

# COPOLYMERIZATION OF ETHYLENE AND 1-OLEFINS IN SUPERCRITICAL CO<sub>2</sub> BY AN ELECTRON POOR Ni(II) COMPLEX

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## Introduction

Late transition metal catalysts for polymerization of olefins have been studied intensely.<sup>1</sup> Due to their functional group tolerance, polymerizations can be carried out in oxygenated reaction media, amongst others dense carbon dioxide. Dense carbon dioxide, that is liquid or supercritical CO<sub>2</sub> (scCO<sub>2</sub>), possesses unique properties, such as the possibility of variation of its density and solvent processing, dense carbon dioxide can be useful as a solvent or suspension medium. It can be removed conveniently by reducing the medium density, resulting in a dry polymer powder.

Ethylene polymerization has been studied in scCO<sub>2</sub> with cationic Pd(II)-diimine catalysts.<sup>3</sup> Highly branched amorphous polyethylene is obtained invariably, which is due to a high rate of 'chain walking' compared to the rate of chain growth. An activity of 2×10<sup>3</sup> TO h<sup>-1</sup> was reported under the conditions studied.<sup>3</sup> We have reported ethylene homopolymerization with CO<sub>2</sub>-soluble neutral Ni(II) salicylaldiminato complexes.<sup>4</sup> Activities of up to 5×10<sup>3</sup> TO h<sup>-1</sup> were observed under the conditions studied. Linear semicrystalline polyethylenes with molecular weights up to M<sub>n</sub> = 2.4×10<sup>4</sup> g mol<sup>-1</sup> were obtained. Polymer crystallinities could be varied in a limited range via the choice of catalyst, by introduction of methyl branches as a result of 'chain walking'. However, with increased branching molecular weights decrease, as β-hydride elimination is a key step both for chain walking and chain transfer.

By copolymerization polymer crystallinities could be controlled over a wide range, and without an intrinsic correlation with molecular weight. This requires a suitable catalyst.

## Experimental

**Materials.** Complex **1** was prepared according to [5]. All manipulations were performed under inert atmosphere using standard schlenk techniques. NMR spectra of polyolefins were obtained in 1,1,2,2-tetrachloroethane-d<sub>2</sub> at 130°C. The branching structure was assigned according to [6]. Differential scanning calorimetry (DSC) was performed on a Netzsch Phoenix 204 F1 at a heating/cooling rate of 10 K min<sup>-1</sup>. DSC data reported are from second heating cycles. Polymer crystallinities were calculated based on a melt enthalpy of 293 J g<sup>-1</sup> for 100% crystalline polyethylene. Gel permeation chromatography (GPC) was performed in 1,2,4-trichlorobenzene at 160°C on a Polymer Laboratories 220 instrument equipped with PLgel Olexis-columns. Data reported were referenced to linear polyethylene standards.

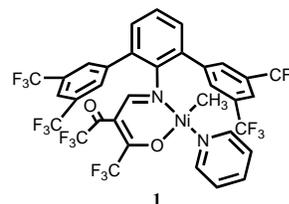
**Solubility measurements** were carried out as reported previously [7] in a custom-made setup at the LPCM CNRS-UMR 5803 in Bordeaux. Briefly, a magnetically stirred 5.5 cm<sup>3</sup> titanium cell with two silicon windows for the infrared (IR) absorption measurements (path length 25 mm), and two sapphire windows for direct observation of the solution to ensure that there is no demixing in the sample was employed. Pressures up to 50 MPa can be adjusted by a hydraulic system via a stainless steel capillary. Single beam IR spectra were obtained in the spectral range 400-6000 cm<sup>-1</sup> with 2 cm<sup>-1</sup> resolution by Fourier transformation of 50 accumulated interferograms acquired with a Biorad FTS-60A interferometer. Spectra were collected at 50°C at 6 to 35 MPa. The concentration of the solute was determined employing the Beer-Lambert law from the intensity of characteristic IR bands of the solute. The overall procedure was: 1) identification of suitable characteristic vibrational bands; 2) determination of the molar extinction coefficient for these bands, with a small quantity of solute completely solubilized at 50°C and 35 MPa (ρ = 0.9 g cm<sup>-3</sup>); 3) determination of the solubility with an excess of solute from the intensity of the selected bands.

**Typical polymerization.** Polymerizations were carried out in a high-pressure view cell supplied by NWA GmbH, Lörrach, Germany. The mechanically stirred stainless steel cell with an internal volume of 30 to 60 cm<sup>3</sup> adjustable by means of a piston operated by a hydraulic system is suited up to 100 MPa and 473.15 K. The cell is heated by two stainless steel cartridge heaters located in cavities in the cell wall, controlled by a thermocouple inside the cell. The pressure was measured with a bourdon type manometer. Gases were pumped into the cell by high pressure pumps up to the

desired pressure (up to 60 MPa for CO<sub>2</sub> and up to 40 MPa for ethylene). The rate of the ethylene addition was controlled by a two way HPLC valve, with an internal loop volume of 1 mL. The quantity of gases introduced was estimated by the piston position and the pressure. Prior to a polymerization experiment, the reactor was heated under a low pressure of CO<sub>2</sub> to the desired temperature for 30 min, and flushed 3 times with CO<sub>2</sub>. The solid catalyst precursor and the comonomer were added via a modified syringe. The reactor was filled with CO<sub>2</sub> to the desired pressure (10 MPa). Under continuous stirring the pressure was increased (to 30 MPa) by decreasing the cell volume, and the ethylene was added at continuous pressure. Polymerisations were carried out at a pressure of 65 MPa, obtained by decreasing the volume of the reactor.

