

# Living Olefin Polymerisation and Block Copolymer Synthesis in the Presence of a Single-site Catalyst Containing a Phenoxyimine Ligand

Marc-Stephan Weiser,\* Rolf Mülhaupt

**Summary:** A new phenoxyimine catalyst (Bis-(N-(3',5'-diiodo-salicylidene)-2,6-difluoroaniline)-titanium(IV)-dichloride) has been synthesised and characterised. 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 on-line polymerisation kinetics and linear growth of number-average molar mass with polymerisation time. A block copolymer of the type PE-block-P(E-co-P) was prepared and characterised by CRYSTAF analysis and AFM micrographs.

**Keywords:** block copolymer; living olefin polymerisation; on-line polymerisation kinetics; phenoxyimine catalyst

## Introduction

Since the pioneering days of Ziegler and Natta several successful attempts were made to initiate living olefin homo- and copolymerisation by preventing chain termination and chain transfer reactions [1]. The first generation of living olefin polymerisation process were based upon catalysts with poor activities operating at low temperatures. For example, in 1979 Doi *et al.* obtained living syndiotactic poly(propylene) using  $[V(acac)_3]$  activated by diethyl aluminiumchloride at temperatures below  $-65^\circ\text{C}$  [2]. Modern single site catalysts exhibit much higher activities and produce block copolymers in industrial processes. Recently T. Fujita *et al.* at Mitsui Chemicals, Inc. found a new class of single site catalysts, the so-called "FI catalysts", useful for living olefin polymerisation [3]. Their phenoxyimine titanium(IV) dichloride complexes bearing two 3'-substituted

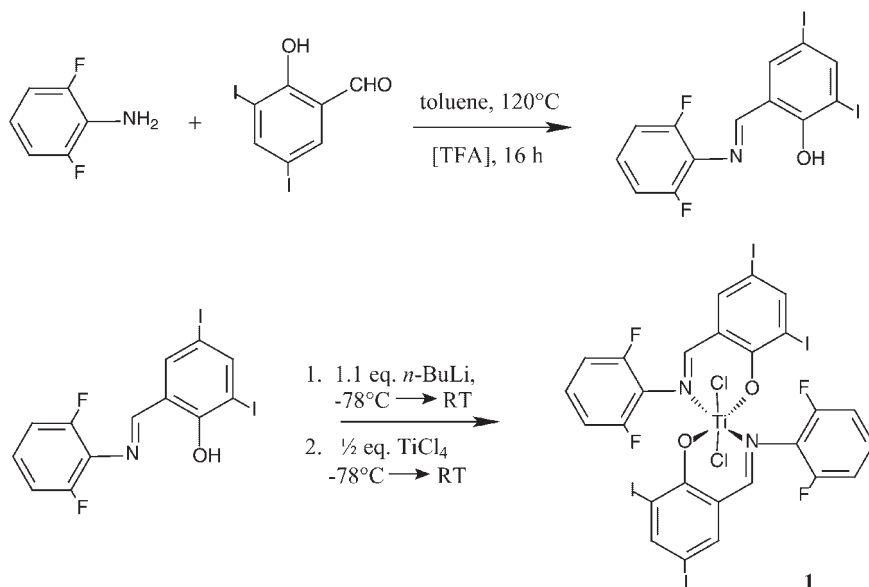
salicylidene anilinato ligands gave remarkably high catalyst activities in living ethylene polymerisation and enabled the synthesis of block copolymers when the anilinato ring was substituted by fluorine atoms in both *ortho* positions [4].

## Results and Discussion

Here we report the synthesis of the phenoxyimine catalyst (bis-(N-(3',5'-diiodo-salicylidene)-2,6-difluoroaniline)-titanium(IV)-dichloride) (**1**), which was synthesised and characterised by means of NMR and mass spectroscopy as well as elementary analysis. The ligand was prepared by Schiff-base reaction of the corresponding aldehyde and 2,6-difluoroaniline. It was deprotonated by *n*-butyllithium and reacted with  $\frac{1}{2}$  eq. of  $\text{TiCl}_4$  to give **1** in 55% yield. This complex was claimed by T. Fujita *et al.* in patent [5], but has not yet been reported in open literature. The synthesis of the complex is shown in Scheme 1.

