

Binary *ansa*-lanthanidocenes/dialkylmagnesium systems versus single-component catalyst: Controlled synthesis of end-capped syndiotactic oligostyrenes

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Abstract

Combinations of the *ansa*-chloroneodymocene precursor $[(\text{Cp}-\text{CMe}_2-\text{Flu})\text{Nd}(\mu\text{-Cl})_2]$ (**2**) and a dialkylmagnesium (1–100 equiv. versus Nd) have been explored for styrene oligomerization and compared to the single-component polymerization catalyst $[\text{Cp}-\text{CMe}_2-\text{Flu}]\text{Nd}(\text{allyl})(\text{THF})$ (**1**). Binary systems derived from **2** and $\text{Mg}(n\text{-Bu})_2$ or $\text{Mg}(\text{allyl})_2$ are moderately active at 60 °C (1–8 kg PS mol Nd⁻¹ h⁻¹), yielding soluble oligostyrenes ($M_n = 1600\text{--}6500$ g mol⁻¹, $M_w/M_n = 1.3\text{--}2.5$), which have an unprecedented high degree of syndiotacticity ($P_r = 94\%$, determined by ¹³C NMR spectroscopy) and are selectively end-capped by butyl or allyl groups (identified by ¹H NMR and/or MALDI-TOF-MS). The formation of the oligostyrenes is proposed to arise exclusively from a coordination/insertion mechanism, involving *in situ* generated Nd-alkyl species that are active for syndiotactic styrene polymerization and undergo chain transfer via transmetalation to excess dialkylmagnesium reagent.

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1. Introduction

Combinations of simple, readily available chlorolanthanidocenes or homoleptic lanthanide alkoxide precursors with dialkylmagnesium reagents have been shown to be effective catalysts for the polymerization of ethylene, α -olefins, styrene and methacrylates [1,2]. Because they feature single-site and “living-controlled” characteristics, those versatile binary systems enable also the synthesis of original materials such as high molecular weight poly(ethylene-*b*-methyl methacrylate) [2b,c] and poly(butadiene-*b*-glycidyl methacrylate) [2e] diblock copolymers. More, in many cases, such *in situ* alkylation of lanthanide precursors by dialkylmagnesium reagents provides a useful method for the formation of higher dialkylmagnesium

derivatives, thanks to a rapid, reversible transfer of growing polymeryl chains from the lanthanide to magnesium centers [1d].

Recently, we reported on a new family of neutral allyl *ansa*-lanthanidocene complexes supported by the cyclopentadienyl/fluorenyl ligand $[\text{Cp}-\text{CMe}_2-\text{Flu}]^{2-}$ (Fig. 1, **1**) that are efficient single-component, single-site catalysts for the highly syndiospecific (>99%, *rrrr*) polymerization of styrene and its copolymerization with ethylene to produce unique sPS-PE materials [3]. In this contribution, we describe the performance of binary catalyst systems based on a related *ansa*-lanthanidocene chloro-precursor (**2**) and a dialkylmagnesium activator for the oligo/polymerization of styrene. To the best of our knowledge, soluble, highly syndiotactic oligostyrenes are reported for the first time. Dialkylmagnesium has been used as co-activator, in order to compare the binary system versus the single-component allyl *ansa*-lanthanidocene catalyst as well as to prepare new functional highly syndiotactic oligostyrenes end-capped with terminal allyl groups.

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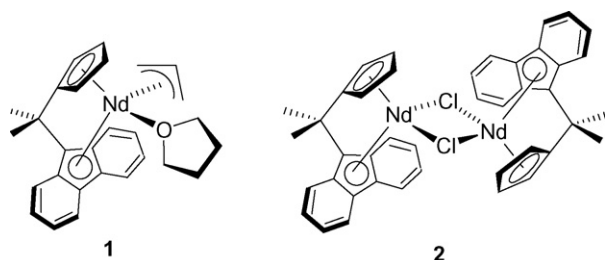


Fig. 1. Lanthanidocene (pre)catalysts for syndiospecific styrene polymerization.

