

Syndiospecific Polymerization Catalysts for Styrene Based on Rare Earth Metal Half-Sandwich Complexes

Julia Hitzbleck,¹ Klaus Beckerle,¹ Jun Okuda,^{*1} Tobias Halbach,² Rolf Mühlhaupt²

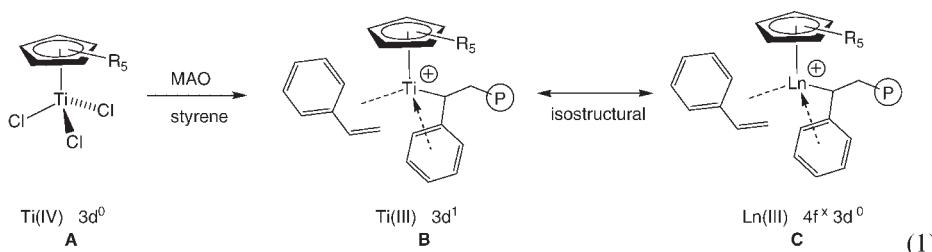
Summary: In the presence of an trialkyl aluminum cocatalyst the activation of scandium, yttrium and lutetium mono(cyclopentadienyl) complexes with various substituted cyclopentadienyl ligands by $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ results in highly efficient catalysts for the syndiospecific polymerization of styrene. As active species half-sandwich alkyl cations is assumed that is isostructural with the mono(cyclopentadienyl) titanium alkyl cation originally proposed by Zambelli.

Keywords: living polymerization; polystyrene; rare earth metal catalysts; stereospecific polymers

Introduction

Polystyrene is one of the important polymer materials used for various applications today. Although isotactic polystyrene has been known since the 1950s, only recently did syndiotactic polystyrene (sPS), first reported by Ishihara et al. at Idemitsu in 1986, receive attention due to its higher melting point and crystallization rate compared to isotactic polystyrene. The standard mono(cyclopentadienyl) titanium catalysts of type $\text{Cp}'\text{TiCl}_3/\text{MAO}$ ($\text{Cp}'=\text{C}_5\text{H}_5$ or

C_5Me_5) produce syndiotactic polystyrene in high yield,^[1,2] but only show poor results for the copolymerization of styrene with ethylene.^[3–6] This observation has been attributed to the different oxidation states of the active species. Whereas α -olefins and ethylene are assumed to be polymerized by the initially formed titanium(IV) complex **A**, the reduction product of the MAO-activated catalyst system, a cationic titanium(III) complex $[\text{Cp}'\text{TiMe}]^+\text{B}$, has been proposed as the active species in syndiospecific styrene polymerization (Equation 1).^[7]



¹ Institut für Anorganische Chemie, RWTH Aachen University, Landoltweg 1, D-52074 Aachen, Germany

² Freiburger Materialforschungszentrum und Institut für Makromolekulare Chemie der Albert-Ludwigs-Universität Freiburg, Stefan-Meier-Str. 21, D-79104 Freiburg i. Br., Germany

Co- and terpolymers of styrene with a variety of α -olefins often show enhanced mechanical properties as for example good visco-elasticity, a major advantage over the brittleness of sPS. Therefore more efficient copolymerization catalysts are needed to further improve the polystyrene properties

by precise control of monomer incorporation, molecular weight distribution as well as stereoregularity of the comonomer sequences. The development of homogeneous single-site polymerization catalysts allows living polymerization under controlled conditions and thus could lead to the production of materials with specific microstructure and unique properties.

The active species of rare earth metal half-sandwich catalysts **C** (Equation 1) are isostructural to the half-sandwich titanium(III) species **B** and such compounds have thus recently received increased interest due to their high activity and selectivity.^[8–13] Recent reports on half-sandwich rare earth metal dialkyl complexes $[\text{Ln}(\eta^5\text{-C}_5\text{Me}_4\text{SiMe}_3)(\text{CH}_2\text{SiMe}_3)_2(\text{THF})]$ ($\text{Ln} = \text{Sc, Y, Gd, Lu}$), a class of compounds previously prepared in our group, documented high polymerization activity for styrene upon activation with $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$.^[14,15] However, the resulting charge separated species $[\text{Ln}(\eta^5\text{-C}_5\text{Me}_4\text{SiMe}_3)(\text{CH}_2\text{SiMe}_3)_2(\text{THF})]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ is highly unstable in benzene or toluene and separates out of solution as a red oil, impeding characterization by NMR spectroscopy.^[14] Experiments in our laboratory have shown improved stability of the cationic complex in the presence of an aluminum alkyl as well as the crucial role of the aluminum alkyl cocatalyst in the syndiospecific polymerization styrene.

