

# Nickel(II) and Palladium(II) Complexes with $\alpha$ -Dioxime Ligands as Catalysts for the Vinyl Polymerization of Norbornene in Combination with Methylaluminumoxane, Tris(pentafluorophenyl)borane, or Triethylaluminum Cocatalyst Systems\*

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Received 31 January 2002; accepted 24 July 2002

**ABSTRACT:** Nickel(II) and palladium(II) complexes with  $\alpha$ -dioxime ligands dimethylglyoxime, diphenylglyoxime, and 1,2-cyclohexanedionedioxime represent six new precatalysts for the polymerization of norbornene that can be activated with methylaluminumoxane (MAO), the organo-Lewis acid tris(pentafluorophenyl)borane [B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>], and triethylaluminum (TEA) AlEt<sub>3</sub>. The palladium but not the nickel precatalysts could also be activated by B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> alone, whereas two of the three nickel precatalysts but none of the palladium systems are somewhat active with only TEA as a cocatalyst. It was possible to achieve very high polymerization activities up to  $3.2 \cdot 10^7$  g<sub>polymer</sub>/mol<sub>metal</sub> · h. With the system B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>/AlEt<sub>3</sub>, the activation process can be formulated as the following two-step reaction: (1) B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> and TEA lead to an aryl/alkyl group exchange and result in the formation of Al(C<sub>6</sub>F<sub>5</sub>)<sub>n</sub>Et<sub>3-n</sub> and B(C<sub>6</sub>F<sub>5</sub>)<sub>3-n</sub>Et<sub>n</sub>; and (2) Al(C<sub>6</sub>F<sub>5</sub>)<sub>n</sub>Et<sub>3-n</sub> will then react with the precatalysts to form the active species for the polymerization of norbornene. Variation of the B:Al ratio shows that Al(C<sub>6</sub>F<sub>5</sub>)Et<sub>2</sub> is sufficient for high activation. Gel permeation chromatography indicated that it was possible to control the molar mass of poly(norbornene)s by TEA or 1-dodecene as chain-transfer agents; the molar mass can be varied in the number-average molecular weight range from  $2 \cdot 10^3$  to  $9 \cdot 10^5$  g · mol<sup>-1</sup>. © 2002 Wiley Periodicals, Inc. *J Polym Sci Part A: Polym Chem* 40: 3604–3614, 2002

**Keywords:** chain transfer; polyolefins; transition metal chemistry; norbornene; nickel catalysts; palladium catalysts

## INTRODUCTION

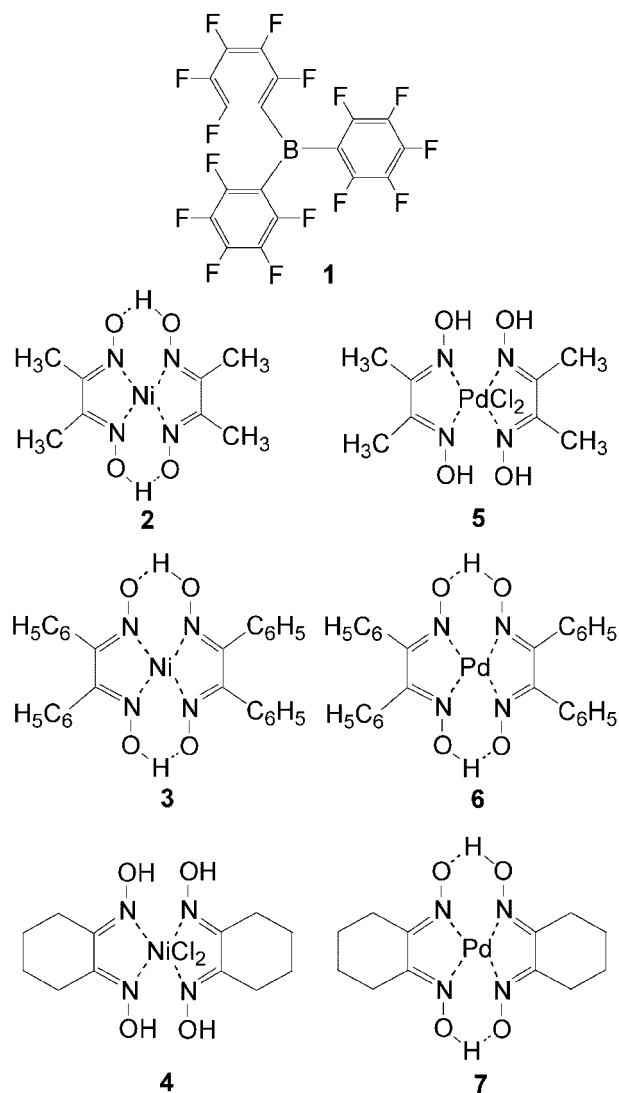
Norbornene (Nb) (bicyclo[2.2.1]hept-2-ene) can be polymerized via ring-opening metathesis poly-

merization (ROMP),<sup>1–3</sup> cationic or radical polymerization,<sup>4–7</sup> and by olefin addition polymerization (vinyl-type polymerization). In the latter, the bicyclic structural unit remains intact, and only the double bond of the  $\pi$  component is opened. Catalysts containing the metals titanium,<sup>8,9</sup> zirconium,<sup>10–14</sup> and chromium<sup>15</sup> as well as the late transition metals cobalt,<sup>16–18</sup> nickel,<sup>19–31</sup> and palladium<sup>32–44</sup> are described in the literature for the vinyl-type polymerization of Nb.<sup>45–52</sup> The late

\*Dedicated to Prof. Walter Heitz on the occasion of his 70th birthday.

