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Heterogenized “Ligand-Free” Lanthanide Catalysts for the Homo- and Copolymerization of Ethylene and 1,3-Butadiene

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Received December 10, 2004; Revised Manuscript Received February 4, 2005

ABSTRACT: Silica-supported lanthanide catalysts have been prepared from the reaction of dehydroxylated silica and tris(bis(trimethylsilyl)amido)lanthanides $\text{Ln}[\text{N}(\text{SiMe}_3)_2]_3$ ($\text{Ln} = \text{Sc}, \text{Y}, \text{La}, \text{Nd}, \text{Sm}, \text{Gd}, \text{Dy}$). On activation with Al^iBu_3 (TIBA), the compounds catalyze the polymerization of ethylene, with the scandium catalyst showing the highest activity. There is an inverse relationship between ionic radius of the lanthanide metal and the activity of the resulting catalyst. The polymer produced was highly linear and of high molecular weight. Activation with magnesium alkyls was less effective but gave polyethylene of slightly higher molecular weight. The supported lanthanides, when activated with TIBA, were also active for the polymerization of 1,3-butadiene, with very high molecular weight polymers being produced. In all cases the polymer was found to be predominately 1,4-cis (typically 85–90% by diad analysis), with only scandium producing a much higher level of 1,4-trans units. The system was also shown to copolymerize ethylene and butadiene, with large differences in the polymeric products depending on the both the choice of the lanthanide and the feed ratio of the monomer. With both neodymium and dysprosium multiblock polymers consisting of 1,4-cis, 1,4-trans, and ethylene blocks were obtained. With scandium two distinct modes of polymerization were detected, with both multiblock 1,4-cis and a somewhat alternating ethylene/1,4-trans block structure observed in the ^{13}C NMR spectra.

Introduction

Organolanthanide complexes of the type Cp_2LnR ($\text{R} = \text{H}, \text{alkyl}$) have received much attention as highly efficient catalysts for the polymerization of ethylene.¹ Perhaps the greatest advantage of these complexes is the intrinsic high polymerization activity, with no need for an activator such as methylaluminoxane or $\text{B}(\text{C}_6\text{F}_5)_3$, even if the activity tends to be short-lived.^{1c,d} To overcome this problem, there is considerable interest in developing organolanthanide complexes with non-Cp ancillary ligands. One approach has been the use of the tris(pyrazolyl)borate ligand, with the complexes $\text{Tp}^{\text{Me}}\text{YR}_2(\text{THF})$ ($\text{Tp}^{\text{Me}} = \text{tris}(1,3\text{-dimethyl-1-pyrazolyl})\text{-borohydride}$, $\text{R} = \text{CH}_3, \text{C}_6\text{H}_5, ^i\text{Bu}, \text{CH}_2\text{Si}(\text{CH}_3)_3$) found to readily catalyze ethylene polymerization, with $\text{Tp}^{\text{Me}}\text{Y-}^i\text{Bu}_2(\text{THF})$ achieving an activity of 3.0 kg PE ($\text{mol Y}^{-1} \text{h}^{-1}$ at 8.3 bar and 25 °C).² Another tridentate nitrogen donor ligand, 1,4,7-trimethyl-1,4,7-triazacyclonane ($9\text{N}3^*$), has been used to prepare complexes $(9\text{N}3^*)\text{LnMe}_3$ ($\text{Ln} = \text{Y}, \text{Sc}$). The scandium complex reacted with $[\text{HMe}_2\text{-PhN}][\text{B}(\text{C}_6\text{F}_5)_4]$ to generate methane and dimethylaniline; exposure of a tetrahydrofuran solution of this not fully characterized product to ethylene resulted in the slow formation of a polyethylene precipitate.³ Scandium complexes of β -diketiminato (“nacnac”) ligands have also been used as precursors and give active catalysts. Thus, treatment of the complex $(\text{nacnac})\text{ScMe}_2$ (where $\text{nacnac} = \text{ArNC}(^i\text{Bu})\text{CHC}(^i\text{Bu})\text{NAr}$, $\text{Ar} = 2,6\text{-diisopropylphenyl}$) with 1 equiv of $\text{B}(\text{C}_6\text{F}_5)_3$ generated an ion paired complex which exhibited an activity of 14 kg PE ($\text{mol Sc}^{-1} \text{h}^{-1} \text{bar}^{-1}$ at 50 °C and 20.7 bar).⁴ An amido-functionalized triazacyclonane complex $[\text{N},\text{N}'\text{-}$

$\text{R}_2\text{-tacn-N''-(CH}_2)_2\text{N}^i\text{Bu}]\text{Y}(\text{CH}_2\text{SiMe}_3)_2$ ($\text{R} = \text{Me}, ^i\text{Pr}$; $\text{tacn} = 1,4,7\text{-triazacyclononane}$) produced a very active system on activation with $[\text{HMe}_2\text{PhN}][\text{B}(\text{C}_6\text{F}_5)_4]$, with a productivity of 1790 kg PE ($\text{mol Y}^{-1} \text{h}^{-1} \text{bar}^{-1}$). All these last three systems have needed an activator.⁵

Several attempts have been made to use oxygen-based ligands, with the rationale that the high oxophilicity of the lanthanides may lead to more robust complexes. Calixarenes have been used with a range of lanthanide metals, with a neodymium complex based on calix[6]-arene in combination with TIBA giving an activity of 3.3 kg PE ($\text{mol Nd}^{-1} \text{h}^{-1} \text{bar}^{-1}$ (80 °C, 12 bar)).⁶ However, the results for other lanthanides were much poorer, with only dysprosium providing complexes with a comparable activity. The neodymium alkoxide complex $\text{Nd}_3(\mu_3\text{-O}^i\text{Bu})_2(\mu_2\text{-O}^i\text{Bu})_3(\text{O}^i\text{Bu})_4(\text{THF})_2$, when activated by 1 equiv of a dialkylmagnesium reagent, gave an activity of 5–20 kg PE ($\text{mol Nd}^{-1} \text{h}^{-1} \text{bar}^{-1}$ under mild conditions (0 °C and 1.1 bar); however, this catalyst system seems to be very sensitive to the polymerization conditions, with much reduced activity above 0 °C and a tendency to catalyst deactivation.⁷