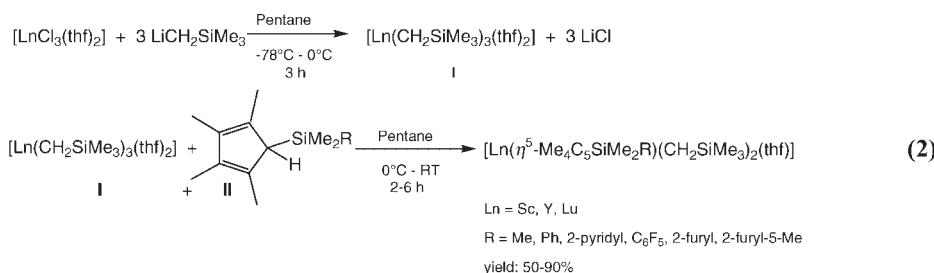
Results and Discussion

A variety of rare earth metal half-sandwich complexes with different silyl-substituents

on the cyclopentadienyl ring was obtained by σ -bond metathesis between the respective metal tris(trimethylsilylmethyl) complexes **I** and substituted cyclopentadienes **II** to give compounds of the general formula $[\text{Ln}(\eta^5\text{-C}_5\text{Me}_4\text{SiMe}_2\text{R})(\text{CH}_2\text{SiMe}_3)_2(\text{THF})_n]$ ($\text{Ln} = \text{Sc, Y, Lu}$; $\text{R} = \text{Me, Ph, 2-pyridyl, C}_6\text{F}_5, 2\text{-furyl, 2-furyl-5-Me}$) (Equation 2).^[10,11] Recrystallization from pentane at -40°C afforded most complexes as crystalline solids in good yield.

The mono(cyclopentadienyl) complexes have been characterized by spectroscopic and analytical methods and show the expected signals for the ligands and donors coordinated to the metal center. X-ray crystallography revealed their molecular structures with representative examples shown in Figures 1 and 2.

The solid-state structures of the half-sandwich complexes display the generally observed piano-stool geometry, with an η^5 -coordinated cyclopentadienyl ring in the apical position of a trigonal pyramid and the remaining three ligands in the basal plane. The overall coordination geometry is independent from the size of the metal center as seen in the corresponding scandium and yttrium complexes **1** and **2** in Figure 1. In contrast to this observation, in the case of potentially intramolecularly coordinating substituents the smaller size of scandium compared to the larger yttrium and lutetium metal centers ($\text{Sc} = 0.745 \text{ \AA}$, $\text{Lu} = 0.861 \text{ \AA}$, $\text{Y} = 0.900 \text{ \AA}$; $\text{CN} = 6$) leads to differences in the overall coordination geometry.^[16] The 2-furyl substituent in $[\text{Lu}(\eta^5\text{-C}_5\text{Me}_4\text{SiMe}_2\text{(2-furyl)})(\text{CH}_2\text{SiMe}_3)_2(\text{THF})]$ (**4**) for example



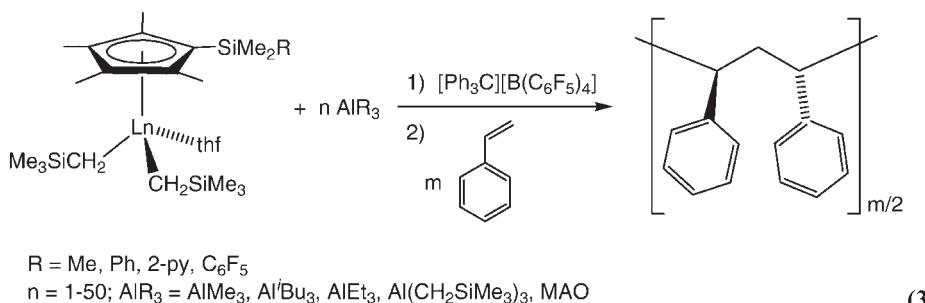
coordinates to the metal center, whereas in $[\text{Sc}(\eta^5\text{-C}_5\text{Me}_4\text{SiMe}_2(2\text{-furyl-5-Me})(\text{CH}_2\text{SiMe}_3)_2(\text{THF})]$ (**3**) the metal center is sterically saturated and shows the 2-furyl-5-Me group pointing away from the metal. This can be attributed to the smaller size of scandium, which is not able to accommodate the second donor. In addition, the tethered furyl group coordinates to the metal under strain and thus shows even more decreased donor strength, forfeiting replacement of the THF ligand (Figure 2). Differences in activity were also observed between scandium and the heavier congener, since analogs of **3** could not be obtained for yttrium and lutetium. In contrast, the larger metals showed C–H activation and only yne-enolates as products of an unusual ring-opening reaction were isolable $[\text{Ln}(\eta^5\text{-C}_5\text{Me}_4\text{SiMe}_2(\text{C}=\text{C}-\text{CH}=\text{COMe})(\text{CH}_2\text{SiMe}_3)_2(\text{THF})]$.^[11]

