

Grafted lanthanide amides: Versatile catalysts for various transformations

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Available online 18 May 2006

Abstract

A series of silica-supported lanthanide (yttrium, lanthanum, neodymium and samarium) silylamides have been prepared using supports dehydroxylated at 250, 500 and 700 °C. According to the silica dehydroxylation temperature, different surface species distributions were obtained. These solids, under proper conditions, polymerise methyl methacrylate, ethylene, ϵ -caprolactone and isoprene. In the case of methyl methacrylate, structure–activity and -selectivity relationships for the surface species could be determined, while in the case of ethylene, no such information could be deduced, even if strong support effect was observed. These materials are also active in homocoupling of benzaldehyde to benzyl benzoate (Tischenko reaction) and in dimerisation of 1-heptyne into enyne. In these latter two cases, recycling of the catalytic system was successful. © 2006 Elsevier B.V. All rights reserved.

Keywords: Lanthanides; Silica; Supported catalysts; Polymerisation; Tischenko reaction; Alkyne dimerisation

1. Introduction

The grafting of homogeneous (molecular) catalysts to generate supported analogues is a subject of constant interest. Indeed, heterogenisation is a most desired process, for reasons specific to each class of reactions. Regarding transition metals-mediated olefin polymerisation processes, the interest lies mostly within the chemical engineering field: the main advantage of new heterogeneous systems, when compared to homogeneous ones, is the possibility to be directly implemented into already operating plants, which majoritarily utilise heterogeneous catalysts (“Ziegler-Natta catalysts”), affording polymer particles of convenient morphology [1]. In the case of fine chemicals synthesis, easy separation of the catalysts from the products is of particular importance, when considering for instance the produced compounds purity grade, or the need to efficiently recover a costly catalyst bearing expensive chiral ligands [2]. Moreover,

the reduced solvent consumption due to easier solid–liquid separation procedures makes such an approach most particularly interesting, bearing in mind the constant demand for greener chemical processes.

Among the metals applied within the field of catalysis, rare-earths (including scandium and yttrium) have been the subject of constant attention, due to their interesting features: they are able to mediate a broad variety of reactions [3], have a low to moderate cost, and are non-toxic. Despite these promising properties, wider application has frequently been hampered by the high sensitivity of (organometallic) catalytic precursors [4], or by the complexity of their synthesis which requires special care: alkyl and hydride derivatives are very sensitive compounds [5]. However, among the various reported lanthanide complex classes, amido derivatives are particularly attractive: derivatives of the type $\text{Ln}[\text{NR}'_2]_3$ ($\text{R}' = \text{SiMe}_3$) are easily synthetically accessible, reasonably sensitive to moisture and oxygen, and known for the most of the lanthanide series [6]. They have been successfully used as catalysts or catalytic precursors in several fields [7]. This owes much to the reactivity of the Ln-NR_2 function which offers a convenient entry into other classes of compounds: it can afford alkyl derivatives by reaction with alkylating agents [8], or react with protic reagents as alcohols [9] or cyclopentadienyl deriva-

Abbreviations: AA, alkylating agent; BEM, butyl-ethylmagnesium; MMA, methyl methacrylate; TIBA, triisobutylaluminium

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tives [10], thus (in situ) affording catalytically active species otherwise difficult to generate directly.

We have recently shown that controllable grafting of the homoleptic lanthanide silylamides $\text{Ln}[\text{NR}'_2]_3$ onto dehydroxylated silica can be achieved, and that the support heat treatment directly affects the catalytic behaviour of a lanthanum amide-based system in MMA polymerisation [11]. We present here our results on the catalytic properties of a series of grafted lanthanide (yttrium, lanthanum, neodymium and samarium) amides, showing that these species (1) initiate the polymerisation of MMA, ethylene, isoprene and ϵ -caprolactone, (2) are active, like their homogeneous precursors, in the Tischenko and terminal alkynes dimerisation reactions, and (3) constitute recyclable catalytic systems in the case of these latter organic couplings.

2. Experimental

2.1. General procedures

All experiments were carried out under an argon atmosphere in a M-Braun glove box or by using standard Schlenk techniques. Lanthanide chlorides were purchased from Strem Chemicals. Solvents, 1-heptyne and benzaldehyde were dried under nitrogen or argon using conventional reagents, degassed by freeze–pump–thaw cycles and stored in the glove box over 3A molecular sieves. Rare-earth silylamides were prepared by following literature procedures [6]. Methyl methacrylate, isoprene and ϵ -caprolactone were distilled and degassed shortly before use. Ethylene was used as received from Air Liquide. Tri-*iso*-butyl-aluminum (TIBA), di-*n*-butyl-magnesium (as 1 M solution in heptane) and *n*-butyl-lithium (as 1.6 M solution in hexanes) were obtained from Aldrich. Lithium tetra-butyl-aluminate was synthesized by following a literature procedure [12]. Liquid-state NMR analyses were run on a Bruker Avance 300. Gas chromatography analyses were performed on a Chrompack CP9001 gas chromatograph under N_2 flow with a CPSil 8 CB column (15 m length, 0.32 mm diameter, 0.25 μm film thickness). Elemental analyses were carried out at the Service Central d'Analyse du CNRS (metals), and in the Service d'Analyse Élémentaire, LSEO, Université de Bourgogne (C, H, N). Aerosil 380 silica (specific area 380 $\text{m}^2 \text{g}^{-1}$) was subjected to heating under secondary vacuum at the desired temperature (250 or 500 °C) during 15 h, or to a prior 15 h heating period at 500 °C followed by 4 h heating at 700 °C. Scanning electron microscope (SEM) investigations were carried out on a Hitachi S4700 SEM FEG (field emission gun).

2.2. Typical preparation of a grafted catalyst

A “double-Schlenk” glassware was loaded in the glove box with the chosen molecular precursor $\text{Ln}[\text{NR}'_2]_3$ (1 mmol) dissolved in 10 mL toluene in one compartment, and with silica (1 g) suspended in 10 mL toluene in the other compartment. The complex solution was added to the support by filtering through the sintered glass separating the two Schlenk tubes, and the reaction mixture was stirred for 15 h at room temperature. The supernatant was then separated by filtration into the other com-

partment, and toluene was gas-phase transferred by trap-to-trap distillation back into the compartment containing the modified support in order to wash away the residual molecular precursor. This operation was repeated twice again. The resulting powder was then dried under secondary vacuum (10^{-6} mmHg) for 6 h at 80 °C.

2.3. Typical ethylene polymerisation

A solution of TIBA (300 mg) in 16 mL toluene was introduced in a thermostated (90 °C) glass reactor equipped with a powerful mechanical stirrer. Ethylene inlet allowed to saturate continuously the inner medium at 1.1 bar. A suspension of La_{-250} (240 mg containing 6.55% La, 113 μmol) in 4 mL toluene was prepared in the glove box and injected through a septum into the polymerisation reactor. The ethylene consumption was then monitored with a mass flowmeter. The polymerisation was stopped after 2 h by hydrolysis with acidic methanol (100 mL with 1 mL concentrated HCl). The solid material was recovered by filtration, washed with pure methanol, dried and weighed (364 mg). This material contained silica which has lost the $\text{La}[\text{N}(\text{TMS})_2]_2$ functional groups and thus representing $[240 \text{ mg} - (0.113 \text{ mmol} \times 459 \text{ mg/mmol})] = 188 \text{ mg}$. The calculated mass of polyethylene is then $(364 - 188) = 176 \text{ mg}$. Integration of the mass flowmeter signal gave 165 mg of consumed ethylene.