**1** was activated by methylaluminumoxane (Ti/Al-ratio 1:2500) and was used as catalyst in living olefin polymerisation of

Freiburger Materialforschungszentrum und Institut für Makromolekulare Chemie, Albert-Ludwigs-University Freiburg, Stefan-Meier-Straße 21, D-79104 Freiburg i. Br., Germany  
E-mail: marc.weiser@fmf.uni-freiburg.de

**Scheme 1.**

Synthesis of (Bis-(N-(3',5'-diiodo-salicylidene)-2,6-difluoro-aniline)-titanium(IV)-dichloride) (**1**).

ethylene and propylene, for the preparation of polyethylene and poly(propylene) homopolymers as well as PE-*block*-P(E-co-P) block copolymers with very high molecular weight containing one crystalline PE and one amorphous flexible atactic P(E-co-P) block. The activity for ethylene polymerisation is very high (1,000 kg PE/mol Ti · h), the activity in propylene polymerisation is considerably lower. On-line kinetics showed that mass consumption of

the monomer gas was constant during polymerisation time and a constant activity for the catalyst was observed. As can be seen in Table 1, the obtained homopolymers showed very high molecular weights ( $M_n = 3.5 \cdot 10^6$  g/mol for the polyethylene) and very low polydispersities (PE:  $M_w/M_n = 1.57$ ). Molar masses and polydispersities were determined by high temperature size exclusion chromatography (HT-SEC) indicating the living character of the

**Table 1.**

Results of the polymers obtained by **1**/MAO.

	polyethylene	poly(propylene)	PE- <i>block</i> -P(E-co-P)
polymerisation time / min.	30 <sup>a</sup>	120 <sup>b</sup>	10/60 <sup>c</sup>
catalyst activity / g/(mmol · h)	1,000	24	n. d.
$M_n$ / kg/mol	3,500	200	2,000
$M_w/M_n$	1.57	1.17	1.60
$T_m/^\circ\text{C}$	133	–	133
$T_g/^\circ\text{C}$	–	–8.6	< –60
$\Delta H_m$ / J/g	135	–	89

<sup>a</sup> 25  $\mu\text{mol/L}$  **1**, 250 mL toluene, MAO, Al/Ti = 2,500:1, 2 bar, 25 °C.

<sup>b</sup> 40  $\mu\text{mol/L}$  **1**, 250 mL toluene, MAO, Al/Ti = 2,500:1, 2 bar, 25 °C.

<sup>c</sup> 33  $\mu\text{mol/L}$  **1**, 300 mL toluene, MAO, Al/Ti = 2,500:1, 2 bar, 25 °C, first block: 10 min.; second block: 60 min.  
n. d.: not determined.

polymerisation. NMR spectra showed that linear polymers were obtained. The polymers were analysed by DSC. The polyethylene showed low crystallinity, the poly(propylene) obtained was atactic.

The formation of block copolymers was confirmed by means of morphology studies and CRYSTAF experiments. The formation of atactic regions of 30–50 nm in diameter derived from the poly(propylene) domains can be seen within the matrix of crystalline polyethylene (see Figure 1). In CRYSTAF experiments which were carried out at the Deutsches Kunststoffinstitut in Darmstadt a single crystallisation peak was detected at 87.3 °C which is a lightly lower crystallisation temperature than expected for pure PE, showing that a block copolymer and no blend is present in the obtained product (see Figure 2). No fraction of atactic poly(propylene) could be isolated by Soxhlet extraction with *i*-hexane as well as with *n*-heptane.