As reported previously, cationic half-sandwich complexes of the rare earth metals are active catalysts for the polymerization of styrene and a variety of other α -olefins.^[14,15,17] Nonetheless, we could demonstrate that the addition of an aluminum alkyl prior to activation of the catalyst is crucial for the stability of the cationic species formed and thus for the polymerization activity of such catalyst systems. Therefore, a revised polymerization protocol was used for the following studies (Equation 3).

increasing amount of the aluminum cocatalyst a rise in the polymerization activity was observed (\sim 1–5 equivalents, depending on the nature of the alkyl group; Figure 3 and 4).

Nonetheless, a larger excess (>5 –10 equiv.; Figure 4) inhibited the catalyst activity most likely due to formation of a dormant state in which the active site on the metal center is blocked by a bridging aluminum species, similar to the dimer $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{Sm}(\mu\text{-Me})\text{AlMe}_2(\mu\text{-Me})_2\text{Sm}(\eta^5\text{-C}_5\text{Me}_5)_2]$.^[19] Related reports have occurred in the literature for the polymerization of styrene with the system $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{TiMe}_3]/\text{B}(\text{C}_6\text{F}_5)_4/\text{Al}(\text{C}_8\text{H}_{17})_3$.^[20] In the absence of n-octylaluminum no stereoselectivity was obtained; but an increase of the Al/Ti ratio over 2 led to a decrease in polymerization activity. Furthermore, use of TMA almost completely inhibited the polymerization activity possibly due to formation of the adduct $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{Ti}(\mu\text{-Me})_3\text{AlMe}]$.^[20] As depicted in Figure 4, this effect is more pronounced for the smaller aluminum alkyls (TMA, MAO) and also explains the decreased activity of DIBALH compared to TIBAL by formation of a possibly hydride bridged species.

It could be shown that the aluminum alkyl itself does not activate the catalyst since no polymerization activity was observed in the absence of the borate activator. However, subsequent addition of



In the absence of the aluminum alkyl reagent only atactic polystyrene could be obtained in low yield, possibly resulting from the trityl borate activator.^[18] With

trityl borate led to abstraction of one alkyl ligand on the metal center, thereby generating an open site on the catalyst. The nature of the aluminum alkyl cocatalyst

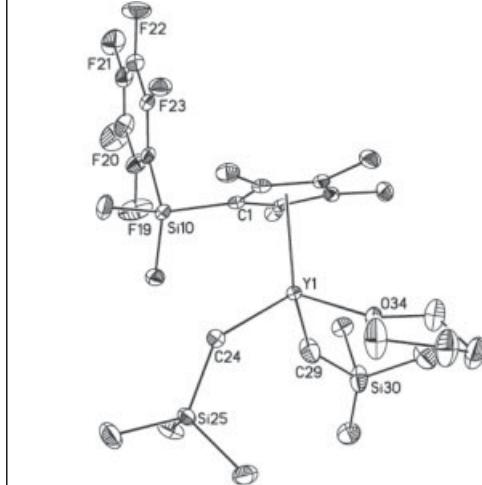
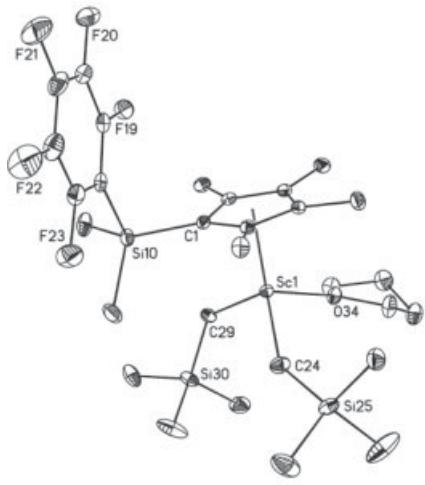


Figure 1.

