Borane Activators for Nickel Catalysts for Olefin Polymerization

Paul-Gerhard Lassahn, Christoph Janiak, and Jae-Seung Oh

Abstract

Activation of Ni(acetylacetonate)\(_2\) and Ni(2-ethylhexanoate)\(_2\) with B(C\(_6\)F\(_5\))\(_3\) and BtCöFs\(^+/\)) triethylaluminium leads to highly active catalyst systems for the vinyl polymerization of norbornene.

Introduction

In recent years, an extraordinary amount of research has been directed toward the development of single-site metallocene olefin polymerization catalysts [1 - 4]. An important cocatalyst for the activation of early transition-metal group IV metallocene catalysts is tris(pentafluorophenyl)borane B(C\(_6\)F\(_5\))\(_3\) (1) [1]. The borane abstracts an alkyl or hydride group from the metallocene pre-catalysts, becomes an anion and generates a cationic, 14-valence-electron metallocenium species as a highly active olefin polymerization catalyst.

Currently, the late transition metals, in particular nickel and palladium, are seeing a renewed interest as olefin polymerization catalysts [5 - 7]. Some of these late transition-metal complexes are cationic species with weakly bound ligands [6, 8]. Hence, they are active (mostly towards ethene polymerization) without the help of a cocatalyst. Others have to be activated by methylalumoxane (MAO) [9] or by so-called phosphine scavengers, such as Ni(cod)\(_2\) or rhodium complexes to abstract phosphorus-bound ligands [10].

During our work we became aware that borane activators were also claimed in a patent by Goodall et al. [12]. They have also been communicated by the same author at conferences [13] but not published in regular journals. A careful literature search did not reveal any journal publications by Goodall on borane activators for late transition metals. Only in a recent paper by Bazan et al. 1 was used as a cocatalyst for nickel complexes in the polymerization of ethene [14]. Thus, the results reported here represent the first more detailed disclosure in the open literature. Activation by MAO has been described before [15].

The homopolymer vinyl-poly(norbomene) (5) is of interest as a specialty polymer with good mechanical strength, heat resistivity, and optical transparency, e.g. for deep ultraviolet photoresists, inter-
The results of the polymerization of norbornene with different catalytic systems (complexes and activators) are summarized in Table 1 and Fig. 1.

The nickel complexes 3 and 4 can be transformed into highly active catalysts for the vinyl polymerization of norbornene (Nb) with the precatalysts 3 and 4 in combination with different cocatalysts.