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*Journal of Polymer Science: Part A: Polymer Chemistry*, Vol. 40, 3604–3614 (2002)  
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Scheme 1

transition-metal complexes are commonly activated by methylaluminumoxane (MAO),<sup>20–23,33,45</sup> except for the cationic palladium complexes  $[\text{Pd}(\text{NCR})_4]^{2+}2\text{L}^-$  (NCR: weakly bound nitrile ligand; L: “noncoordinating” counterion).<sup>34–44</sup> Another possibility to activate late transition-metal complexes is the organo-Lewis acid tris(pentafluorophenyl)borane,  $\text{B}(\text{C}_6\text{F}_5)_3$  (**1**), with or without triethylaluminum (TEA).<sup>19,32,46–52</sup> This cocatalyst system was first mentioned for the activation of early transition-metal group IV metallocene catalysts in olefin polymerization<sup>53–59</sup> and recently in the activation process of late transition-metal complexes for the polymerization of cyclopentene<sup>60</sup> and ethene.<sup>61</sup> In the polymerization of

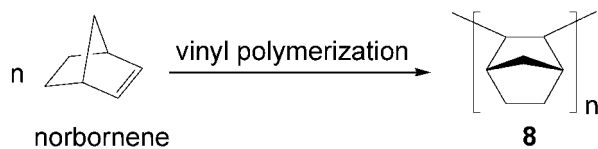
Nb or Nb derivatives, respectively, in the copolymerization of ethylene and Nb-type monomers, the cocatalyst system  $\text{B}(\text{C}_6\text{F}_5)_3/\text{TEA}$  has been described only in a series of patents of the B.F. Goodrich Co.<sup>46–51</sup> and communicated at conferences.<sup>52</sup> This research addresses an investigation on the vinyl-type polymerization of Nb in the presence of a series of simple nickel(II) and palladium(II) precatalysts with different kinds of  $\alpha$ -dioxime ligands (dimethylglyoxime, diphenylglyoxime, and 1,2-cyclohexanedione dioxime). The precatalysts bis(dimethylglyoximate)nickel(II) (**2**), bis(diphenylglyoximate)nickel(II) (**3**), dichlorobis(1,2-cyclohexanedione-dioximate)nickel(II) (**4**), dichlorobis(dimethylglyoximate)palladium(II) (**5**), bis(diphenylglyoximate)palladium(II) (**6**), and bis(1,2-cyclohexanedione-dioximate)palladium(II) (**7**) have not been described for the Nb polymerization before<sup>62</sup> and can be activated with different cocatalyst systems, especially MAO and the combination of  $\text{B}(\text{C}_6\text{F}_5)_3$  and TEA. After activation of the precatalysts **2–7** with the cocatalysts MAO and  $\text{B}(\text{C}_6\text{F}_5)_3/\text{TEA}$ , the partly soluble  $\alpha$ -dioximate complexes became soluble, and the polymerizations were carried out in a homogeneous phase.

The homopolymer vinyl-poly(norbornene) (**8**) is of interest as a specialty polymer with good mechanical strength, heat resistivity, and optical transparency, for example, for deep ultraviolet photoresists, interlevel dielectrics in microelectronics applications, or as a cover layer for liquid-crystal displays.<sup>45,63</sup>

## EXPERIMENTAL

### General Procedures

All work involving air- and/or moisture-sensitive compounds was carried out with standard vacuum, Schlenk, or drybox techniques. IR spectra (KBr pellets) were measured on a Bruker Optik IFS 25. Gel permeation chromatography (GPC) analyses were performed on a PL-GPC 220 (columns PL gel 10  $\mu\text{m}$  Mixed-B) with polymer solu-



Scheme 2

tions in 1,2,4-trichlorobenzene (concentration of 2–3 g/mL). GPC was measured at 140 °C with an injection volume of 200  $\mu$ L and a flow rate of 1 mL/min. Powder diffractograms of the polyNb samples were obtained by a Siemens X-ray spectrometer with Cu  $K\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ). Scans were collected in a  $2\theta$  range from 2 to 60°.  $^{19}\text{F}$  NMR spectra were recorded on a Bruker Avance DPX200 (188.29 MHz) with calibration against an external standard of  $\text{CDFCl}_2$ .

## Materials

Palladium(II) chloride (Merck-Schuchardt),  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  (Acros), dimethylglyoxime (Merck), diphenylglyoxime (Aldrich), 1,2-cyclohexanedione dioxime (Aldrich), 1-dodecene (Aldrich), tris(pentafluorophenyl)borane,  $\text{B}(\text{C}_6\text{F}_5)_3$  **1** (Aldrich), MAO (10% solution in toluene, Witco), and TEA (1 mol/L solution in hexane, Merck-Schuchardt) were used as received. Toluene was dried over sodium metal and methylene chloride over  $\text{CaH}_2$  and distilled under nitrogen prior to use. Nb (bicyclo[2.2.1]hept-2-ene) (Aldrich) was purified by distillation and used as a solution in toluene.  $\text{PdCl}_2(\text{CH}_3\text{CN})_2$  was prepared according to a procedure given by Khrasch et al.<sup>64</sup>

## Preparation of the Precatalysts

Complexes **2–7** were prepared by adding a solution of the ligand in ethanol to a solution of  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  or  $\text{PdCl}_2(\text{CH}_3\text{CN})_2$ , respectively, in ethanol. The resulting precipitates were washed with diethylether and dried *in vacuo*. The yields were in the range of 81–92%, and the purities were controlled by CHN analysis.

## Polymerization Procedures

### General

The precatalysts were suspended in methylene chloride via ultrasonication. Polymerizations were conducted at room temperature in a water bath to ensure a constant temperature during the reaction. The polymerization mixture was stirred with a magnetic stirrer. Polymerization runs were carried out at least three to five times to ensure reproducibility. The IR spectra of the poly(Nb)s obtained with the precatalysts **2–7** showed the absence of bands at 1620–1680  $\text{cm}^{-1}$ ,

which would be indicative of double bonds. This ensured a vinyl-type instead of ROMP.

### General Procedure for the Polymerization of Nb with MAO as a Cocatalyst

A Schlenk-flask was charged with Nb or the Nb/1-dodecene solution, and the MAO solution was added. After 1 min the suspension of the precatalyst was added via syringe to start the polymerization. The polymerization was stopped through the addition of 30 mL of a 10:1 methanol/concentrated HCl mixture. The precipitated polymer was filtered, washed with methanol, and dried *in vacuo* for 5 h.

### General Procedure for the Polymerization of Nb with $\text{B}(\text{C}_6\text{F}_5)_3$ or TEA Alone and $\text{B}(\text{C}_6\text{F}_5)_3/\text{TEA}$ As Cocatalysts

A Schlenk flask was charged with the Nb solution and the suspension of the precatalyst. Addition of the cocatalyst components [ $\text{B}(\text{C}_6\text{F}_5)_3$  and TEA] started the polymerization. The polymerization was stopped through the addition of 40 mL of a 10:1 methanol/concentrated HCl mixture. The precipitated polymer was filtered, washed with methanol, and dried *in vacuo* for 5 h.