## Experimental

### General

Toluene was distilled from sodium/potassium, heptane was distilled from sodium. Both were kept under argon. 3,5-Diiodosalicylaldehyde (97%, *Sigma-Aldrich Chem-*

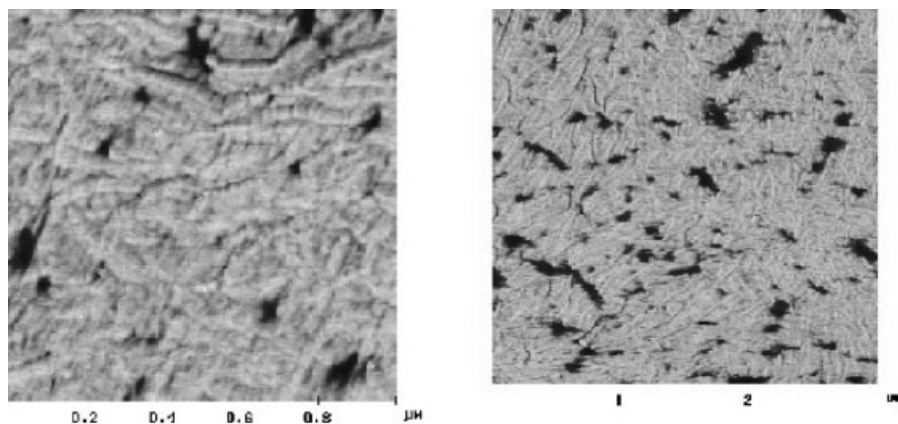
*icals*), 2,6-difluoro-aniline (97%, *Sigma-Aldrich Chemicals*) and titanium tetrachloride (>99%, *Fluka*) were used as received. *n*-Butyllithium was purchased as solution in hexane (1.6-M) from *Sigma-Aldrich Chemicals*. Methylaluminoxane was purchased as solution in toluene (10% g/v; 4.97 wt % Al) from *Crompton GmbH*. Ethylene (3.0) and propene (2.5) were obtained from *Messer-Griesheim*.

### Synthesis of N-(3',5'-diiodo-salicylidene)-2,6-difluoroaniline

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* flash chromatography over silicagel 60 (40–63 µm, *Merck*) / Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed and the imine was dried *in vacuo* over night (yield: 6.75 g, 86%).

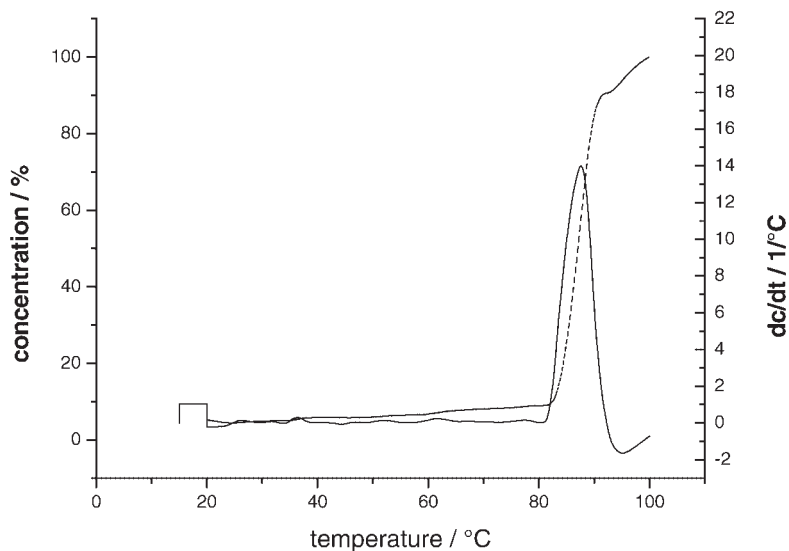
### Synthesis and Characterisation of 1

1.00 g N-(3',5'-diiodo-salicylidene)-2,6-difluoroaniline (2.062 mmol) were dissolved in toluene under argon atmosphere



**Figure 1.**

AFM images of PE-P(E-co-P) block copolymer (received from polymerisation using 10 µmol **1**, MAO with ratio Ti/Al = 1:2500, 300 mL toluene, 25 °C, 2 bar, 10 min. ethylene, then 1 h propylene, propene content in the block copolymer: 8 %). Left image: side length 1 µm, right below: side length 3 µm.



