

The synthesis and X-ray structure of a phenoxyimine catalyst tailored for living olefin polymerisation and the synthesis of ultra-high molecular weight polyethylene and atactic polypropylene

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Abstract

A phenoxyimine catalyst (bis-(*N*-(3',5'-diiodo-salicylidene)-2,6-difluoroaniline)-titanium(IV)-dichloride has been synthesised. The ligand as well as the complex have been fully characterised. An X-ray structure of the titanium complex was obtained. After activation with MAO, it was used as highly active catalyst in living olefin polymerisation of ethylene and propylene. Ultra-high molecular weight polyethylene and atactic polypropylene of low polydispersity were obtained. The living character of the polymerisation was shown by online polymerisation kinetics and linear growth of number-average molar mass with polymerisation time. In addition, the influence of hydrogen as a chain transfer agent was studied in living olefin polymerisation.

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1. Introduction

Group IV metal catalysts have proven to be excellent reagents for the preparation of polyolefins of high stereoselectivity at very high activities [1]. Non-metallocene group IV metal complexes as catalysts for living olefin polymerisation have been of great research interest in recent years [2,3]. Living polymerisation enables the access to very high molecular weight polymers of low molecular mass distribution, controlled reaction conditions and the sequential synthesis of block copolymers [4,5].

Research in living olefin polymerisation has been known for more than 20 years. Doi et al. obtained syndiotactic poly(propylene) using $[V(acac)_3]$ as catalyst activated by diethyl aluminiumchloride at temperatures below -65°C

[6,7]. This became known as the first reaction fulfilling all criteria for a living olefin polymerisation [5]. This technique was used later to synthesise terminally functionalised poly(propylene)s [8–11] which were also used as macromonomers [12]. Sequential addition of monomers lead to block copolymers of propene, ethylene, styrene, THF and methyl methacrylate [8,13,14]. All block copolymers showed very narrow molecular weight distributions.

After Doi's pioneering contributions, different metal complexes were used as catalysts for living olefin polymerisation, including bridged lanthanide cyclopentadienyl complexes [15–18], cobalt half sandwich complexes [19,20], niobium diene complexes [21] and nickel- α -diimine complexes [22]. Yasuda et al. managed to synthesise block copolymers of ethylene and polar comonomers in which the polymerisation mechanism changes during the reaction [23]. At very low temperatures even polymerisations mediated by metallocene catalysts fulfil criteria of a living polymerisation [24–26].

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Recently, Fujita et al. at Mitsui Chemicals Inc. found a new class of catalysts for living olefin polymerisation, the so-called FI catalysts [5,27–29]. They described the synthesis of phenoxyimine titanium(IV) dichloride complexes bearing two 3'-substituted salicylidene anilinato ligands which when activated by methylaluminoxane show extremely high activity in living ethylene polymerisation and enable the synthesis of block copolymers when the anilinato ring is substituted by fluorine atoms in both *ortho*-positions [30–32]. It was claimed, that the living effect in polymerisation was achieved by a weak attractive interaction of the fluorine atoms in the ligands with a β -hydrogen atom of the growing polymer chain, resulting in preventing termination [2,33]. The presence of [C–H–F–C]-interactions in related complexes was verified by spectroscopic and crystallographic techniques [34,35].

In this paper, we describe the synthesis of a phenoxyimine catalyst for living olefin polymerisation tailored for the synthesis of ultra-high molecular weight polyethylene and atactic polypropylene of low polydispersity. The living behaviour of the catalyst during ethylene and propylene polymerisation was proven by online monitoring of polymerisation kinetics and SEC analyses. The influence of temperature and pressure on the living behaviour of the catalyst were studied. In the presence of hydrogen a broadening of the molar mass distribution was observed.

2. Experimental

2.1. Solvents and chemicals

Toluene was distilled from sodium/potassium, heptane was distilled from sodium. Both were kept under argon. All other solvents were lab-grade and used as received. Ethene (3.0), propene (2.5) and hydrogen (5.0) were obtained from Messer-Griesheim. 3,5-Diiodo-salicylaldehyde (97%, Sigma–Aldrich Chemicals), 2,6-difluoro-aniline (97%, Sigma–Aldrich Chemicals) and titanium tetrachloride (>99%, Fluka) were used as received. *n*-Butyllithium was purchased as solution in hexane (1.6 M) from Sigma–Aldrich Chemicals. Methylaluminoxane was purchased as solution in toluene (10% g/v; 4.97 wt% Al) from Crompton GmbH.

