

Silica-supported lanthanide silylamides for methyl methacrylate polymerisation: controlled grafting induces controlled reactivity

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Lanthanide silylamides were grafted onto non-porous silica dehydroxylated at various temperatures, and the surface species nature and relative distribution were correlated with MMA polymerisation activity and selectivity.

Within the field of catalytic polymerisation, lanthanide complexes have attracted considerable attention, owing to their outstanding performances, which range from extremely high activities to the generation of unprecedented polymer architectures.¹ A key feature regarding the catalytic behaviour of such species lies in the nature of their coordination sphere, which may be tuned to adjust their reactivity. Bearing in mind the advantages of heterogeneous catalysis, highly favoured regarding large-scale applications, the synthesis of grafted lanthanide catalysts would be highly desirable. Moreover, it is of considerable interest to be able to control the nature of the obtained grafted species, which could not only allow a deeper understanding of their structure–activity relationships, but could also pave the way to homogeneous-like coordination sphere modifications in order to tune the catalyst's performances.²

As demonstrated by Anwender and collaborators, lanthanide (extended) silylamide complexes can be grafted onto (mesoporous) silica, generating through Ln–N bond protonolysis mixtures of mono- and digrafted lanthanide amide surface species (similar to surface species **A** and **B** on Scheme 1). These may relieve their coordinative unsaturation by interaction with a neighbouring siloxane oxygen atom. Noteworthy is the reaction of $\equiv\text{Si}-\text{OH}$ with the released $\text{HN}(\text{SiR}_3)_2$, which concomitantly generates $\equiv\text{Si}-\text{O}-\text{SiR}_3$ groups.³ Since from a coordination chemistry point

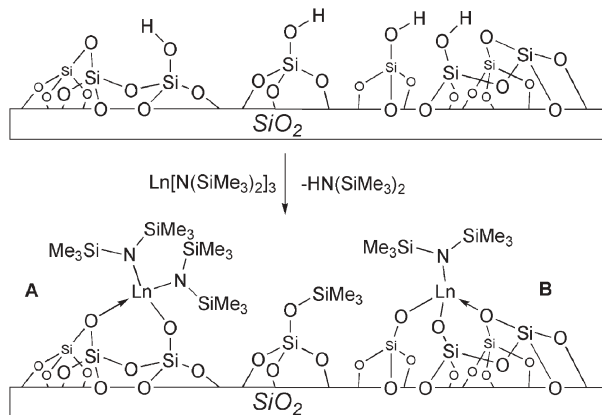
of view a silica surface may behave as a monodentate or a bidentate siloxide ligand, depending on the extent of its dehydroxylation, we have examined the influence of this key parameter on the nature and distribution of surface species.⁴

As molecular precursors, we chose to graft $\text{Ln}[\text{N}(\text{SiMe}_3)_2]_3$ complexes, devoid of a donor ligand within their coordination sphere and available over a wide range of the lanthanide series members.⁵ The selected non-porous silica support, Aerosil 380 (Degussa, specific area $380 \text{ m}^2 \text{ g}^{-1}$), was subjected to dehydroxylation by heating under a secondary vacuum at various temperatures: 250, 500 and 700 °C, respectively yielding materials **1a**, **2a** and **3a**. Such a treatment affects both the nature and the quantity of the residual OH groups.⁶ With increasing treatment temperature, their distribution goes from clusters of hydroxyls to isolated silanols, while the OH contents (in $\text{mmol}_{\text{OH}} \cdot \text{g}^{-1}$) decreases: 2.22 for **1a**, 1.13 for **2a** and 0.62 for **3a**, as shown by bisalkylmagnesium titration.⁷

Grafting of $\text{La}[\text{N}(\text{SiMe}_3)_2]_3$ **4** was carried out by impregnation in toluene on **1a–3a**.† After three successive washings and extensive drying under a secondary vacuum, the modified silicas **1b–3b** were obtained as colourless powders. Qualitative NMR analysis of the toluene phase showed the presence of released hexamethyldisilazane along with unreacted lanthanum starting material.

