Polymer evaluation methods

DSC was performed with a differential scanning calorimeter DSC 204 F1 Phoenix («NETZSCH») in helium atmosphere. The analyses were performed at the heating rate of 10 °C min^{-1} in the temperature range of 50–200 °C. The heating cycle was run twice. In the first scan, samples were heated and then cooled to room temperature. In the second scan, samples were reheated at the same rate. The characteristic melting temperatures and the heat of fusion for UHMWPE are given according to the first and second heating. For copolymers, only the results of the second scan were reported because the first scan was influenced by the mechanical and thermal history of samples.

Viscosity-average molecular weight of synthesized UHMWPE samples was calculated with the Mark–Houwink equation: $M_v = 5.37 \times 10^4$ $[\eta]^{1.37}$ [24], where M_v = viscosity-average molecular weight (g mol^{-1}); $[\eta]$ = intrinsic viscosity in decalin at 135 °C (dL g^{-1}); $[\eta] = (2\eta_{sp} - 2\ln\eta_r)^{1/2}/0.056$ (η_{sp}—specific viscosity decalin at 135 °C; η_r—relative viscosity in decalin at 135 °C; $\eta_r = \eta_{sp} + 1$).

Gel permeation chromatographic (GPC) analysis of polymers was carried out at 135 °C with a Waters GPCV-2000 chromatograph equipped with two columns (PLgel, 5 µ and Mixed-C, 3007.5 mm) and a refractometer. 1,2,4-Trichlorobenzene was used as a solvent; the elution rate was 1 mL min^{-1}. Molecular weights (MWs) of polymer products were determined using the universal calibration dependence relative to polystyrene standards with a narrow MW distribution: for polystyrene $K = 2.88 \times 10^{-4}$, $\alpha = 0.64$; for PE, $K = 6.14 \times 10^{-4}$, $\alpha = 0.67$.

^{13}C NMR spectra of ethylene/1-octene and ethylene/1-hexene copolymers (~5 wt% solutions in *o*-dichlorobenzene) were recorded at 100 °C on a Bruker Avance-400 spectrometer at 10.613 MHz. The relaxation delay was 15 s; the number of scans varied from 500 to 2000. The signal assignment in the ^{13}C NMR spectra was based on the literature data [25, 26].

IR spectra of polymers (thin films) were recorded on a PerkinElmer Spectrum 100 spectrophotometer. 1-Hexene content in the ethylene/l-hexene copolymer was estimated by FT-IR method using the $A_{CH3}^{1379}/A_{CH2}^{1369}$ absorbance ratios [27] in accordance with the methodology [28].

The degree of crystallinity was calculated using DSC data, as the ratio between crystalline peak area and the entire area under the curve in the 2θ region (15°–35°), excluding support and air dissipation.

Results and discussion

Synthesis of (4*R*,5*R*)-2,2-dimethyl-α,α,α′,α′-tetrakis(3,5-bis-(trifluoromethyl)-phenyl)-1,3-dioxolan-4,5-dimethanol **1** was performed according to reported methods [21]. Direct interaction of ligand **1** with dichloro(diisopropoxy)titanium ($TiCl_2(O^iPr)_2$) results in the one step formation of titanium(IV) dichloride complex **2** (Scheme 1). The complex contains two coordinated isopropanol molecules, which are eliminated upon cocatalyst addition to yield vacant coordination sites, as in the previously described cases [19]. The results of elemental analysis, the ^1H, ^{19}F, ^{13}C NMR and IR data of complex **2** are consistent with the structure proposed in Scheme 1.

Thus, the signals of OH protons, observed at 2.56 ppm in the spectrum of the ligand **1**, disappear in the ^1H NMR spectrum of the complex **2**, but signals of coordinated isopropanol molecules appear at 3.86 (–CH–), 1.10 ppm (–CH_3).

The ^{19}F NMR spectrum of the complex and the ligand contains a signal typical for CF_3 fragments (−65.58 ppm—for **1** and −63.67 ppm—for **2**). In the IR spectrum of the complex **2**, valence vibrations of the Ti–O bond are observed at 550 cm^{-1} and 620 cm^{-1}.