2. Results and discussion

The *ansa*-neodymocene $[(\text{Cp}-\text{CMe}_2-\text{Flu})\text{Nd}(\mu\text{-Cl})_2]_2$ (**2**) was prepared as reported previously by transmetallation between $\text{NdCl}_3(\text{THF})_2$ and $[\text{Flu}-\text{CMe}_2-\text{Cp}]\text{Li}$ in diethylether [4]. This chloro precursor was activated for styrene polymerization by addition of a dialkylmagnesium reagent. Representative results obtained with di(*n*-butyl)magnesium and diallylmagnesium are summarized in Table 1.

The reactions were carried out in bulk styrene, using a minimal amount of toluene for preparing the catalyst, since early investigations have shown that this solvent and other aromatic hydrocarbons have a detrimental influence on catalytic activity. This is probably due to competitive coordination of such solvents onto the active species that blocks the subsequent attack of the π -system of incoming styrene monomer units [3a,b,5]. Also, the conversions were deliberately kept at low levels to produce relatively low molecular weights polymers ($M_n < 6000 \text{ g mol}^{-1}$) that do not precipitate during the reaction course. The oligomerizations were carried out at 60°C , which allows a direct comparison between the binary Nd–Mg systems and parent single-component catalysts, e.g. $[\text{Cp}-\text{CMe}_2-\text{Flu}]\text{Nd}(\text{allyl})(\text{THF})$ (**1**) [3a,b]. No significant differences in activity were observed upon using 1–100 equiv. of either $\text{Mg}(n\text{-Bu})_2$ or $\text{Mg}(\text{allyl})_2$ as activators ($1\text{--}8 \text{ kg PS mol Nd}^{-1} \text{ h}^{-1}$) and both binary systems appear ca. 2 orders of magnitude less active than the single-site complex **1** ($1700 \text{ kg PS mol Nd}^{-1} \text{ h}^{-1}$). On the other hand, the similar performances of the **2**/ $\text{Mg}(n\text{-Bu})_2$ and **2**/ $\text{Mg}(\text{allyl})_2$ systems were unexpected because so far only discrete *allyl* complexes

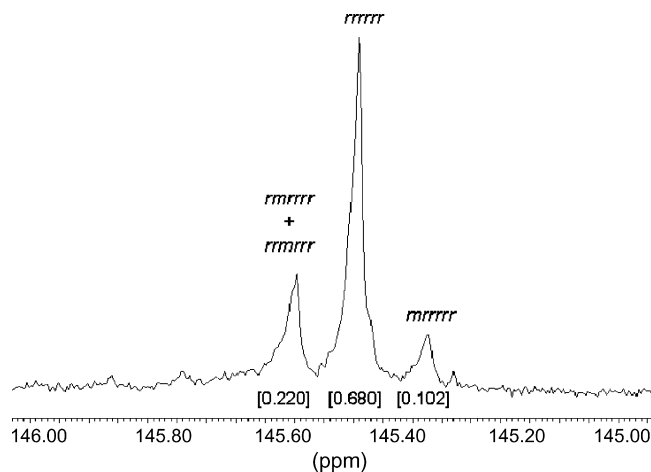


Fig. 2. Phenyl *ipso*-carbon region of the ^{13}C NMR spectrum (CDCl_3 , 40°C , 125 MHz) of oligostyrenes with assignments of heptads (entry 1) (data in square brackets are integral values).

such as **1** were found active for styrene polymerization under these conditions; i.e., no activity was detected with the yttrium carbyl complexes $[\text{Cp}-\text{CMe}_2-\text{Flu}]\text{Y}(\text{R})(\text{THF})$ ($\text{R} = \text{CH}_2\text{SiMe}_3$, $\text{CH}(\text{SiMe}_3)_2$).