For production-scale polyolefin processes heterogeneous catalysts are preferred, not least because the resulting polymer morphology replicates that of the catalyst particles.^{8,9} Solid polymerization catalysts have been successfully prepared from group IV metallocenes and their derivatives as well as by supporting early transition metal oxides (V, Cr, Mo, and W) on silica and other related oxide surfaces. By far, the most active combination of these is Cr on silica,¹⁰ which accounts for around one-third of the current production of high-density polyethylene.¹¹ Supported La and Nd tris(allyl) complexes with a variety of surfaces and conditions have been used in the gas-phase polymerization of 1,3-butadiene to give polybutadiene with high 1,4-cis con-

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tent.¹² However, to our knowledge, very little work has been reported on the use of silica-supported lanthanide organometallic complexes as 1-alkene polymerization catalysts.¹³

The synthesis of diene/olefin copolymers is difficult, principally because the two classes of monomer show very different coordination and reactivity characteristics. Specifically, dienes tend to be stronger binding ligands and are well-known to act as poisons for 1-alkene polymerization catalysts. However, a small number of systems have been reported for 1,3-butadiene/ethylene polymerization. The first copolymerization of E and BD was reported by Natta.¹⁴ Homogeneous vanadium¹⁵ and heterogeneous titanium¹⁶ systems have been shown to copolymerize E and BD at room temperature and above, giving polymers with a multiblock structure and low incorporation of BD. Most metallocene catalysts display low activities and tend to generate copolymers that contain a mixture of unsaturated 1,4-enriched BD and methylene-1,2-cyclopentane units.¹⁷ Longo et al. recently described the cyclo-copolymerization of BD and E with a C_2 -symmetric zirconocene to produce a copolymer where the BD gave rise to methylene-1,2-cyclopropane rings.¹⁸ Boisson et al. used neodymocene complexes activated with $BuLi/AlHBu_2$ and other alkylating agents to prepare E-BD copolymers with almost alternating or six-ring structures,¹⁹ whereas Waymouth showed that E/BD copolymerization catalyzed by the dual-site metallocene $Me_2Si(Ind)(Flu)-ZrCl_2$ allowed the preparation of a copolymer where 1,2-cyclopentane rings are separated by three methylene units.²⁰

We now report a catalyst system based on the simple impregnation of silica with lanthanide amides, $Ln[N(SiMe_2)_3]$ ($Ln = Sc, Y, La, Nd, Sm, Gd, Dy$), and activated by TIBA, and the reactivity of these catalysts in the polymerization of ethylene, the production of high 1,4-*cis*-polybutadiene, the copolymerization of ethylene with butadiene, and the influence of ethylene on the stereochemistry of butadiene incorporation.

Experimental Section

General Considerations. All manipulations were performed under an atmosphere of dry nitrogen using standard Schlenk line techniques. Solvents were distilled under nitrogen from sodium (toluene), sodium benzophenone (diethyl ether, tetrahydrofuran), and sodium-potassium alloy (light petroleum, bp 40–60 °C). Deuterated solvents were degassed by several freeze-thaw cycles and stored over 4 Å molecular sieves. Ethylene was purified by passing through a $CaCl_2/P_2O_5$ column followed by $NaAlEt_4$ on glass wool. Butadiene was used without purification. NMR spectra were recorded on a Bruker DPX300 spectrometer. 1H NMR spectra (300.1 MHz) were referenced to residual solvent protons of the deuterated solvent used; ^{13}C NMR spectra were referenced internally to the D-coupled ^{13}C resonances of the NMR solvent. $LnCl_3(thf)_n$ were prepared from the corresponding oxides following a literature procedure.²¹ The silica support was Vulkasil S, a gift from Bayer AG Leverkusen, with a surface area of 175 ± 20 m²/g.

Synthesis of $Ln[N(SiMe_2)_3]_3$. Lanthanide amido complexes were synthesized via a modification of the literature method as described below for yttrium.²² A solution of $HN(SiMe_2)_3$ (10.7 g, 66.2 mmol, 13.8 mL) in tetrahydrofuran (100 mL) at –78 °C was treated with $nBuLi$ (41.4 mL, 1.6 M in hexanes, 66.2 mmol). The reaction was allowed to reach room temperature, stirred for 1 h, and re-cooled to –78 °C, and solid YCl_3 (4.17 g, 21.4 mmol) was added in small portions over ca. 10 min. After stirring the mixture for 16 h at room temperature, volatiles were removed in vacuo to give a white sticky solid. This was heated in vacuo at ca. 80 °C for 4 h and

extracted with light petroleum (100 mL). Concentration of the filtrate to ca. 50 mL and cooling to –20 °C afforded $Y[N(SiMe_2)_3]_3$ as colorless needle-shaped crystals, yield 7.12 g (58.4%). The amides of Sc, La, Nd, Sm, Gd, and Dy were all obtained in similar yields.

