Polymer Communication

In situ generated half-lanthanidocene based catalysts for the controlled oligomerisation of styrene: Selectivity, block copolymerisation and chain transfer

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Abstract

The Cp*Nd(BH$_4$)$_2$(THF)$_2$/n-butylethylmagnesium combination affords a controlled and syndioselective oligomerisation of styrene. Living oligostyrenes can be used as macromonomers for block copolymerisation, leading to the unprecedented synthesis of a (polystyrene)-*block*-(1,4-*trans* polyisoprene) copolymer. Reversible transmetallation between the neodymium and the magnesium atom is further established with a transfer efficiency close to 100%.
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1. Introduction

The syndiotactic polymerisation of styrene reported for the first time 20 years ago [1] is now well-documented. Although titanium based precatalysts combined to alumoxanes have been studied extensively, with an emphasis on half-titanocenes [2,3], the discovery of a highly syndiospecific living system has only been reported recently, using half-calciumocenes [4,5]. Besides, the search for new versatile catalysts affording copolymerisations has found a new breath with the rare earth elements, using the strategy of changing the ligand environment of the metal [6–9]. Simple rare earth precatalysts in combination with a cocatalyst have also been applied successfully to the polymerisation of styrene [10–13] as well as half-lanthanidocenes [9,14,15], lanthanidocenes [16,17] and allyl complexes [17,18]. Only one lanthanide mediated controlled

"living" polymerisation of styrene has been reported so far to our knowledge, leading to the unprecedented incorporation of syndiotactic sequences in styrene–ethylene copolymers [14,15].

Borohydrido lanthanide complexes are an emerging class of simple polymerisation precatalysts. They are known as valuable precursors in organometallic chemistry. They give rise to well-defined X-ray characterized compounds. They are more reactive and more soluble than their chloro homologues, and allow ^{1}H NMR monitoring [19–23]. Another reason for the growing interest in borohydrido catalysts lies in their versatility and the related applicative potentialities for copolymerisations. They are indeed known as precatalysts for the polymerisation of dienes [24,25] and olefins [26] as well as initiators for polar monomers such as cyclic esters [27] and acrylates [28,29]. We reported recently the polymerisation of styrene by trisborohydrido complexes of the rare earths [30] and we present herein, in the course of our on-going research, preliminary results of the activity of an *in-situ* generated borohydrido half-neodymocene catalyst. This system affords not

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only a controlled oligomerisation of styrene, that leads to the unprecedented synthesis of a polystyrene-*block*-(1,4-*trans* polyisoprene (98%)) copolymer, but also well-controlled reversible chain transfer to magnesium.

2. Experimental section

2.1. Materials

All operations were performed under dry argon by using Schlenk techniques. Toluene was dried over sodium/benzophenone and distilled over molecular sieves before use. Styrene (99% from Aldrich) was dried over calcium hydride, distilled twice over molecular sieves and once just before use. *n*-Butylethylmagnesium (20 wt%. in heptane from Texas Alkyl) was used as received. The complex Cp*Nd(BH$_4$)$_2$(THF)$_2$ was synthesized according to literature procedures [22,23].

2.2. Polymerisation

In a glove box, the borohydrido complex was weighed in a vessel. Toluene, styrene and *n*-butylethylmagnesium were added in the flask in this order using syringes. The mixture was magnetically stirred at the reaction temperature for a given time, diluted in toluene and the resulting solution was poured into ethanol, leading to the precipitation of an off-white polymer. Solvents were evaporated under partial vacuum, and the product was dried under vacuum for 48 h.

For the copolymerisation experiments and the subsequent styrene addition, the flask was reintroduced in the glove box after the first run of the reaction (20 h at 50 °C). Half of the mixture was separated for analysis and 1 ml monomer (isoprene or styrene) was introduced in the second half remaining in the flask. After the given reaction time (2 h for isoprene and 20 h for styrene, 50 °C), the procedure described above was used to isolate the product.