2.4. Typical methyl methacrylate polymerisation

In the glove box, to a stirred 5 mL toluene suspension of La_{-250} (41 mg, 19 μmol La) was added 1 mL of MMA (9.4 mmol, 490 equivalents). After 16 h, the viscous reaction mixture 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 (167 mg, 18%).

2.5. Isoprene polymerisation

In the glove box, to a stirred 5 mL toluene suspension of Nd_{-700} (100 mg, 29 μmol of neodymium) in a sealable vial was added a solution of 33 μmol of BEM (1.1 equiv./Nd) in 5 mL toluene (this solution was prepared from 21 mg of a 20 wt.% BEM solution in heptane). The suspended solid turned from light blue to pale yellow. After 1 min stirring at room temperature, 1 mL isoprene (10 mmol, 344 equivalents/Nd) was added, and the sealed vial was taken out of the glove box to be heated at 85 °C, which caused rapid colour change of the solid to bright green and increasing viscosity of the reaction mixture. After 2 h, the reaction was quenched by pouring into 200 mL EtOH. The precipitated white solid was redissolved in CH_2Cl_2 , filtered and precipitated into EtOH, to afford 165 mg of a gummy solid (yield: 24%). ^1H NMR (CDCl_3 , RT) analysis showed a structure of 93% 1,4-insertion type, with a *cis*-content of 70%. A blank reaction carried out under the same conditions with dehydroxylated silica and BEM resulted in negligible polymer formation (yield < 1%).

2.6. ϵ -Caprolactone polymerisation test

In the glove box, to a stirred 5 mL toluene suspension of La₋₅₀₀ (127 mg, 41 μ mol La) was added a solution of 3 g of ϵ -caprolactone (26 mmol, 630 equiv.) in 2 mL toluene. Exothermic polymerisation occurred instantaneously, causing the reaction mixture to turn into a compact block. Separation of the formed polymer from solvents and catalyst remains was not attempted.

2.7. Typical Tischenko reaction

In the glove box, to a stirred 5 mL toluene suspension of Sm₋₇₀₀ (70 mg, 20 μ mol Sm) was added a solution of 212 mg of benzaldehyde (2 mmol, 100 equiv.) and 50 mg of durene as internal standard in 5 mL toluene. The reaction course was followed by GC injections of toluene dissolved reaction mixture aliquots. Identification of the benzylbenzoate product was checked by ¹H NMR.

2.8. Typical 1-heptyne dimerisation

A sealable reaction ampoule was loaded in the glove box with 300 mg of Y₋₇₀₀ (83 μ mol Y) suspended in 3 mL toluene. After addition of a 160 mg solution of 1-heptyne (1.66 mmol, 20 equiv./Y) in 7 mL toluene, the sealed reaction vessel was heated at 100 °C. A colour change of the suspended solid to orange occurred gradually. After 15 h, total conversion of 1-heptyne was checked by GC analysis of the reaction mixture. Separation of the organic products was carried out in air: the supernatant was separated by filtration, the solid was washed with two 5 mL portions of toluene, and the collected liquid fractions were evaporated to dryness under primary vacuum to afford a pale yellow oil (151 mg). NMR analysis showed presence of the tail-to-head dimer and of the tail-to-head-to-head trimer, in respective 82/18 ratio.

3. Grafted lanthanide amides preparation

As demonstrated in the work of Anwender and collaborators, lanthanides amides can be grafted onto silica and aluminosilicate [13]. The grafting reaction is the protonolysis of the Ln–N bond by surface silanols, which generates covalent \equiv Si–O–Ln anchoring points. Depending on the concentration of the surface silanols during the grafting process, a Ln[NR'₂]₃ molecule can react with one or two silanols, thus affording monosiloxide species A or bisiloxide species B, respectively (Scheme 1). Concomitantly, the released hexamethyldisilazane also reacts

Table 1
Elemental analysis data

Catalyst	%Ln	<i>n</i> (Ln) (g) ^a	%N	N/Ln ^b	%A ^c	%B ^c
La ₋₂₅₀	6.55	0.472	0.82	1.24	25	75
La ₋₅₀₀	4.52	0.325	0.66	1.45	45	55
La ₋₇₀₀	3.80	0.274	0.80	2.09	100	0
Nd ₋₂₅₀	6.76	0.469	0.81	1.23	25	75
Nd ₋₅₀₀	4.80	0.333	0.65	1.39	40	60
Nd ₋₇₀₀	4.12	0.286	0.79	1.98	100	0
Y ₋₇₀₀	2.47	0.278	0.80	2.06	100	0
Sm ₋₇₀₀	4.27	0.284	0.80	2.02	100	0

^a Millimoles of lanthanide per gram of material.

^b Molar ratio.

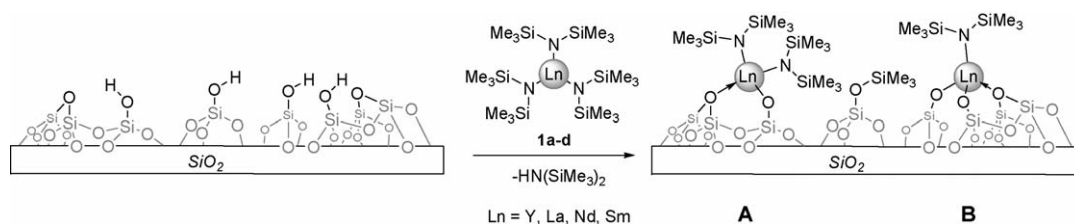
^c Estimated values \pm 5%.

with surface SiOH to generate trimethylsilyl-capped silanols [14].

It is known that the distribution and nature of the surface silanol types vary according to the followed silica dehydroxylation procedure [15]. Indeed, silica dehydroxylated at low temperatures (typically 250 °C) mostly bears vicinal silanol groups, while on silica dehydroxylated at high temperatures (e.g. 700 °C), silanols are almost exclusively of the isolated type. Thus the support dehydroxylation temperature directly affects the mono- versus bigrafted species ratio obtained when grafting a molecular precursor onto the considered material [16]. This controlled grafting, which we have demonstrated for the lanthanum trisilylamide case, has been extended to yttrium, neodymium and samarium.

Grafting of the lanthanide amides Ln[NR'₂]₃ (Ln = Y, La, Nd, Sm) onto silica was performed by impregnation in toluene. Sample treatment ensured that excess molecular precursor and organic by-products were separated from the modified silica. In the case of lanthanum and neodymium, three different support heat pre-treatments were used: 250, 500 and 700 °C. For the yttrium and samarium derivatives, only silica treated at 700 °C was chosen as a support. In the following text, these materials will be referred to as metal_{-temp}, where “metal” is the considered lanthanide, and “temp” is the support dehydroxylation temperature. Results of elemental analyses for the resulting materials have been gathered in Table 1.