Catalyst Preparation. Silica was dehydroxylated at 500 °C in vacuo for 6 h. A solution of the desired amount of lanthanide amide complex (ca. 0.1 mmol) in light petroleum (40 mL) was transferred to a stirred suspension of the dehydroxylated silica (ca. 0.5 g) in the same solvent (20 mL). In the case of colored metal amides the reaction could be visually followed since the color was transferred from the solution to the solid. The mixture was stirred for 30 min, filtered, and dried in vacuo for 10 min to give the catalysts Ln/SiO_2 (**1**, $Ln = Y$; **2**, $Ln = La$; **3**, $Ln = Nd$; **4**, $Ln = Sm$; **5**, $Ln = Gd$; **6**, $Ln = Sc$; **7**, $Ln = Dy$). The filtrate was free of residual lanthanide amide (by NMR), and the impregnation was quantitative. $(SiO_2)_{60}YNSi_2C_6H_{18}$: Anal. Calcd: C, 1.87; H, 0.47; N, 0.36. Found: C, 1.92; H, 0.48; N, 0.34. $(SiO_2)_{55}DyNSi_2C_6H_{18}$: Anal. Calcd: C, 1.99; H, 0.50; N, 0.39. Found: C, 2.26; H, 0.52; N, 0.36.

The solids were washed with light petroleum (1×20 mL), suspended in toluene (10 mL), and treated with either Al^iBu_3 (0.5 mmol) or $MgBu_2$ (0.2 mmol) for 30 min. These suspensions were then introduced into the autoclave via a pressure buret.

Ethylene Polymerization. The polymerization experiments were conducted in a glass autoclave at 7 bar ethylene pressure. The autoclave was predried at 110 °C in vacuo for at least 4 h, cooled to room temperature, charged with toluene (400 mL), followed by either Al^iBu_3 (1.0 mmol) or $MgBu_2$ (0.4 mmol), and heated to the desired polymerization temperature. The reaction was terminated by the addition of methanol (10 mL). The content of the autoclave was poured into methanol (500 mL) and acidified with dilute HCl. The precipitated polymer was filtered off, washed with methanol, and dried for 16 h at 60 °C.

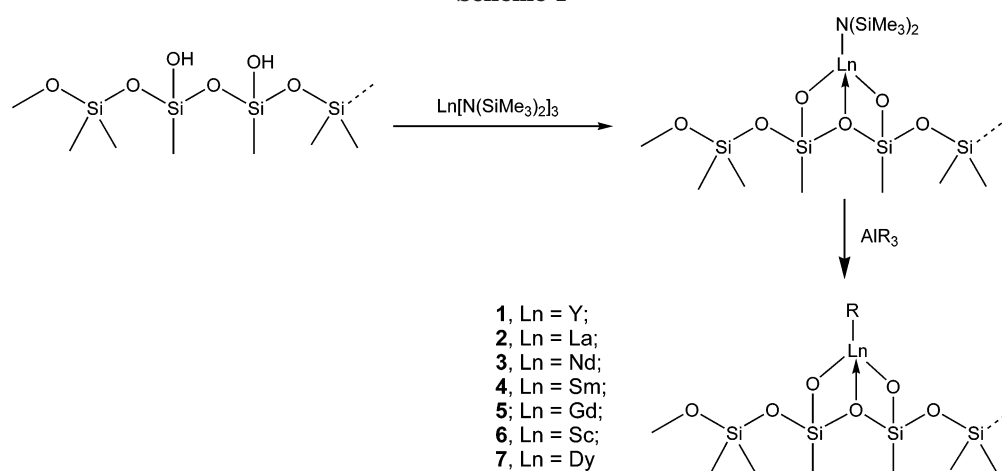
Butadiene Polymerization. The polymerization experiments were conducted in a thick-walled glass tube equipped with magnetic stirrer and sealed with a Teflon bellows valve. 1,3-Butadiene (10 mL, 6.2 g, 115 mmol) was condensed into the reactor at –78 °C, and TIBA (0.4 mL) was injected by syringe. This mixture was allowed to stir at –78 °C for 10 min. The freshly prepared supported lanthanide catalyst was suspended in light petroleum (2.5 mL), treated with TIBA (0.2 mL, stirred for 30 min, and then rapidly transferred into the polymerization vessel, which was then sealed and placed in a water bath at 50 °C. The reaction was terminated by the release of the excess pressure and the addition of methanol (5 mL). The resultant polymer was washed with acidified methanol, to which a trace of 4-methyl-2,6-ditertbutylphenol as antioxidant had been added, and dried at 60 °C for 16 h. The resulting PBD was difficult to dissolve. Polymer microstructure was determined by triad analysis from the 1H and ^{13}C NMR spectra in $CDCl_3$ or at 100 °C in a mixture of HCl_2CCl_2H and DCl_2CCl_2D (50:50).

Ethylene/Butadiene Copolymerizations. Reactions were performed in a Büchi autoclave at 50 °C under 2 bar of ethylene. $Ln[N(SiMe_2)_3]_3$ (200 μ mol) supported on silica was used in combination with 30 equiv of TIBA. The reactor was first loaded with the appropriate amount of toluene and 1.0 mL of TIBA. BD was then condensed into the toluene solution; the use of a flow meter allowed accurate control of the amount of BD added. Once the desired volume of BD was loaded, the toluene solution was saturated with ethene under a pressure of 2 bar. The supported lanthanide catalyst was freshly prepared as described and injected into the autoclave via a pressure buret. The polymerizations were quenched with methanol, and the polymers were precipitated with acidified MeOH, filtered, and dried under vacuum at 60 °C.