### Table 1. Polymerization of norbornene (Nb) with the precatalysts 3 and 4 in combination with different cocatalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Time [min]</th>
<th>Conversion [%]</th>
<th>Activity [g polymer/mol catalyst]</th>
<th>$M_n$ [g mol$^{-1}$]</th>
<th>$M_v$ [g mol$^{-1}$]</th>
<th>$M_n/M_v$</th>
</tr>
</thead>
<tbody>
<tr>
<td>MAO/3 $^b$</td>
<td>1</td>
<td>28.0</td>
<td>1.6 x 10$^5$</td>
<td>5.1 x 10$^5$</td>
<td>3.2</td>
<td></td>
</tr>
<tr>
<td>3/B(C$_6$F$_5$)$_3$/TEA $^c$</td>
<td>1</td>
<td>54.8</td>
<td>3.1 x 10$^5$</td>
<td>8.2 x 10$^4$</td>
<td>3.2</td>
<td></td>
</tr>
<tr>
<td>3/TEA/B(C$_6$F$_5$)$_3$ $^c$</td>
<td>1</td>
<td>18.8</td>
<td>1.1 x 10$^5$</td>
<td>2.3 x 10$^5$</td>
<td>1.8</td>
<td></td>
</tr>
<tr>
<td>3/B(C$_6$F$_5$)$_3$ $^d$</td>
<td>1</td>
<td>98.9</td>
<td>5.6 x 10$^5$</td>
<td>5.1 x 10$^5$</td>
<td>2.3 $^f$</td>
<td></td>
</tr>
<tr>
<td>3/TEA $^e$</td>
<td>60</td>
<td>-</td>
<td>no activity observed</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>3/B(C$_6$H$_5$)$_3$ $^d$</td>
<td>1</td>
<td>26.7</td>
<td>1.5 x 10$^6$</td>
<td>3.1 x 10$^5$</td>
<td>2.7</td>
<td></td>
</tr>
<tr>
<td>4/B(C$_6$F$_5$)$_3$/TEA $^c$</td>
<td>2</td>
<td>56.9</td>
<td>1.6 x 10$^5$</td>
<td>1.7 x 10$^5$</td>
<td>4.5 $^g$</td>
<td></td>
</tr>
<tr>
<td>4/TEA/B(C$_6$F$_5$)$_3$ $^c$</td>
<td>2</td>
<td>13.3</td>
<td>3.8 x 10$^5$</td>
<td>2.0 x 10$^5$</td>
<td>2.0</td>
<td></td>
</tr>
<tr>
<td>4/B(C$_6$F$_5$)$_3$ $^d$</td>
<td>60</td>
<td>66.7</td>
<td>6.3 x 10$^4$</td>
<td>2.7 x 10$^5$</td>
<td>6.0 x 10$^5$</td>
<td>2.2 $^f$</td>
</tr>
<tr>
<td>4/TEA $^e$</td>
<td>60</td>
<td>-</td>
<td>no activity observed</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>4/B(C$_6$H$_5$)$_3$ $^d$</td>
<td>60</td>
<td>-</td>
<td>no activity observed</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>4/B(C$_6$H$_5$)$_3$/TEA $^e$</td>
<td>60</td>
<td>-</td>
<td>no activity observed</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>

$a$ The ordering of the components refers to the order of addition to the monomer solution; $^b$ 10.6 mmol Nb, [Cat]:[Nb] = 1:1000, total volume: 10.0 ml; $^c$ 30.1 mmol Nb, [Cat]:[Nb] = 1:1000, [Cat]:[B]:[Al] = 1:9:10, total volume: 40.0 ml; $^d$ 30.1 mmol Nb, [Cat]:[Nb] = 1:1000, [Cat]:[B] = 1:9, total volume: 40.0 ml; $^e$ 30.1 mmol Nb, [Cat]:[Nb] = 1:1000, [Cat]:[Al] = 1:10, total volume: 40.0 ml; $^f$ the samples were not completely soluble in 1,2,4-trichlorobenzene; the GPC data corresponds to the data of the soluble part of the polymer; $^g$ bimodal molar mass distribution.

**Experimental Section**

**Materials and instruments**

Nickel(II)(acetylacetonate)$_2$ (Merck), nickel(II)(2-ethylhexanoate)$_2$ (Aldrich), triphenylborane B(C$_6$H$_5$)$_3$ (Aldrich), tris(pentafluorophenyl)borane B(C$_6$F$_5$)$_3$ (Aldrich), methylalumoxane (10% solution in toluene, Witco), and triethylaluminium (TEA, 1 molar solution in hexane, Merck-Schuchardt) were used as received. Toluene was dried over sodium metal and distilled under nitrogen. Norbornene (bicyclo[2.2.1]hept-2-ene) (Aldrich) was purified by distillation and used as a solution in toluene. All work involving air- and/or moisture-sensitive compounds was carried out by using standard vacuum, Schlenk or drybox techniques.

IR spectra (KBr pellet) were measured on a Bruker Optik IFS 25. Gel permeation chromatography (GPC) analyses were performed on a polymer solution in 1,2,4-trichlorobenzene (concentration of 2 - 3 g/ml). The GPC was measured at 140°C with an injection volume of 200 µl and with a rate of 1 ml/min.