It appears that the metal content is similar for materials prepared from the same support: 0.47, 0.33 and 0.28 mmol of grafted metal per gram of support dehydroxylated at 250, 500 and 700 °C, respectively. This indicates that grafting proceeds with similar efficiency over the studied lanthanide series. The decrease of metal content with increasing dehydroxylation temperature is also consistent with decreasing silanol contents, from



Scheme 1. Reaction of Ln[NR'₂]₃ with silica surface.

2.22 to 0.62 mmol of silanol per gram on silica dehydroxylated at 250 and 700 °C, respectively [17]. The N/Ln value is also varying with silica dehydroxylation temperature, and is not metal dependant, since close values are observed for different metals grafted onto the same support, revealing similar grafting chemistry. The A and B species proportions can be extracted from the N/Ln figure, which is a combination of both species contributions [18]. Values of 2 and 1 for N/Ln are expected for A and B, respectively. It appears that on silica dehydroxylated at 250 and 500 °C, species A and B are both present, the bigrafted surface species being the major one, while on silica dehydroxylated at 700 °C, only monografted species is formed, which is consistent with the isolated silanols being the only reactive sites on such a support.

4. Grafted lanthanide silylamides as polymerisation catalysts

4.1. Methyl methacrylate polymerisation

4.1.1. Results

Lanthanide amide functionalities have been described as initiators of MMA polymerisation in the absence of activator [7a,19]. Michaël addition of the Ln–N moiety on the methyl methacrylate C–C double bond generates the propagating enolate species [20]. Both activity and selectivity are highly dependant on the metal nature and on its coordination sphere. It seemed therefore of interest to investigate the Ln_{temp} materials performances in this reaction, and, if possible, to assess the properties of the grafted monosiloxybisamido (A) and bisiloxyamido (B) lanthanide species regarding polymerisation activity and polymer tacticity.

As appears in Table 2, supported catalysts afford moderately to highly isotactic PMMA, and marked differences originate from variations of the support dehydroxylation temperature. For a similar support, neodymium affords higher activity and

Table 2
MMA polymerisation results

Run	Catalyst	Yield (%)	TON	%mm ^a	%mr ^a	%rr ^a	M _n ^b	PDI ^b
1	La ₂₅₀	18	88	92	4	4	55800	1.90
2	La ₂₅₀ ^c	10	49	87	8	5	13000	16.07
3	La ₅₀₀	22	108	87	8	5	86000	2.43
4	La ₇₀₀	28	137	77	13	10	73000	2.05
5	La ₇₀₀ ^d	42	206	56	33	11	30000	2.82
6	La ₇₀₀ ^e	27	132	85	7	8	n.d. ^f	n.d. ^f
7	Nd ₂₅₀	17	83	92	4	4	35000	4.42
8	Nd ₅₀₀	18	88	86	6	8	10000	29.65
9	Nd ₇₀₀	21	103	66	15	19	6900	10.55
10	La[NR' ₂] ₃	62	310	28	48	24	14800	3.01

Reaction conditions: *n*(Ln) = 19 μmol, 1 mL MMA, MMA/Ln, mol/mol = 490, 5 mL PhMe, 16 h, 23 °C unless otherwise stated.

^a From ¹H NMR.

^b From GPC.

^c Reaction temperature 0 °C.

^d 1 equivalent BEM per La.

^e 1 equivalent O=PPh₃ per La.

^f N.D.: not determined.

comparable to lower selectivity than lanthanum. Both for the lanthanum and the neodymium series, the order of activity is Ln₂₅₀ < Ln₅₀₀ < Ln₇₀₀. The percentage of isotactic triads in the produced polymers again depends on the support heating pre-treatment, according to the order Ln₇₀₀ < Ln₅₀₀ < Ln₂₅₀. Both Ln₂₅₀ (Ln = La and Nd) afford PMMA with as high as 92% of mm triads. As a comparison, under the same reaction conditions, the homogeneous catalyst La[NR'₂]₃ gives rise to higher activity, but produces atactic PMMA, thus emphasizing the beneficial support effect on the stereoselectivity of the polymerisation process. The Michaël addition of the lanthanide enolate nucleophile into the incoming monomer double bond is most sensitive to the presence of the surface, which acts as a bulky siloxide ligand [21].

Regarding mass distribution, lanthanum systems afford rather well controlled polymerisation with relatively low polydispersities (PDI), contrary to neodymium systems, where no efficient control on the produced masses is exerted, as shown by the high PDI values. In the case of La₂₅₀, lowering the reaction temperature down to 0 °C (run 2) leads to a loss in activity, selectivity and mass control.

In an attempt to ensure a more efficient initiation by prealably generating a Ln-alkyl bond, reaction with one equivalent of butylethylmagnesium was carried out before the addition of MMA (run 5). Alkoxy-lanthanide-magnesium dialkyl combinations have been described as efficient PMMA initiating systems [22]. In our case, the observed activity was higher, at the expense of the selectivity: the afforded PMMA was less isotactic than the one produced in absence of BEM. This is probably due to a MgR₂ induced polymerisation, which can also take place together with the lanthanide amide-initiated polymerisation, as assessed by a decreased molecular weight associated with a higher conversion (magnesium dialkyls are known to polymerise MMA: see Ref. [22]).

Performance of La₇₀₀ in terms of stereoselectivity can be improved by addition of an equivalent of triphenylphosphine oxide, which increases the isotacticity (mm%) from 77 to 85%, without loss of activity (run 6). Interestingly, we have demonstrated that the grafted species present on the surface of La₇₀₀, namely (≡Si–O)La[NR'₂]₂, reacts with O=PPh₃ to afford the corresponding mono-adduct, (≡Si–O)La[NR'₂]₂(O=PPh₃) [23]. It may be expected that surface species with a different coordination sphere have different selectivity, which in this case proves to be beneficial from the stereoselectivity point of view. This shows that coordination sphere modifications may be efficiently applied to improve catalytic performances of the grafted catalyst, a most promising perspective.

4.1.2. Site-specific activity and selectivity

By taking into account the mono- and bigrafted species proportions for the studied Ln_{temp} catalysts (Table 1), site-specific activities and selectivities can be extracted, while keeping in mind the experimental errors. Table 3 presents the calculated values of TON (in 16 h), and triads distributions for lanthanum and neodymium A and B surface species. As could be guessed from the raw data, monografted bisilylamides are more active than their bigrafted counterparts by a factor 1.8–1.4. Thus, sim-

Table 3
Activities and selectivities for mono- and bigrafted lanthanide silylamides

	La		Nd	
	A	B	A	B
TON	137	78	108	75
%mm	77	97	66	99
%mr	13	2	15	1
%rr	10	1	19	0
2[mm]/[mr]	1.54	1	2.53	198
4[mm] × [rr]/[mr] ²	18.2	97	22.3	0

ple considerations on the metal electrophilicity are not the main origin of the observed activity difference, since bigrafted species are expected to be more electrophilic than monografted ones due to the electron withdrawing surface siloxide ligands. The reactivity difference may be due to the fact that the amido group is much less prone to the Michaël addition in a more electrophilic surface species, which may disfavour the initiation step. Large polydispersities and much higher Mn values than those expected support that initiation, not propagation, is the rate determining step in this process.