Results and Discussion

The lanthanide amido complexes $Ln[N(SiMe_2)_3]_3$ ($Ln = Sc, Y, La, Nd, Sm, Gd, Dy$) were prepared by a variation of the literature route.²² It has been shown

Scheme 1

Table 1. Ethylene Polymerization with $\text{Ln}[\text{N}(\text{SiMe}_3)_2]_3/\text{SiO}_2/\text{TIBA}$ Catalysts^a

run	support (g)	Ln	ionic radius (Å)	yield (g)	productivity ^b	M_w^c	M_w/M_n^c
1	0.508	Sc	0.68	47.2	67.4	960 000	17
2	0.526	Gd	0.94	14.8	21.1	901 000	13
3	0.511	Sm	0.96	7.28	10.4	991 000	25
4	0.433	Nd	0.99	1.89	3.13	741 000	19
5	0.462	La	1.06	4.70	6.71	938 000	16
6	0.606	Dy	0.91	12.03	17.1	n.d.	n.d.
7	0.508	Y	0.88	22.96	32.9	979 000	62

^a Conditions: $\text{Ln}[\text{N}(\text{SiMe}_3)_2]_3$ 100 μmol , TIBA 1.5 mmol, temperature 80 °C, time 1 h 7 bar ethene pressure. ^b In kg (mol metal)⁻¹ h⁻¹ bar⁻¹. ^c Determined by gel permeation chromatography in 1,2,4-trichlorobenzene at 140 °C using polystyrene standards.

that the reaction of LnCl_3 with 3 equiv of $\text{LiN}(\text{SiMe}_3)_2$ results in the formation of $[(\text{Me}_3\text{Si})_2\text{N}]_3\text{LnClLi}(\text{THF})$ as the first reaction product.²³ Several purification routes have been reported, including sublimation, repeated recrystallization from light petroleum or hexane, or recrystallization, heating in a dinitrogen stream at 100 °C, and further recrystallization. However, we find that reacting 3 equiv of $\text{LiN}(\text{SiMe}_3)_2$ with LnCl_3 in tetrahydrofuran solution for 24 h at room temperature, removal of the volatile solvents, heating of the solid residues at 100 °C in vacuo for ca. 3 h followed by extraction with light petroleum, and cooling to -20 °C affords the complexes in high yield and good purity.

The silica support was partially dehydroxylated by heating in vacuo at 500 °C for 6 h. It has been shown²⁴ that under such conditions only isolated silanol groups remain, with an average surface concentration of between 5.5 and 1 nm². Lanthanide metal silylamides can be conveniently grafted onto silica supports suspended in hexane.²⁵ In this work, a quantity of the lanthanide amide complex dissolved in light petroleum was added to a slurry of silica in the same solvent (Scheme 1). In the case of colored amido complexes (Nd (blue), Sm (pale yellow), Dy (pale green)) the petroleum solution quickly became colorless. After stirring for 30 min the filtrate contained no detectable amounts of residual amido complex, and the impregnation was therefore assumed to be quantitative. The solid catalyst precursor was filtered off, washed with light petroleum, and dried in vacuo for 15 min. The presence of $\text{HN}(\text{SiMe}_3)_2$ in the filtrate was confirmed by NMR analysis. This method provided catalysts with ca. 1–1.2 mol % metal loading.

To provide further evidence for the presence of the supported amide on the silica, the yttrium-impregnated catalyst was studied using solid-state magic-angle ²⁹Si NMR spectroscopy. A sample of dehydroxylated silica treated with $\text{Y}[\text{N}(\text{SiMe}_3)_2]_3$ showed only a single reso-

nance at δ -110 associated with the quaternary SiO_4 units of the silica; no distinct signal for the silanol groups could be detected. By contrast, in the supported material the δ -110 resonance was accompanied by a much smaller signal at δ 14.3, assigned to the surface-bound yttrium amide ligand. A second, smaller peak at δ 9.8 is assigned to surface silylation by $\text{HN}(\text{SiMe}_3)_2$ formed during the impregnation process.²⁶

Ethylene Polymerization. Lanthanide silylamide complexes readily undergo ligand exchange with aluminum alkyls, resulting in the formation of lanthanide alkyl species.²⁷ Thus, the catalyst precursors were activated by stirring the supported amides in toluene containing 5 equiv of TIBA for 30 min. ¹H NMR analysis of the resulting toluene supernatant showed the presence of aluminum silylamido products and indicated that amide/alkyl ligand exchange had occurred. To minimize catalyst deterioration, all catalysts were activated in situ and used as freshly prepared suspensions.

The ethylene polymerization activity of the activated lanthanide alkyl/ SiO_2 catalysts was tested at 80 °C under 7 bar ethylene pressure in the presence of 15 equiv of TIBA per Ln acting as scavenger. The results are assembled in Table 1. All seven lanthanides catalysts were found to be active, with scandium achieving a productivity of 67.4 kg PE (mol metal)⁻¹ h⁻¹ bar⁻¹. By contrast, under identical conditions homogeneous mixtures of $\text{Ln}[\text{N}(\text{SiMe}_3)_2]_3$ and TIBA are catalytically inactive.

Surprisingly, there is an inverse relationship between the Ln^{3+} ionic radius and catalytic activity (Figure 1): scandium, with the smallest ionic radius (0.68 Å), proved to be by far the most active, while for the larger lanthanides the activities are much lower; for example, lanthanum with an ionic radius of 1.06 Å shows only one-tenth of the productivity of scandium, 6.7 kg PE

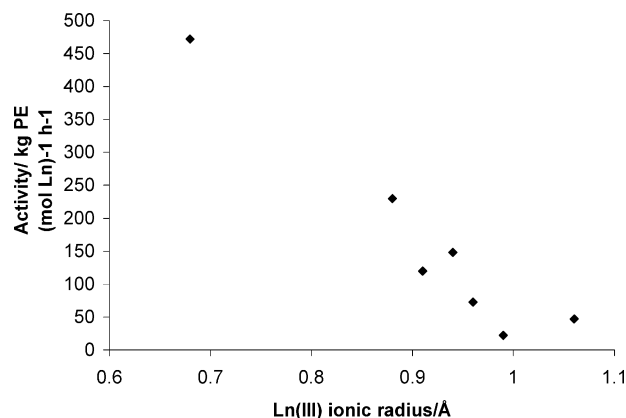


Figure 1. Ethylene polymerization activity of Ln/SiO₂/TIBA catalysts as a function of the Ln³⁺ ionic radius.