Molecular structures of $[\text{Ln}(\eta^5\text{-C}_5\text{Me}_4\text{SiMe}_2\text{C}_6\text{F}_5)(\text{CH}_2\text{SiMe}_3)_2(\text{THF})]$ ($\text{Ln} = \text{Sc}$, **1**; Y , **2**). Selected bond distances and angles for $\text{Ln} = \text{Sc}$, **1**; Y , **2** respectively: $\text{Ln}(1)\text{-C}(24)$ 2.201(2), 2.404(4) Å; $\text{Ln}(1)\text{-C}(29)$ 2.263(2), 2.364(5) Å; $\text{Ln}(1)\text{-O}(34)$ 2.164(2), 2.313(3) Å; $\text{Ln}(1)\text{-C}(1-5)$ 2.463(2)-2.542(2), 2.611(4)-2.689(4) Å; $\text{C}(24)\text{-Ln}(1)\text{-C}(29)$ 106.36(7)°, 107.5(2)°; $\text{O}(34)\text{-Ln}(1)\text{-C}(24)$ 100.96(7)°, 95.85(2)°; $\text{O}(34)\text{-Ln}(1)\text{-C}(29)$ 97.10(6)°, 102.4(2)°.

strongly influenced the polymerization activity and thus it seems likely that the active species in the polymerization process is an aluminum alkyl stabilized, bimetallic

complex. Interestingly, use of $\text{Al}(\text{CH}_2\text{SiMe}_3)_3$ produced syndiotactically enriched polystyrene (Figure 5a), whereas all other cocatalysts yielded purely syndiotactic

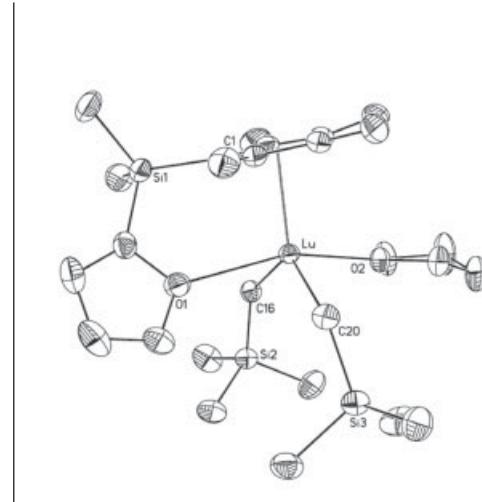
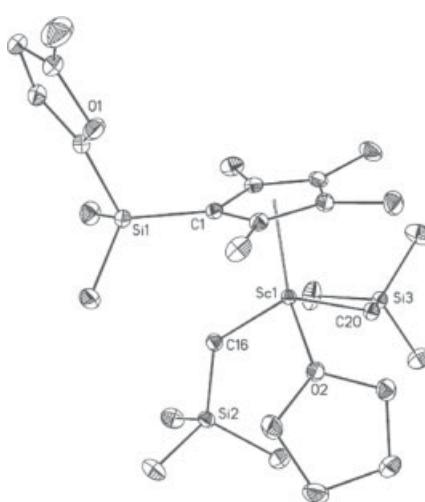
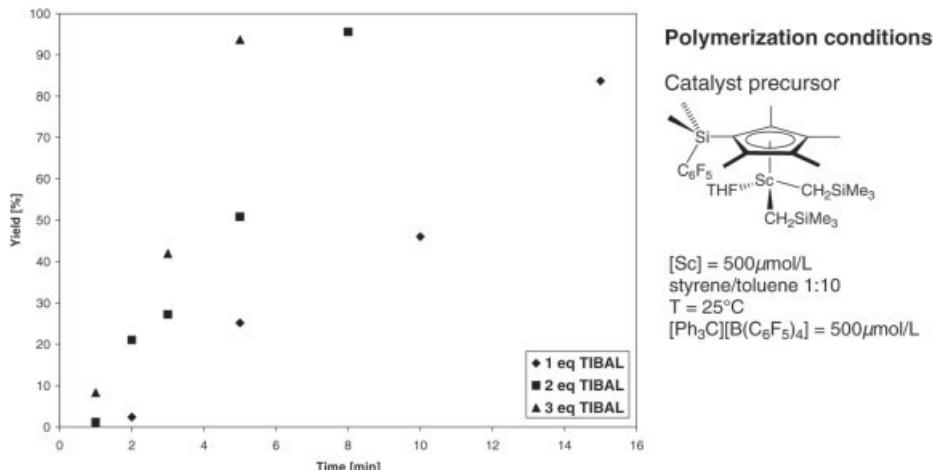
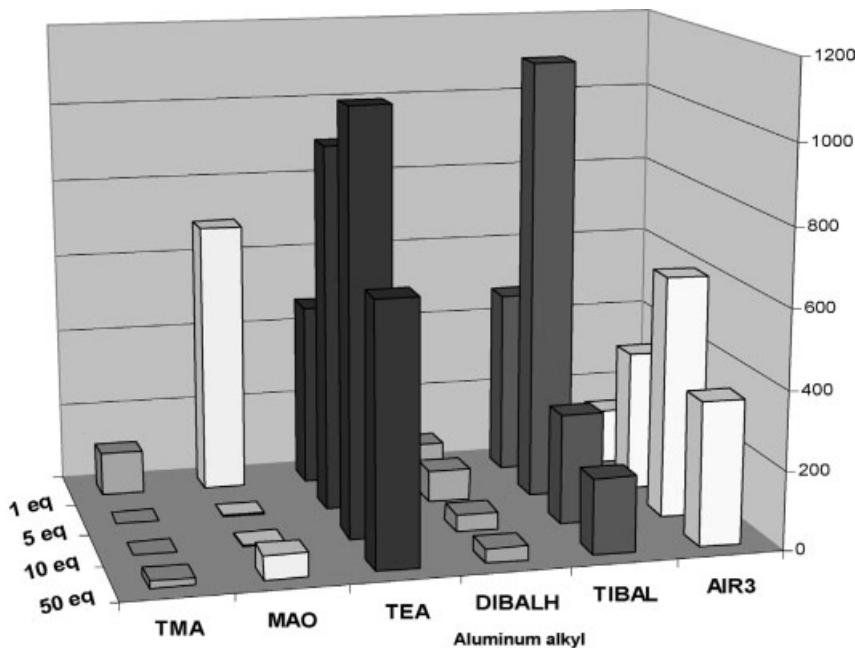