## RESULTS AND DISCUSSION

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

The polymerization activities of the new precatalysts **2–7** with the different cocatalysts covered a range from  $1.5 \cdot 10^3$  [**2**/ $\text{B}(\text{C}_6\text{F}_5)_3/\text{TEA}$ ] to  $3.2 \cdot 10^7$   $\text{g}_{\text{polymer}}/\text{mol}_{\text{metal}} \cdot \text{h}$  [**5**/ $\text{B}(\text{C}_6\text{F}_5)_3/\text{TEA}$ ]. The nickel complexes **2** and **4** were less active than the comparable palladium complexes **5** and **7**. With the diphenylglyoximate ligand, the nickel complex **3** became more active than the palladium analogue **6**. Upon changing the cocatalyst system from MAO to  $\text{B}(\text{C}_6\text{F}_5)_3/\text{TEA}$ , the activities dropped in the cases of nickel systems and the Pd complex **7** and increased with the palladium systems **5** and **6**. Similar monomer conversions and activities are obtained by  $\text{B}(\text{C}_6\text{F}_5)_3/\text{TEA}$  instead of MAO, but much lower cocatalyst quantities are required with precatalysts **3** and **5–7** (molar ratios of metal:borane:TEA = 1:9:10 and metal:MAO = 1:100). Therefore, fewer cocatalyst residues remain in the polymer. This leads to more

**Table 1.** Polymerization of Nb with Precatalysts **2–7** at Room Temperature in a Toluene/Methylene Chloride Solution<sup>a</sup>

Catalyst	Time (min)	Conversion (%)	Activity (g <sub>polymer</sub> /mol <sub>metal</sub> · h)	M <sub>n</sub> (g · mol <sup>-1</sup> )	M <sub>w</sub> (g · mol <sup>-1</sup> )	M <sub>w</sub> /M <sub>n</sub>
<b>2</b> /MAO <sup>b</sup>	5	10.0	1.1 · 10 <sup>5</sup>	1.2 · 10 <sup>6</sup>	2.2 · 10 <sup>6</sup>	1.9
<b>3</b> /MAO <sup>b</sup>	5	30.8	3.5 · 10 <sup>5</sup>	8.9 · 10 <sup>5</sup>	1.6 · 10 <sup>6</sup>	1.8
<b>4</b> /MAO <sup>b</sup>	1	6.2	3.5 · 10 <sup>5</sup>	1.3 · 10 <sup>6</sup>	2.4 · 10 <sup>6</sup>	1.9
<b>5</b> /MAO <sup>b</sup>	1/6	66.6	2.3 · 10 <sup>7</sup>		Not soluble	
<b>6</b> /MAO <sup>b</sup>	5	1.0	1.2 · 10 <sup>4</sup>		Not soluble	
<b>7</b> /MAO <sup>b</sup>	1	15.9	9.0 · 10 <sup>5</sup>		Not soluble	
<b>2–7</b> /— <sup>c</sup>	60	—	No activity observed	—	—	—
<b>2</b> /B(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub> /TEA <sup>d</sup>	60	1.5	1.5 · 10 <sup>3</sup>	4.0 · 10 <sup>5</sup>	1.5 · 10 <sup>6</sup>	3.7
<b>3</b> /B(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub> /TEA <sup>d</sup>	5	18.3	2.1 · 10 <sup>5</sup>	2.0 · 10 <sup>5</sup>	4.7 · 10 <sup>5</sup>	2.4
<b>4</b> /B(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub> /TEA <sup>d</sup>	10	6.1	3.5 · 10 <sup>4</sup>	3.4 · 10 <sup>5</sup>	7.2 · 10 <sup>5</sup>	2.1
<b>5</b> /B(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub> /TEA <sup>d</sup>	1/6	92.8	3.2 · 10 <sup>7</sup>		Not soluble	
<b>6</b> /B(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub> /TEA <sup>d</sup>	10	4.5	2.6 · 10 <sup>4</sup>		Not soluble	
<b>7</b> /B(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub> /TEA <sup>d</sup>	2	13.3	3.8 · 10 <sup>5</sup>		Not soluble	
<b>2, 5–7</b> /—/TEA <sup>e</sup>	60	—	No activity observed	—	—	—
<b>3</b> /—/TEA <sup>e</sup>	60	3.3	3.1 · 10 <sup>3</sup>		Not measured	
<b>4</b> /—/TEA <sup>e</sup>	60	1.8	1.7 · 10 <sup>3</sup>		Not measured	
<b>2</b> /B(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub> /— <sup>f</sup>	60	—	No activity observed	—	—	—
<b>3, 4</b> /B(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub> /— <sup>f</sup>	60	Traces	—	—	—	—
<b>5</b> /B(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub> /— <sup>f</sup>	15	50.5	1.9 · 10 <sup>5</sup>		Not soluble	
<b>6</b> /B(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub> /— <sup>f</sup>	60	16.1	1.5 · 10 <sup>4</sup>		Not soluble	
<b>7</b> /B(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub> /— <sup>f</sup>	30	16.9	3.2 · 10 <sup>4</sup>		Not soluble	

<sup>a</sup> Toluene/CH<sub>2</sub>Cl<sub>2</sub> = 1/1 (v/v) for the polymerizations with MAO and **3/1** for the polymerizations with B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> and TEA.

<sup>b</sup> About 10.6 mmol of Nb, molar ratio Ni:Nb = 1:1000, Ni:Al = 1:100, and total volume: 10.0 mL.

<sup>c</sup> About 10.6 mmol of Nb, Ni:Nb = 1:1000, and total volume: 10.0 mL.