2.3. Measurements

The ^{1}H spectrum of 1,4-*trans* polyisoprene was recorded on a AC 300 Bruker spectrometer at room temperature in CDCl$_3$. Other spectra were recorded on a AC 400 Bruker spectrometer at 380 K and 400 K in tetrachloroethane-d_2. The chemical shifts were calibrated using the residual resonances of the solvent. Size exclusion chromatography (SEC) was performed (i) in THF as eluent at 20 °C using a Waters SIS HPLC-pump, a Waters 410 refractometer and Waters styragel column (HR2, HR3, HR4, HR5E) and (ii) in trichlorobenzene as eluent at 135 °C using a Waters 150C PLUS device with coupled refractometer and viscosity detectors. The number-average molecular weight and polydispersity index were calculated using polystyrene standards. Both analyses lead to similar results for all entries except entries 4 and 7 where a number-average

molecular weight of 11,000 and 3500 and a PDI of 1.6 and 1.4, respectively, were measured at room temperature.

3. Results and discussion

Typical experiments conducted in toluene at 50 °C are summarized in Table 1. The reaction is quantitative in several hours and syndioselective (85% from NMR as detailed in Appendix). The analysis of the molecular weight distribution shows a rather low and constant polydispersity along the reaction time (entries 1−3), indicating a well-controlled oligomerisation. The resulting molecular weights are close to the theoretical ones assuming two growing chains per magnesium, *i.e.*, one growing chain per alkyl group. The living character of the reaction was checked by a second addition of monomer after 20 h reaction. Deactivated chains can be noticed in Fig. 1, characteristic of a partially living system. The higher apparent polydispersity observed after the second addition of styrene (Fig. 1(a)) can be attributed to the presence of such deactivated chains. The selectivity of the reaction was found to be unchanged.

The potentiality of the living oligostyrenes as macroinitiators for block copolymerisation was assessed with isoprene (Fig. 1(b)), and the resulting polyisoprene block shows a high 1,4-*trans* microstructure (98% from NMR analysis detailed in Appendix), together with a narrow polydispersity (1.2). Such a polystyrene-*block*-(1,4-*trans* polyisoprene) copolymer has never been synthesized so far to our knowledge.

The occurrence of transmetallation is further established by increasing the Mg/Nd ratio up to 10 (entries 5−7 in Table 1). The reaction is slower (entries 5 and 6), but remains quantitative. The narrow polydispersity and the control over the molecular weight are preserved in the course of the transfer reactions. The selectivity was found to be unchanged, in accordance with coordination−insertion processes taking place around the neodymium atom. All alkyl fragments of *n*-butylethylmagnesium introduced are involved in the chain transfer, highlighting a process which can be considered as a polystyrene catalyzed chain growth on magnesium, similar to that observed between lanthanidocene catalysts and magnesium

Table 1

Polymerisation of styrene with Cp*Nd(BH$_4$)$_2$(THF)$_2$ and *n*-butylethylmagnesium

Entry[a]	St/Nd	Mg/Nd	Time (h)	Conversion (%)	$\overline{M}_n$ calc.[b] (g/mol)	$\overline{M}_n$[c] (g/mol)	PDI[d]
1	100	1	2	31	1600	1400	1.3
2	108	1.05	8	59	3100	2700	1.2
3	100	1	20	97	5000	3800	1.3
4	440	1	20	81	18500	16000	1.2
5	440	10	20	24	550	560	1.2
6	475	10.8	90	99	2300	2100	1.3
7	2000	10	90	82	8500	8300	1.2

[a] Reactions conducted at 50 °C with 0.5 ml styrene in 0.5 ml toluene.
[b] Expected molecular weight assuming two growing chains per magnesium.
[c] Number-average molecular weight measured by SEC.
[d] Polydispersity index measured by SEC (PDI $= \overline{M}_w/\overline{M}_n$).