Figure 2.

Molecular structures of $[\text{Ln}(\eta^5\text{-C}_5\text{Me}_4\text{SiMe}_2\{2\text{-furyl-5-R}\})(\text{CH}_2\text{SiMe}_3)_2(\text{THF})]$ ($\text{Ln} = \text{Sc}$, **3**, $\text{R} = \text{Me}$; $\text{Ln} = \text{Lu}$, **4**)^[11] ($\text{R} = \text{H}$). Selected bond distances and angles for $\text{Ln} = \text{Sc}$ **3**, Lu **4** respectively: $\text{Ln}(1)\text{-C}(16)$ 2.244(2), 2.373(4) Å; $\text{Ln}(1)\text{-C}(20)$ 2.228(2), 2.381(4) Å; $\text{Lu}(1)\text{-O}(1)$ 2.659(3) Å; $\text{Ln}(1)\text{-O}(2)$ 2.171(1), 2.305(3) Å; $\text{Ln}(1)\text{-C}(1-5)$ 2.480(2)-2.541(2), 2.568(4)-2.727(4) Å; $\text{C}(16)\text{-Ln}(1)\text{-C}(20)$ 103.93(5)°, 124.4(2)°; $\text{O}(2)\text{-Ln}(1)\text{-C}(16)$ 103.76(4)°, 90.12(2)°; $\text{O}(2)\text{-Ln}(1)\text{-C}(20)$ 95.74(4)°, 89.3(2)°; $\text{O}(1)\text{-Lu}(1)\text{-O}(2)$ 162.0(1)°.

**Figure 3.**

Styrene polymerization in dependence of equivalents TIBAL (triisobutylaluminum).

**Figure 4.**

Polymerization activity as a function of aluminum alkyl concentration. TMA = trimethylaluminum, MAO = methylalumoxane, TEA = triethylaluminum, DIBALH = diisobutylaluminum hydride, TIBAL = triisobutylaluminum, AlR_3 = tris(trimethylsilylmethyl)aluminum. Polymerization conditions: $[\text{Sc}(\eta^5\text{C}_5\text{Me}_4\text{SiMe}_2\text{C}_6\text{F}_5)(\text{CH}_2\text{SiMe}_3)_2(\text{THF})] = 500 \mu\text{mol/L}$, $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4] = 500 \mu\text{mol/L}$, styrene: toluene $1:10$, $t = 10 \text{ min}$, $T = 25^\circ\text{C}$.