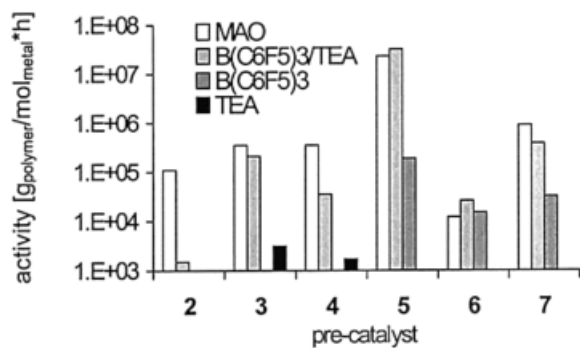
<sup>d</sup> Around 30.1 mmol of Nb, Ni:Nb = 1:1000, Ni:B:Al = 1:9:10, and total volume: 40.0 mL.

<sup>e</sup> Approximately 30.1 mmol of Nb, Ni:Nb = 1:1000, Ni:Al = 1:10, and total volume: 40.0 mL.

<sup>f</sup> About 30.1 mmol of Nb, Ni:Nb = 1:1000, Ni:B = 1:9, and total volume: 40.0 mL.

advantages for the prospective optical applications of poly(Nb).

Also, B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> can function as a sole activator only toward the palladium precatalysts, but this resulted in a decrease of the polymerization activ-

**Figure 1.** Polymerization activities of **2–7** with different cocatalyst systems in the polymerization of Nb; see Table 1 for details.

ities. Activation with the aluminium compound TEA was only possible for the nickel complexes **3** and **4** and showed the expected dramatic decrease of the activity. The activity trends are difficult to explain in the absence of more profound knowledge of the active species. Generally, the active species in MAO- or B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>-activated Ni or Pd complexes are not well known.<sup>45</sup> Some of the following investigations aimed at increasing understanding of the activation process of these precatalysts.

The polymer solubilities were as expected from the literature.<sup>19,32,34–36,45,46</sup> Polymers obtained with the nickel precatalysts **2**, **3**, and **4** were soluble in 1,2,4-trichlorobenzene with a concentration of 2–3 mg/mL, whereas the palladium-derived polymers were insoluble in common solvents. Thus, only GPC data of the nickel-catalyzed polymers are available. The number-average molecular weight ( $M_n$ ) was between 8.9 ·

**Table 2.** Polymerization of Nb with Precatalysts **2–7** in Combination with MAO at Room Temperature in Toluene<sup>a</sup>

Catalyst	Time (min)	Conversion (%)	Activity (g <sub>polymer</sub> /mol <sub>metal</sub> · h)	M <sub>n</sub> (g · mol <sup>-1</sup> )	M <sub>w</sub> (g · mol <sup>-1</sup> )	M <sub>w</sub> /M <sub>n</sub>
<b>2</b> /MAO	5	3.1	3.5 · 10 <sup>4</sup>	4.7 · 10 <sup>5</sup>	1.2 · 10 <sup>6</sup>	2.5
<b>3</b> /MAO	5	24.3	2.8 · 10 <sup>5</sup>	4.5 · 10 <sup>5</sup>	9.6 · 10 <sup>5</sup>	2.1
<b>4</b> /MAO	5	6.0	6.8 · 10 <sup>4</sup>	4.7 · 10 <sup>5</sup>	1.1 · 10 <sup>6</sup>	2.4
<b>5</b> /MAO	1/6	53.0	1.8 · 10 <sup>7</sup>		Not soluble	
<b>6</b> /MAO	60	5.0	4.7 · 10 <sup>3</sup>		Not soluble	
<b>7</b> /MAO	1	15.4	8.7 · 10 <sup>5</sup>		Not soluble	

<sup>a</sup> About 10.6 mmol of Nb, molar ratio Ni:Nb = 1:1000, Ni:Al = 1:100, and total volume: 10.0 mL.

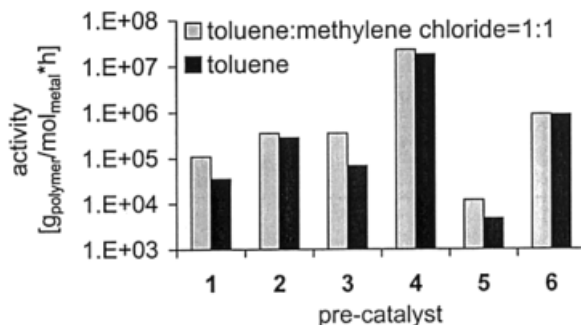
10<sup>5</sup> and 1.3 · 10<sup>6</sup> g · mol<sup>-1</sup> for activation with MAO and between 2.0 · 10<sup>5</sup> and 4.0 · 10<sup>5</sup> g · mol<sup>-1</sup> for activation with the cocatalyst system B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>/TEA. Therefore, the average chain length for the polymers lay between 9500 and 14,000 monomer units with MAO and between 2100 and 4200 monomer units with B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>/TEA (M<sub>Nb</sub> = 94.16 g · mol<sup>-1</sup>). This is due to the action of TEA as a chain-transfer agent.<sup>65–67</sup> TEA is a better reaction partner for the alkyl exchange than MAO.<sup>65</sup> The turnover frequency for the insertion reaction can be calculated to at least 1 s<sup>-1</sup> [2/B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>/TEA] and 230 s<sup>-1</sup> for the more-active systems. The polymer samples displayed a monomodal molar mass distribution. The molar mass distribution  $Q = M_w/M_n$  for the polymer samples is rather narrow and close to a value of 2 with the exception of the system 2/B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>/TEA ( $Q = 3.7$ ). A value of  $Q = 2$  is the theoretical dispersity for a Schulz–Flory-type distribution arising from an ideally behaved polymerization reaction with a chain-termination reaction.<sup>68</sup> A dispersity of  $Q \approx 2$  indicates a single-site character, that is, a highly homogeneous structure of the active catalyst species.

The powder diffractograms were measured for all polymer samples listed in Table 1 and displayed two broad halos that can be attributed to a short-range order. The occurrence of two halos is characteristic for poly(Nb)s, and the corresponding distances amount to 4.7 and 8.6 Å.<sup>69</sup> No traces of Bragg reflections, characteristic of crystalline regions, are revealed, and the poly(Nb)s are therefore noncrystalline. The polymer obtained with the catalytic system 6/B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>/TEA exhibited two additional weak halos corresponding to distances of 6.0 and 13 Å.