(a)

M_n 7900
PDI 1.78
Conv. (97+72)%

M_n 3200
PDI 1.31
Conv. 97%

(b)

M_n 28800
PDI 1.20
Conv. (98+97)%
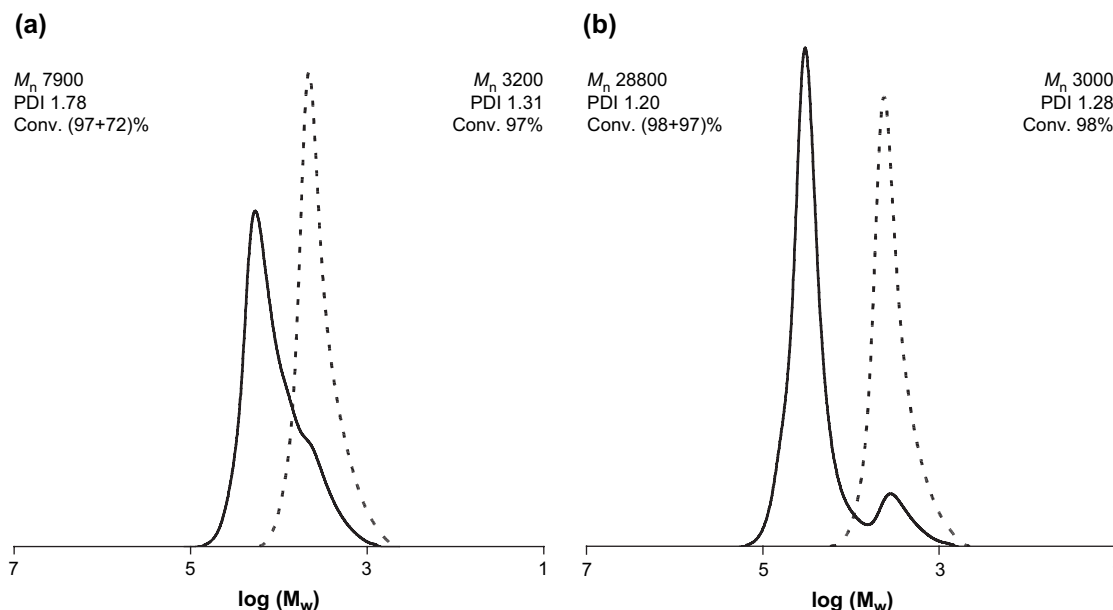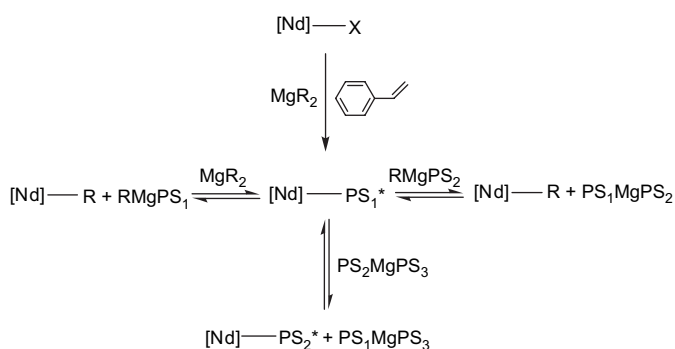
M_n 3000
PDI 1.28
Conv. 98%

Fig. 1. Molecular weight distribution of polystyrene (conditions similar to entry 3) before (dot lines) and after subsequent addition of styrene (a) or isoprene (b).

Scheme 1. Mechanism of the transfer polymerisation of styrene in the presence of half-lanthanidocene/dialkylmagnesium systems. X represents a BH_4 group and PS_i* a growing polystyrene chain.

dialkyl during ethylene polymerisation [31]. If polyethylene catalyzed chain growth (CCG) [32] on zinc has also been achieved, polystyrene chain transfer to aluminium [33,34] and reversible transfer to magnesium [13,16] occurred only with a partial transfer efficiency. The mechanism of the reaction is summarized in Scheme 1.

