Highly trans-stereospecific Isoprene Polymerization by Neodymium Borohydrido Catalysts

Fanny Bonnet, Marc Visseaux, Angela Pereira, Denise Barbier-Baudry

Highly *trans*-stereospecific Isoprene Polymerization by Neodymium Borohydrido Catalysts[†]

Fanny BONNET[a], *Marc VISSEAUX*[b]*, *Angela PEREIRA*[a], *and Denise BARBIER-BAUDRY*[a]

[a]Laboratoire de Synthèse et d'Electrosynthèse Organométallique (LSEO) – UMR 5188 CNRS, Université de Bourgogne, BP 47870, 21078 Dijon cedex, France.

[b]Laboratoire de Catalyse de Lille – UMR 8010 CNRS, ENSCL, Université des Sciences et Technologies de Lille, BP 108, 59652 Villeneuve d'Ascq cedex, France

marc.visseaux@ensc-lille.fr

fanny.bonnet@chemistry.oxford.ac.uk

aspereira@dq.ua.pt

denise.baudry@u-bourgogne.fr

tel. +33 (0)3 20 43 43 43 poste 5085. Fax : +33 (0) 3 20 43 65 85

[†] A part of this work was preliminarily reported to : *Macromol. Rapid Commun*. **2004**, 25, 873-877 (rapid communication).

Abstract.

Highly stereospecific polymerization of isoprene was achieved using borohydrido neodymium complexes. In combination with stoichiometric amounts of dialkylmagnesium, $Nd(BH_4)_3(THF)_3$ (**1**) and $Cp^{*'}Nd(BH_4)_2(THF)_2$ (**2**) ($Cp^{*'} = C_5Me_4nPr$) afford very efficient catalysts. Activity reaches 37300 g polyisoprene/mol Nd/h. Half-lanthanidocene **2** gives rise to polyisoprene 98.5 % *trans*-regular, the highest content yet described for a homogeneous organometallic catalyst. NMR experiments argue for the formation of bimetallic $Nd(\mu\text{-}BH_4)Mg$ active species.

Keywords: neodymium, rare-earths, *trans*-polyisoprene, borohydride, stereospecific polymerization.

Introduction

Rare earth complexes have been involved in a great number of reports dealing with conjugated dienes polymerization since the 1980's. [1-4] Whereas *cis*-diene polymerization has been to a large extent more studied, *trans*-polymerization has seen a renewed interest only recently, after the pioneer work of Natta. [5] *Trans*-1,4-polydienes, [6] and particularly 1,4-*trans*-polyisoprene, produced naturally as gutta-percha rubber, appear well-suited for the elaboration of high-performances tires. [7] Moreover, *trans*-polymerization may also allow incorporation of α-olefin into a polydiene chain, affording high value-added copolymers. [8-10]

Lanthanide-based isoprene polymerization catalysts are obtained by the reaction of a lanthanide precursor, selected among readily available carboxylates (versatates), [11] halides, [12,13] or alkoxides, [14] with an Al or Mg co-catalyst. *Trans*-sterospecificity is generally related to the use of Nd/Mg combinations, [15,16] but such catalysts do not allow living polymerization. This had just been achieved by means of an organometallic initiator, $(CMe_2C_5H_4)_2Sm(allyl)MgCl_2(ether)_2LiCl(ether)$, [17] which gives rise to polyisoprene with molecular weights that are well controlled, and have quite narrow polydispersity indices (1.5–1.8). The polymer was also 95 % *trans*-regular and it was assumed that such stereospecificity could be related to steric hindrance around the samarium atom in the trimetallic catalyst.

Only recently, lanthanide trisborohydrides, $Ln(BH_4)_3(THF)_3$, have been used as valuable precursors for organometallic syntheses. [18,19] The presence of a borohydride ligand in the coordination sphere of a lanthanide generally ensures the formation of neutral rather than ionic "ate" species, and isolation of adducts containing less coordinated THF than in the chloro homologues. For instance, well-defined early half-lanthanidocenes have been isolated readily from $Ln(BH_4)_3(THF)_3$ (Ln = Sm, Nd) as starting materials. [18,20] These trisborohydrides behave like pseudo-halides and display several advantages, in particular their higher solubility in apolar solvents, respective to traditional $LnCl_3(THF)_3$. Also, they are easily available in one step from trichlorides, and the BH_4 ligand affords a typical pattern by ^1H NMR, allowing easier NMR analysis and monitoring, particularly in the case of paramagnetic lanthanides.

It was thus of interest to study the ability of lanthanide borohydrido complexes as precatalysts for isoprene polymerization. We present here a complete study, using inorganic $Nd(BH_4)_3(THF)_3$ (**1**) as an alternative to generic LnX_3 (X = Cl, OR, OCOR), and organometallic half-lanthanidocene $Cp^{*'}Nd(BH_4)_2(THF)_2$ (**2**) ($Cp^{*'} = C_5Me_4nPr$), both associated to dialkylmagnesium derivatives, for

such a purpose. Additional information about the molecular structure of active catalytic species is obtained from NMR experiments.