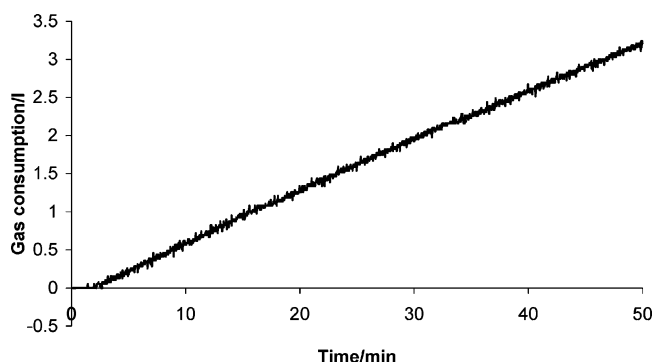


Figure 2. Ethylene consumption curve for the Sc[N(SiMe₃)₂]₃/SiO₂/TIBA catalyst.

(mol metal)⁻¹ h⁻¹ bar⁻¹. This activity trend is the opposite of that displayed by the homogeneous system [Ln(CH₂SiMe₃)₃(THF)₂]/TIBA/2[NMe₂HPh][B(C₆F₅)₄], where the largest lanthanide investigated, terbium, was found to be the most active, at 899 kg PE (mol metal)⁻¹ h⁻¹ bar⁻¹.²⁸

However, whereas the peak activity values of the Ln/SiO₂ catalysts are lower than those of some homogeneous systems, these silica supported catalysts show remarkably long-term stability and maintain their productivity for extended periods of time. Thus, the rate of ethylene consumption for the system Sc[N(SiMe₃)₂]₃/SiO₂/TIBA remained almost constant throughout a 50 min experiment (Figure 2).

In several lanthanide catalytic systems magnesium alkyls have been used as activators, in preference to aluminum alkyls. For example, Gromada et al.⁷ found that activation of Nd₃(μ₃-O^tBu)₂(μ₂-O^tBu)₃(O^tBu)₄(THF)₂ with di(*n*-hexyl)magnesium at 0 °C showed an optimum at a Mg/Nd ratio of 1:1, to give a catalyst with an ethylene polymerization activity of 5–10 kg PE (mol metal)⁻¹ h⁻¹ bar⁻¹, while no activity was observed when a variety of aluminum alkyls or Grignard reagents were used. This Nd catalyst also differs from the Ln/SiO₂ system described above in being sensitive to deactivation and shows a rapid loss of activity after ca. 10 min.

The silica-supported lanthanide amide catalysts were therefore tested with just 1 equiv of MgBu₂. At a Mg/Ln ratio of 1:1 only low yields of polymeric products were obtained, and it was found that 3 equiv of MgR₂ was needed to achieve reasonable activities (Table 2). As was the case with TIBA as activator, there is an inverse relationship between ionic radius and polymerization activity; scandium proved to be most active,

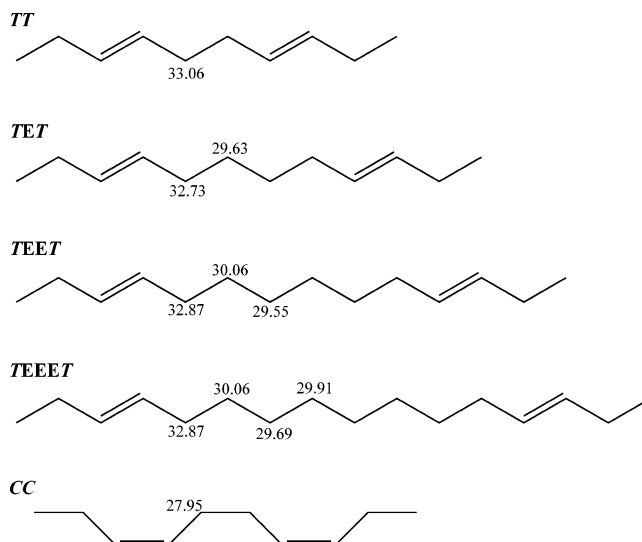


Figure 3. Assignment of saturated carbons in E/BD copolymers (¹³C NMR chemical shifts in ppm).³¹

at 13.1 kg (mol metal)⁻¹ h⁻¹ bar⁻¹. In all cases, however, the activities of the Ln/SiO₂ catalysts activated with magnesium alkyls decreased with time and remained substantially below those with TIBA as activator.

The molecular weights of the polymers were very high, with \bar{M}_w being usually close to 10⁶ g mol⁻¹ for the system with TIBA and slightly higher than 10⁶ g mol⁻¹ when dibutylmagnesium was used as cocatalyst. Only the neodymium/TIBA catalyst gave slightly lower molecular weights (7.4 × 10⁵ g mol⁻¹, entry 4). The polydispersities were very broad, and \bar{M}_w/\bar{M}_n was typically >10. The polyethylene samples showed melt transitions on first heating at 140–141 °C and at 138 °C after annealing, indicative of linear high-density polyethylene of very high molecular weight.