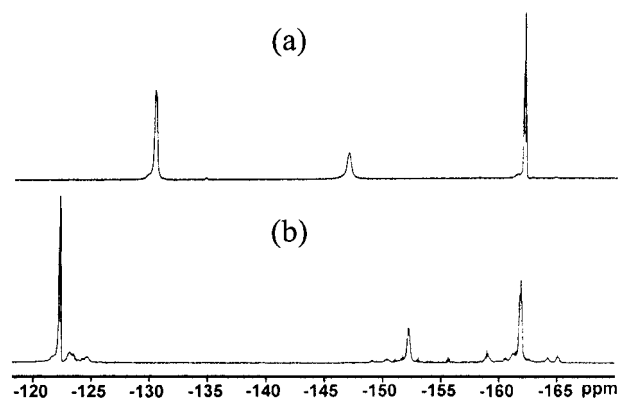
To receive information about the active species using the precatalysts **2–7**, the polarity of the

solvent was decreased by changing the solvent from a toluene/methylene chloride mixture (1:1 v/v) to toluene. In the polymerization of Nb with cobalt(II) complexes in chlorobenzene, small amounts of toluene decreased the polymerization activity by factors of 10–40.<sup>18</sup> The data in Table 2 in comparison with Table 1 and their graphical presentation in Figure 2 show that there is a slight decrease in the polymerization activity when reducing the polarity of the solvent by going from toluene/CH<sub>2</sub>Cl<sub>2</sub> to toluene alone.

This suggests a complex cation/MAO anion pair as the active species. A more polar solvent (CH<sub>2</sub>Cl<sub>2</sub>) allows for a better ion-pair separation, thus increasing the accessibility and activity of the cation. The decrease in activity in toluene is accompanied by a decrease in polymer molar mass and a slight increase in polymer dispersity. The decrease in activity corresponds to a decrease in the chain-propagation rate ( $k_p$ ) and a relative increase in the rate of chain transfer/termination ( $k_T$ ). The mean degree of polymerization,  $P_n$ ,



**Figure 2.** Influence of the polarity of the solvent in the polymerization of Nb with precatalysts **2–7** in combination with MAO; see Tables 1 (toluene/CH<sub>2</sub>Cl<sub>2</sub>) and 2 (toluene) for details.



**Figure 3.**  $^{19}\text{F}$  NMR spectra: (a)  $\text{B}(\text{C}_6\text{F}_5)_3$ , **1**, and (b)  $\text{B}(\text{C}_6\text{F}_5)_3$  with TEA in a molar ratio of B:Al = 9:10.

which is proportional to  $M_n$ , is given by the ratio of the growth rate to the rate of transfer,  $M_n \sim P_n \approx k_p/k_t$ .<sup>68,70,71</sup>

The high Lewis acidity of **1** with its perfluorinated phenyl ligands plays an important role in the formation of the active species. In a recent publication, we have shown that in the case of the highly active nickel systems bis(acetylacetonato)nickel(II) and bis(2-ethylhexanoato)nickel(II), the change to the weaker Lewis acid  $\text{B}(\text{C}_6\text{H}_5)_3$  exhibited no polymerization activity within 60 min.<sup>19</sup> The combination of  $\text{B}(\text{C}_6\text{F}_5)_3$  and  $\text{AlMe}_3$  led to a facile aryl/alkyl group exchange and resulted in the formation of  $\text{Al}(\text{C}_6\text{F}_5)_3$  as the main product.<sup>72,73</sup>  $\text{B}(\text{C}_6\text{F}_5)_3$  in combination with TEA

should undergo an analogous ligand-exchange reaction, and the  $^{19}\text{F}$  NMR spectrum showed the expected signals of  $\text{Al}(\text{C}_6\text{F}_5)_3$  at  $-122.3$  ppm (*ortho*-F),  $-152.2$  ppm (*para*-F), and  $-161.7$  ppm (*meta*-F) (see Fig. 3). Also, the  $^{19}\text{F}$  NMR spectrum revealed the formation of dimeric aluminium species of the type  $[\text{Al}(\text{C}_6\text{F}_5)_n\text{Et}_{3-n}]_2$  ( $x = 1-2$ ) as side products.

Therefore, the metal complex precatalysts in combination with  $\text{B}(\text{C}_6\text{F}_5)_3$  and TEA will not be activated by the Lewis acid  $\text{B}(\text{C}_6\text{F}_5)_3$  but instead by the Lewis acids  $\text{Al}(\text{C}_6\text{F}_5)_n\text{Et}_{3-n}$  as the reaction product of a ligand-exchange reaction between  $\text{B}(\text{C}_6\text{F}_5)_3$  and TEA.

In the following investigations, we only focused on the nickel(II) precatalyst **3**. This precatalyst gave polymerization activities in the range of  $10^5$   $\text{g}_{\text{polymer}}/\text{mol}_{\text{metal}} \cdot \text{h}$  both with MAO and  $\text{B}(\text{C}_6\text{F}_5)_3/\text{TEA}$  so that changes in activity with polymerization parameters could be followed in either direction. To increase understanding of the activation process of precatalyst **3** with  $\text{B}(\text{C}_6\text{F}_5)_3$  with TEA, the influence of the molar ratio of  $\text{B}(\text{C}_6\text{F}_5)_3$  on the polymerization activity was investigated (see Table 3 and Fig. 4).

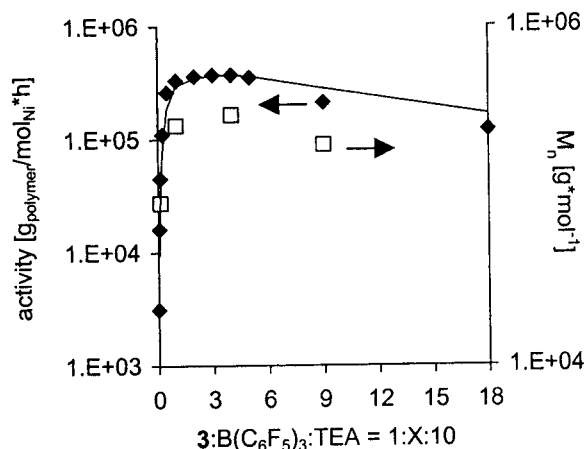
The shallow maximum in the polymerization activity around a molar ratio Ni:B:Al  $\approx$  1:3:10 is somewhat surprising. The decrease in activity toward higher amounts of borane could be explained by a deactivating interaction with the active complex, for example, an abstraction of the second glyoximate ligand or a certain deactivat-

