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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 $[(Cp–CMe_2–Flu)Nd(\mu\text{-}Cl)]_2$ (**2**) and a dialkylmagnesium (1–100 equiv. versus Nd) have been explored for styrene oligomerization and compared to the single-component polymerization catalyst $[Cp–CMe_2–Flu]Nd(allyl)(THF)$ (**1**). Binary systems derived from **2** and $Mg(n\text{-}Bu)_2$ or $Mg(allyl)_2$ are moderately active at 60 °C (1–8 kg PS mol Nd^{-1} h^{-1}), yielding soluble oligostyrenes ($M_n = 1600–6500$ g mol^{-1}, $M_w/M_n = 1.3–2.5$), which have an unprecedented high degree of syndiotacticity ($P_r = 94\%$, determined by ^{13}C NMR spectroscopy) and are selectively end-capped by butyl or allyl groups (identified by ^{1}H 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 transmetallation to excess dialkylmagnesium reagent.

Keywords: Catalysis; Neodymium; Polymerization; Styrene; Tacticity

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 $[Cp–CMe_2–Flu]^{2-}$ (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. Diallylmagnesium 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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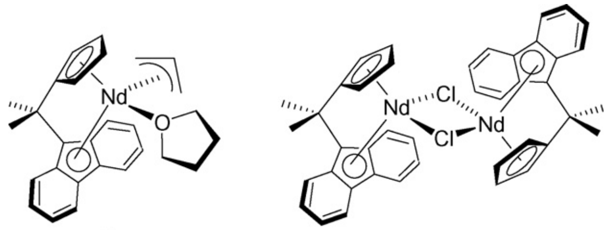

1 **2**

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

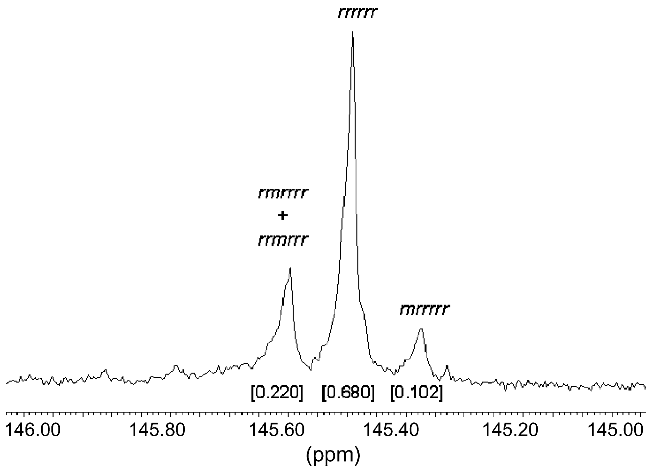

Fig. 2. Phenyl *ipso*-carbon region of the ^{13}C NMR spectrum ($CDCl_3$, 40 °C, 125 MHz) of oligostyrenes with assignments of heptads (entry 1) (data in square brackets are integral values).

2. Results and discussion

The *ansa*-neodymocene $[(Cp–CMe_2–Flu)Nd(\mu\text{-}Cl)]_2$ (**2**) was prepared as reported previously by transmetallation between $NdCl_3(THF)_2$ and $[Flu–CMe_2–Cp]Li_2$ 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 ($M_n < 6000\,g\,mol^{-1}$) 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. $[Cp–CMe_2–Flu]Nd(allyl)(THF)$ (**1**) [3a,b]. No significant differences in activity were observed upon using 1–100 equiv. of either $Mg(n\text{-}Bu)_2$ or $Mg(allyl)_2$ as activators (1–8 kg PS mol $Nd^{-1}\,h^{-1}$) and both binary systems appear ca. 2 orders of magnitude less active than the single-site complex **1** (1700 kg PS mol $Nd^{-1}\,h^{-1}$). On the other hand, the similar performances of the **2**/$Mg(n\text{-}Bu)_2$ and **2**/$Mg(allyl)_2$ systems were unexpected because so far only discrete *allyl* complexes such as **1** were found active for styrene polymerization under these conditions; i.e., no activity was detected with the yttrium carbyl complexes $[Cp–CMe_2–Flu]Y(R)(THF)$ ($R = CH_2SiMe_3$, $CH(SiMe_3)_2$).

The oligostyrenes prepared from both $Mg(n\text{-}Bu)_2$ and $Mg(allyl)_2$ 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* ($\delta = 145.44$ ppm) and minor *rrmrrr*, *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 $[(Cp–CMe_2–Flu)Nd(\mu\text{-}Cl)]_2/MgR_2$ 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: conv × ([St]/[Nd]) × 104 /M_n.