The oligostyrenes prepared from both $\text{Mg}(n\text{-Bu})_2$ and $\text{Mg}(\text{allyl})_2$ are highly syndiotactic as determined by ^{13}C NMR spectroscopy. As depicted in Fig. 2, the aromatic *ipso*-carbon region of the high-field ^{13}C NMR spectra of the oligostyrenes shows only few signals assigned to one major *rrrrrr* ($\delta = 145.44 \text{ ppm}$) and minor *rmrrrr*, *rmrrrr* and *mrrrrr* heptads [6]. The relative intensities of those match well with the first-order Markovian (Bernoullian) statistics of the chain-end stereocontrol, giving a probability of racemic linkage between styrene units P_r of 0.93–0.94 [7]. This observation indicates that the binary combinations **1**/ MgR_2 actually generate catalytic species that act similarly to the single-component allyl complex **1**, in particular with the same syndiospecificity. It argues against other contributions to the production of oligostyrenes, e.g. radical routes [2] which would lead to atactic materials. Remarkably, the oligostyrenes prepared in this work have good solubility in chloroform, THF and toluene, despite their high syndiotacticity.

Table 1
Styrene oligomerization promoted by $[(\text{Cp}-\text{CMe}_2-\text{Flu})\text{Nd}(\mu\text{-Cl})_2]/\text{MgR}_2$ combinations^a

Entry	MgR ₂	[Mg]/[Nd]	[St]/[Nd]	PSt (%)	M_n^b	M_w/M_n^b	Chains/Nd ^c
1	MgBu ₂	1	830	5	6500	1.5	0.67
2	MgBu ₂	14	810	10	4400	1.4	1.9
3	MgBu ₂	38	690	12	2700	1.3	3.2
4	MgBu ₂	54	630	12	2600	1.2	3.0
5	MgBu ₂	144	660	17	3000	1.2	3.9
6	Mg(allyl) ₂	1	800	2	4400	2.8	0.38
7	Mg(allyl) ₂	13	750	8	3300	1.3	1.9
8	Mg(allyl) ₂	36	670	6	2400	2.4	1.7
9	Mg(allyl) ₂	62	730	14	2600	1.2	4.0
10	Mg(allyl) ₂	154	940	6	1600	1.2	3.7

^a Reactions conducted for 1 h at 60°C using 10–60 μmol of Nd in neat styrene.

^b Determined by GPC in THF at 20°C using polystyrene standards.

^c Number of polymer chains per Nd as determined from the relation: $\text{conv} \times ([\text{St}]/[\text{Nd}]) \times 104/M_n$.

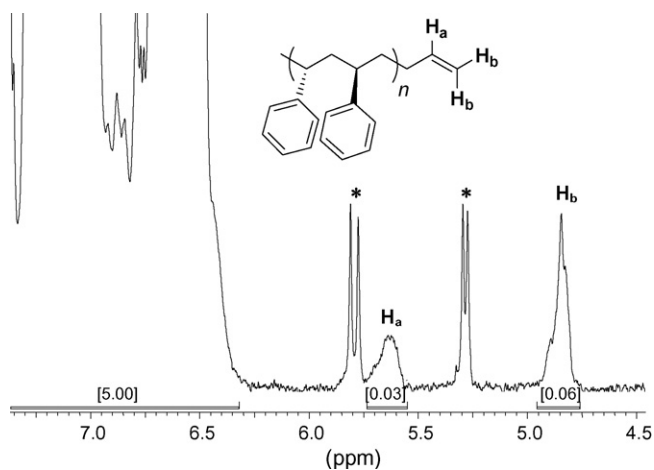


Fig. 3. ^1H NMR spectrum (500 MHz, 25°C , CDCl_3) of oligostyrenes produced from $\mathbf{2}/\text{Mg}(\text{allyl})_2$ (Table 1, entry 7) ($M_n = 3300 \text{ g mol}^{-1}$ according to GPC; 3500 g mol^{-1} by ^1H NMR) (asterisk (*) stands for residual styrene monomer resonances).