**Table 3.** Influence of the  $\text{B}(\text{C}_6\text{F}_5)_3$  Amount with Nickel Pre-catalyst **3**<sup>a</sup>

Molar ratio Ni:B:Al <sup>b</sup>	Conversion (%)	Activity ( $\text{g}_{\text{polymer}}/\text{mol}_{\text{Ni}} \cdot \text{h}$ )	$M_n$ ( $\text{g} \cdot \text{mol}^{-1}$ )	$M_w$ ( $\text{g} \cdot \text{mol}^{-1}$ )	$M_w/M_n$
1:18:10	10.2	$1.2 \cdot 10^5$		Not measured	
1:9:10	18.3	$2.1 \cdot 10^5$	$2.0 \cdot 10^5$	$4.7 \cdot 10^5$	2.4
1:5:10	30.6	$3.5 \cdot 10^5$		Not measured	
1:4:10	32.5	$3.7 \cdot 10^5$	$3.0 \cdot 10^5$	$5.5 \cdot 10^5$	1.8
1:3:10	32.2	$3.7 \cdot 10^5$		Not measured	
1:2:10	32.0	$3.6 \cdot 10^5$		Not measured	
1:1:10	28.8	$3.3 \cdot 10^5$	$2.6 \cdot 10^5$	$5.0 \cdot 10^5$	1.9
1:0.5:10	22.9	$2.6 \cdot 10^5$		Not measured	
1:0.25:10	9.8	$1.1 \cdot 10^5$		Not measured	
1:0.125:10	4.0	$4.5 \cdot 10^4$	$9.1 \cdot 10^4$	$2.5 \cdot 10^5$	2.7
1:0.0625:10	1.5	$1.6 \cdot 10^4$		Not measured	
1:0:10	0.3	$3.1 \cdot 10^3$		Not measured	

<sup>a</sup> About 30 mmol of Nb, molar ratio Ni:Nb = 1:1000, toluene:methylene chloride solution = 3:1 (v/v), room temperature, total volume: 40.0 mL, and reaction time. 5 min.

<sup>b</sup> Al as TEA.



**Figure 4.** Influence of the  $B(C_6F_5)_3$  amount with nickel precatalyst **3** and TEA in the polymerization of Nb; see Table 3 for details.

ing role of  $B(C_6F_5)_3$  in general. The observation that  $\mathbf{3}/B(C_6F_5)_3$  indicates nothing and  $\mathbf{3}/TEA$  shows very little activity underscores the necessity of the formation of  $Al(C_6F_5)_3$ ,  $Al(C_6F_5)_2Et$ , and  $Al(C_6F_5)Et_2$  as the actual activators in the equilibrium mixture  $B(C_6F_5)_3 + AlEt_3 \leftrightarrow BEt_3 + Al(C_6F_5)_3$ . Consequently, a high polymerization activity down to a molar ratio of Ni:B:Al = 1:1:10 revealed that an excess of the cocatalyst  $B(C_6F_5)_3$  is not necessary or desirable to obtain good polymerization activities. However, a further decrease of the tris(pentafluorophenyl)borane amount resulted in a drastic but expected drop of the activity. Again, a decrease in activity is accompanied by a decrease in molar mass of the

polymer and a slight increase in the molar mass distribution (see preceding information).

In turn, the influence of the aluminium amount was investigated by a Ni:B [ $\mathbf{3}:B(C_6F_5)_3$ ] molar ratio of 1:1 and different amounts of TEA to elucidate the function of TEA in the activation process, the role as scavenger toward impurities, and as a chain-transfer agent (Table 4 and Fig. 5).

An increase in the amount of aluminium from Ni:B:Al = 1:1:1 on leads to a strong increase in polymerization activity up to a molar ratio of 1:1:5. From there the increase levels off but continues steadily with a small gradient up to Ni:B:Al = 1:1:100, the final ratio that was investigated. This indicates that the formation of  $Al(C_6F_5)Et_2$  is sufficient as an activator. The formation and action of  $Al(C_6F_5)_3$  or  $Al(C_6F_5)_2Et$  is not required.  $Al(C_6F_5)Et_2$  is the main species at excess TEA over  $B(C_6F_5)_3$ . In addition, higher amounts of TEA work as scavenger toward impurities. A molar ratio of B:Al = 1:1 already results in the formation of  $Al(C_6F_5)_3$ , but the scavenging action is less prominent and the polymerization activity decreases accordingly. Alternatively, it cannot be ruled out that  $Al(C_6F_5)Et_2$ , which forms at Al excess (e.g., B:Al = 1:>3), is a more potent activator than  $Al(C_6F_5)_3$ , which is present at low Al ratios (B:Al  $\approx$  1:1). The molar mass of the polymer samples is inversely proportional to the amount of TEA because of the action of TEA as a chain-transfer agent.<sup>65–67</sup>

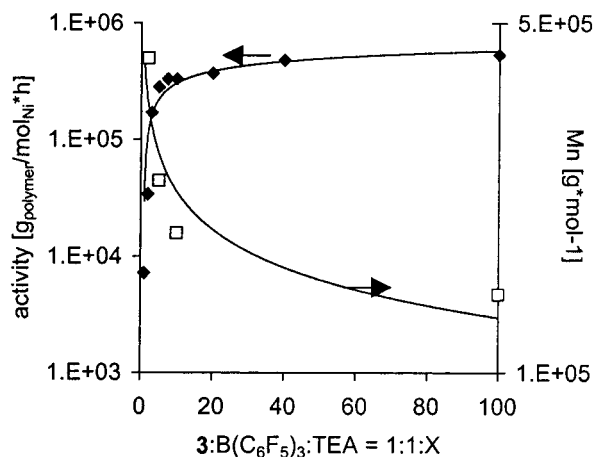
Precatalyst **3** could also be activated with TEA alone, allowing for the possibility to investigate the influence of TEA (Table 5 and Fig. 6). Yet

