Borane activators for nickel catalysts for olefin polymerization

Paul-Gerhard Lassahn[a], Christoph Janiak[a], and Jae-Seung Oh[b]

[a] Institut für Anorganische Chemie, Universität Freiburg, Albertstr.21, D-79104 Freiburg, Germany

[b] LG Chem Research Park, 104-1,Moonji-dong, Yusong-gu, Taejon 305-380, Korea

Reprint requests to Prof. Dr. C. Janiak. Fax: +49(0)761-2036147. E-mail: janiak@uni-freiburg.de

Activation of Ni(acetylacetonate)$_2$ and Ni(2-ethylhexanoate)$_2$ with B(C$_6$F$_5$)$_3$ and B(C$_6$F$_5$)$_3$/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 [1,2,3,4]. 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 [5,6,7]. 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

1

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].

Here, we describe the use of the organo-Lewis acid tris(pentafluorophenyl)borane, B(C$_6$F$_5$)$_3$ (**1**) [11], and **1**/TEA, in comparison with MAO or triphenylborane, B(C$_6$H$_5$)$_3$ (**2**) as an activator towards the nickel complexes Ni(II)(acetylacetonate)$_2$ (**3**) and Ni(II)(2-ethylhexanoate)$_2$ (**4**) in the vinyl polymerization of norbornene.

((drawings 1-4 here))

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. was **1** 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(norbornene) (**5**) is of interest as a specialty polymer with good mechanical strength, heat resistivity, and optical transparency, e.g. for deep ultraviolet photoresists, interlevel dielectrics in microelectronics applications or as cover layers for liquid-crystal displays. Catalysts described in the literature for the vinyl homo-polymerization of norbornene are commonly activated with methylalumoxane (MAO) except for the cationic palladium-complexes [Pd(NCR)$_4$]$^{2+}$2L$^-$ (NCR: weakly bound nitrile-ligand; L: „non"-coordinating counter ion) [15].

((drawing 5 here))

Experimental

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 pre-catalyst 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 poly(norbornene)s 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

The results of the polymerization of norbornene with the different catalytic systems (complexes and activators) are summarized in Table 1 and Figure 1.

((Table 1 and Fig. 1 here))

The nickel complexes **3** and **4** can be transformed into highly active catalysts for the vinyl polymerization of norbornene in combination with appropriate borane-containing cocatalysts.

Both precatalysts **3** and **4** exhibit a higher or comparable activity with $B(C_6F_5)_3$/TEA and with MAO. Complex **3** also shows a strong increase in activity with $B(C_6F_5)_3$ alone relative to MAO activation. Within one minute a monomer conversion of nearly 100% could be achieved from the catalyst **3/1**. We point out that the required cocatalyst quantities were much less for **1** than for MAO in order to reach similar monomer conversions and activities (molar ratios of metal:borane = 1:9 and metal:MAO = 1:100). This leads to fewer cocatalyst residues in the polymer which is highly advantageous for prospective optical applications of poly(norbornene). An activation of **3** with the cocatalyst system **1**/TEA decreased the conversion and the polymerization activity in comparison to the polymerization with the cocatalyst **1** alone. Changing the sequence of addition of the catalytical components from **3**→**1**→TEA to **3**→TEA→**1** led to a further drop in the polymerization activity. Thus, TEA appears to be somewhat deactivating at least towards **3**.

With the precatalyst **4**, the cocatalyst combination of **1**/TEA delivered nearly the same polymerization results as the cocatalyst MAO. Again, the molar ratio of metal:borane (1:9) was much lower than that of metal:MAO (1:100). Changing the sequence of addition from **4**→**1**→TEA to **4**→TEA→**1** resulted in a decrease of the polymerization activity by a factor of 4. The activation of **4** by the borane **1** alone resulted in only a low polymerization activity. Still, it is important to note that **1** can function as a sole activator towards the nickel complexes **3** and **4**. Further investigations are clearly necessary to understand the role of TEA.