Regarding stereoselection, it also appears that higher control is exerted during MMA polymerisation by the bigrafted amide. Both La and Nd bipodal species afford highly isotactic PMMA, with [mm] contents of 97 and 99%, respectively. Explanation could be found in steric effects, and/or in the more rigid structure of the catalytic centre B, when compared to monopodal site A. Both A and B seem to operate via enantiomorphic site control rather than via chain-end control mechanism, according to triad tests (Table 3).

4.1.3. Scanning electron microscope investigations

Over the different runs, initiation efficiency appears to be rather low, when comparing the obtained molar masses with corresponding theoretical ones. In order to enquire about this fact, scanning electronic microscopy (SEM) was used on unseparated polymer–silica mixture obtained from solvent evaporation after a run involving La₂₅₀. SEM pictures show the presence of particles with a smooth polymer-like surface (Fig. 1a). Closer analysis of such a particle, which had been torn open by accidental mechanical treatment, shows that if its outside layer seems to be covered by PMMA, its inner part consists of Aerosil particles with a size range of 20–50 nm, devoid of distinguishable quantity of PMMA (Fig. 1b). Such an observation tends to indicate that only a fraction of the starting catalyst has been able to initiate MMA polymerisation, and that the particles of catalysts did not “explode” like this is the case when classical Ziegler–Natta catalysts react with ethylene (if no latter agglomeration took place).

4.2. Ethylene polymerisation

4.2.1. Results

As shown by Bochmann and co-workers, lanthanide silylamides grafted onto silica are active as ethylene polymerisation catalysts [24]. We explored the potential of our materials regard-

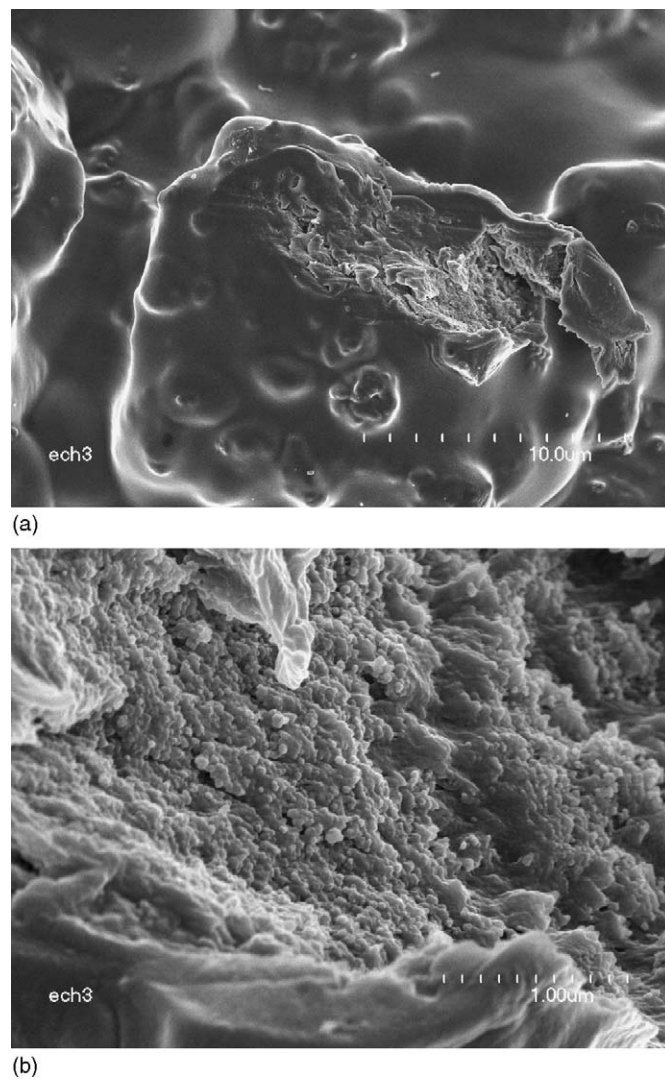


Fig. 1. SEM pictures of crude reaction mixture between La₂₅₀ and MMA.

ing this reaction, in order to probe whether the same “support effect” due to site-specific activity would be observed for this reaction as in the case of MMA polymerisation.

Ethylene polymerisation experiments were conducted at atmospheric pressure, 90 °C and in suspension in toluene with mechanical stirring. On the Gibson scale [25], our systems activities are to be considered as very low to low, ranging from 0.1 to 1.24 kg_{PE} mol_{Ln} h⁻¹ (Table 4). Ethylene consumption started immediately upon mixing the silica-supported catalyst precursor and the alkylating agent in the glass reactor. Maximum activities were recorded within the first minutes of each run. Then, irreversible decrease of ethylene consumption was invariably observed. Some experiments (runs 2, 3 and 8 in Table 4) were found to have undetectable ethylene consumption after 20–40 min (vide infra), the others were arbitrarily stopped after 2 h although the catalytic systems were not completely dead. During these latter runs, the morphology of the particles in suspension gradually changed from free flowing thin particles to massive gelatinous clots. Moreover, the progressive shift of the specific gravity of these particles during the polymerisation

Table 4
Ethylene polymerisation results

run	Catalyst	PE ^a (mg)	Activity ^b (kg/mol/h)	Inst. act. ^c (kg/mol/h)
1	La ₋₂₅₀	165	0.73	0.45
2	La ₋₂₅₀ ^d	26	0.12	0
3	La ₋₂₅₀ ^e	10	0.04	0
4	La ₋₇₀₀	157	0.69	0.45
5	Nd ₋₂₅₀	137	0.61	0.30
6	Nd ₋₅₀₀	230	1.02	0.40
7	Nd ₋₇₀₀	280	1.24	0.50
8	Nd[NR' ₂] ₃	10	0.04	0

Reaction conditions: $n(\text{Ln}) = 113 \mu\text{mol}$, tri-isobutylaluminium as alkylating agent (AA) unless otherwise specified; $n(\text{AA}) = 1.5 \text{ mmol}$, AA/Ln, mol/mol = 13.3, 20 mL PhMe, ethylene pressure = 1.1 bar, 2 h, 90 °C.

^a Consumed ethylene obtained by integrating the mass flowmeter signal.

^b Calculated for a 2 h reaction time even if monomer consumption stopped before this time.

^c Instantaneous consumption rate of ethylene after 2 h, as measured with a mass flowmeter.

^d AA: lithium tetrabutylaluminate.

^e AA: di-*n*-butylmagnesium

process made them to move from the lower to the higher part of the vortex. In most cases, white polyethylene fibres were seen to coil around the mechanical stirrer.