Results and Discussion

$Nd(BH_4)_3(THF)_3$ [21] has been used as a single-component initiator for ε-caprolactone polymerization. [22,23] It behaves in that case like a hydride, via Ring Opening Polymerization. In a preliminary paper, we reported that $Nd(BH_4)_3(THF)_3$ (**1**) is active as well toward isoprene, but only in the presence of specific alkylating agents, whereas no activity was observed with **1** alone. [24] The catalyst displayed *trans*-stereospecificity, and among the possible reasons for such a control, the formation of a sterically hindered bimetallic Nd-Mg species allowing only a single coordination of the diene was retained. It was thus of interest to study the influence of a bulky and electron-rich ligand in the coordination sphere of Nd for such catalysis, and we studied the ability of recently prepared $Cp^*'Nd(BH_4)_2(THF)_2$ (**2**) ($Cp^*' = C_5Me_4(n\text{Pr})$) for this purpose. [20] The synthesis of this complex, a rare example of monocyclopentadienyl derivatives of early lanthanides, had been achieved straightforwardly from $Nd(BH_4)_3(THF)_3$ according to equation 1, without the comproportionation usually observed with these elements, particularly with chloride complexes. [25]

(Equation 1)

As expected, **2**, combined with equivalent amounts of $Mg(n\text{Bu})_2$ displayed good efficiency along with higher *trans*-stereospecificity for isoprene polymerization.

Selected experiments are gathered in Table 1. Runs 1-4 and runs 5-12 were carried out starting respectively from **1** and **2**.

(Table 1)

Activity. The monomer conversion is mostly quantitative in less than 3 hours, depending on the monomer/catalyst ratio and the amount of co-catalyst. The average activity reaches 15600 g polymer/mol Nd/h with **1** (run 3) which is in all cases higher than that obtained with neodymium trichloride based catalysts. [13,15,26] With **2** (run 8) a better activity, 37300 g polymer/mol Nd/h, is observed, markedly higher than those mentioned in the literature for *trans*-specific similar polymerizations (range from 1000 to 10000 g polyisoprene/mol catalyst/h). The activities of *cis*-processes, kinetically favored, [27] are by two orders of magnitude higher. [28,29]

The higher activity of catalytic system obtained with precatalyst **2** might be ascribed to the smaller quantity of coordinated THF than in **1**. However, a more convincing explanation is the presence of the electron-rich Cp*' ligand, which favors η^3-η^1 allylic rearrangement, hence allowing faster chain migration. [30]

The **2**/Mg(*n*Bu)$_2$ catalytic system appears less successful in the presence of a large excess of dialkylmagnesium (run 11); a very poorly soluble material, likely cross-linked, is obtained. Obviously the quasi-living character is no more retained in such conditions. Competition between Mg(*n*Bu)$_2$ and isoprene monomer during the coordination step may account for such a result. A blank test conducted with Mg(*n*Bu)$_2$ alone did not afford any polymer in the same experimental conditions (run 13).

In the presence of a 50/50 isoprene/1-hexene mixture, no incorporation of olefin in the polymer occurred (pure polyisoprene is quantitatively obtained, run 12) and **2**/Mg(*n*Bu)$_2$ catalyst is inactive as well toward 1-hexene homopolymerization in our experimental conditions. Actually, the very few lanthanide catalysts allowing α-olefin polymerization all consist of electronic deficient complexes. [31] Such a finding may account here for a too important electronic donor environment in Cp*'Nd(BH$_4$)$_2$(THF)$_2$/Mg(*n*Bu)$_2$ despite the presence of only one cyclopentadienyl ligand.

Macromolecular data. As reported in table 1, both catalysts display a good control of the polymerization process, *i.e.* M_n values close to theoretical ones, and molecular weight distributions typical of a single-site mechanism. Calculated molecular weights take into account the number of equivalent of Mg co-catalyst added, *i.e.* the number of chains growing on the metal. SEC analyses were performed against polystyrene standards, but we established that such experimental values were close to the real ones for *trans*-polyisoprenes, since they were in accordance with values determined by ^{1}H NMR for allyl terminated samples. [8,32] With precatalyst **1**, each equivalents of dialkylmagnesium give rise to initiation of one single growing chain (runs 1-4). In the presence of two (run 3) or three (run 4) Mg per Nd, two and three chains are initiated on the lanthanide metal, respectively. Addition of a slight stoichiometric default (runs 5-7) or excess (runs 8-9) of dialkylmagnesium to precatalyst **2** affords molecular weights close to the expected ones. All these results are in accordance with a quasi-living process, indicating that: i) only one alkyl group per MgR$_2$ is transferred from the Mg atom to the Nd one to create an active bond and initiate polymerization, ii) then, most of Nd-R formed species are active. Such a behavior features a main difference with the well-known double alkyl-transfer reaction in lanthanide/MgR$_2$ dual component catalysts. [33]

SEC analysis shows monomodal profiles (in very few cases a slight shoulder at high M_n values could be observed). A typical chromatogram (run 5) is displayed on figure 1. Especially with catalyst prepared from **2** (runs 5-10), M_w/ M_n values are very close to the ideal value of 1: they are in the 1.15-1.3 range, which confirms the single-site catalyst character deduced from molecular weights.