**Typical polymerization procedure**

Polymerizations were conducted at room temperature in a water bath to ensure a constant temperature. The precatalyst solutions in toluene followed by the co-catalyst components were added via syringe to the norbornene / toluene solution and the mixture was stirred with a magnetic stirrer. The polymerizations were stopped by addition of a 10:1 methanol / conc. HCl mixture. The precipitated polymer was filtered, washed with methanol and dried in vacuo for 5 h. The IR spectra of the polymer obtained with the catalysts 3 and 4 showed the absence of bands for double bonds in the range 1620 to 1680 cm$^{-1}$. This ensured the vinyl-type polymerization instead of a ring-opening metathesis polymerization (ROMP).

**Results and Discussion**
We admit that the work is still empirical at this stage and we cannot, as yet, provide a detailed mechanistic understanding. But we hope that this report may help to initiate such mechanistic investigations. We note that first reports on metalloocene/MAO catalysts [16] or on the 2,6-bis(imino)pyridyliron and cobalt/MAO catalysts for ethene polymerization [17] were also empirical only. Mechanistic investigations with MAO as cocatalyst cause the problem that proposals for mechanism and active species are difficult to verify since the exact composition and structure of MAO are still not entirely clear [4,18].

The polymerizations with the well-defined catalyst 1 in combination with or without TEA opens the door for mechanistic investigations. It may be envisioned that the oxophilic borane will coordinate to the oxygen donor atom and, thereby, create vacant coordination sites. The start species may be a nickel hydride formed by traces of appropriate impurities, such as water.

The high Lewis acidity of 1 with its perfluorated phenyl-ligands plays an important role in this kind of activation. No polymerization activity was observed by using the weaker Lewis acid 2 as a catalyst for the polymerization of norbornene with the precatalysts 3 and 4.

Usually the norbornene polymers obtained with the nickel catalysts 3 and 4 were soluble in 1,2,4-trichlorobenzene with a concentration of 2 - 3 mg/ml, and it was possible to characterize the samples with GPC. However, an activation of 3 and 4 with 1 alone resulted in polymers which were only partly soluble in 1,2,4-trichlorobenzene. This decrease in the solubility may either be caused by a higher molar mass fraction or by more stereoregularty polymer fractions. The polymer samples displayed a monomodal molar mass distribution with the exception of the polymers catalyzed with the system 4 / B(C_6F_5)_3 / TEA (bimodal molar mass distribution with $M_w = 1.1 \cdot 10^6$ and $M_w = 1.1 \cdot 10^5$ g·mol^{-1}). The molar mass ($M_n$) is rather high, when taking into account the metal-to-monomer ratio of 1:1000. An $M_n$ of $5.1 \cdot 10^5$ g·mol^{-1} for the polymerization of norbornene ($M_{norbornene} = 94.16$ g·mol^{-1}) with the system 3 / B(C_6F_5)_3 corresponds to an average chain length of about 5400 monomer units. If each active metal center gives rise to a minimum of one chain then the fraction of active metal atoms is at most about 18%. An average chain length of 5400 monomer units reached after 60 s translates into...
a turnover frequency for the insertion reaction of about 90 s⁻¹. Similarly, the system \(3 / \text{B(C₆F₅)₃} / \text{TEA}\) would give a fraction of active metal atoms of 63% because of the lower \(M_n\) (8.2·10⁴ g·mol⁻¹, 870 monomer units average). With more than one chain per metal atom, the fraction of catalytically active centers would be lowered, of course. The calculated fraction of active metal atoms and the turnover frequency of the other polymerizations are between 6% to 16% and 18 s⁻¹ to 55 s⁻¹, respectively.

The molar mass distribution \(Q = M_M / M_n\) for monomodal distributions was usually rather narrow, often with a dispersion of around 2. A value of \(Q \approx 2\) is the theoretical dispersity for a Schulz-Flory type distribution arising from an ideally behaved polymerization reaction with a chain-termination reaction. A dispersity of \(Q \approx 2\) would then indicate a single-site character, i.e. a highly homogeneous structure of the active catalyst species. At present we can, however, not rule out a living polymerization with a broadening of the dispersion due to polymer precipitation and diffusion control in the increasingly viscous reaction mixture.

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