Butadiene Polymerization. Synthetic rubber is commonly produced via the conversion of 1,3-butadiene into 1,4-*cis*-polybutadiene using Ziegler–Natta catalysts in the liquid phase. However, this reaction can also be performed in a heterogeneous catalytic gas-phase process with supported neodymium Ziegler catalysts¹² as well as with supported lanthanide allyl complexes in combination with methylalumoxane (MAO).²⁹ Recently studies, including the use of DRIFTS investigations, have been made of the gas-phase polymerization of 1,3-butadiene on supported neodymium and lanthanum allyl complexes.^{29a}

In agreement with these earlier results, our Ln-[N(SiMe₃)₂]₃/SiO₂/TIBA catalysts showed good activity for the polymerization of 1,3-butadiene. The polymerization reactions were carried out in a sealed pressure tube at 50 °C with 10 mL of butadiene. The catalysts were prepared as described for ethylene polymerizations, then suspended in light petroleum (5 mL), and treated with TIBA for 30 min. This suspension was added to a mixture of the condensed butadiene and TIBA at -78 °C; the tubes were sealed and then heated rapidly to 50 °C. The reactions were terminated by releasing the pressure and the addition of methanol. The results are collected in Table 3.

The most striking feature is that all the different lanthanides tested achieved very similar polymerization results, both in terms of activity and also in the stereochemistry of the resulting polybutadiene. The catalysts gave turnover numbers (TON) typically of ca.

Table 2. Ethylene Polymerization with $\text{Ln}[\text{N}(\text{SiMe}_3)_2]_3/\text{SiO}_2$ Catalysts Activated with MgBu_2^a

run	support (g)	Ln	ionic radius (Å)	yield (g)	productivity ^c	M_w^d	M_w/M_n^d
8 ^b	0.504	Sc	0.68	9.23	13.2	1 030 000	10
9	0.993	Gd	0.94	15.5	11.1	1 330 000	30
10	0.944	Sm	0.96	10.8	7.69	1 150 000	41
11	0.915	Nd	0.99	4.84	3.47	1 350 000	14
12	0.999	La	1.06	4.90	3.50	1 260 000	11

^a Conditions: $\text{Ln}[\text{N}(\text{SiMe}_3)_2]_3$ 200 μmol , MgBu_2 600 μmol , temperature 80 °C, time 1 h 7 bar ethene pressure. ^b $\text{Sc}[\text{N}(\text{SiMe}_3)_2]_3$ 100 μmol . ^c In $\text{kg mol}^{-1} \text{h}^{-1} \text{bar}^{-1}$. ^d Determined by gel permeation chromatography in 1,2,4-trichlorobenzene using polystyrene standards.

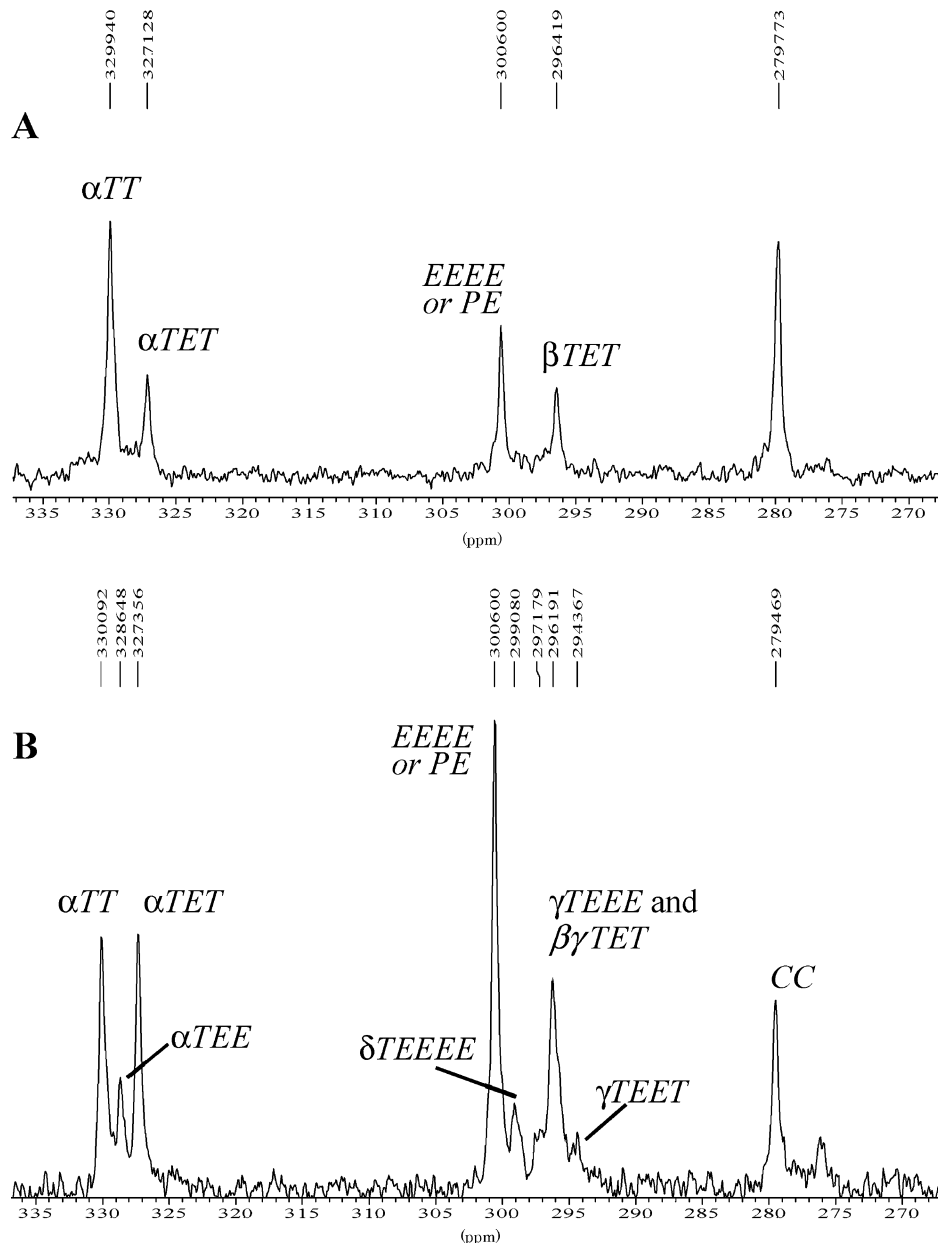


Figure 4. ^{13}C $\{^1\text{H}\}$ NMR spectra of E/BD copolymers prepared with catalyst **6**: (A) 51 mol % BD (Table 4, entry 22); (B) 21 mol % of BD (entry 23).