4.2.2. Alkylating agent influence

Alkylating agent influence was probed for the La₋₂₅₀ system. Marked sensitivity to the choice of the organometallic derivative used was observed: TIBA affords the most active catalytic system, still active after 2 h of reaction, while lithium tetrabutylaluminate and, to a larger extent, di-*n*-butylmagnesium lead to poorly active systems, stopping after 40 and 20 min, respectively (Fig. 2). Bochmann already pointed out that TIBA affords a more productive system than magnesium bisalkyl, at lower Mg/Ln. Significant leaching (58%) was detected by ICP in the supernatant and collected washing fractions in the case of dialkylmagnesium (run 3), while aluminium-based activators did not cause similar metal extraction (4% and 3% leaching in runs 1 and 2, respectively). These results illustrate the deli-

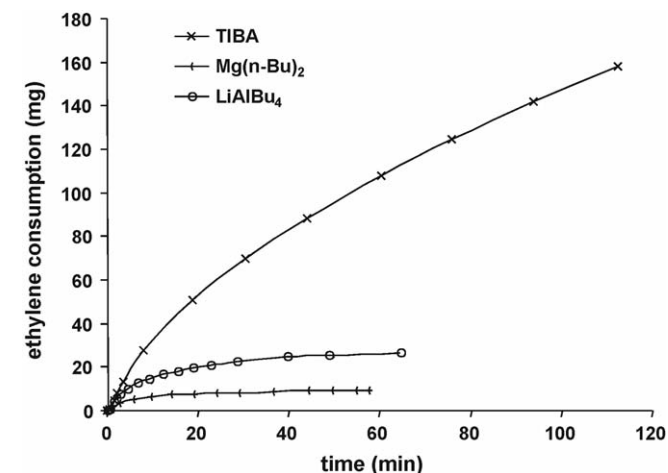


Fig. 2. Kinetics of ethylene polymerisation by La₋₂₅₀: alkylating agent influence. Experimental conditions: see Table 4.

cate dependency of activity on the combination of the alkylating agent and the metal centre. Too strong an alkylating agent causes metal extraction from the surface through transmetalation and blocks activity (provided that leached species are inactive toward ethylene), while weaker organometallic reagents may simply form adducts unable to afford reactive Ln–C bonds necessary for monomer insertion.

4.2.3. Influence of support and nature of the metal centre

Ethylene polymerisation studies were carried out on the La_{-temp} and Nd_{-temp} (temp = 250, 500 and 700) materials activated with excess TIBA. These form systems of modest but sustained activity, still consuming ethylene after 120 min (Fig. 3). Neodymium catalysts are generally more productive than the lanthanum ones, at the exception of the Ln₋₂₅₀ materials, which are comparable, lanthanum being slightly more efficient than neodymium in this case. In related studies on lanthanide amides grafted onto silica dehydroxylated at 500 °C, it has been observed that the lanthanum system was more active than the neodymium one [24]. However, activities are in the same range.

While lanthanum silylamides grafted onto silica dehydroxylated at 250 and 700 °C behave similarly, significant support effect is observed for neodymium-based systems, where activity evolves as Nd₋₂₅₀ < Nd₋₅₀₀ < Nd₋₇₀₀. No direct correlation between grafted species distribution and activity could be drawn from these data. However, coordination sphere considerations seem to be of major importance regarding these systems activity, since molecular catalyst Nd[NR'₂]₃ behaves poorly in ethylene polymerisation, stopping monomer consumption after 20 min. Thus, silica does not merely act as a catalyst carrier, but plays some role in the catalytic activity. At least two effects may be identified: the first one is the ligand change from amido to siloxy, which should enhance the reactivity by increasing the electrophilicity of the metal center, the second one being a grafting effect, by which, in contrast with homogeneous catalysis, where aggregates are prone to be formed, mainly isolated, mononuclear species should be present at the silica surface. Active site isolation, by preventing aggregation of alkyl lanthanide species, may thus avoid the involvement of bimetallic (or polymetallic) deactivation pathways.

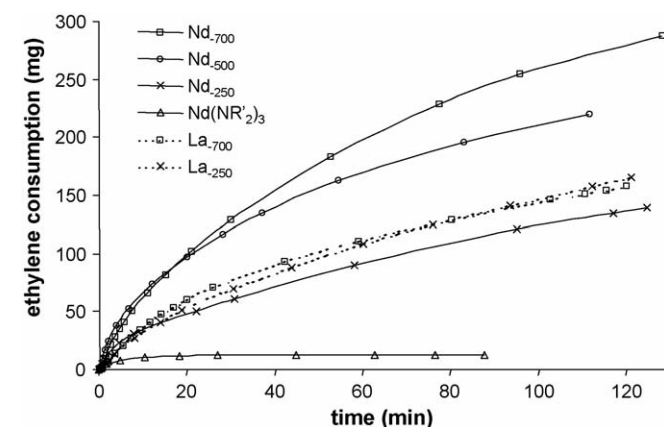


Fig. 3. Kinetics of ethylene polymerisation by Ln_{-temp}-TIBA systems. Experimental conditions: see Table 4.

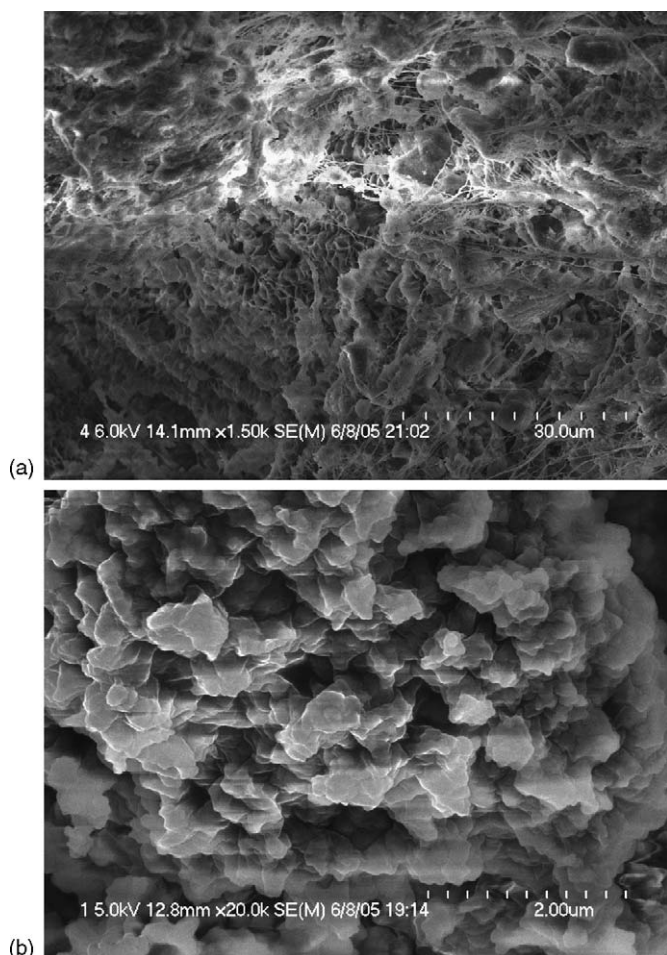


Fig. 4. SEM pictures of crude material obtained from La₇₀₀ catalytic run.

4.2.4. Scanning electron microscope investigations

Scanning electronic microscopy investigations were carried out on precipitated polymer obtained from La₇₀₀ (run 4). SEM pictures confirm the macroscopic observation of both particles and fibres of polymer in the solid (Fig. 4a). Closer examination of the particles reveals that they consist of polymer-like aggregates which size ranges from 200 to 500 nm, about ten times larger than the starting Aerosil particles (Fig. 4b). These observations are consistent with “exploding grain” model as a polyethylene particle formation mechanism, while the fibres may either originate from extrusion of silica particle supported polyethylene or from homogeneously produced polymer (from leaching catalyst).