**Table 4.** Influence of the TEA Amount with Nickel Precatalyst **3**<sup>a</sup>

Molar Ratio Ni:B:Al <sup>b</sup>	Conversion (%)	Activity ( $g_{\text{polymer}}/\text{mol}_{\text{Ni}} \cdot \text{h}$ )	$M_n$ ( $g \cdot \text{mol}^{-1}$ )	$M_w$ ( $g \cdot \text{mol}^{-1}$ )	$M_w/M_n$
1:1:1	0.6	$7.2 \cdot 10^3$		Not measured	
1:1:2	3.0	$3.4 \cdot 10^4$	$4.6 \cdot 10^5$	$8.8 \cdot 10^5$	1.9
1:1:3	14.6	$1.7 \cdot 10^5$		Not measured	
1:1:5	24.6	$2.8 \cdot 10^5$	$3.2 \cdot 10^5$	$6.5 \cdot 10^5$	2.1
1:1:7.5	28.9	$3.3 \cdot 10^5$		Not measured	
1:1:10	28.8	$3.3 \cdot 10^5$	$2.6 \cdot 10^5$	$5.0 \cdot 10^5$	1.9
1:1:20	32.5	$3.7 \cdot 10^5$		Not measured	
1:1:40	42.0	$4.8 \cdot 10^5$		Not measured	
1:1:100	46.6	$5.3 \cdot 10^5$	$1.9 \cdot 10^5$	$4.1 \cdot 10^5$	2.1

<sup>a</sup> 30 mmol of Nb, molar ratio Ni:Nb = 1:1000, toluene:methylene chloride solution = 3:1 (v/v), room temperature, total volume: 40.0 mL, and reaction time: 5 min.

<sup>b</sup> B as  $B(C_6F_5)_3$ .



**Figure 5.** Influence of the aluminium amount with nickel precatalyst **3** and  $B(C_6F_5)_3$  in the polymerization of Nb; see Table 4 for details.

without borane the activity of **3**/TEA is rather low and decreases even further with an increasing excess of aluminum alkyl. An excess of TEA apparently leads to a deactivation of the active species.<sup>74</sup>

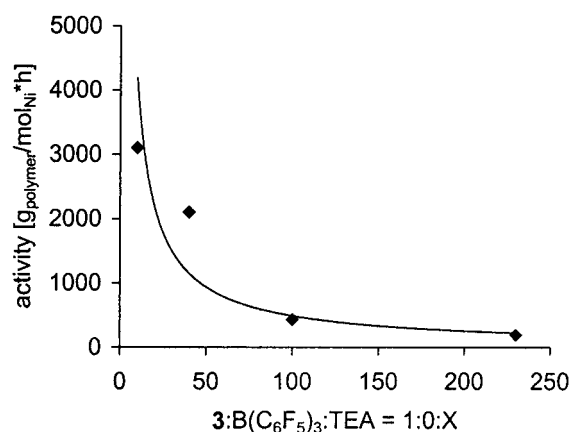
The activation of **3** requires the action of  $Al(C_6F_5)_nEt_{3-n}$  species [generated *in situ* from  $B(C_6F_5)_3/TEA$ ] with excess TEA to give high polymerization activities.

The molar mass of polymers is of some importance for physical properties and potential applications. The aforementioned polymerization series have shown that it was possible to influence the molar mass of the poly(Nb)s with TEA as a chain-transfer agent (see Figs. 4 and 5). Another possibility to control the molar mass of polymers is the addition of  $\alpha$ -olefins as chain-transfer agents. The insertion of the  $\alpha$ -olefin into the metal chain end should serve to terminate the chain-

**Table 5.** Influence of the TEA Amount with Nickel Precatalyst **3** without  $B(C_6F_5)_3$ <sup>a</sup>

Molar Ratio Ni:B:Al	Conversion (%)	Activity ( $g_{\text{polymer}}/\text{mol}_{\text{Ni}} \cdot \text{h}$ )
1:0:10	3.3	$3.1 \cdot 10^3$
1:0:40	2.2	$2.1 \cdot 10^3$
1:0:100	0.5	$4.3 \cdot 10^2$
1:0:230	0.2	$1.9 \cdot 10^2$

<sup>a</sup> 30 mmol of Nb, molar ratio Ni:Nb = 1:1000, toluene: methylene chloride solution = 3:1 (v/v), room temperature, total volume: 40.0 mL, and reaction time: 60 min.



**Figure 6.** Influence of the TEA amount with nickel precatalyst **3** without  $B(C_6F_5)_3$  in the polymerization of Nb; see Table 5 for details.

propagation process by  $\beta$ -hydride elimination.<sup>30,31</sup> Here, 1-dodecene was used in the polymerization of Nb with the catalytic system **3**/MAO to control the molar mass of the polymers obtained (Table 6, Figs. 7 and 8). Because of the increasing amount of 1-dodecene and the decreasing Nb concentration, it was not possible to investigate this series with a constant polymerization time of 5 min so that a direct comparison of the molar mass values of the poly(Nb)s should be done with care.

The polymerizations with the chain-transfer agent 1-dodecene exhibited nearly constant activities while adding up to 10%  $\alpha$ -olefin relative to Nb to the polymerization mixture. Further increase of the amount of 1-dodecene led to the expected drop of the polymerization activity because of the concomitant decrease in Nb concentration. It is possible to compare the GPC investigations in the addition range of 0–1% 1-dodecene because of the constant polymerization time of 5 min. Figure 8 displays the influence of 1-dodecene on the  $M_n$  of the polymers. The more  $\alpha$ -olefin was added, the lower the molar mass. Surprisingly, the addition of 1-dodecene up to 1% also led to broadening of the polymer dispersity. This broadening is explained such that only part of the polymer chains are terminated with a low molar mass through the insertion of 1-dodecene. Because of its small amount and increasing solution viscosity, 1-dodecene is not readily available to terminate each growing chain at the same early stage. Hence, the polymerization continues to give chains of higher molar mass. An increased amount of 1-dodecene up to 80% relative to Nb

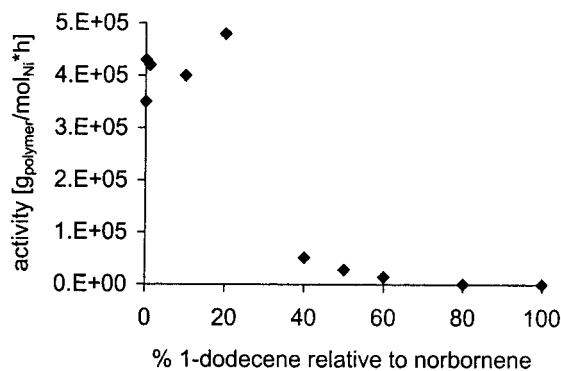


**Table 6.** Addition of 1-Dodecene to the Polymerization Mixture with Precatalyst **3** in Combination with MAO<sup>a</sup>