## Result and Discussion

Complex **1** with a chelating enolatoimine ligand bearing an electron-withdrawing trifluoromethyl and trifluoroacetyl substituent has recently been found to be very active for ethylene polymerization in toluene as well as in aqueous emulsions.<sup>5,8</sup> Moderately branched polyethylenes of typically M<sub>w</sub> 3×10<sup>4</sup> g mol<sup>-1</sup> (M<sub>w</sub>/M<sub>n</sub> 2.0-2.5) and T<sub>m</sub> of 106-112°C are obtained.



**1** appeared promising for copolymerization in scCO<sub>2</sub> as 1) the six trifluoromethyl groups should provide solubility in the medium; 2) the compatibility with aqueous emulsions suggests stability also towards CO<sub>2</sub>; 3) the pronounced capability to insert also into secondary alkyl species, evidenced by the methyl branching of the polyethylenes formed with **1**, suggests that **1** should also be suited for 1-olefin copolymerization.<sup>9</sup>

As the cell used for solubility studies could not be charged under an inert atmosphere, solubility studies were not carried out with **1** but with the corresponding ligand, 3-[(2,6-Di(3,5-bis(trifluoromethyl)phenyl)phenyl)-amino]methylene]-1,1,1,5,5,5-hexafluoropentane-2,4-dione. Solubilities at 50 °C were 0.1 mmol L<sup>-1</sup> at ρ(CO<sub>2</sub>) = 0.22 g mL<sup>-1</sup>; 7.4 mmol L<sup>-1</sup> at ρ(CO<sub>2</sub>) = 0.38 g mL<sup>-1</sup>; and > 9.2 mmol L<sup>-1</sup> at ρ(CO<sub>2</sub>) = 0.70 g mL<sup>-1</sup>. This suggests that **1** indeed is soluble under the typical conditions of polymerization experiments (vide infra).

Polymerization of ethylene, and copolymerization with 1-hexene (H) and norbornene (NB) in scCO<sub>2</sub> was studied (Table 1). An immediate onset of turbidity was observed after reaching reaction conditions due to precipitation of the polyethylene formed. This shows that no induction period occurs, and polymerization starts immediately. After decompression of the reaction mixture, the polymers were obtained in dry form.

Table 1. Polymerization In scCO<sub>2</sub>.<sup>[a]</sup>

entry	1	2	3	4
ethylene [g]	9	3	3	7
comonomer	-	3.4 g H	1 g NB	1 g NB
TOF <sup>[b]</sup>	23200	4280	780	2000
polymer yield [g]	3.75	1.10	0.25	0.60
M <sub>n</sub> <sup>[c]</sup> [g mol <sup>-1</sup> ]	83800	15000	27300	16400
M <sub>w</sub> /M <sub>n</sub> <sup>[c]</sup>	1.9	5.7	2.4	7.0
T <sub>m</sub> <sup>[d]</sup> [°C]	117	105	71	94
crystallinity <sup>[d]</sup>	43%	36%	<20%	24%
X <sub>comon.</sub> <sup>[e]</sup> [mol-%]	-	1%	6%	2.5%

<sup>[a]</sup> Reaction conditions: 10 μmol **1**, 50°C, 65 MPa, 1 h. <sup>[b]</sup> TOF = average turnover frequency, in mol (olefin converted) mol(Ni)<sup>-1</sup>h<sup>-1</sup>. <sup>[c]</sup> Determined by GPC. <sup>[d]</sup> Determined by DSC. <sup>[e]</sup> Determined by <sup>13</sup>C NMR.<sup>5</sup>

A remarkably high average polymerization activity of 2.3×10<sup>4</sup> TO h<sup>-1</sup> is observed, at the same time polymer with a molecular weight approaching 10<sup>5</sup> g mol<sup>-1</sup> is obtained (entry 1). As expected,<sup>9,10</sup> comonomer incorporation results in reduced catalyst activities due to a slow insertion of the bulky comonomer and/or a slow insertion into the bulky alkyl species formed after comonomer

insertion, but catalyst activities are still reasonable. As observed for polymerizations in organic solvents with other neutral Ni(II) complexes, ethylene incorporation is preferred over comonomer incorporation; the ratio of comonomer incorporated in the polymer ( $X_{\text{comon.}}$ ) is much lower than its molar fraction in the reaction mixture. Nonetheless, crystallinity can be reduced substantially by comonomer incorporation, and the melting point varied over a large range (entries 2 to 4). Note that in addition to the branches introduced with the comonomer, all polymer possess ca. 10 methyl branches originating from ethylene monomer, which also somewhat reduce crystallinity.

## Conclusion

Catalyst precursor **1** enables catalytic ethylene polymerization in supercritical carbon dioxide with unprecedented catalyst activities, affording higher molecular weight polymer. Control of polymer crystallinity, and melting point, over a wide range is possible by copolymerization with 1-hexene or norbornene.

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