A chain-end analysis of the oligomers was undertaken to identify the role of the MgR_2 reagent in those binary catalytic systems. In fact, the ^1H NMR spectrum of oligostyrenes prepared from the $\mathbf{2}/\text{Mg}(\text{allyl})_2$ combination features two signals at δ 5.64 ppm (1H) and 4.84 ppm (2H) that are characteristic for the vinyl moiety of an allyl end-group (Fig. 3) [8]. The oligostyrenes were also characterized by MALDI-TOF mass spectrometry to confirm the terminus groups [9]. As shown in Fig. 4, the oligomers prepared with the $\mathbf{2}/\text{Mg}(\text{allyl})_2$ system feature a single distribution of peaks, which actually correspond to oligostyrene chains cationized by Ag^+ with an allyl end-group and a H termination chain end from methanol during the work-up procedure using acidic methanol [10]. Similarly, the MALDI-TOF-MS spectrum of oligostyrenes prepared with the $\mathbf{2}/\text{Mg}(n\text{-Bu})_2$ system feature a major distribution of peaks, of which the molecular weight is consistent with the calculated molecular weights for the on-matrix compounds $(\text{H})(\text{C}_8\text{H}_8)_n(\text{C}_4\text{H}_{10})\text{Ag}^+$, where n represents the degree of polymerization (Fig. 5) [11]. A lower intensity series of peaks was found to correspond to polystyrene chains capped with an ethyl

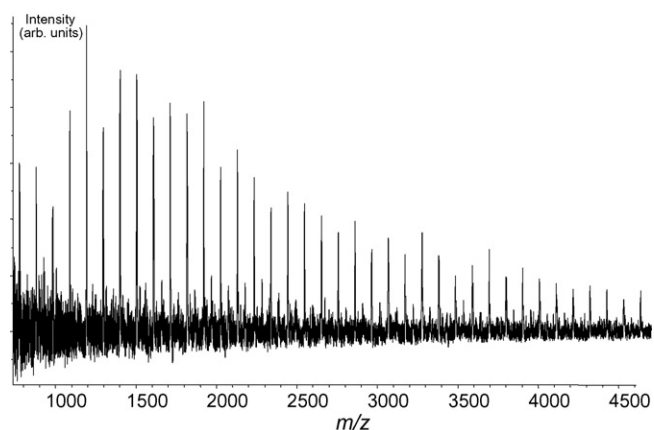


Fig. 4. MALDI-TOF mass spectrum of oligostyrenes produced from $\mathbf{2}/\text{Mg}(\text{allyl})_2$ (Table 1, entry 7) (polymer doped with AgOTf , dithranol matrix).

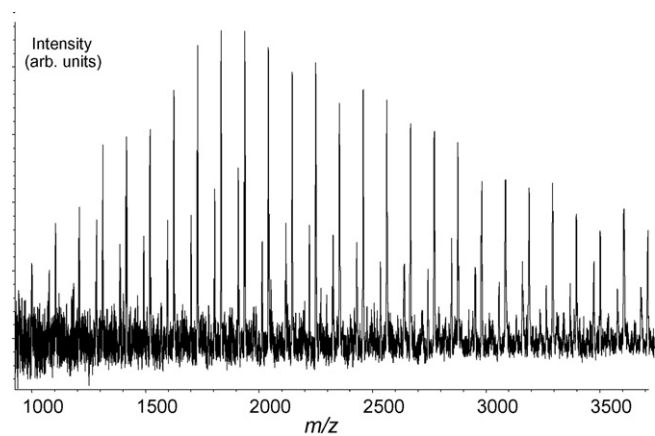
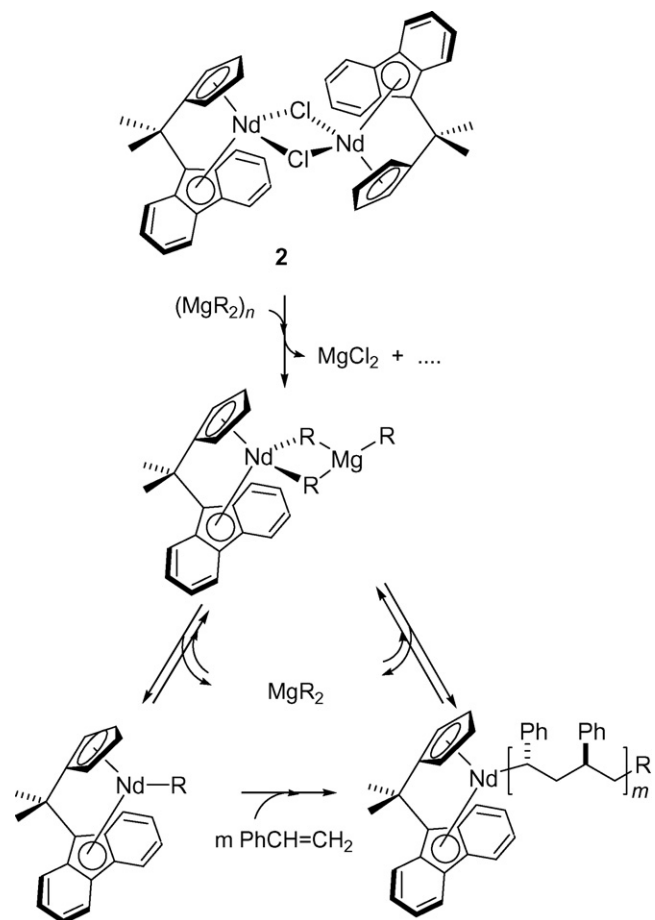