2.2. Characterisations

NMR spectra were recorded by Dr. M. Kowalski (macromolecular institute of the Albert-Ludwigs-Universität in Freiburg/Br.) on a Bruker ARX 300 spectrometer (299.87 MHz) using the solvent peaks as reference for ^1H spectra and ^{13}C spectra and external standard for the ^{19}F spectrum. High temperature NMR spectra were recorded at 120 °C. Several NMR spectra were recorded on a Bruker Avance 300 spectrometer at the Institut Le Bel in Strasbourg. Mass spectrometry and elemental analysis were carried out in the institute for organic chemistry and biochemistry of the Albert-Ludwigs-Universität in Frei-

burg/Br. by Dr. J. Wörth and C. Warth, respectively, E. Hickl. A Finnigan TSQ7000 and a Vario EL for elementary analysis were used. High temperature size exclusion chromatography was carried out by U. Westphal using a triple column set (PLgel mixed-bed) and 1,2,4-trichlorobenzene stabilised with 2 mg/mL of Irganox 1010 as solvent at 145 °C. Molecular weight distributions were analysed by light scattering, viscosimetry and refractive index. Calibration was carried out against linear PS standards using a calibration transfer for polyethylene samples. Glass transition temperatures and melting points of the obtained polymers were detected using a Seiko 6200 differential scanning calorimeter (DSC).

2.3. Synthesis and characterisation of *N*-(3',5'-diiodo-salicylidene)-2,6-difluoroaniline (**1**)

5.23 g 3,5-Diiodo-salicylidene (14.0 mmol) were dissolved in toluene under argon atmosphere in a double-necked 250 mL Schlenk round bottom flask equipped with a Dean-Stark trap and a reflux cooler. 13.9 mmol (1.80 g, 1.51 mL) of 2,6-difluoroaniline and two drops of trifluoroacetic acid were added and the reaction mixture was heated to 120 °C for 16 h. After cooling, the product was isolated via flush chromatography over silica gel 60 (40–63 μm , Merck)/ Na_2SO_4 . The solvent was reduced to few mL and the ligand was crystallised from the concentrated solution. The bright red crystals were dried in vacuo over night (yield: 7.71 g, 98%). ^1H NMR (CDCl_3): δ = 14.09 (s, 1H, OH), δ = 8.73 (s, 1H, HC=N), δ = 8.10 (d, 4J = 2 Hz, 1H, salicyl-*H*), δ = 7.65 (d, 4J = 2 Hz, 1H, salicyl-*H*), δ = 7.10–7.25 (m, 1H, aniline-*H*), δ = 6.92–7.06 (m, 2H, aniline-*H*); ^{13}C NMR: δ = 165.7 (HC=N), δ = 160.1 (C–OH), δ = 157.9 and δ = 154.5 (d, $^2J(\text{C};\text{F})$ = 256 Hz, C–F), δ = 149.7 and δ = 140.9 (salicyl-CH), δ = 127.7 (t, $^3J(\text{C};\text{F})$ = 10 Hz, C–N), δ = 123.7 (C–CH=N), δ = 120.8, δ = 112.1 (d, $^2J(\text{C};\text{H})$ = 7 Hz, aniline-CH), δ = 87.3, δ = 80.1 (C–I); ^{19}F NMR: δ = –122.1, $^3J(\text{F};\text{H})$ = 12.4 Hz; $^4J(\text{F};\text{H})$ = 11.4 Hz ($^{19}\text{F}\{^1\text{H}\}$ -decoupled spectrum).

The solid state molecular structure of **1** was determined using a Bruker AXS Smart CCD diffractometer with monochromatic Mo $\text{K}\alpha$ -radiation. The structure was solved using the programme SHELXS-97, the refinement was done using the programmes SHELXL-93 and SHELXL-97. The positions of the iodine were solved directly, the other atoms (except hydrogen) were calculated by Fourier synthesis.