We have evaluated catalytic activity of compound **2** in ethylene polymerization. The complex **2** produces almost linear polyethylene, as indicated by the low branching degree determined by ^{13}C NMR and IR analysis. PE samples were insoluble in hot 1,2,4-trichlorobenzene so molecular weight was determined by viscometric method in decalin; the viscosity-average molecular weights are in the range of 1.94–3.25×10^6, which allows to attribute it to UHMWPE. An increase in the reaction temperature from 30 to 50 °C is accompanied by a 30% increase in
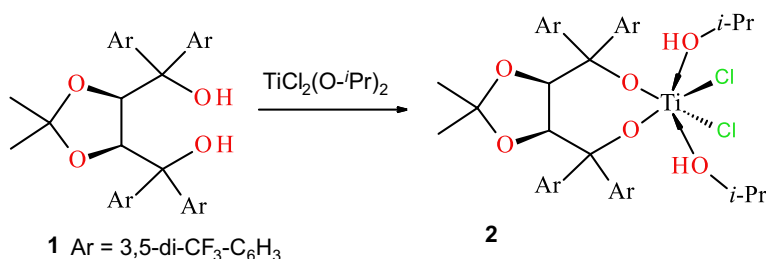

Scheme 1 Synthesis of titanium(IV) dichloride TADDOL complex **2**

the activity, but further increase in the temperature to 70 °C leads to the deactivation of the catalytic system (Fig. 2a). These data indicate moderate thermal stability of the catalytic system.

The melting points of the polyethylene samples were measured by DSC (Table 1). The melting points are in the range of 141–143 °C at first heating run, which significantly exceeds the usual values for polyethylene. Such high values of T_m, as well as the thermal exo-effect observed on the DSC curves, are typical for disentangled UHMWPE [29, 30].

The **2**/MAO catalytic system produces UHMWPE with moderate productivity (1500–4500 kg mol(Ti)$^{-1}$ [C$_2$H$_4$]$^{-1}$ h^{-1} atm^{-1}), compared to structurally related TADDOL pre-catalysts **F** [19], as well as complexes with 1,2- and 1,4-diolate ligands [10, 11] and derivatives of 2-hydroxymethylphenol [31, 32], that were practically inactive in the presence of MAO (Fig. 1. Compounds **A**–**F**). Since the catalytic activity of the titanium(IV) TADDOL complexes has a tendency to increase with the increased acidity of the hydroxyl groups [11], we have compared the catalytic performances of complex **2** with other structurally related titanium(IV) TADDOL complexes **F** (Fig. 1). However, the studied complexes **2** (Scheme 1) and **F** (Fig. 1) do not obey this trend.

The results obtained in entries 1–3 of Table 1 are promising, so we have studied the catalytic behavior of this system in the copolymerization of ethylene with higher α-olefins. 1-Octene was used as the monomer, since the ethylene–octene copolymer (EOC), a relatively novel polyolefin elastomer, developed by Dow Chemical Company with metallocene catalysis, is attracting a lot of attention from both research and industry. Among ethylene-based elastomers, EOC is characterized by an excellent compatibility with polyolefins, such as polyethylene (PE) and polypropylene (PP), lower level of crystallinity and a higher flexibility. Based on these properties, EOC is currently being used as an impact modifier of PP to replace ethylene propylene rubber (EPR) and ethylene propylene diene rubber (EPDM) [33].
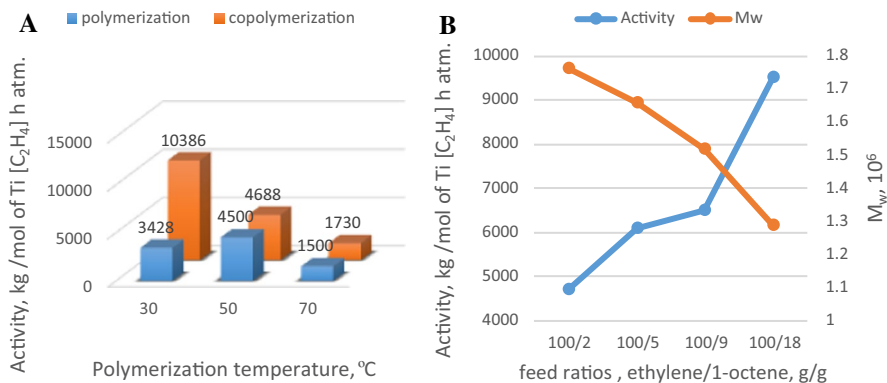
Fig. 2 **a** Activities of the catalytic systems in ethylene polymerization and its copolymerization with 1-octene versus the polymerization temperature. **b** Activities of the catalytic systems and M_w of copolymers versus ethylene/1-octene feed ratio