4.3. ϵ -Caprolactone and isoprene polymerisation explorative attempts

Further tests were carried out regarding the polymerisation abilities of some of the grafted catalysts. When contacted with 600 equivalents of ϵ -caprolactone, La₅₀₀ rapidly polymerises the monomer to afford a compact gummy solid. Viscosity is too high to afford complete conversion. The nature of the polymer was checked by ¹H and ¹³C NMR. Such high activities are common for rare-earth catalysts. No attempt was made to control the

polydispersity of the obtained polylactone. Such a study with similar catalysts has been described by Spitz and co-workers [26]. Ring-opening polymerisation of ϵ -caprolactone is initiated by nucleophilic attack of the amido onto the monomer carbonyl group, generating the alkoxide propagating species [27].

We also checked that isoprene could be polymerised into mostly 1,4-*cis*-polyisoprene. Contacting a suspension of Nd₇₀₀ with 1.2 equivalent of BEM leads to a colour change of the solid from pale blue to light yellow. Addition of 350 equivalents of isoprene and further heating at 85 °C affords a quick colour change to bright green. The supernatant remained colourless, as observed when stirring was stopped. After 2 h of reaction, and further quenching and polymer separation, a gummy solid is obtained, with a corresponding 24% yield and a modest activity of 2.9 kg_{pol} mol⁻¹ h⁻¹. NMR analysis reveals a structure of mostly (93%) 1,4-type, with a *cis* content of 70% [28]. The observed green colour is characteristic of the formation of a lanthanide π -allylic moiety, the active species postulated for this type of catalysis [29]. Obtention of this propagating species proceeds first by MgR₂ alkylation of the metal amido function, followed by alkyl insertion into the diene monomer.

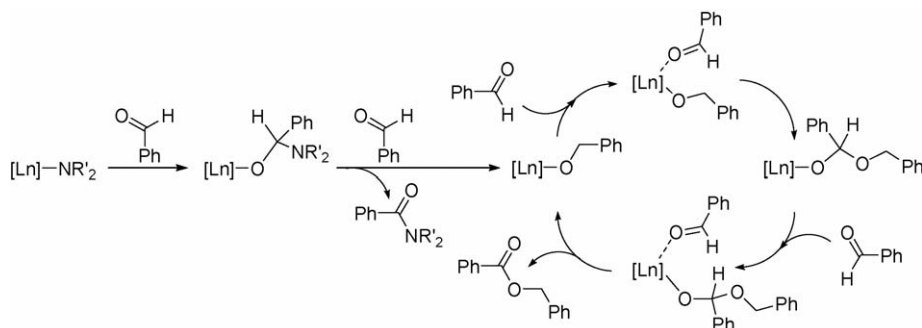
5. Grafted lanthanide silylamides as aldehydes and alkynes coupling catalysts

5.1. Tischenko reaction

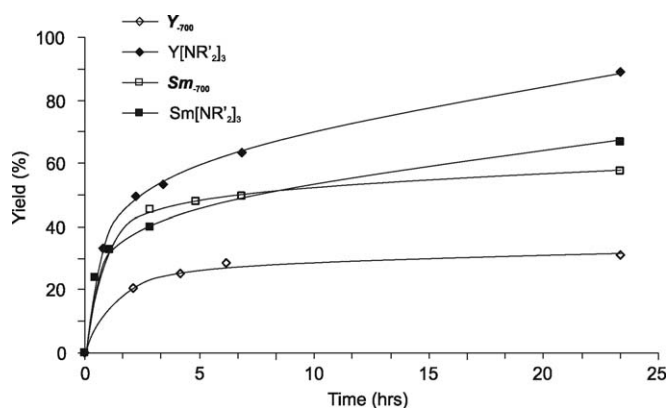
Recent reports from the P. Roesky group [7b,30] have shown that lanthanide silylamides are among the best catalysts precursors for the Tischenko reaction, which converts aldehydes into esters:



The actual catalyst is an alkoxide derivative, generated by consecutive amide nucleophilic attack on a first benzaldehyde molecule and α -hydride transfer to a second incoming benzaldehyde substrate to release *N,N*-bis(trimethylsilyl)benzylamide. The catalytic cycle involves similar elementary steps, the nucleophilic addition onto the first PhCHO incoming substrate being done by the alkoxide ligand, to afford in fine benzyl benzoate and regenerate the benzylic alkoxide species (Scheme 2). We studied the reactivity of the Y₇₀₀ and Sm₇₀₀ solids, which bear only monografted A-type bisamide species, toward benzaldehyde. These were tested with a substrate/metal ratio of 100, in toluene at room temperature, for 24 h. Conversions of 31 and 57 equivalents of benzaldehyde per lanthanide were achieved for yttrium and samarium, respectively. Separation of the supernatant and addition of benzaldehyde showed no activity after 15 h, showing that the actual active species lies on the silica surface. Supported catalysts proved to be less effective than their trisamido precursors, which achieved higher conversions: 89% for Y[NR'₂]₃ and 67% for Sm[NR'₂]₃, under similar experimental conditions. Follow-up of the reaction by gas chromatography shows that in the case of grafted catalyst Y₇₀₀ and Sm₇₀₀, yield reaches a plateau after about 6 h, a result which probably comes from an inhibition process by the reaction product



Scheme 2. Generation of the active species and mechanism of the Tischenko reaction.

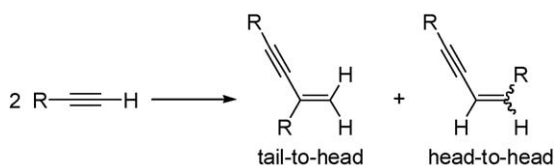
Fig. 5. Tischenko reaction. Reaction conditions: $n(\text{Ln}) = 113 \mu\text{mol}$, benzaldehyde 11.3 mmol (100 equiv.), durene as internal standard, 10 mL toluene, 25 °C.

(Fig. 5). This behaviour may be explained by the different nature of the active sites: the homogeneous catalyst is most probably a lanthanide cluster, since benzylato ligands are way too small to afford monomeric complexes [9]. On the other hand, surface lanthanide alkoxides are mononuclear, due to grafting-imposed site isolation. In the Tischenko reaction, such a situation may prove detrimental to catalytic efficiency.

Recycling of the Sm catalyst was studied. After 3 h reaction time at room temperature, the supernatant was separated from the catalytic solid by filtration. The modified silica was further washed with toluene, after which a fresh substrate solution was introduced. The first run afforded 38% conversion, while the next two cycles afforded 16% and 15% conversion, respectively. Thus, grafted Sm catalyst was able to convert a total of 69 equivalents of benzaldehyde over the different runs in an overall reaction time of 9 h, which is higher than the compared performance of the homogeneous amide.