800–1500 mol BD (mol metal) $^{-1} \text{h}^{-1}$ and produced predominantly 1,4-*cis*-polybutadiene. It is possible that under these conditions the polymerization was mass-transport-limited since during the course of the polymerization a sticky mass of polymer formed around the magnetic follower and made efficient polymerization difficult.

Unusually, the metal employed seemed to have little effect on the polymer stereochemistry. Neodymium has long been known to produce polybutadiene with very high 1,4-*cis* stereoselectivity,³⁰ yet in the present system

the performance of the Nd/SiO₂ catalyst was, if anything, among the worst, in terms of both activity and stereoselectivity. The reason for this behavior is unclear at this time. The only exception was scandium, which generated polybutadiene with a high 1,4-*trans* content of up to ca. 40 mol %.

The polybutadienes produced with these catalysts are only sparingly soluble in all solvents. This is not unusual for high-molecular-weight PBD but precluded accurate molecular weight determinations. The polymers were however sufficiently soluble to carry out the

Table 3. Butadiene Polymerizations with Ln[N(SiMe₃)₂]₃/SiO₂/TIBA Catalysts^a

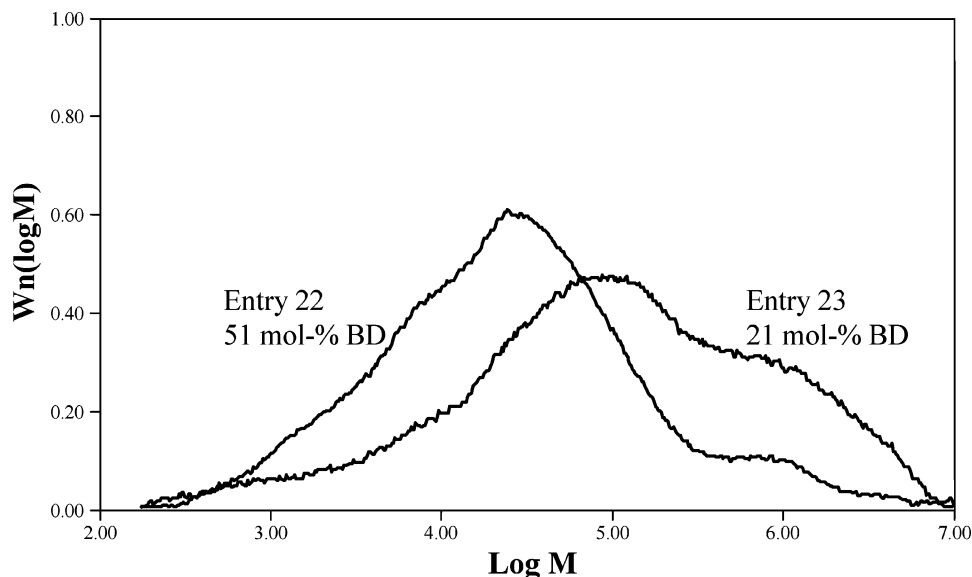
run	Ln	time (min)	yield (g)	conversion (%)	TON ^b	1,4-cis ^c (%)	1,4-trans ^c (%)	1,2 ^c (%)
13	Sc	30	1.378	22.2	1020	60.2	36.7	3.1
14	Y	30	2.487	40.0	1840	81.3	13.7	5.0
15	Sm	30	1.992	32.1	1470	89.2	6.7	4.1
16	La	30	2.057	33.1	1520	85.2	9.8	5.0
17	Nd	30	0.894	14.4	661	84.9	11.2	3.9
18	Gd	30	1.119	18.0	827	91.2	4.9	3.9
19	Dy	30	2.107	33.9	1560	90.0	3.8	6.2

^a Conditions: Ln[N(SiMe₃)₂]₃ 50 μ mol, TIBA 0.75 mmol, temperature 50 °C. ^b In mol BD mol Ln⁻¹ h⁻¹. ^c Determined by diad analysis of the ¹H and ¹³C NMR spectra of the polymers in 1,1,2,2-tetrachloroethane-*d*₂ at 100 °C.

Table 4. Ethylene/Butadiene Copolymerizations with the System Ln[N(SiMe₃)₂]₃/SiO₂/TIBA^a

entry	Ln	E feed ^b	BD feed ^c	<i>t</i> (min)	yield (g)	E pol ^d	1,4-cis pol ^d	1,4-trans pol ^d	1,2 pol ^d	\bar{M}_w	\bar{M}_w/\bar{M}_n	<i>T</i> _m (°C)
20	Sc ^e	2		60	6.16	100				858 000	30	138
21	Sc		1.7	30	2.07		57.7	37.3	4.9	60 500	5.6	70
22	Sc	2	1.7	45	2.54	49.0	20.3	27.8	2.8	147 000	21	44; 125
23	Sc	2	0.8	45	2.30	79.0	6.5	13.5	0.9	537 000	51	126
24	Sc	2	0.4	45	1.94	94.1	n.d.	n.d.	0.4	631 000	41	128
25	Nd		1.7	45	3.67		84.5	11.2	3.9	16 000	3.9	66
26	Nd	2	1.7	45	2.65	10.3	70.5	14.1	5.0	25 000	5.2	n.d.
27	Nd ^e	2	0.4	45	0.35	42.1	32.4	25.5	~0	10 000	3.7	75; 126
28	Dy	2	1.7	45	2.39	33.0	47.0	13.3	6.7	98 000	9.3	126

^a Polymerization conditions: 110 mL of toluene, 50 °C, Al/Ln = 30. ^b Ethene pressure [bar]. ^c BD in [mol L⁻¹]. ^d Molar percentage in the copolymer as determined by ¹H and ¹³C {¹H} NMR [mol %]. ^e 100 μ mol of Ln[N(SiMe₃)₂]₃.