Table 1 Ethylene polymerization and copolymerization with 1-hexene and 1-octene by complex **2**/MAO

Run	Comonomer (g g^{-1})	[Al]/[Ti]	T (°C)	A^a	T_m^b (°C)	χ^c (%)	M_w, M_n^d	M_w/M_n	Comonomer content (%)^e
1	–	500	30	3428	143.2	82.3	3.25×10^{6f}	–	–
2	–	500	50	4500	141.9	80.1	2.19×10^{6f}	–	–
3	–	500	70	1500	140.4	76.4	1.94×10^{6f}	–	–
4	1-Octene, 100/2	500	50	4688	139.8	65.6	1.76×10^6 2.91×10^5	6.07	1.1
5	1-Octene, 100/5	500	50	6075	134.2	53.7	1.66×10^6 4.84×10^5	3.43	1.5
6	1-Octene, 100/9	500	50	6500	129.1	52.6	1.52×10^6 2.28×10^5	6.63	1.9
7	1-Octene, 100/18	500	50	9506	126.4	40.7	1.29×10^6 4.25×10^5	3.04	3.5
8	1-Octene, 100/18	250	50	5525	124.5	40.4	1.69×10^5 0.50×10^4	3.38	3.2
9	1-Octene, 100/18	1000	50	10,063	125.4	39.6	2.11×10^5 3.71×10^4	5.69	4.5
10	1-Octene, 100/18	2000	50	8038	125.9	35.4	9.64×10^5 1.88×10^4	5.14	7.8
11	1-octene, 100/9	500	30	10,386	130.1	65.2	1.86×10^6 2.26×10^5	8.23	1.9
12	1-Octene, 100/9	500	70	1730	127.6	51.7	4.82×10^5 8.95×10^4	5.38	1.8
13^g	1-Octene, 100/9	500	50	10,875	128.1	62.8	6.74×10^5 2.35×10^5	2.87	2.5
14	1-Hexene, 100/5	500	50	12,531	132.4	68.8	1.40×10^6 2.02×10^5	6.96	6.2

Experiments were carried out in 60 mL of hexane with 5×10^{-5} mol of pre-catalyst at a constant ethylene pressure of 1 atm for 1 h, cocatalyst—MAO

^{a}Activity, kg of PE mol^{-1} h^{-1} [C$_2$H$_4$]$^{-1}$ atm^{-1}

^{b}Melting points were determined by DSC, and the values for the second heating runs are given

^{c}Determined by DSC; second heating run (runs 1–3), first heating run (runs 4–14)

^{d}Determined by gel permeation chromatography (GPC)

^{e}Determined by ^{13}C NMR data

^{f}Viscosity-average molecular weight

^{g}Comonomers were fed to the reactor in a stepwise fashion; first, 1-octene was introduced, after 60 min—ethylene

Insofar as the maximum activity (4500 kg mol^{-1} of Ti [C$_2$H$_4$] h atm.) was recorded during ethylene polymerization at 50 °C; the optimization of the copolymerization conditions was carried out at this temperature. Copolymerization was performed at a variety of feed ratios (runs 4–7, Table 1; Fig. 2b) to investigate how the different concentrations of comonomer affect the catalytic activity and properties of the copolymers.

The increase in 1-octene content in the feed is beneficial both to productivity and the comonomer inclusion, while the molecular weight of the polymer is reduced. In this case, the comonomer synergistic effect is clearly evident: The productivity of this system in copolymerization is about twice higher than those observed in ethylene homopolymerization (entry 7 vs 2).