2.4. Synthesis and characterisation of bis-(*N*-(3',5'-diiodo-salicylidene)-2,6-difluoroaniline)-titanium(IV)-dichloride (**2**)

1.00 g *N*-(3',5'-diiodo-salicylidene)-2,6-difluoroaniline (2.062 mmol) were dissolved in toluene under argon atmosphere to give a yellow solution. At –78 °C 1.1 equiv. *n*-butyllithium (1.6-M solution in hexane, 1.5 mL) was added and the red reaction mixture was warmed to ambient

temperature and stirred for 3 h. At -78°C 1/2 equiv. (196 mg, 1.03 mmol) titanium tetrachloride were injected through a septum. The solution was warmed to ambient temperature and stirred for 16 h. Then the reaction mixture was filtered over Na_2SO_4 . The amount of solvent was reduced to 10 mL and poured in stirring *n*-heptane to precipitate the complex. The Schlenk flask was placed in the refrigerator at 4°C for two days. Then the solid was isolated, washed twice with cold heptane and once with few mL of cold toluene. Then **2** was dried in vacuo over night (yield: 610 mg, 55%). Complex **2** was recrystallised from toluene to give orange needles. Single crystals for X-ray analysis could not be obtained. ^1H NMR (toluene- d_8): $\delta = 8.47$ (s, 1H, $\text{HC}=\text{N}$), $\delta = 7.69$ – 8.04 (m, 2H, salicyl-*H*), $\delta = 6.46$ – 6.88 (m, 3H, aniline-*H*); ^{13}C NMR: $\delta = 176.5$ ($\text{HC}=\text{N}$), $\delta = 142.1$, $\delta = 136.7$ (salicyl-CH), $\delta = 111.8$ (aniline-CH), $\delta = 103.6$ (aniline-CH); ^{19}F NMR: $\delta = -111.9$, $\delta = -112.9$. MS(EI), m/z (%): 1086 (<1%, M^+); 374 (100%). Elemental analysis: (theor.) C, 28.73%; H, 1.11%; N, 2.58%; (Exp.) C, 28.36%; H, 1.37%; N, 2.15%.

2.5. Crystallisation of **2** · THF

To 50 mg (1.09×10^{-4} mol) of *N*-(3',5'-diiodo-salicylidene)-2,6-difluoroaniline dissolved in 4 mL of THF were added 1.54 equiv. (4 mg) of NaH. The reaction mixture was stirred for 6 h. The excess of NaH was removed by filtration over celite. To the limpid yellow solution obtained 0.5 equiv. of TiCl_4 (10.2 mg) previously dissolved in 2 mL of THF to give a white suspension were added and the mixture was stirred for 16 h at ambient temperature. The solution was dried under vacuum, redissolved in THF and filtered over celite to separate the sodium chloride. The solvent was reduced under vacuum to 2 mL to permit the growing of the crystals.

The solid state molecular structure of **2** was determined using a Nonius Kappa-CCD area detector diffractometer (Mo $\text{K}\alpha$ radiation; 0.71073 \AA). The complete conditions of data collection (DENZO software) [36] and structure refinement are given within the supporting information. The structure was solved using direct method and refined against F^2 using the SHELXL-97 software [37]. The absorption was non-corrected. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were introduced as fixed contribution (SHELX-97).

2.6. General procedure for the polymerisation

The polymerisation was carried out using a semi-automated 600 mL polymerisation reactor (multi-purpose polymerisation reactor) from Labeq AG. Polymerisation was carried out at 25°C , in 300 mL of toluene at ethylene pressure of 2 bar. MAO was used as cocatalyst, using a ratio $\text{Ti}/\text{Al} = 1:2500$. The reactor was filled with toluene and half the amount of cocatalyst (methylaluminoxane as solution in toluene, 10% g/v). Then the atmosphere was satu-

rated with 2 bar of ethylene (gas feed 150 g/h) and the reactor was thermostated to 25°C . $7.5 \mu\text{mol}$ (8.15 mg) of **2** were dissolved in few mL of toluene and activated by the remaining amount of MAO. The solution of the activated catalyst was injected by syringe using a slight argon over-pressure. After a certain period of time, the reactor content was drained and the polymer was precipitated by pouring the reaction mixture in methanol/aq. HCl (5% v/v). The polymer was filtered, washed with methanol and dried in vacuo over night at 60°C . Propylene polymerisation was carried out in analogous manner.