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 metallocene/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 cocatalyst **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 cocatalyst 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 stereoregulary polymer fractions. The polymer samples displayed a monomodal molar mass distribution with the exception of the polymers catalyzed with the system **4**/B(C$_6$F$_5$)$_3$/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$_6$F$_5$)$_3$ 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**/B(C$_6$F$_5$)$_3$/TEA would give a fraction of active metal atoms of 63% because of the lower M$_n$ ($8.2 \cdot 10^4$ 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 $Q = M_w/M_n$ 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.

[1] E.Y.-X. Chen, T.J. Marks, Chem. Rev. **100**, 1391 (2000).

[2] G.W. Coates, Chem. Rev. **100**, 1223 (2000).

[3] W. Kaminsky, Macromol. Chem. Phys. **197**, 3907 (1996).

[4] C. Janiak "Metallocene Catalysts for Olefin Polymerization" in A. Togni, R.L. Halterman (eds.): Metallocenes, p. 547, Wiley-VCH, Weinheim (1998).

[5] S.D. Ittel, L.K. Johnson, M. Brookhart, Chem. Rev. **100**, 1169 (2000).

[6] S. Mecking, Coord. Chem. Rev. **203**, 325 (2000).

[7] S. Mecking, Angew. Chem. Int. Ed. **40**, 534 (2001).

[8] see for example: Z. Guan, P.M. Cotts, E.F. McCord, S. J. McLain, Science **283**, 2059 (1999); S.Y. Desjardins, K.J. Cavell, J.L. Hoare, B.W. Skelton, A.N. Sobolev, A.H. White, W. Keim, J. Organomet. Chem. **544**, 163 (1997); A. Held, F.M. Bauers, S. Mecking, Chem. Commun. 301 (2000).

[9] see for examples: C.M. Killian, L.K. Johnson, M. Brookhart, Organometallics **16**, 2005 (1997); D.P. Gates, S.A. Svejda, E. Onate, C.M. Killian, L.K. Johnson, P.S. White, M. Brookhart, Macromolecules **33**, 2320 (2000).

[10] see for examples: U. Klabunde, S.D. Ittel, J. Mol. Catal. **41**, 123 (1987); K. Kurtev, A. Tomov, J. Mol. Catal. **88**, 141 (1994).

[11] C. Janiak, L. Braun, T.G. Scharmann, F. Girgsdies, Acta Crystallogr. **C54**, 1722 (1998).

[12] L.H. McIntosh III, B.L. Goodall, R.A. Shick, S. Jayaraman, Patent US5912313 (1999) B.F. Goodrich Company (USA), Chem. Abstr. **127**, 110414m (1997).

[13] B.L. Goodall, B.F. Goodrich Company (USA), Book of Abstracts, 215th ACS National Meeting, Dallas, March 29-April 2 (1998), Conference Meeting Abstract, INOR-263. American Chemical Society, Washington DC

[14] B.Y. Lee, G.C. Bazan, J. Vela, Z.J.A. Komon, X. Bu, J. Am. Chem. Soc. **123**, 5352 (2001).

[15] C. Janiak, P.G. Lassahn, J. Mol. Catal. A: Chem. **166**, 193 (2001). C. Janiak, P.G. Lassahn, Macromol. Rapid Commun. **22**, 479 (2001).

[16] A. Andresen, H.-G. Cordes, J. Herwig, W. Kaminsky, A. Merck, R. Mottweiler, J. Pein, Hj. Sinn, H.-J. Vollmer, Angew. Chem. **88**, 689 (1976).

[17] G. J. P. Britovsek, V. C. Gibson, B. S. Kimberley, P. J. Maddox, S. J. McTavish, G. A. Solan, A. J. P. White, D. J. Williams, Chem. Commun. 849 (1998).

[18] C. Janiak, B. Rieger, R. Voelkel, H.-G. Braun, J. Polym. Sci., Polym. Chem. **31**, 2959 (1993).

Figure Caption

Fig. 1. Polymerization activities of **3** and **4** with different cocatalyst in the polymerization of norbornene. Detailed conditions are given in Table 1. The ordering of the cocatalyst components $B(C_6F_5)_3$ and TEA in the legend refers to the order of addition to the reaction solution.