Unlike the polymerization process, the maximum productivity of the catalytic system in copolymerization is achieved at 30 °C. An increase in temperature to 50–70 °C is accompanied by a significant decrease in activity (entries 6, 11–12, Table 1, Fig. 2a). The polymer with higher M_W (1.86×10^6, entry 11) was produced at the lowest polymerization temperature (30 °C).

The DSC analysis of the copolymers shows one sole melting point in the range of 125.4–139.8 °C, which is significantly lower than the melting points of homopolymers (140.4–143.2 °C).

Analysis of the copolymer samples by GPC revealed that catalytic system 2/MAO produces high molecular weight copolymers. (M_w values are in the range 1.69×10^5–1.86×10^6.) All copolymers have a broad molecular weight distribution (Table 1, Fig. 3). The latter is explained by the presence of several types of active sites in the catalytic system.

The effect of [Al]/[Ti] molar ratio on the catalytic activity and properties of the resulting polymer was investigated. The activity grows with the ratio increase up to [Al]/[Ti] = 1000:1 reaching 10,063 kg mol(Ti)$^{-1}$ [C$_2$H$_4$]$^{-1}$ h^{-1} atm^{-1} (Table 1, entry 9); further growth up to 2000:1 leads to a decrease in activity. Such a phenomenon can be well clarified by the influence of the Al concentration on the termination of polymer chains. Interestingly, the degree of inclusion of the comonomer monotonically increases with growth in [Al]/[Ti] molar ratio, reaching a maximum—7.8% at molar ratio 2000:1.

The preparation of polyoctene-b-poly(ethylene-*co*-1-octene) block copolymer was attempted by a sequential addition polymerization procedure: To prepare a
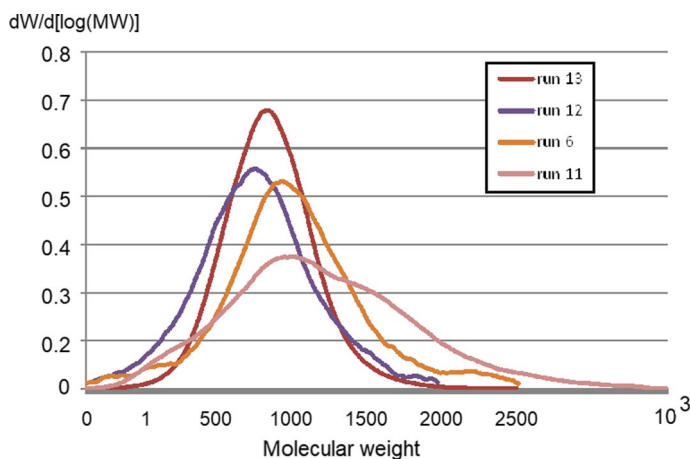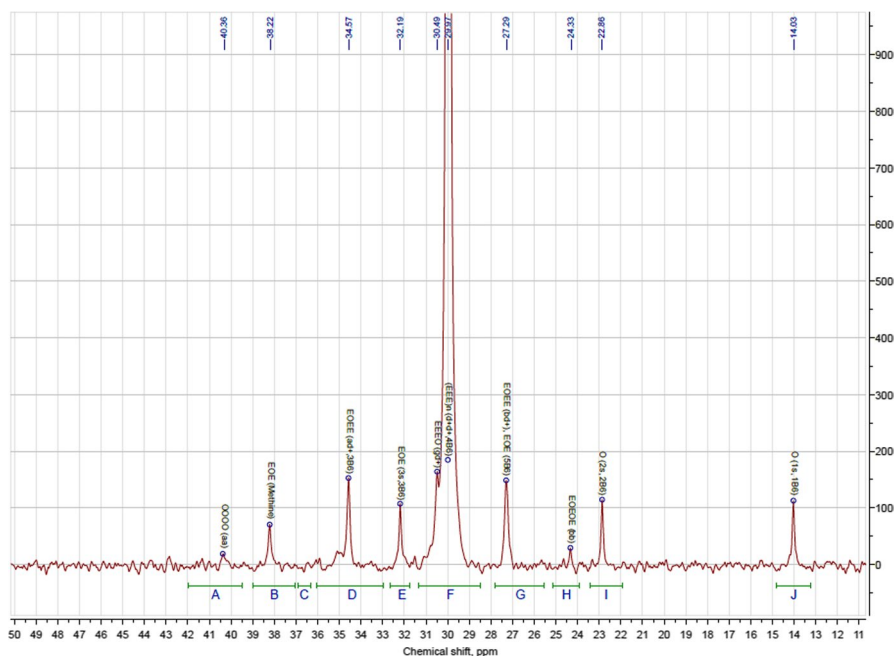