Fig. 5. MALDI-TOF mass spectrum of oligostyrenes produced from $\mathbf{2}/\text{Mg}(n\text{-Bu})_2$ (Table 1, entry 2) (polymer doped with AgOTf , dithranol matrix).

head group, i.e. $(\text{H})(\text{C}_8\text{H}_8)_n(\text{C}_2\text{H}_5)\text{Ag}^+$ [11], reflecting the presence of MgEtBu as a contaminant in $\text{Mg}(n\text{-Bu})_2$ due to the way the latter is prepared [12]. These results are consistent with our previous observations in the case of styrene oligomerization promoted by other lanthanide/dialkylmagnesium systems [1f,2g] and confirm that MgR_2 acts as an alkylating agent of the *ansa*-chloroneodymocene precursor $\mathbf{2}$ and a transfer agent during polymerization (Scheme 1).



Scheme 1. *In situ* generation of active alkyl-Nd species and transmetalation processes.

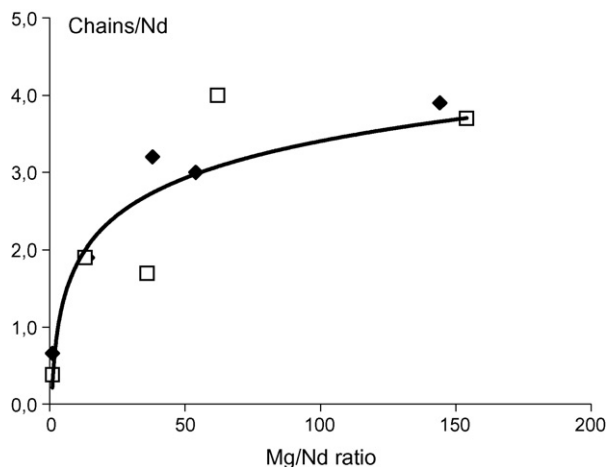


Fig. 6. Number of oligostyrene chains as a function of the MgR_2/Nd ratio: (\square) $\text{Mg}(\text{allyl})_2$; (\blacklozenge) $\text{Mg}(n\text{-Bu})_2$ (see Table 1 for details).

The average number molecular weights (M_n) of the prepared oligostyrenes are in the range 1600–6500 g mol^{-1} , as determined by GPC versus polystyrene standards. The M_n values determined by $^1\text{H NMR}$, based on the relative intensity of the resonances for terminal allyl groups, were in close agreement; e.g., entry 7: $M_{n,\text{GPC}} = 3300 \text{ g mol}^{-1}$ and $M_{n,\text{NMR}} = 3500 \text{ g mol}^{-1}$ (see Fig. 3). The molecular weight distributions are monomodal and rather narrow, ranging for most from 1.2 to 1.5, with two exceptions. Such polydispersity values, which fall in the usual range for binary lanthanide–magnesium poly/oligomerization systems [1,2], are indicative of a single-site catalyst behavior. However, the experimental M_n values are systematically higher than those calculated, considering the styrene-to-Nd and Mg-to-Nd ratios. This reflects modest initiation and chain transfer efficiencies. The initiation efficiency of the *in situ* generated butyl(allyl)-neodymocene, as estimated from experiments performed with 1 equiv. of the MgR_2 activator, is ca. 38 (allyl)–66% (butyl) (Table 1, entries 1 and 6). These initiation efficiency values are similar to those determined for the single-component catalyst **2** (ca. 33–56%) [3b]. The chain transfer efficiency, expressed by the number of oligostyrenes chains par Nd center (Table 1), as a function of the dialkylmagnesium-to-Nd ratio is illustrated in Fig. 6. Obviously, effective chain transfer takes place in the range $1 < [\text{MgR}_2]/[\text{Nd}] < 10$, equally with $\text{Mg}(n\text{-Bu})_2$ (entry 2) and $\text{Mg}(\text{allyl})_2$ (entry 7), but shows afterwards a saturation limit with a plateau observed at $[\text{MgR}_2]/[\text{Nd}] > 20$.