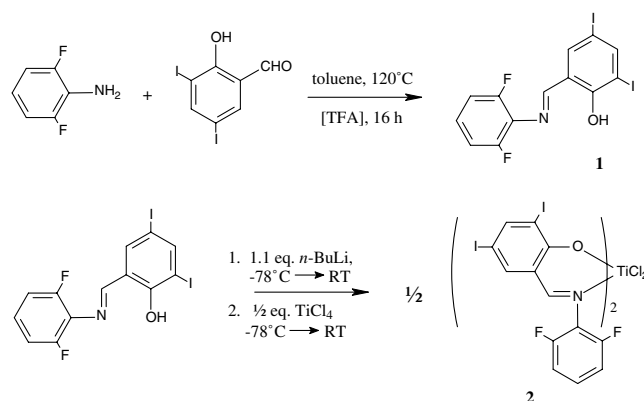
3. Results and discussion

The ligand *N*-(3',5'-diiodo-salicylidene)-2,6-difluoroaniline (**1**) was synthesised by Schiff-base formation of the 3,5-diiodo-salicylaldehyde and 2,6-difluoroaniline according to Scheme 1. The purified ligand was deprotonated by 1.1 equiv. of *n*-butyllithium at -78°C and brought to reaction with 1/2 equiv. of TiCl_4 to form complex **2** (bis-(*N*-(3',5'-diiodo-salicylidene)-2,6-difluoroaniline)-titanium-(IV)-dichloride) with 55% yield. The complex was claimed by Fujita et al. in patent [38] but to our knowledge has not yet been reported to the open literature.

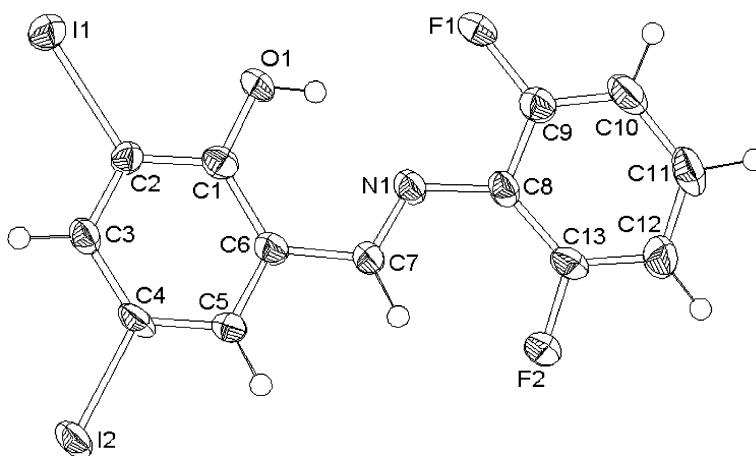
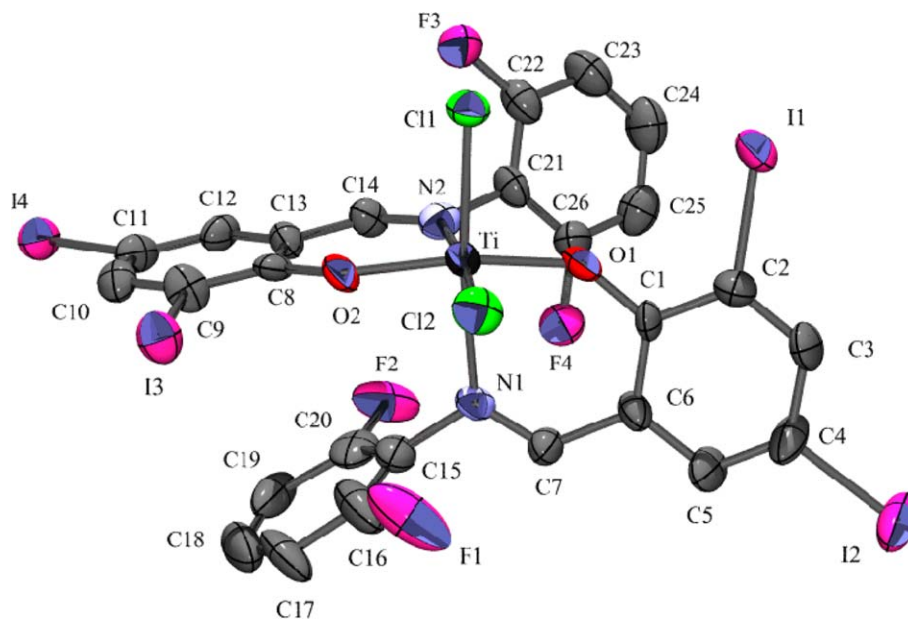
1 was characterised by means of NMR spectroscopy, showing good consistence with the expected analytical data. A crystal structure was obtained and is shown in Fig. 1. The ligand is slightly bent due to packing effects.