Elemental analyses of **1b–3b** show decreasing lanthanum content with increasing dehydroxylation temperature: 6.55% in **1b**, 4.52% in **2b**, and 3.79% in **3b**, as expected from the decrease in surface silanol concentration. The corresponding molar loadings (0.47, 0.32 and 0.27 $\text{mmol}_{\text{La}} \cdot \text{g}^{-1}$, respectively) are significantly lower than the maximal expected loadings. This difference may arise not only from the side reaction of silanol silylation which lowers the number of available grafting sites, but also from surface crowding by the bulky silylamide species, which may cause incomplete consumption of surface silanols by preventing efficient contact with the molecular precursor **4**. The N–La molar ratio increases with the pre-treatment temperature,† indicating a modification in the relative proportions of monografted ($\equiv\text{Si}-\text{O}-\text{La}[\text{N}(\text{SiMe}_3)_2]_2(\text{Si}-\text{O}-\text{Si})_x$ (**A**) and digrafted ($\equiv\text{Si}-\text{O}-\text{La}[\text{N}(\text{SiMe}_3)_2]_2(\text{Si}-\text{O}-\text{Si})_y$ (**B**) species. Thus, the **A–B** ratio can be estimated to go from *ca.* 25 : 75 in **1b**, to *ca.* 55 : 45 in **2b** and *ca.* 100 : 0 in **3b**. This confirms that surface species distribution can indeed be controlled and, moreover, that a monografted lanthanum silylamide can be selectively obtained (while bearing in mind the accuracy of the elemental analysis). Such a result parallels the observations made on surface organometallic chemistry involving transition metals.²

Compared with the starting materials, DRIFT spectra show, for the three lanthanum-grafted silicas, the quasi-total disappearance



Scheme 1 Grafting of lanthanide silylamides onto dehydroxylated silica.

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of the isolated silanol peak (3746 cm^{-1}) as well as, in the cases of **1b** and **2b**, the decrease of the vicinal silanol band intensity (Fig. 1). Broad absorptions in the O–H stretching region (3650 cm^{-1}) indicate the presence of residual interacting $\equiv\text{Si-OH}$ moieties. In agreement with the above mentioned low surface coverage rate, this could arise from their interaction with neighbouring bulky lanthanide surface species. These spectral features are accompanied by the formation of bands at 2956 and 2900 cm^{-1} (medium to weak intensities, $\nu_{\text{C-H}}$) with a shoulder at 2820 cm^{-1} , and 1596 and 1496 cm^{-1} (weak intensities, $\delta_{\text{C-H}}$) which is consistent with grafting of $\text{La}[\text{N}(\text{SiMe}_3)_2]_3$ and silanol group silylation.

The ^1H MAS NMR spectra of materials **1b–3b** all present a single peak at 0.10 ppm , corresponding to SiMe_3 protons (Fig. 2). This is to be compared with the 0.21 ppm value for the ^1H MAS NMR spectrum of **4**. Besides negligible chemical shift differences (*ca.* 0.01 ppm), the only distinctive feature between the various samples' spectra is the SiMe_3 peak half-height width, narrowing with increasing pre-treatment temperature: 300 Hz for **1b**, 220 Hz for **2b** and 140 Hz for **3b**. This is most probably due to overlapping La-N-SiMe_3 and $\equiv\text{Si-O-SiMe}_3$ peaks in different relative proportions. Indeed, the ^1H MAS NMR spectrum of the paramagnetic Nd-grafted silica **3c**, prepared from **3a** and $\text{Nd}[\text{N}(\text{SiMe}_3)_2]_3$ (**5**) shows distinct signals for the $\text{Nd-N}(\text{SiMe}_3)_2$ groups (-6.7 ppm , $\Delta\nu_{1/2} = 5600\text{ Hz}$, **5**: -6.30 ppm) and $\equiv\text{Si-O-SiMe}_3$ (0.08 ppm). The ^{13}C CP-MAS spectrum obtained for the La series consists of a single peak centred at 2.7 ppm , which is also in agreement with the presence of SiMe_3 groups on the surface.

Heteroleptic lanthanide(III) amido complexes are known to be catalytically active in methyl methacrylate (MMA) polymerisation.⁸ After initiation by 1,4-addition of Ln-N on a MMA monomer, polymer growth occurs by successive conjugated additions, the postulated active species being a lanthanide enolate.⁹ Grafted lanthanide amides **1b–3b** catalyse MMA polymerisation, affording high molecular weight poly(methyl methacrylate) (PMMA) with polydispersity indexes around 2 (Table 1).^{†10} Their activity depends on the silica pre-treatment temperature: indeed, for similar lanthanum content, **3b** is 1.5 times more active than **1b**. However, the supported catalysts are less productive than their molecular precursor **4**, while allowing a better control over the molecular weight distribution. Most interestingly, grafted catalysts produce isotactic-rich PMMA: the [mm] triad percentage