5.2. Terminal alkynes dimerisation

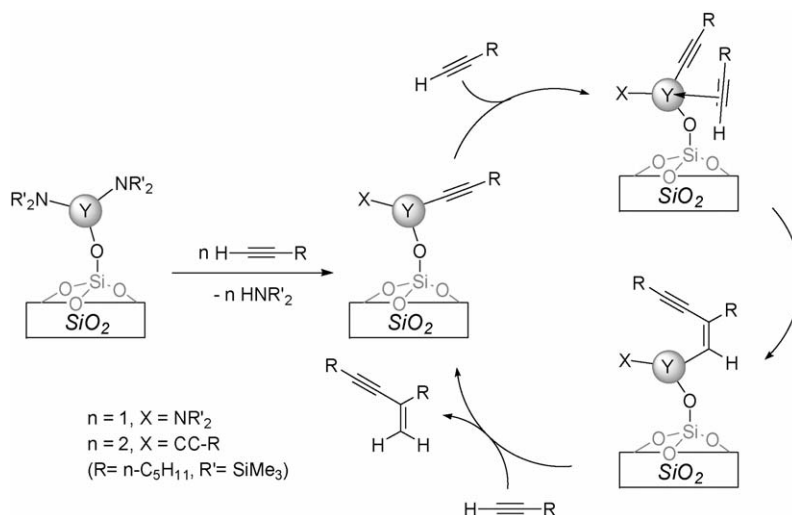
Rare-earth complexes have been reported as active catalysts for the terminal alkynes dimerisation [31], a most interesting entry into the synthesis of enynes [32].



It has been shown that this reaction could be selectively catalysed by lanthanide amides such as $\text{Y}[\text{NR}'_2]_3$ [33]. The mechanism proceeds by generation of the active species by amido lanthanide bond protonolysis by a terminal alkyne ($\text{p}K_{\text{a}}(\text{HNR}'_2)$: 30 and $\text{p}K_{\text{a}}(\text{HC}\equiv\text{CR}) \approx 25$), to generate acetylide compounds. Insertion of the acetylide nucleophile into the alkyne triple bond generates an yne-ynylidene complex. This key step directs the product selectivity: a 1,2 addition leads to tail-to-head dimer, while a 2,1 addition affords the head-to-head enyne. In the final step, protonolysis from incoming alkyne releases enyne and regenerates acetylide active species. Further reaction on the enyne yields di(en)yne type alkyne trimers.

In order to enquire further on the compared ability of our supported catalytic systems and molecular analogues, we have studied the reactivity of the Y_{-700} catalysts toward 1-heptyne dimerisation. Heating the catalyst at 100 °C in the presence of 20 equivalents of the terminal alkyne substrate affords a bright orange solid and a clear supernatant. Complete conversion of the substrate was reached, as shown by GC analysis of the reaction mixture. The selectivity of the products, as determined by ^1H NMR, was 82% of tail-to-head dimer and 18% of the tail-head-head trimer, obtained by two consecutive 1,2 acetylide insertions [34]. Comparatively, under similar conditions, molecular catalyst $\text{Y}[\text{NR}'_2]_3$ affords complete conversion, and selectivity to tail-to-head and head-to-head dimers of 92% and 8%, respectively.

Recycling of the catalytic system was probed, as in the case of the heterogeneous Tischenko reaction. The orange material separated from the supernatant was contacted with a fresh substrate solution, and afforded under similar reaction conditions total conversion and complete selectivity to tail-to-head dimer. Identical results were obtained from the third run. The change in selectivity between the first and second runs can be due to the separation of $\text{HN}(\text{SiMe}_3)_2$ released during the activation step (protonolysis of the $\text{Ln}-\text{N}$ bond by the alkyne $\equiv\text{C}-\text{H}$, Scheme 3) from the reaction mixture between the first and second runs: amine derivatives were shown by Takaki and co-workers to affect the selectivity of the related homogeneous system. The observed selectivity for the tail-to-head dimer may be originating from the surface acting as a bulky ligand, which would induce favourable orientation of the substrate within the lanthanide ligand sphere prior to acetylide migration into the coordinated triple bond. Steric effects have been reported to play a major role in this reaction [35].



Scheme 3. Active species generation and proposed mechanism for yttrium-mediated alkyne dimerisation.

Thus, simple grafting of the yttrium trisamide afforded a recyclable and more selective catalytic system. It is however necessary to mention that its capacity regarding activity under higher substrate to catalyst ratio has still to be examined. Recyclable lanthanide systems able to perform the same reaction have already been described, but the arduous multi-steps synthesis and the high sensitivity of the precursors seem highly detrimental to wide use and practical application of this system [36].

6. Conclusion

Lanthanide silylamides supported onto silica proved to be able to mediate a large variety of reactions, thereby demonstrating their effectiveness as versatile catalysts. Regarding polymerisation applications, a strong effect of the support heat pretreatment, and hence, of the lanthanide surface species nature and distribution, has been observed. We have been able to evaluate the respective activity and selectivity for monografted and bigrafted lanthanum and neodymium amides in methyl methacrylate polymerisation. These solids were also shown to be active for the Tischenko and alkyne dimerisation reactions. Moreover, they proved to be recyclable catalytic systems, with even an improvement of the selectivity in the case of the alkyne dimerisation.

The broad scope of reactions mediated by these catalysts owes a lot to the reactivity of the lanthanide-amido function, which can react with various reagents to afford a wide range of catalytically active species: enolate, alkyl, allyl, alkoxide and acetylide. The possibility of ligand sphere modifications to introduce spectator ligands around the metal centre to tune its reactivity constitutes a promising development of these systems, which is currently under investigation in our laboratory.

Acknowledgments

We thank the CNRS and the Ministère de l'Éducation Nationale et de la Recherche for their financial support, and Anne-Marie Cazé for the GPC measurements. Dr. Olivier Coute-

lier is acknowledged for helpful assistance in gas chromatography and fruitful discussions. We thank a referee for a helpful remark.

References

- [1] H. Knuutila, A. Lehtinen, A. Nummala-Pakarinen, *Adv. Polym. Sci.* 169 (2004) 13–27.
- [2] (a) B. Pugin, B.H.-U. Blaser, in: E.N. Jacobsen, A. Pfaltz, H. Yamamoto (Eds.), *Comprehensive Asymmetric Catalysis*, 3, Springer-Verlag, Berlin, 1999, pp. 1367–1375; (b) G. Oehme, in: E.N. Jacobsen, A. Pfaltz, H. Yamamoto (Eds.), *Comprehensive Asymmetric Catalysis*, 3, Springer-Verlag, Berlin, 1999, pp. 1377–1386.
- [3] (a) K. Mikami, M. Terada, H. Matsuzawa, *Angew. Chem. Int. Ed.* 41 (2002) 3554–3572; (b) G.A. Molander, J.A.C. Romero, *Chem. Rev.* 102 (2002) 2161–2186; (c) J. Inanaga, H. Furuno, T. Hayano, *Chem. Rev.* 102 (2002) 2211–2226.
- [4] See for example: W.J. Evans, J.D. Feldman, J.W. Ziller, *J. Am. Chem. Soc.* 118 (1996) 4581–4584.
- [5] (a) G. Jeske, H. Lauke, H. Mauermann, P.N. Swepston, H. Schumann, T.J. Marks, *J. Am. Chem. Soc.* 107 (1985) 8091–8103; (b) G. Jeske, L.E. Schock, P.N. Swepston, H. Schumann, T.J. Marks, *J. Am. Chem. Soc.* 107 (1985) 8103–8110.
- [6] (a) D.C. Bradley, J.S. Ghotra, F.A. Hart, *J. Chem. Soc., Chem. Commun.* 6 (1972) 349–350; (b) D.C. Bradley, J.S. Ghotra, F.A. Hart, *J. Chem. Soc., Dalton* (1973) 1021–1023; (c) P.W. Roesky, *Z. Anorg. Allg. Chem.* 629 (2003) 1881–1894.
- [7] (a) M.A. Giardello, Y. Yamamoto, L. Brard, T.J. Marks, *J. Am. Chem. Soc.* 117 (1995) 3276–3277; (b) H. Berberich, P.W. Roesky, *Angew. Chem. Int. Ed.* 37 (1998) 1569–1571; (c) Y.K. Kim, T. Livinghouse, J.E. Bercaw, *Tetrahedron Lett.* 42 (2001) 2933–2935; (d) Y.K. Kim, T. Livinghouse, *Angew. Chem. Int. Ed.* 41 (2002) 3645–3647; (e) D.V. Gribkov, K.C. Hultsch, F. Hampel, *Chem. Eur. J.* 9 (2003) 4796–4810; (f) A.M. Kawaoka, M.R. Douglass, T.J. Marks, *Organometallics* 22 (2003) 4630–4632; (g) M. Suzuki, N. Kata, M. Kanai, M. Shibasaki, *Org. Lett.* 7 (2005) 2527–2530.
- [8] I. Nagl, M. Widenmeyer, E. Herdtweck, G. Raudaschl-Sieber, R. Anwander, *Micropor. Mesopor. Mater.* 44–45 (2001) 311–319.