Complex **2** was characterised by means of NMR spectroscopy, mass spectrometry and elementary analysis, showing good consistence with the expected analytical data. Complex **2** was crystallised from THF solution and a crystal structure was obtained. The crystal structure is shown in Fig. 2. One solvent molecule is disordered within the crystals. In Fig. 2 it has been removed for clarity.

Complex **2** was activated by 2500 equiv. (Al/Ti) of methylaluminoxane and used as catalyst for living ethylene and propylene polymerisation. The activity for ethylene polymerisation is very high (1000 kg PE/mol Ti h), the activity in propylene polymerisation is considerably lower. The data is displayed in Table 1.



Scheme 1. Synthesis of complex **2**.

Fig. 1. An ORTEP view of the crystal structure of **1** (CCDC No. 286033).Fig. 2. An ORTEP view of the crystal structure of **2** (CCDC No. 286034).Table 1
Results of the homopolymerisation using **2**/MAO

	Polyethylene	Polypropylene
Polymerisation time (min) ^a	30	120 ^b
Catalyst activity (g polymer/mmol Ti h)	1000	24
M_w (g/mol)	5.5×10^6	230000
M_w/M_n	1.57	1.17
T_g (°C)	Not determined	−8.6 °C
T_m (°C)	133	None
ΔH_m (J/g)	135	None
Crystallinity (%)	47	None

^a 25 $\mu\text{mol/L}$ **2**, 250 mL toluene, MAO, Al/Ti = 2500:1, 2 bar, 25 °C.^b 40 $\mu\text{mol/L}$ **2**.

N-(3',5'-diiodo-salicylidene)-2,6-difluoroaniline was chosen as the ligand to achieve the synthesis of atactic polypropylene. Therefore, a ligand with less steric bulk in the 3'-position of the salicylidene ring was chosen [39].

The obtained polyethylenes show extremely high molecular weights (up to $M_w = 5.5 \times 10^6$ g/mol for 30 min polymerisation time) and low polydispersities ($M_w/M_n \leq 1.57$, at polymerisation times below 15 min: $M_w/M_n \approx 1.33$), indicating the living character of the polymerisation. At longer polymerisation times transfer reactions to MAO might occur as well as hindered monomer diffusion due to heterogeneity, which lead to a slight broadening of the molar mass distribution. A linear dependency of number-average molecular weight and time can be observed (Table 2 and Fig. 3). For poly(propylene) the obtained molar mass is lower due to the much lower catalyst activity. As atactic poly(propylene) does not precipitate from solution the reaction mixture does not get heterogeneous like in case of polyethylene and the obtained polydispersity of the product is even smaller ($M_w/M_n = 1.17$).