**Figure 2.**

CRYSTAF analysis of PE-*block*-P(E-*co*-P) received from polymerisation using 10  $\mu\text{mol}$  **1**, MAO with ratio Ti/Al = 1:2500, 300 mL toluene, 25 °C, 2 bar, 10 min. ethylene, then 1 h propylene, propene content in the block copolymer: 8%.

to give a yellow solution. At  $-78^\circ\text{C}$  1.1 eq. *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 hours. At  $-78^\circ\text{C}$   $\frac{1}{2}$  eq. (196 mg, 1.03 mmol) titanium tetrachloride were injected through a septum. The solution was warmed to ambient temperature and stirred for 16 hours. Then the reaction mixture was filtered over  $\text{Na}_2\text{SO}_4$ . The amount 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  $4^\circ\text{C}$  for two days. Then the solid was isolated, washed twice with cold heptane and once with few mL of cold toluene. Then **1** was dried *in vacuo* over night (yield: 610 mg, 55%). **1** was recrystallised from toluene to give orange needles.

#### General Procedure for the Homopolymerisation

The polymerisations were carried out using a semi-automated 600 mL polymerisation reactor (Multi-purpose polymerisation reactor) from Labeq AG. Polymerisation were carried out at  $25^\circ\text{C}$ , in 300 mL of

toluene at ethylene pressure of 2 bar. MAO was used as cocatalyst, using a ratio Ti/Al = 1:2,500. The reactor was filled with toluene and half the amount of cocatalyst (methylaluminoxane as solution in toluene, 10% g/v). Then the atmosphere was saturated with 2 bar of ethylene (gas feed 150 g/h) and the reactor was thermostated to  $25^\circ\text{C}$ . 7.5  $\mu\text{mol}$  (8.15 mg) of **1** 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 1 h, the reactor content was drained and the polymer was precipitated by pouring the reaction mixture in methanol/aq. HCl. The polymer was filtered and dried *in vacuo* over night at  $60^\circ\text{C}$ .

#### Procedure for the Copolymerisation

Polymerisations were carried out as described above. After injecting the toluene solution of the activated catalyst, the reaction mixture was stirred for 10 minutes at  $25^\circ\text{C}$  and 2 bar of ethylene pressure. After the preparation of the polyethylene segment, the atmosphere was evaporated and the propylene gas feed

(100 g/h) was initiated. The polymerisation was continued for 1 hour. Then the reactor content was drained and the polymer was isolated as described above.

### Analytical Techniques

NMR spectra were recorded on a Bruker ARX 300 spectrometer (299.87 MHz) using the solvent peaks as reference for  $^1\text{H}$ -spectra and  $^{13}\text{C}$ -spectra and external standard for the  $^{19}\text{F}$ -spectrum. High temperature spectra were recorded at 120 °C. Mass spectrometry and elementary analysis were carried out in the institute for organic chemistry and biochemistry of the Albert-Ludwigs-Universität in Freiburg/Br. A Finnigan TSQ7000 and a Vario EL for elemental analysis were used. HT-SEC was carried out using a triple column set (PLgel mixed-bed) and 1,2,4-trichlorobenzene stabilised with 2 mg/mL of Irganox 1010 as solvent at 140 °C. Molecular weight distributions were analysed by light scattering, viscosimetry and refractive index. Glass transition temperatures and melting points of the obtained polymers were detected using a Seiko 6200 differential scanning calorimetry (DSC). Atomic Force Microscopy (AFM) experiments were performed with a Nanoscope III scanning probe microscope. Images were taken at the fundamental resonance frequency of the Si cantilever (300 MHz). The flat surfaces that were examined were obtained by cutting the sample with a Diatome diamond knife at –45 °C using a ultramicrotome (Ultracut E, Reichert & Jung) equipped with a cryochamber. A CRYSTAF apparatus, model 200 from PolymerChar S. A., was used for fractionation. Samples (20 mg) were dissolved in 30 mL of distilled 1,2-dichlorobenzene at 160 °C. After dissolution, the temperature was decreased at a rate of 0.1 °C/min.