Fig. 3 GPC curves of ethylene/1-octene copolymers obtained in entries 6, 11, 12, 13

polyoctene segment, 1-octene was added to the activated complex and after 1 h, a sample of the reaction mass was taken for analysis. According to GPC data, the polyoctene segment had the following characteristics: M_w: 1.59×10^3; M_n: 1.11×10^3; M_w/M_n: 1.42. After that, the ethylene feed was started to produce a poly(ethylene-*co*-1-octene) segment [34]. As a result, a semicrystalline high molecular weight polymer was obtained with high efficiency 10,875 kg mol(Ti)$^{-1}$ $[C_2H_4]^{-1}$ h^{-1} atm^{-1} (Table 1, entry 13). The content of 1-octene was amounted to 2.5%; the polymer is characterized by a rather narrow MWD − 2.87 (the smallest value in this series). The composition and structure of ethylene/1-octene block copolymer was confirmed by ^{13}C NMR using the method of Randall et al. [25, 26] (Fig. 4).

The values of $r1 = 10.48$ and $r2 = 0.2358$ calculated according to [26], indicate that reactivity of these monomers differs in ≈ 44 times. The consequence of this is the block nature of the resulting copolymer: $r1 \times r2 = 2.47$. The presence of long ethylene sequences in polymer chains leads to the formation of a crystalline phase based on PE.

The copolymerization of ethylene with 1-hexene takes place with twice productivity compared to ethylene/1-octene copolymerization (12,531 and 6075 k g mol(Ti)$^{-1}$ $[C_2H_4]^{-1}$ h^{-1} atm^{-1}; Table 1, entries 5 vs 14), which is obviously explained by the higher reactivity of the 1-hexene comonomer.

Fig. 4 ^{13}C NMR (10.613 MHz) spectrum of ethylene/1-octene copolymer produced with **2**/MAO (Table 1, entry 13, $T = 50$ °C; [Al]/[Ti] = 500; [C$_8$H$_{16}$] = 9.0 mass%)

Conclusion

We have synthesized and fully characterized a new TADDOLate Ti(IV) complex—(*4R,5R*)-2,2-dimethyl-α,α,α′,α′-tetrakis-[bis-(3,5-trifluoromethyl)phenyl]-1,3-dioxolane-4,5-dimethanolato-titanium(IV) dichloride. This complex displayed moderate catalytic activity toward ethylene polymerization in the presence of MAO as a cocatalyst and produced UHMWPE with M_w 1.94–3.25×10⁶ even at elevated reaction temperature.

The reaction conditions in ethylene copolymerization (the temperature, ethylene/α-olefin and Al/Ti ratios) at a constant concentration of complex **2** have been optimized. Comonomer incorporation and polymer MW can be controlled in a wide range by the variation of the reaction parameters. Both the productivity of the catalytic system and the degree of comonomer content increase with increasing concentration of the latter in the feed mixture.

This effect of the [Al]/[Ti] ratio on the composition of the copolymers can be explained by two reasons: 1—With an increase in the Al/Ti molar ratio above 500, the chain transfer reaction to the cocatalyst (MAO) becomes noticeable; 2—there is a change in the composition and structure of the active center(s).

The obtained results confirm our assumption that the introduction of electron-withdrawing fluorine-containing substituents into the ligand structure is accompanied by an increase in the catalytic activity of the corresponding titanium complexes.

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