Table 2

Dependency of number-average molar mass on polymerisation time for living ethylene polymerisation on **2**/MAO

Polymerisation time (min)	3	5	10	15	30
M_n (kg/mol)	400	625	1100	1800	3500
M_w/M_n	1.33	1.34	1.33	1.32	1.57

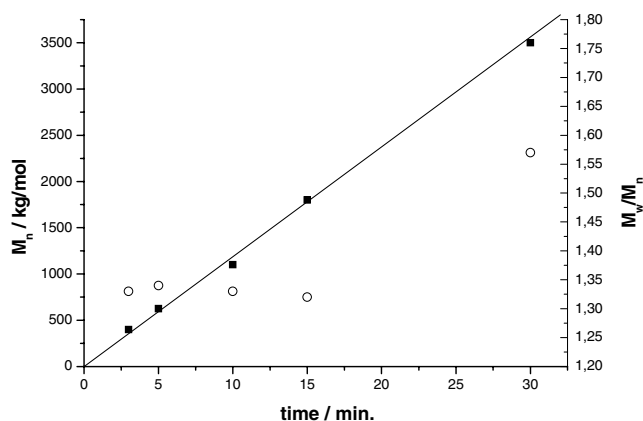


Fig. 3. Plot of number average molar mass (■) and polydispersity index M_w/M_n (○) of polyethylene obtained by **2**/MAO versus time (20–25 $\mu\text{mol/L}$ **2**, 250 mL toluene, MAO, Al/Ti = 2500:1, 2 bar, 25 °C).

A linear consumption of ethylene and a constant catalyst activity was detected by on-line kinetics measured by mass flow meter (Fig. 4). As the consumption of propylene is very low due to low catalyst activity a long time run has been performed showing a constant catalytic activity for up to 16 h. As the activated catalyst solution is injected by over-pressure a certain period is needed until the over-pressure in the gas phase has been consumed and new propylene is flowing into the reactor vessel, starting the on-line kinetic measurement. Therefore, no flow of ethylene is

detected within the first 3 h. Afterward a constant mass flow can be seen (Fig. 5).

NMR spectra showed that linear polymers are obtained. The polymers were analysed by DSC. The polyethylene showed a melting temperature of 133 °C and relatively low crystallinity, the poly(propylene) obtained was atactic and amorphous with a glass transition temperature of –8.6 °C as expected due to the ligand design.

Ethylene polymerisation was carried out at different pressure and temperature to study the influence of the polymerisation parameters. The results are shown in Table 3.

There seems to be an optimum in temperature for the living polymerisation on **2**/MAO at 25 °C. At higher as well as at lower temperature control of the polymerisation is worse resulting in lower average-number molecular weight, higher polydispersity and in unconstant catalyst activity at least at higher temperature. A constant catalyst activity can only be observed at temperatures below 50 °C. At 50 and 70 °C a high initial activity is followed by a continuous decline. Although the overall activity is still higher than at 25 °C (Fig. 6), it is not constant in regard to polymerisation time. Polymerisation conditions no longer fulfill living criteria.

A possible explanation for this behaviour relates to the presence of different isomers of the catalyst. Phenoxyimine complexes can arrange in five different isomeric structures, two of which are predominant in solution. They differ in the positioning of one of the ligands, having either the oxygen or the nitrogen atom in the axial position (structures referred to as (a) and (b) in Scheme 2). It was assumed, that after activation only structural isomer (b) is present [3]. At lower temperature the process of isomerisation might be slower, resulting in different activation times, different growth of the polymer chains and therefore, a broadened molar mass distribution although a constant mass flow and a constant catalyst activity are observed.

