

# Polymorphism of a nickel polymerization catalyst

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Dedicated to Prof. Erker on the occasion of his 60th birthday.

## Abstract

Two polymorphs of an highly active nickel(II) salicylaldiminato polymerization catalyst are reported, which to our knowledge represent the first examples of polymorphism of catalytically active polymerization catalysts. The two structures differ significantly in the coordination geometry of the central metal atom. Lattice energy calculations were used to analyze the different solid state structures. © 2007 Elsevier B.V. All rights reserved.

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## 1. Introduction

For many organic and inorganic compounds different crystal structures, i.e. polymorphic forms, are known. This is of great economic importance since separate patents can be obtained for different polymorphic forms. It is especially important in the field of pharmaceuticals or organic pigments, where it might lead to a prolonged patent protection. In one case Glaxo could maintain the patent for “Zantac” (sales of 3.3 billion US-\$ in 1992) for some additional years due to a patent on an (unintentionally formed) polymorphic form, which lasted longer than the patent on the molecule itself [1].

Similar cases are known for organic pigments, where usually an extensive polymorph-screening is conducted

[2,3]. While for pharmaceuticals the registration depends on the polymorphic form, an individual registration of polymorphic forms is not necessary for color pigments and fine chemicals. The solid state properties depend on the polymeric form. This is not only true for pigments (for which e.g. color shade and light stability depend on the crystal phase [4]) but also for heterogeneous catalysts, where the catalytic activity may strongly depend on the crystal structure [5–8].

Several studies show that possible crystal structures for simple organic molecules can nowadays be predicted with quite good accuracy [9–14]. But it is almost impossible to decide which of the predicted crystal structures will be formed during an experiment and what procedure leads to one particular polymorphic form [15]. In contrast to organic or inorganic substances much less attention had been paid to the polymorphism of organometallic compounds [16–19] although for certain compounds more than 10 different forms are known [20]. Organometallic compounds are involved as catalysts, precatalysts or intermediates in many homogeneous and heterogeneous processes. Therefore the question of polymorphism may also become

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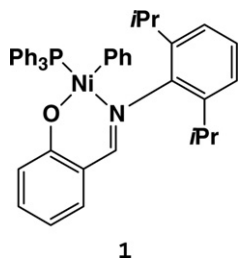


Fig. 1. Nickel complex **1**.

more and more important in this field. We want to report one example, a nickel(II) polymerization catalyst (**1**, Fig. 1) where we were able to obtain and fully characterize two polymorphic forms.

Since the mid-1990s the area of transition metal catalyzed olefin polymerization was extended by highly active nickel(II) catalysts [21–24]. In his seminal work Brookhart et al. introduced the class of nickel diimine catalyst, which are able to produce linear to highly branched polyethylene [25]. Analogous to metallocenes they are activated by methyl aluminoxane (MAO). In contrast, the Grubbs group later developed new neutral catalyst systems, which in most cases are active without the need for a cocatalyst like MAO. This is a great advantage over the previously known catalysts because now also functionalized monomers can be employed in polymerization reactions [26,27]. This class of neutral, highly active catalysts is based on salicylaldiminato ligands. In our study we investigate one representative of this interesting class of catalysts, which has gotten a lot of attention during the last years [28,29].

## 2. Results and discussion

Compound **1** could be obtained by the reaction [26] of the sodium salt of the ligand with *trans*-[NiCl(Ph)(PPh<sub>3</sub>)<sub>2</sub>], for which we recently developed a straight-forward one-pot synthesis [30]. During our work with **1** we surprisingly found that some of the yellow product obtained from the synthesis changes its color to red over the period of some days. From a crystal growth screening using different solvent systems we succeeded to gain yellow single-crystals (**1<sub>yellow</sub>**) from slow diffusion of hexane into a concentrated solution in toluene. On the other hand red crystals (**1<sub>red</sub>**) could be obtained by slow evaporation of a toluene solution. It should be noted, that solutions of **1** show an intense red color. Elemental analysis of both substances showed good agreement with the calculated values. A single crystal analysis of both crystals revealed two polymorphic forms of **1**.

The central coordination geometry is depicted in Fig. 2; important geometric data of both structures are given in Table 1. Two different views from the side (A) and from on top (B) are provided to better describe the differences between the structures.

One interesting difference in the solid state structures is a stronger distortion of the square-planar coordination

geometry in **1<sub>red</sub>**. The tendency towards a tetrahedral environment in this structure is obvious from the smaller P–Ni–N– and O–Ni–C angles. Furthermore, the arrangement of the phenolate ring (C11–C16) differs significantly relative to the nickel coordination plane. In **1<sub>yellow</sub>** the nickel plane is almost coplanar with the phenolate whereas in **1<sub>red</sub>** the salicylaldimine moiety is strongly bent away. The angle between the planes N1–Ni–O1 and O1–C16–C11–C1–N1 differs significantly (red: 31.09(8)°; yellow: 14.3(1)).

Furthermore, one isopropyl group in **1<sub>red</sub>** reveals a disorder on two orientations. Lattice energy calculations show that both orientations result in very similar lattice energies, which explains the disorder in the solid state (see Section 4). The polymorphic structures observed herein are best described as conformational polymorphs, since the molecule crystallizes in different conformations [19].

Looking at the molecular conformations in the solid state the question arises if they are simply a consequence of packing effects. In other words, is the formation of the yellow crystal phase from a red solution favorable because of a higher lattice energy? Lattice energy calculations using the software CRYSCA [31] show, that this is not the case. The lattice energy (without intramolecular terms) of the yellow polymorph is about 13 kJ/mol higher than that of the red form (for details see Section 4). This is consistent with the lower density of the yellow form; hence the molecular packing is less efficient.

To get further insight into the thermodynamic properties of both crystal phases we looked at the crystallization behavior of **1**. The yellow crystals grow by slow diffusion of hexane into a concentrated solution of **1** in toluene, whereas the red crystals are formed by slow evaporation from toluene. As noted before, we observed that some of the yellow powder obtained from the synthesis from toluene/hexane turns red after some days. This implies that **1<sub>yellow</sub>** is only the metastable kinetic crystallization product. This is converted to the red form if some crystal seeds of the latter are present. This means that **1<sub>red</sub>** is the thermodynamically more stable form in the solid state. Solutions of **1** show a deep red color, therefore also in solution the conformation of **1<sub>red</sub>** should be present in noticeable amounts.

Aside from the X-ray structure determinations the conformational flexibility is also evident from <sup>1</sup>H NMR spectroscopy. Besides the main signals of **1<sub>red</sub>** (corresponding to published data [26]) small resonances of a second species are visible (with about 8% intensity from NMR integration). They are strongly shifted to lower field ( $\delta = 4.28$  for –CH–, 1.48 and 1.28 ppm for –CH<sub>3</sub>). Similar results were observed for complexes with halogen substituted ligands [32,33]. A low temperature NMR measurement showed that indeed the second resonances are temperature dependent and presumably caused by **1<sub>yellow</sub>**. No further resonances are visible in a <sup>1</sup>H NMR spectrum at –100 °C in CD<sub>2</sub>Cl<sub>2</sub>. This does not change even after warming the NMR tube to RT again for some minutes. The signals of the second species arise only slowly and are not complete

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