- [9] R. Anwander, *Top. Curr. Chem.* 179 (1996) 149–245.
- [10] (a) J. Eppinger, M. Spiegler, W. Hieringer, W.A. Herrmann, R. Anwander, *J. Am. Chem. Soc.* 122 (2000) 3080–3096;
(b) A.K. Dash, A. Razavi, A. Mortreux, C.W. Lehmann, J.-F. Carpentier, *Organometallics* 21 (2002) 3238–3249.
- [11] R.M. Gauvin, A. Mortreux, *Chem. Commun.* (2005) 1146–1148.
- [12] E.C. Ashby, G.E. Heinsohn, *J. Org. Chem.* 38 (1973) 4343–4344.
- [13] (a) R. Anwander, R. Roesky, *J. Chem. Soc. Dalton Trans.* (1997) 137–138;
(b) R. Anwander, O. Runte, J. Eppinger, G. Gestberger, E. Herdtweck, M. Spiegler, *J. Chem. Soc. Dalton Trans.* (1998) 847–858.
- [14] (a) N.R.E.N. Impens, P. van der Voort, E.F. Vansant, *Micropor. Mesopor. Mater.* 28 (1999) 217–232;
(b) W. Hertl, M.L. Hair, *J. Phys. Chem.* 75 (1971) 2181–2185;
(c) D.W. Windorf, G.E. Maciel, *J. Phys. Chem.* 86 (1982) 5208–5219.
- [15] R.S. McDonald, *J. Phys. Chem.* 62 (1958) 1168–1178.
- [16] L. Lefort, M. Chabanas, O. Maury, D. Meunier, C. Copéret, J. Thivolle-Cazat, J.-M. Basset, *J. Organomet. Chem.* 593–594 (2000) 96–100.
- [17] L.T. Zhuravlev, *Langmuir* 3 (1987) 316–318.
- [18] $N/Ln = (2\%A + \%B)/100$ and $\%A + \%B = 100$, thus $\%A = 100[(N/Ln) - 1]$ and $\%B = 100[2 - (N/Ln)]$.
- [19] (a) L. Mao, Q. Shen, *J. Polym. Sci., Part A: Polym. Chem.* 36 (1998) 1593–1597;
(b) F. Estler, G. Eickerling, E. Herdtweck, R. Anwander, *Organometallics* 22 (2003) 1212–1222;
(c) S.-L. Zhou, S.-W. Wang, G.-S. Yang, X.-Y. Liu, E.-H. Sheng, K.-H. Zhang, L. Cheng, Z.-X. Huang, *Polyhedron* 22 (2003) 1019–1024.
- [20] H. Yasuda, H. Yamamoto, K. Yokota, S. Miyake, A. Nakamura, *J. Am. Chem. Soc.* 114 (1992) 4908–4910.
- [21] Steric factors have been shown to considerably affect the PMMA tacticity in zirconocene-based systems: P.A. Cameron, V.C. Gibson, A.J. Graham, *Macromolecules* 33 (2000) 4329–4335.
- [22] J. Gromada, C. Fouga, T. Chenal, A. Mortreux, J.-F. Carpentier, *Macromol. Chem. Phys.* 203 (2002) 550–555.
- [23] R. M. Gauvin, R. Ali Hassan, A. Mortreux, L. Delevoye, submitted for publication.
- [24] T.J. Woodman, Y. Sarazin, G. Fink, K. Hauschild, M. Bochmann, *Macromolecules* 38 (2005) 3060–3067.
- [25] G.J.P. Britovsek, V.C. Gibson, D.F. Wass, *Angew. Chem. Int. Ed. Engl.* 38 (1999) 428–447.
- [26] K. Tortosa, T. Hamaide, C. Boisson, R. Spitz, *Macromol. Chem. Phys.* 2 (2001) 1156–1160.
- [27] E. Ihara, M. Morimoto, H. Yasuda, *Macromolecules* 28 (1995) 7886–7892.
- [28] W. Dong, T. Masuda, *J. Polym. Sci. Part A: Polym. Chem.* 40 (2002) 1838–1844.
- [29] S. Maiwald, H. Weissenborn, C. Sommer, G. Müller, R. Taube, *J. Organomet. Chem.* 640 (1–2) (2001) 1–9.
- [30] M.B. Bürgstein, H. Berberich, P.W. Roesky, *Chem. Eur. J.* 7 (2001) 3078–3085.
- [31] (a) M.E. Thompson, S.M. Baxter, A.R. Bulls, B.J. Burger, M.C. Nolan, B.D. Santasiero, W.P. Schaefer, J.E. Bercaw, *J. Am. Chem. Soc.* 109 (1987) 203–219;
(b) K.H. Den Haan, Y. Wielstra, J.H. Teuben, *Organometallics* 6 (1987) 2053–2060;
(c) H.J. Heeres, J.H. Teuben, *Organometallics* 10 (1991) 1980–1986.
- [32] B.M. Trost, *Angew. Chem., Int. Ed. Engl.* 34 (1995) 259–281.
- [33] (a) K. Komeyama, K. Takehira, K. Takaki, *Synthesis* (2004) 1062–1066;
(b) K. Komeyama, T. Kawabata, K. Takehira, K. Takaki, *J. Org. Chem.* 70 (2005) 7260–7266.
- [34] A. Haskel, J.Q. Wang, T. Straub, T.G. Neyroud, M.S. Eisen, *J. Am. Chem. Soc.* 121 (1999) 3025–3034.
- [35] R. Duchateau, C.T. van Wee, J.H. Teuben, *Organometallics* 15 (1996) 2291–2302.
- [36] M. Nishiura, Z. Hou, Y. Wakatsuki, T. Yamaki, T. Miyamoto, *J. Am. Chem. Soc.* 125 (2003) 1184–1185.