4. Conclusion

The oligomerisation of styrene using Cp*Nd(BH$_4$)$_2$(THF)$_2$/n-butylethylmagnesium presents the following features:

- A controlled character, both in terms of molecular weight and polydispersity;
- A pseudo-living character;

- A syndioselectivity close to 85%;
- Reversible transmetallation with a transfer efficiency close to 100%, which is to our knowledge the first example of a polystyrene CCG reaction.

This versatile catalytic system affords finally the synthesis of new polystyrene-*block*-(1,4-*trans* polyisoprene) copolymers.

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Appendix. Spectroscopic data

Determination of the selectivity of the reaction

The selectivity of the reaction can be established from the ^{13}C NMR spectra in the phenyl *ipso* carbon region: the four heptads of highly syndiotactic polystyrene [35] can be distinguished in Fig. A1. The deconvolution of the spectra is done directly by the NMR software TOPSPIN (Bruker), and leads to the following area proportions of the four heptads, from left to right: 50.4, 11.2, 20.6 and 17.8%. It leads to a syndiotacticity ratio of 86.8% that we consider to be close to 85%. The goodness of fit can be appreciated graphically in Fig. A2.
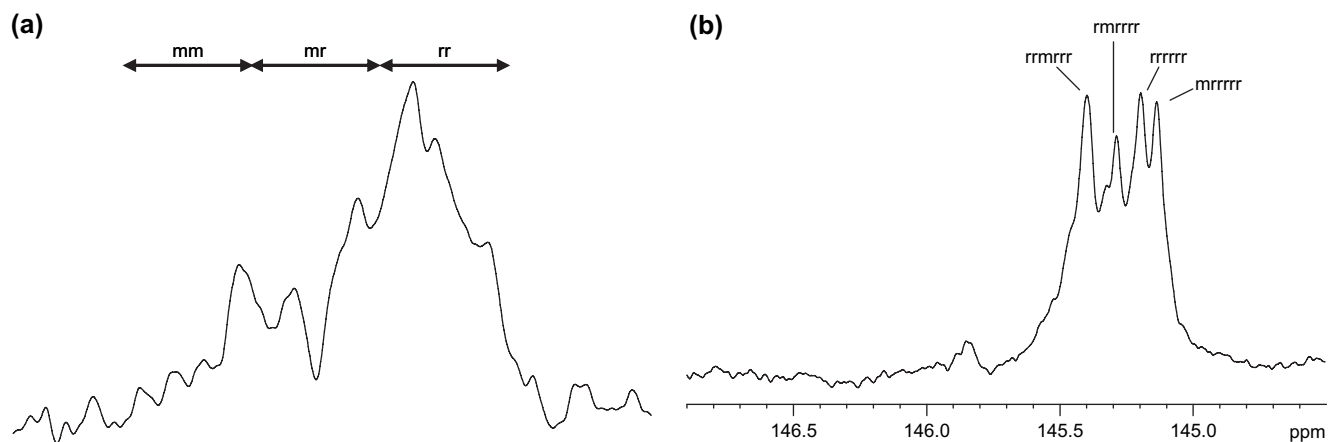
Fig. A1. ^{13}C NMR spectra of polystyrene (400 K in tetrachloroethane-d_2) in the phenyl *ipso* carbon region corresponding to atactic polystyrene (a) and syndio-tactic-rich polystyrene synthesized using the Cp*Nd(BH$_4$)$_2$(THF)$_2$/*n*-butylethylmagnesium combination.
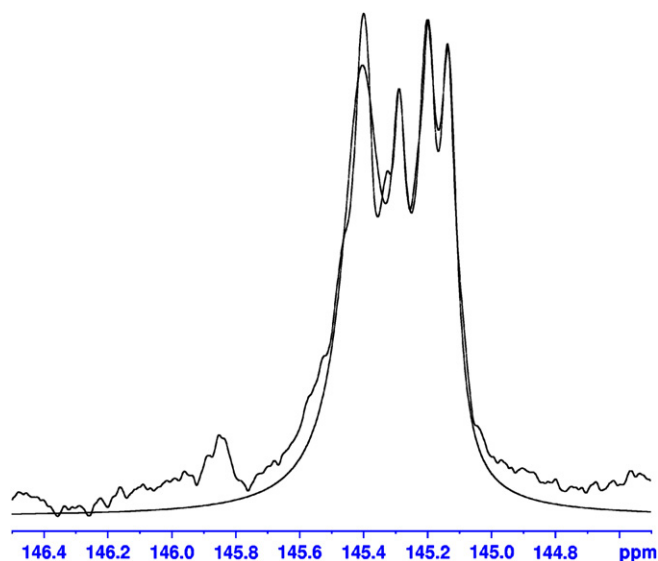