3. Conclusions

Binary combinations of the readily prepared catalyst precursor $[(\text{Cp}-\text{CMe}_2-\text{Flu})\text{Nd}(\mu\text{-Cl})_2]$ (**2**) and a dialkylmagnesium provide a simple way to prepare soluble highly syndiotactic oligostyrenes. Selectively allyl end-capped, syndiotactic oligostyrenes can be efficiently obtained via this procedure upon using dialkylmagnesium. Such materials, which have never been reported to our knowledge, may be used as valuable macromonomers [13] or macromolecular reagents for specific functionalization.

4. Experimental

4.1. General

All manipulations were performed under a purified argon atmosphere using standard Schlenk techniques or in a glovebox. Solvents were distilled from appropriate agents under nitrogen and degassed thoroughly prior to use. $[(\text{Cp}-\text{CMe}_2-\text{Flu})\text{Y}(\mu\text{-Cl})_2]$ (**2**) was prepared following a reported procedure [4]. Diallylmagnesium was prepared from the corresponding Grignard reagent by addition of 0.5 equiv. of 1,4-dioxane in diethyl ether to precipitate MgCl_2 . Di(*n*-butyl)magnesium (1.0 M in heptane, Aldrich) was used as received. Styrene (99%, Aldrich) was distilled over CaH_2 , stored at -20°C under argon, and degassed prior to use.

4.2. Typical procedure for styrene polymerization

In the glovebox, a pre-weighed amount of chloro *ansa*-neodymocene **2** (ca. 30 mg) and dialkylmagnesium were solubilized in toluene (1 mL) and stirred for 20 min at room temperature. Styrene (4.00 mL, 34.8 mmol) was added to the mixture and vigorous stirring at the appropriate temperature was immediately started. After a given time period, the Schlenk tube was opened to air and a 10% solution of HCl in methanol (ca. 1 mL) was added to quench the reaction. The precipitated polymer was washed repeatedly with methanol (ca. 500 mL), filtered and dried *in vacuo* overnight at room temperature.

4.3. Analysis of oligostyrenes

^{13}C NMR analyses of oligostyrenes were performed in CDCl_3 solvent at 40°C in 5 mm tubes on a AM-500 Bruker spectrometer operating at 125 MHz; “quantitative” ^{13}C NMR spectra were recorded in the inverted-gate decoupling-acquisition mode with the following parameters: delay 30 s, acquisition time 1.18 s, number of scans ≥ 2000 . GPC analyses of oligostyrenes were carried out in THF at 20°C in Rennes on a Waters apparatus (flowrate: 1 mL min^{-1} , RI detection) and/or at the research center of Total Petrochemicals in Feluy (Belgium) using PS standards for calibration. MALDI-TOF-MS was performed on a MicroFlex LT spectrometer (Bruker Daltonics) which was operated in the linear mode. The spectra were recorded in the positive-ion mode. The samples were prepared by taking $2 \mu\text{L}$ of a THF solution of the polymer (10 mg PS mL^{-1}) and adding this to $16 \mu\text{L}$ of 1,8-dihydroxy-9(10H)-anthracenone (dithranol, 10 mg mL^{-1} in THF) to which had been added $2 \mu\text{L}$ of $\text{CF}_3\text{SO}_3\text{Ag}$ (2 mg mL^{-1} in THF). A $1 \mu\text{L}$ portion of this mixture was applied to the target and 50–100 single shot spectra were accumulated. Given masses represent the average masses of the Ag^+ adducts. The spectrometer was calibrated with external PS standards ($M_p = 2610$ and 6690 g mol^{-1}).

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