

Extremely Narrow-Dispersed High Molecular Weight Polyethylene from Living Polymerization at Elevated Temperatures with *o*-F Substituted Ti Enolatoimines

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Living polymerization techniques are an essential tool for the synthesis of polymers with controlled architectures, such as monodisperse polymers or blockcopolymers.¹ Polymerization in a living fashion requires the essential absence of chain termination and irreversible transfer. In olefin polymerization, chain transfer (occurring by β -hydride transfer or transfer to cocatalyst) and termination can be suppressed by polymerization at low temperatures.² This, however, results in low catalyst activities and limited molecular weights attainable especially for semicrystalline polymers. Therefore, considerable effort has been directed at the development of new catalysts. Albeit a significant number of catalyst systems with living polymerization characteristics at ambient or elevated temperature have been reported,^{3–10} the synthesis of linear polyethylene (PE) with a high molecular weight and truly narrow distribution remains a challenge.

Phenoxyimine Ti complexes with *o*-fluorine substitution of the N-aryl moiety, discovered by Fujita et al., are highly active versatile catalysts for, e.g., the synthesis of narrowly distributed (ultra high molecular weight) PE and of block copolymers.³ The *o*-F substituents have been suggested to suppress chain transfer by interaction with the β -hydrogen atoms of the growing PE chain.^{3,11} At 25 °C linear PE with M_w/M_n as low as 1.05 was obtained, when a short reaction time (3 min) and diluted ethylene (0.04 atm) were employed for this very reactive system. The PE formed with this narrow distribution has a molecular weight of several 10^4 g mol⁻¹.^{3b,c,f} Living characteristics can be retained for longer reaction times also at 50 °C, as evidenced by a linear increase of molecular weight with time to afford PE with, e.g., M_w/M_n 1.19, M_n 1.4×10^5 g mol⁻¹ after 15 min of polymerization.^{3a} For complexes with other N,O-chelating ligands, however, no living polymerization was observed to result from *o*-F substitution,^{12,13} and living polymerization occurs also for nonfluorinated N,O-chelated Ti complexes.^{3e,4} This prompted us to study the effect of *o*-F substitution in a different type of complex to shed further light on this issue.

Ti(IV) enolatoimine complexes [(N[^]O)₂TiCl₂] substituted in the 2,6-position of the N-aryl moiety were prepared in good yields (70%) by reaction of the corresponding ketoenamines with [Ti(NMe₂)₂Cl₂] and chlorination of the resulting mixed amido-chloro intermediate with BCl₃ (Scheme 1; reaction of the Li salts of the ketoenamines with TiCl₄ did not afford the desired compounds). The unsubstituted analogue **3c** (R = H), which is known to polymerize ethylene in a nonliving fashion, was prepared for comparison as previously reported.¹⁴

In the solid state, **3a** possesses a C₂-symmetric, distorted octahedral geometry (Figure 1). The two oxygen atoms are oriented trans to one another (O–Ti–O angle 164°), while the two nitrogen atoms (N–Ti–N 92°) and the two chlorine atoms are positioned in a cis fashion. The latter is a prerequisite for polymerization catalysis.

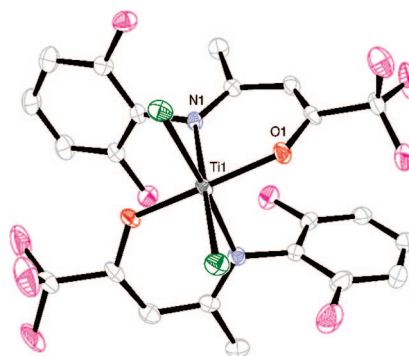
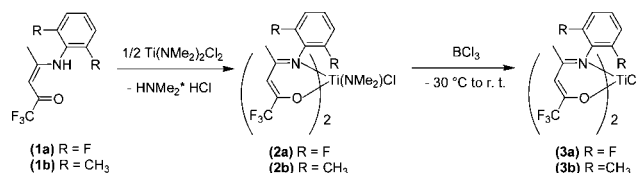


Figure 1. ORTEP plot of the molecular structure of **3a**. Ellipsoids are shown with 50% probability. The H-atoms are not shown for clarity.