Fig. A2. Deconvolution: experimental vs. fitted curve.

Polystyrene-block-(1,4-trans polyisoprene)

The microstructure of the polyisoprene block was determined from NMR spectra according to the following way. The proportion of 1,4 vs. 3,4 sequences is deduced from the =CH vs. =CH$_2$ ratio determined from the ^{1}H NMR spectrum. From Fig. A3, a 98% 1,4 microstructure is assessed for the polyisoprene block, but the presence of styrene signals in the −CH$_3$ zone do not enable a quantitative analysis. The absence of signals that would result from 1,4-*cis* sequences on the ^{13}C NMR spectra (Fig. A4) let us conclude to a 98% 1,4-*trans* and 2% 3,4 microstructure for the polyisoprene block.
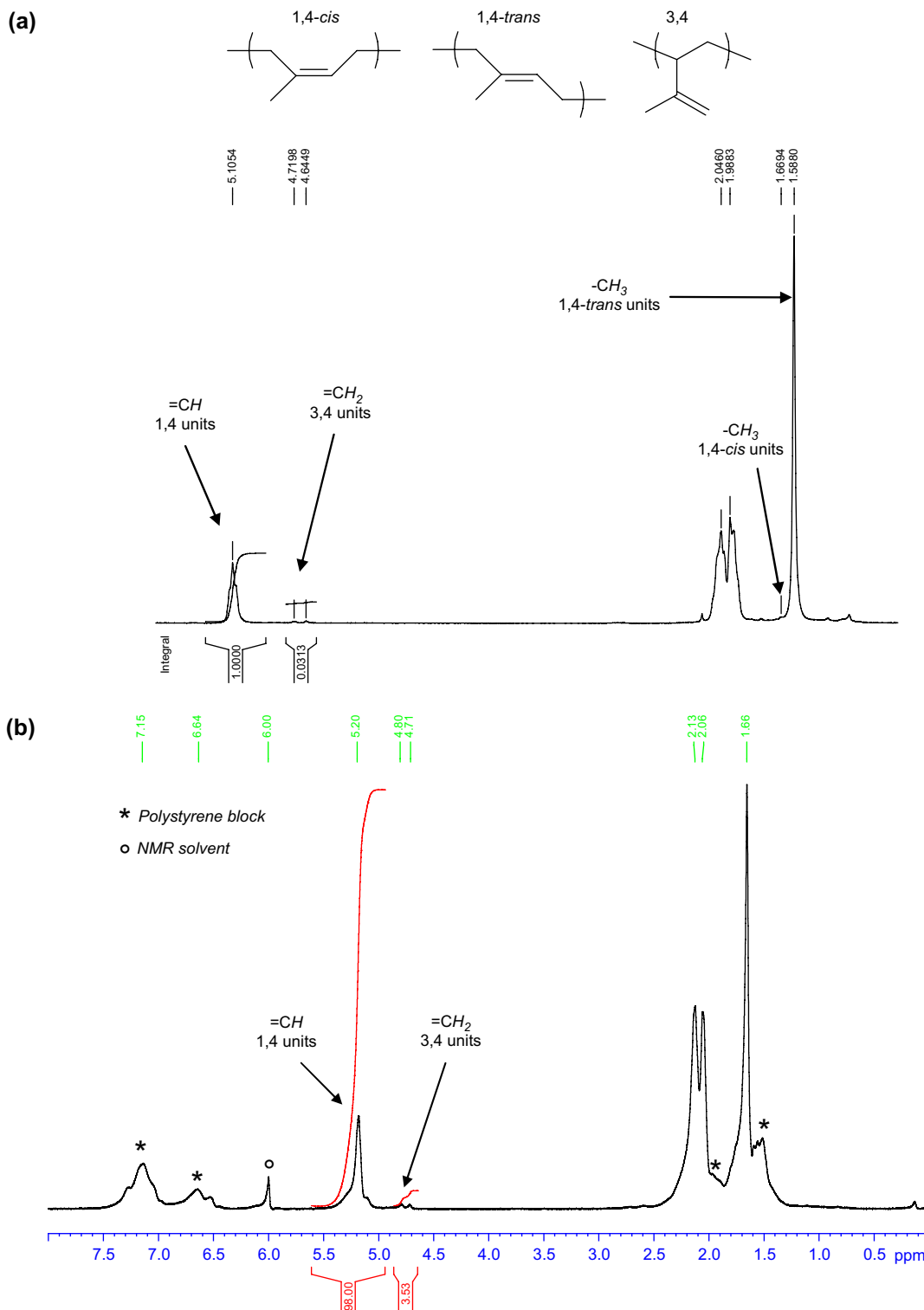
(a)