**Figure 5.** GPC curves for E/BD copolymers obtained with scandium catalyst **6**.

diad analysis of the polymer microstructure by ¹H NMR spectroscopy in tetrachloroethane-*d*₂ at 100 °C.

Ethylene/Butadiene Copolymerizations. The supported catalysts **3** (Nd), **6** (Sc), and **7** (Dy) activated with TIBA were tested for E/BD copolymerizations at 50 °C, under 2 bar ethylene pressure with varying feed concentrations of butadiene. The results are collected in Table 4. All three catalysts promote the copolymerization of E and BD. The yields are generally very similar for all three systems. This may indicate that as for BD homopolymerizations catalysis was hampered by mass-transport effects, and indeed the solutions in the reactor very rapidly became extremely viscous. On the other hand, important differences in catalyst behavior are noticeable, depending on both the element and the monomer feed ratio.

The neodymium catalyst **3** (entries 25–27) produced low molecular weight materials, since \bar{M}_w was never higher than 30 000 g mol⁻¹. The polydispersities of **4**–**6** were surprisingly low compared to the homopolymeri-

zation results. The molecular weight distribution was monomodal, indicating a uniform behavior of the catalytically active centers. ¹H and ¹³C {¹H} NMR spectra showed that the incorporation of BD increased with increasing feed concentration and reached values of nearly 90 mol % (entry 26). As in the PBD homopolymerization, at high BD incorporation (entry 26) the 1,4-cis (*C*) stereochemistry was favored over the 1,4-trans (*T*). On the other hand, lower BD incorporation levels led to increased 1,4-trans units. A multiblock structure was found for all copolymers, as indicated by the presence of dominant peaks in the ¹³C NMR spectrum at δ 33.06 (*TT* diads), 30.06 (polyethylene block), and 27.95 ppm (*CC* diads).³¹ The dysprosium catalyst gave comparatively lower incorporation of the diene (up to ca. 70 mol %), with a preference for 1,4-cis geometry and a multiblock microstructure (entry 28). The molecular weight was higher than with Nd, and the polydispersity was broader.

By contrast, the supported scandium catalyst yielded copolymers with much lower BD contents, typically 5–50 mol %, over the range of feed concentrations investigated. The distribution of 1,4-cis and 1,4-trans units was approximately even. $\{^{13}\text{C}\}$ ^1H NMR analysis showed that the microstructure of these copolymers varied greatly with BD incorporation. Figure 3 shows the various resonances due to saturated carbons observed in the two polymers with higher diene contents, assigned according to Boisson et al.³¹ At low BD contents, determination of the 1,4-cis and 1,4-trans distribution was not possible (entry 24). With 21 mol % of BD in the polymer chain (entry 23), distinct blocks consisting essentially of 1,4-cis units for one part (strong signal at δ 27.98) and of somewhat alternating E/1,4-trans-BD units for the other part (peaks at δ 30.06 and, to a lesser extent, δ 32.71 and 29.64) could be seen (Figure 4, spectrum A). A mixed composition with 1,4-cis and E/1,4-trans blocks was also found for the material containing 51 mol % of BD (entry 22); the E/1,4-trans block exhibited a tendency to random distribution, as indicated by the presence (among others) of all resonances characteristic of *TT*, *TET*, *TEET*, and *TEET* units (Figure 4, spectrum B).

The molecular weights of several hundred thousand g mol^{-1} obtained with the scandium-based system were considerably higher than those obtained with the supported Nd and Dy catalysts; they decreased consistently with increasing BD contents. The molecular weight distributions of the materials with high BD contents prepared with scandium catalysts is particularly broad (entries 22 and 23); the GPC traces show a tendency toward polymodal behavior, in line with the preference of this catalyst for ethylene polymerization (Figure 5).

Conclusion

The reaction of dehydroxylated silica with lanthanide amido complexes provides a convenient synthetic route to solid supported lanthanide systems. In combination with TIBA, the lanthanides are alkylated and are active for the polymerization of ethylene and butadiene and also for the copolymerization of ethylene and butadiene. This catalyst system is characterized by several advantages: the facile synthesis and good thermal stability of the lanthanide amide precursors, the ease of attachment to the support, the good response to aluminum trialkyls as activators, and the remarkably good long-term stability, with hardly any sign of catalyst deactivation in polymerizations over ≥ 1 h. There is an inverse relationship between the activity of the catalysts and the ionic radius of the lanthanide involved. This trend is surprising and as yet unexplained; it is the opposite of that seen with the homogeneous catalyst $[\text{Ln}(\text{CHSiMe}_3)_3(\text{THF})_2]/\text{TIBA}/2[\text{NMMe}_2\text{HPh}][\text{B}(\text{C}_6\text{F}_5)_4]$. This observation, and the fact that homogeneous mixtures of lanthanide amides and TIBA are inactive, provides evidence that the active species in the current system is indeed heterogeneous and not derived from leaching into solution.

The copolymerization of ethylene and butadiene yields mainly block copolymers, although the scandium catalyst afforded some degree of alternating ethylene/butadiene copolymer. The outcome of the copolymerization is highly dependent upon the initial feed ratios of the monomers and also the choice of lanthanide.

Acknowledgment. This work was supported by the Engineering and Physical Sciences Research Council

and the European Union (Contract HPRN-CT2000-00004).

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MA047454R