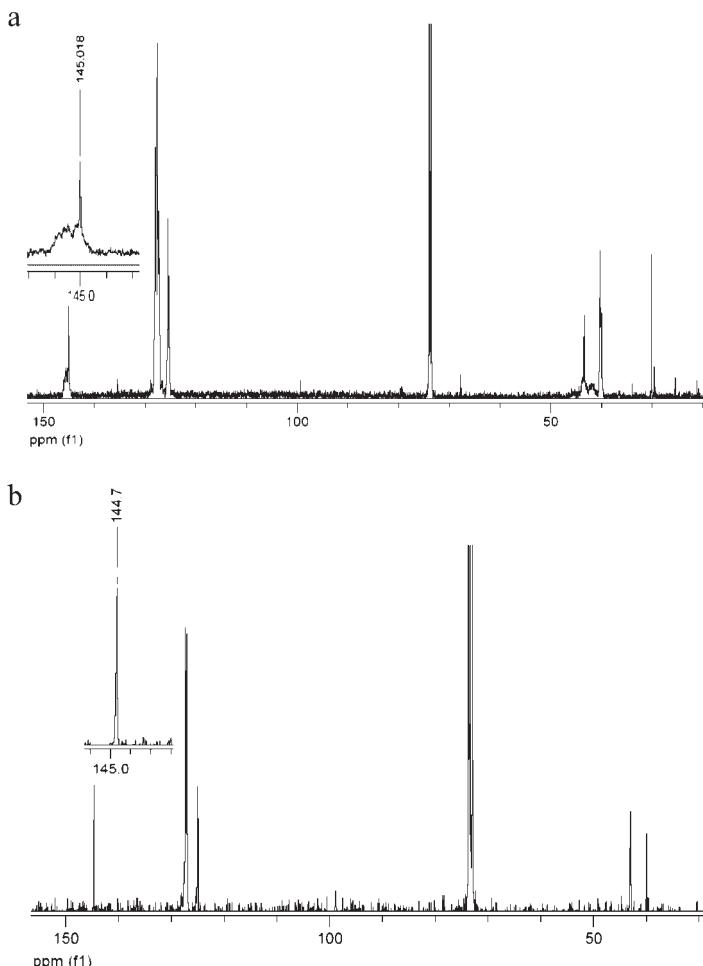


Figure 5.

^{13}C NMR spectra (300 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$) of polymers obtained with $[\text{Sc}(\eta^5\text{-C}_5\text{Me}_4\text{SiMe}_2\text{C}_6\text{F}_5)(\text{CH}_2\text{SiMe}_3)_2(\text{THF})]/\text{AlR}_3/\text{[Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$; a) $\text{AlR}_3 = \text{Al}(\text{CH}_2\text{SiMe}_3)_3$; sPS enriched PS; b) $\text{AlR}_3 = \text{Al}(\text{C}_2\text{H}_5)_3$; sPS.

polystyrene, whenever the polymerization activity was high (Figure 5b).

In addition, ethylene polymerization experiments showed that an increase in borate activator concentration also reduces the catalyst activity,^[21] underpinning that a monocationic, aluminum alkyl-stabilized species is responsible for the polymerization activity.

Conclusion

In summary, syndiotactic polystyrene can be obtained using highly active half-sandwich rare earth metal dialkyl complexes.

The aluminum alkyl cocatalyst plays an important role in the formation of the active species, most likely by stabilizing the electronically and sterically unsaturated metal center. In addition, for polymerization reactions which require a scavenger for residual impurities the same aluminum alkyl as the cocatalyst can be used, without increasing the components in the reaction mixture. With the smallest metal scandium in this series the complexes even show activities comparable to those of the standard $\text{Cp}^*\text{TiCl}_3/\text{MAO}$ catalysts.^[1,2] Such mono(cyclopentadienyl) rare earth metal

complexes have also been reported as highly active for (stereo-)selective co- and terpolymerization of a variety of α -olefins,^[14,15,17] offering systems superior over the currently applied catalysts. Even though the details of the active species in the polymerization process remains to be elucidated, progress towards a better understanding is being made.

Acknowledgements: Financial support by the EU Commission (FP6 project: NMP3-CT-2005-516972), the Deutsche Forschungsgemeinschaft, and the Fonds der Chemischen Industrie is gratefully acknowledged.

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