### Conclusions

The phenoxyimine complex **1** has been synthesised and characterised. After activation with MAO, the catalyst is highly active in living olefin polymerisation for the

preparation of polyethylene and poly(propylene) homopolymers as well as PE-*block*-P(E-*co*-P) block copolymers containing one crystalline PE and one amorphous flexible rubber-like block with very high molecular weight. On-line polymerisation kinetics showed linear mass consumption of the monomer gas and constant catalyst activity as expected for a living system. SEC analyses proved the number-average molar mass being dependent on polymerisation time. The formation of block copolymers was confirmed by means of AFM morphology studies and CRYSTAF experiments.

Living olefin polymerisation offers a new synthetic approach for the preparation of block copolymers which might be useful as compatibilizers in polymer blends for tailoring mechanical properties and the synthesis of new materials. Further studies on a systematic variation of the block lengths and analyses of the block copolymers are carried out at the moment and to be published soon.

**Acknowledgements:** The authors would like to thank Dr. M. Kowalski for NMR analyses, U. Westphal for HT-SEC, Dr. J. Wörth and C. Wirth for recording mass spectra and E. Hickl for carrying out the elementary analysis of **1** as well as A. Warmbold, F. Mießner and M. Strecker for technical assistance. We would especially like to thank L.-C. Heinz and Dr. Robert Brüll for carrying out CRYSTAF analyses of the block copolymers at the Deutsches Kunststoff-Institut in Darmstadt. This work was funded by Basell Polyolefine GmbH, BASF AG, Bundesministerium für Bildung und Forschung (BMBF project number 03C0354A and 03C0354B) and Fonds der Chemischen Industrie.

- [1] Coates, G. W.; Hustad, P. D.; Reinartz, S. *Angew. Chem.* **2002**, 114, 2341.
- [2] (a) Doi, Y.; Ueki, S.; Keii, T. *Macromolecules* **1979**, 12, 814. (b) Doi, Y.; Ueki, S.; Keii, T. *Macromol. Chem.* **1979**, 180, 1359.
- [3] (a) Matsui, S.; Fujita, T. *Catal. Today* **2001**, 66, 63. (b) Suzuki, Y.; Terao, H.; Fujita, T. *Bull. Chem. Soc. Jpn.* **2003**, 76, 1493. (c) Mitani, M.; Saito, J.; Ishii, S.-I.; Nakayama, Y.; Makio, H.; Matsukawa, N.; Matsui, S.; Mohri, J.-I.; Furuyama, R.; Terao, H.; Bando, H.; Tanaka, H.; Fujita, T. *The Chem. Record* **2004**, 4, 137.

- [4] (a) Mitani, M.; Mohri, J.; Yoshida, Y.; Saito, J.; Ishii, S.-I.; Tsuru, K.; Matsui, S.; Furuyama, R.; Nakano, T.; Tanaka, H.; Kojoh, S.-I.; Matsugi, T.; Kashiwa, N.; Fujita, T. *J. Am. Chem. Soc.* **2002**, 124, 3327. (b) Saito, J.; Mitani, M.; Mohri, J.-I.; Yoshida, Y.; Matsui, S.; Ishii, S.-I.; Kojoh, S.-I.; Kashiwa, N.; Fujita, T. *Angew. Chem.* **2001**, 113, 3002. (c) Ishii, S.-I.; Furuyama, R.; Matsukawa, N.; Saito, J.; Mitani, M.; Tanaka, H.; Fujita, T. *Macromol. Rapid Commun.* **2003**, 24, 452. (d) Mitani, M.; Nakano, T.; Fujita, T. *Chem. Eur. J.* **2003**, 9, 2396. (e) Mitani, M.; Fujita, T. *ACS Symp. Series* **2003**, 857, 26.
- [5] Fujita, T.; Tohi, Y.; Mitani, M.; Matsui, S.; Saito, J., Nitabaru, M.; Sugi, K.; Makio, H.; Tsutsui, T. (Mitsui Chemicals, Inc.) *Eur. Pat. Appl.* 1998, 164 pp., EP 0874005 A1 19981028.