Dodecene (%)	Time (min)	Yield (g)	Activity (g <sub>polymer</sub> /mol <sub>Ni</sub> · h)	$M_n$ (g · mol <sup>-1</sup> )	$M_w$ (g · mol <sup>-1</sup> )	$M_w/M_n$
0	5	0.308	$3.5 \cdot 10^5$	$8.9 \cdot 10^5$	$1.6 \cdot 10^6$	1.8
0.1	5	0.377	$4.3 \cdot 10^5$	$2.2 \cdot 10^5$	$8.7 \cdot 10^5$	3.9
1	5	0.375	$4.2 \cdot 10^5$	$5.2 \cdot 10^4$	$3.4 \cdot 10^5$	6.6
10	5	0.352	$4.0 \cdot 10^5$		Not measured	
20	5	0.428	$4.8 \cdot 10^5$	$1.3 \cdot 10^4$	$2.2 \cdot 10^4$	1.7
40	60	0.545	$5.1 \cdot 10^4$	$5.3 \cdot 10^3$	$8.4 \cdot 10^3$	1.6
50	60	0.298	$2.8 \cdot 10^4$	$5.9 \cdot 10^3$	$8.2 \cdot 10^3$	1.4
60	120	0.289	$1.4 \cdot 10^4$	$3.2 \cdot 10^3$	$4.3 \cdot 10^3$	1.3
80	1080	0.057	$3.0 \cdot 10^2$	$2.5 \cdot 10^3$	$3.0 \cdot 10^3$	1.2
100	1440	—	No activity observed	—	—	—

<sup>a</sup> About 10.6 mmol of Nb+1-dodecene, molar ratio Ni:monomers = 1:1000, molar ratio Ni:Al = 1:100, toluene/methylene chloride solution (1/1 v/v), room temperature, and total volume: 10.0 mL.

resulted in a strong but expected reduction of the molar mass of poly(Nb)s down to a value of  $M_n = 2.5 \cdot 10^3 \text{ g} \cdot \text{mol}^{-1}$ . Such an  $M_n$  corresponds to an average chain length of about 25 monomer units, that is, species in the oligomer range. The molar mass distribution  $Q$  for the polymer samples in the polymerizations with amounts of 1-dodecene higher than 40% became extremely narrow with dispersities between 1.6 and 1.2. Dispersities smaller than 2 seem to contradict a Schulz–Flory distribution. However, Schulz–Flory demands a propagation rate independent of the chain length—a prerequisite that is not fulfilled during the first insertion steps.<sup>68</sup> A dispersity of  $Q < 2$  can be explained by a chain-length-dependent insertion rate in the case of oligomeric products. For propene oligomerizations such narrow molar mass dispersions could be reproduced with



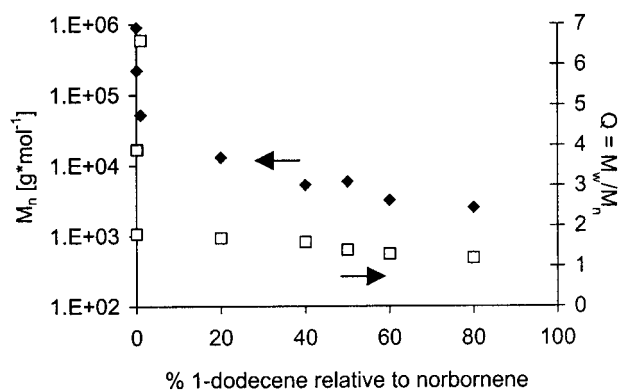
**Figure 7.** Addition of 1-dodecene to the polymerization mixture with precatalyst **3** in combination with MAO; see Table 6 for details.

a model that considers chain propagation and  $\beta$ -hydrogen elimination (for the chain transfer) on the basis of the decreased propagation rate over the first five insertions.<sup>75</sup>

The possibility to synthesize well-defined poly(Nb)s with low molar mass and high solubility may be an important step for the determination of the polymerization mechanism and for investigations concerning the structure of the polymer chain.<sup>76</sup> Investigations, especially NMR experiments, directed toward the activation process of precatalysts and the polymer chain growth will be included in future research.

## CONCLUSIONS

Nb undergoes vinyl polymerization with simple Ni(II) and Pd(II) complexes with different  $\alpha$ -di-



**Figure 8.** Addition of 1-dodecene to the polymerization mixture with precatalyst **3** in combination with MAO; see Table 6 for details.

oxime ligands. These precatalysts can be activated both with MAO and a combination of  $B(C_6F_5)_3/TEA$ . The palladium but not nickel precatalysts could also be activated with  $B(C_6F_5)_3$  alone, whereas two of the three nickel precatalysts but none of the palladium systems become somewhat active using only TEA as a cocatalyst.  $B(C_6F_5)_3$  and TEA led to an aryl/alkyl group exchange and result in the formation of  $Al(C_6F_5)_n-Et_{3-n}$  as the actual high activator from this cocatalyst mixture. The polymerization behavior of **3** was investigated, as an example, to gain insight into the activation process by changing the activation/polymerization parameters in the system **3**/ $B(C_6F_5)_3/TEA$ . From a variation of the B:Al ratio, it became evident that  $Al(C_6F_5)Et_2$  suffices to react with the precatalysts to form the active species. Higher amounts of TEA are beneficial as a scavenger. It was also possible to vary the molar mass of the poly(Nb)s with precatalyst **3** in a range from  $M_n = 2 \cdot 10^3$  to  $9 \cdot 10^5 \text{ g} \cdot \text{mol}^{-1}$  by TEA or 1-dodecene as chain-transfer agents.

The research was supported by the Fonds der Chemischen Industrie and LG Chem (Korea). The authors appreciate a gift of  $PdCl_2$  by Degussa-Hüls AG and a gift of MAO bei Witco GmbH.

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