Scheme 1. Synthesis of Complexes **3a** and **3b**

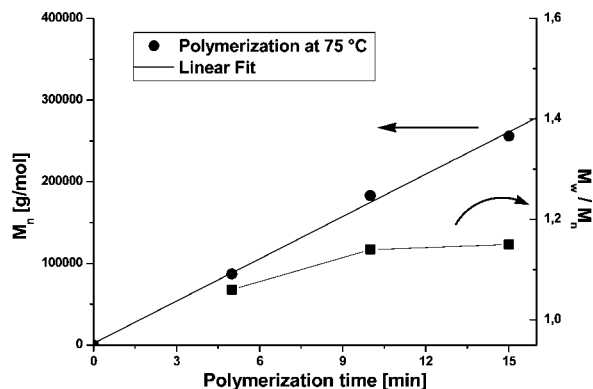


Activation of **3a–c** with an MAO cocatalyst affords ethylene polymerization catalysts (Table 1). Astonishingly, **3a** affords high molecular weight linear PE with an extremely narrow molecular weight distribution of M_w/M_n 1.01 at room temperature (entry 2; cf. Supporting Information (SI) for GPC trace and details of molecular weight determination). The polymer molecular weight determined agrees within experimental error with the theoretical value calculated from the amount of polymer obtained and catalyst precursor employed. This shows that the catalyst precursor is rapidly converted to a single type of active species, chains are initiated simultaneously, and essentially no chain transfer or termination occurs. The catalyst is highly stable during ethylene polymerization. After 1 h of living polymerization, narrowly distributed ultrahigh molecular weight polyethylene is obtained (entry 7).¹⁵ By contrast, a comparatively much broader polydispersity (M_w/M_n 1.45) is observed with the nonfluorinated **3c** (entry 1). The even broader molecular weight distribution obtained with **3b** (R = CH₃, entry 3) supports the fact that the living behavior of **3a** is not due to a steric effect of the *o*-fluorine substituents. Interestingly, relatively high molecular weights are obtained with **3b** and **3c** which exceed the calculated molecular weights for the hypothetical case that the polymerization was living (vide infra). Considering also the broad molecular weight distributions, this suggests that by contrast to the *o*-fluorinated **3a** the catalyst precursors **3b** and **3c** are inefficiently converted to the active species and that actually, by comparison to

Table 1. Results of Ethylene Polymerization with **3a–c**^a

entry	complex	T [°C]	time [min]	TOF [mol(C ₂ H ₄) mol(Ti) ⁻¹ h ⁻¹]	polymer yield [g]	T _m ^b [°C]	M _n ^c [10 ⁴ g mol ⁻¹]	M _n (calcd) [10 ⁴ g mol ⁻¹]	M _w /M _n ^c
1	3c	25	15	21 400	0.15	138	26	(15)	1.45
2	3a	25	15	37 100	0.26	139	27	26	1.01
3	3b	25	15	14 300	0.10	139	19	(10)	2.62
4	3a	0	15	30 000	0.21	140	19	21	1.13
5	3a	50	15	42 900	0.30	139	32	30	1.03
6	3a	75	15	42 900	0.30	139	26	30	1.15
7	3a	25	60	36 100	1.01	137	99	100	1.17

^a Reaction conditions: 1 atm of ethylene pressure, 1 μmol of catalyst, toluene 250 mL, 2000 equiv of MAO (molar ratio). ^b Measured by DSC. ^c Determined by GPC referenced to linear PE (cf. SI for details).

**Figure 2.** Plots of M_n and M_w/M_n versus time for ethylene polymerization at 75 °C with **3a** (reaction conditions as in entry 6).

the *o*-fluorinated analogue, the intrinsic rate of chain growth is higher in the active species, which are prone to chain transfer.

The effect of polymerization temperature was studied (entries 2, 4, 5, and 6). The extremely narrow molecular weight distribution is retained at an elevated temperature of 50 °C. PE with M_w/M_n 1.03 and M_n 3.2×10^5 g mol⁻¹ is obtained after 15 min of polymerization (entry 5). Remarkably, molecular weight control is retained even at 75 °C in polymerization with **3a** (entry 6).

To further confirm the living nature of the polymerization with **3a**, the development of M_n and M_w/M_n over time was studied at 25, 50, and 75 °C (Figure 2 and SI). A linear increase of M_n with polymerization time and narrow molecular weight distributions were observed for all runs, thus corroborating the highly controlled nature of the polymerization.

By comparison to the well studied highly active phenoxyimine catalysts,³ the lower insertion rates with **3a** facilitate control of the polymerization reactions. A generally lower reactivity may also contribute to the stability over time at higher temperatures.

The utility of **3a** is also illustrated by the preparation of block copolymers, with a hard PE block and a soft atactic polypropylene block. After complete ethylene consumption at 25 °C, addition of propylene afforded a block copolymer with apparent M_n 1.9×10^5 g mol⁻¹, M_w/M_n 1.12, PE content 60 wt %. Notably, the living character is also retained at 50 °C (M_n 2.4×10^5 g mol⁻¹, M_w/M_n 1.12, PE content 40 wt %). For details, cf. SI).

In conclusion, the conveniently accessible novel enolatoimine Ti complex **3a** upon MAO activation polymerizes ethylene in a living fashion with unprecedented molecular weight control and temperature stability. This provides viable access to high molecular weight PE with an extremely narrow molecular weight distribution (M_w/M_n 1.01) and corresponding block copolymers. In addition to phenoxyimine Ti complexes, this is another example of a system in which *o*-F substitution appears beneficial for living polymerization of ethylene as well as propylene. Our studies indicate that these

substituents also affect the activation reaction, which is effective only for **3a** but not for analogues lacking *o*-fluorine substitution.

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Supporting Information Available: Preparative procedures and characterization data, X-ray data for **3a**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (15) DSC (SI) shows typical behaviour of UHMWPE. In the first heating trace a narrow melt transition (144 °C) and high crystallinity (76%) are observed for the nascent polymer. In the second heating cycle, crystallinity is much lower (49%) due to entanglement hindering recrystallization from the melt.

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