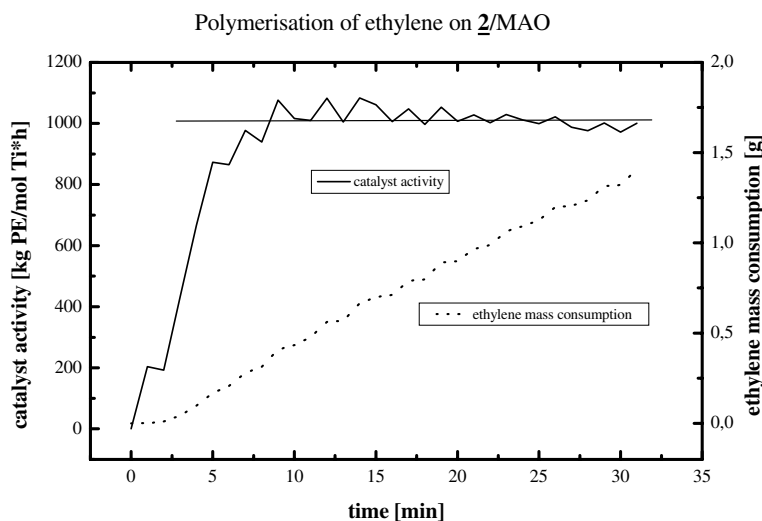


Fig. 4. On-line kinetics of activity (straight line) and mass flow of ethylene (dotted line) during polymerisation on **2**/MAO (20 $\mu\text{mol/L}$ **2**, 250 mL toluene, MAO, Al/Ti = 2500:1, 2 bar, 25 °C, $\frac{1}{2}$ h).

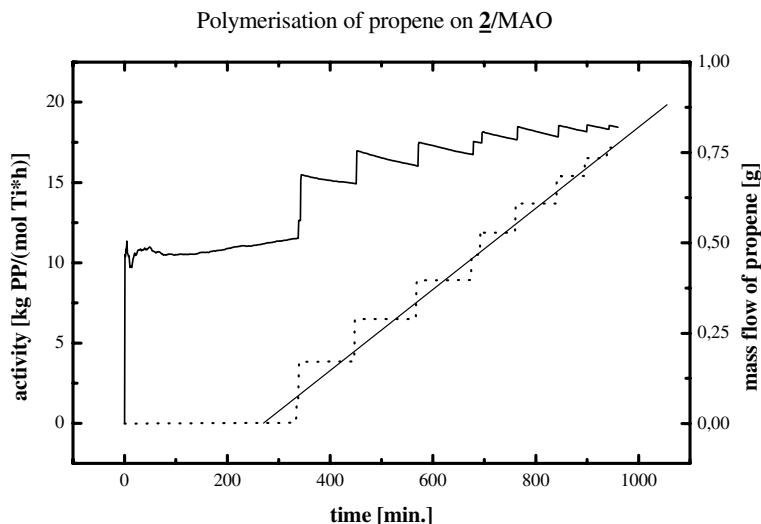


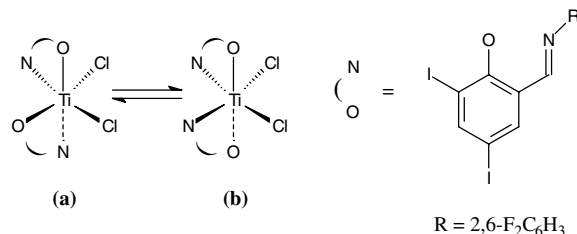
Fig. 5. On-line kinetics of activity (straight line) and mass flow of propene (dotted line) during polymerisation on **2**/MAO (25 $\mu\text{mol/L}$ **2**, 250 mL toluene, MAO, Al/Ti = 2500:1, 2 bar, 25 $^{\circ}\text{C}$, 16 h).

Table 3
Results of the ethylene polymerisation using **2**/MAO^a

T_{pol} ($^{\circ}\text{C}$)	25	25	25	5	50	70
p (bar)	1	1.5	2	2	2	2
Activity	560	740	1000	915	980	1240
M_n (kg/mol)	650	1000	3500	850	700	120
M_w/M_n	2.0	1.6	1.6	1.9	2.0	3.0
T_m ($^{\circ}\text{C}$)	134.3	133.5	133.0	133.8	134.8	135.0
ΔH_m (J/g)	130	123	132	131	138	172

^a 20 $\mu\text{mol/L}$ **2**, 250 mL toluene, MAO, Al/Ti = 2500:1, 30 min.

Whereas the polymerisation temperature has no significant effect on the melting point of the obtained polyethylene, the melting enthalpy rises with higher polymerisation temperature. As more shorter chains are formed a higher level of crystallinity can be achieved. When the ethylene pressure



Scheme 2. Isomers of phenoxyimine complexes in solution.