1,4-*cis*   1,4-*trans*   3,4

5.1054

4.7198
4.6449

2.0460
1.9883

1.6694
1.5880

-CH₃
1,4-*trans* units

=CH
1,4 units

=CH₂
3,4 units

-CH₃
1,4-*cis* units

Integral

1.0000

0.0313

(b)

7.15

6.64

6.00

5.20

4.80
4.71

2.13
2.06

1.66

* *Polystyrene block*

o *NMR solvent*

=CH
1,4 units

=CH₂
3,4 units

*

*

o

*

*

7.5   7.0   6.5   6.0   5.5   5.0   4.5   4.0   3.5   3.0   2.5   2.0   1.5   1.0   0.5 ppm

98.00   3.53

Fig. A3. ¹H NMR spectrum of (a) a 98% 1,4-*trans* polyisoprene at room temperature in CDCl₃ and (b) a polystyrene-*block*-polyisoprene showing a 1,4-*trans* microstructure (380 K, tetrachloroethane-d_2) − both compounds were synthesized using the Cp*Nd(BH₄)₂(THF)₂/*n*-butylethylmagnesium combination.
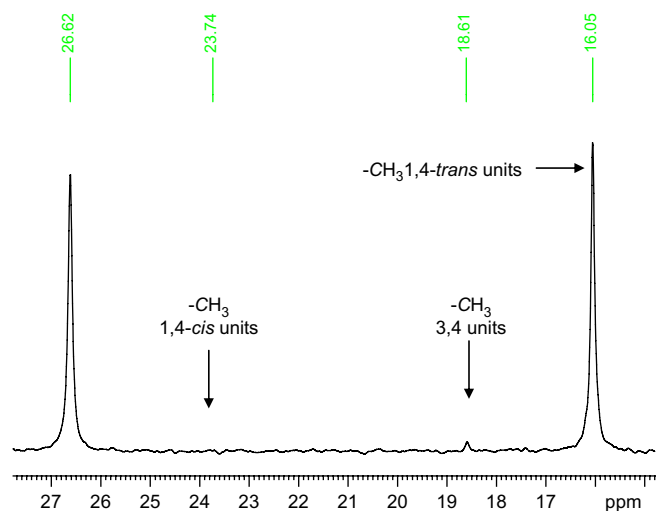
Fig. A4. ^{13}C NMR spectrum (380 K, tetrachloroethane-d_2) of a polystyrene-*block*-polyisoprene showing the absence of 1,4-*cis* units in the polyisoprene block.

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