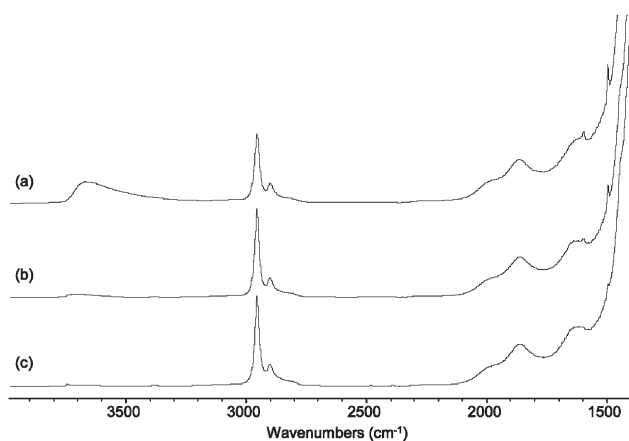


Fig. 1 DRIFT spectra of: (a) **1b**, (b) **2b**, (c) **3b**.

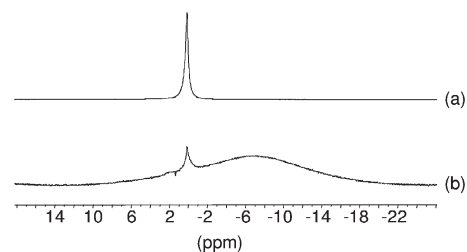


Fig. 2 ^1H MAS NMR spectra of (a) **3b**, (b) **3c** (400 MHz).

Table 1 MMA Polymerisation data^a

Cat.	Yield (%)	mm (%) ^b	mr (%) ^b	rr (%) ^b	M_n^c	PDI ^c
1b	18	92	4	4	56 000	1.90
2b	22	86	8	6	86 000	2.43
3b	28	77	13	19	73 000	2.05
4	62	28	48	24	14 800	3.01

^a $n(\text{La}) = 19\text{ }\mu\text{mol}$, MMA/La , mol/mol = 500, 5 mL PhMe, 16 h, $23\text{ }^\circ\text{C}$;
^b from ^1H NMR; ^c from GPC relative to polystyrene standards.

rises from 77% with **3b** up to 92% with **1b**. Comparatively, **4** yields atactic PMMA under the same conditions, revealing the dramatic effect of the grafting on the catalyst's stereoselectivity.

Moreover, polymerisation activities and selectivities appear to be linearly dependent on the proportions of grafted species **A** and **B**: the activity and stereoselectivity of the **A–B** distribution can be directly assessed from the linear combination of the two different site contributions. Indeed, species **A** and **B** respectively produce PMMA with turnover numbers of 135 and 73, with respective [mm] triad proportions of 77 and 97%.

In conclusion, adjustment of the silica support dehydroxylation temperature allows the controlled synthesis of distributions of mono- and digrafted surface lanthanide silylamides. These proved to be active MMA isotactic polymerisation catalysts, and the activity and selectivity of the two different active sites can be determined. The beneficial effect of the grafting process also reflects in moderate molecular weight distributions. Further developments will be focused on the tuning of the catalyst performances through grafted species coordination sphere modifications. We thank the CNRS and the Ministère de l'Éducation Nationale et de la Recherche for their financial support, Bertrand Revel and Catherine Méliet for NMR measurements and Christophe Dujardin for his kind assistance with DRIFT spectroscopy.

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Notes and references

[†] Typical grafting procedure: molecular precursor (1 mmol) dissolved in 10 mL toluene was added to a silica (1 g) suspension in 10 mL toluene, stirred for 15 h at room temperature, washed three times with 20 mL toluene and dried under a secondary vacuum. Elemental analysis (%): **1b**: La: 6.55, N: 0.82 (N/La = 1.2(4)); **2b**: La: 4.52, N: 0.66 (N/La = 1.4(5)); **3b**: La: 3.80, N: 0.80 (N/La = 2.0(9)); **3c**: Nd: 4.12, N: 0.79 (N/Nd = 1.9(8)).
[‡] Typical polymerisation procedure: to a stirred 5 mL toluene suspension of the catalyst (19 μmol of La) was added 1 mL of MMA; after 16 h, the

reaction was quenched by MeOH–HCl injection. Precipitated PMMA was separated by decantation, sonicated for a few hours, washed extensively with MeOH and dried under vacuum.

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