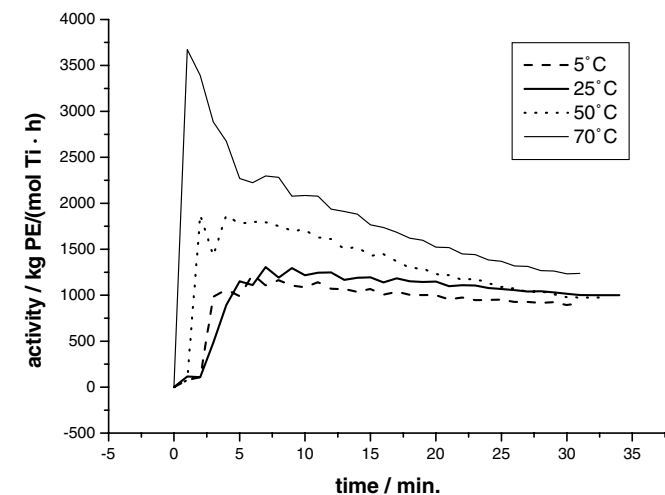


Fig. 6. Activity versus time in ethylene polymerisation on **2**/MAO depending on temperature (20 $\mu\text{mol/L}$ **2**, 250 mL toluene, MAO, Al/Ti = 2500:1, 2 bar, 30 min).

is reduced, catalytic activity declines as well as the molar mass of the obtained polyethylene. The effects of pressure are less significant than the effects of temperature. The activity is nearly constant when being normalised on pressure. But at lower pressure (1 bar) the control of the polymerisation is also lost resulting in polydispersities of $M_w/M_n = 2$.

The presence of hydrogen during ethylene polymerisation on **2**/MAO was studied with the purpose to achieve chain transfer and a regulation of the molar mass. The results are shown in Table 4.

When ethylene polymerisation on **2**/MAO is carried out in the presence of hydrogen a slightly higher catalyst activity can be recognised. Small influence of hydrogen is observed on molar mass of the obtained polymers, but broadening of molar mass distribution gives hint to the loss

Table 4
Results of the ethylene polymerisation in the presence of hydrogen using **2**/MAO^a

Hydrogen pressure (bar)	0	0.5 ^b	1 ^b	2
Catalyst activity (kg PE/mol Ti h)	1000	1470	1350	2000
M_w (g/mol)	5.5×10^6	1.3×10^6	900000	700000
M_w/M_n	1.57	2.00	2.86	2.56
T_m (°C)	132.9	131.2	132.7	130.7
ΔH_m (J/g)	135	144	155	119

^a 25 μ mol/L **2**, 250 mL toluene, MAO, Al/Ti = 2500:1, 2 bar ethylene, 25 °C, 1/2 h.

^b 1 h.

of living polymerisation conditions. Hydrogen seems to be no effective chain transfer agent for phenoxyimine catalysts or suitable for the control of molecular weight. Maybe due to the [C–H–F–C]-interactions between the *ortho*-fluorine atoms of the aniline ring and the β -hydrogen of the growing polymer chain transfer to hydrogen does not occur and the growing polymer chain stays bond to the active catalyst.

4. Conclusions

The family of phenoxyimine catalysts for living ethylene and propylene polymerisation was expanded by the synthesis and characterisation of (bis-(*N*-(3',5'-diiodo-salicylidene)-2,6-difluoroaniline)-titanium(IV)-dichloride. The X-ray structure of the complex has been obtained. After activation with MAO, it was used as highly active catalyst in living olefin polymerisation of ethylene and propylene. Ultra-high molecular weight polyethylene and atactic polypropylene of low polydispersity ($M_w/M_n = 1.17$) were synthesised. The living character of the polymerisation was shown by on-line polymerisation kinetics and linear growth of number-average molar mass with polymerisation time. The influence of temperature, pressure and the presence of hydrogen on the living behaviour of the catalyst were studied. In the presence of hydrogen a broadening of the molar mass distribution was observed. Within the phenoxyimine catalyst family, the phenoxyimine catalyst **2** is able to incorporate propylene very effectively and to produce block copolymers containing flexible atactic polypropylene segments.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorganchem.2006.03.020](https://doi.org/10.1016/j.jorganchem.2006.03.020).

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