Upon addition of an excess of magnesium co-catalyst to **2** (1.7 Mg/Nd, run 10), the experimental M_n value (6600) remains higher than the calculated one (4400) for a mono alkylation (i.e. one active R per MgR_2) with 1.7 Mg per Nd. Since double alkylation (i.e. both R of MgR_2 active) of Nd by $Mg(n\text{Bu})_2$ should provide molecular weights that would be significantly lower than 4400, this occurrence can be discarded.

(Figure 1)

Stereospecificity. Both catalysts are *trans*-stereospecific, as long as the amount of $Mg(n\text{Bu})_2$ remains stoichiometric (Table 2*).* In the presence of 1.7 equivalents of dialkylmagnesium per Nd, the *trans*-stereoregularity falls down to 96.2 % (run 10), whereas no specificity remains when a large excess of co-catalyst is used (run 11), indicating a different polymerization mechanism in that latter case.

(Table 2)

Cp*'$Nd(BH_4)_2(THF)_2$/$Mg(n\text{Bu})_2$ affords up to 98.5 *trans*-steroregularity. To our knowledge, such a *trans*-content is the highest one obtained with a homogeneous single-site catalyst. It is noteworthy that the rate of defects with **2** as precatalyst consists in 3,4-units only (*cis*-1,4 polyisoprene was detected as traces). A typical ^{1}H NMR spectrum is displayed in figure 2 (run 6). DSC thermogram of 98.5 % *trans*-polyisoprene (run 5) exhibits a glass transition at Tg = -71°C. The polymer is highly crystalline as expected (Tm = 47 °C ; $\Delta H = 43$ Jg^{-1}), in accordance with the low rate of defects of the polymer.

(Figure 2)

Microstructure of polyisoprene is 1,4-*trans* at more than 95 % with the $Nd(BH_4)_3(THF)_3$/$Mg(n\text{Bu})_2$ system (runs 1-4). Small quantities of 1,4-*cis* and 3,4 motives (ca. 2-3 % each) are also present.

It is generally admitted that *trans*-polymerization can be related to single coordination of the diene monomer to the metal, [27,34,35] when double coordination of the diene is required to afford *cis*-polydiene.

According to a recent theoretical study related to hindered permethyllanthanidocenes catalysts, the coordination step of the monomer is likely dependent on the steric hindrance around the metal and, as a matter of fact, single η^2 coordination may be preferred. [36] Such an assomption was also made by Spitz and coworkers who polymerized butadiene with neodymocene catalysts. [37] This feature must be specially taken into consideration in the case of isoprene polymerization; it was invoked to account for the 95 % *trans*-specificity obtained with the already mentioned trimetallic ansasamarocene. [17]

One can note that the small amount of 1,4-*cis* polymer obtained with **1**/Mg(*n*Bu)$_2$ disappears when **1** is replaced by **2**; the bulky Cp*' totally prevents η^4 coordination of isoprene to the neodymium atom. As same, although the *trans*-stereoregularity falls down to 96.2 % with a Mg/Nd ratio of 1.7 (run 10), the microstructure reveals the presence of a very low quantity of *cis*-polyisoprene (1.0 %), which agrees well with a disfavored η^4 coordination, likely due to competition between monomer and co-catalyst.

Considering the well-known bridging ability of the borohydride ligand in lanthanides chemistry, [20] the *trans*-stereospecificity can be tentatively correlated to the formation of sterically hindered borohydrido-bridged bimetallic Nd-Mg species. Bimetallic Nd-Mg associations have been frequently observed [38-40] or postulated [15,41] when a magnesium derivative is reacted with a lanthanide complex. It was therefore assumed that bridging Ln(μ-BH$_4$)Mg species could be formed and NMR experiments were undertaken to focus on that point.

^{1}H NMR experiments. For clarity, the cyclopentadienyl ligand exhibiting numerous signals, these experiments were first conducted with **1.** Figure 3 displays ^{1}H NMR spectrum of Nd(BH$_4$)$_3$(THF)$_3$ (**1**) alone (a) and immediately after addition of 1 equivalent of Mg(*n*Bu)$_2$ (1.6 M, heptane) (b), both recorded at 300 K. BH$_4$ signal is shifted from δ = 98 ppm to *ca* 50 ppm. In addition, this new resonance is now very broad, accounting for dynamic exchange between different borohydride groups.

(Figure 3)

We assume that thanks to the bridging ability of the BH$_4$ group, formation of a Nd(μ-BH$_4$)(μ-R)MgR bimetallic species may occur, which corresponds well to the mono alkylation deduced from macromolecular data. A possible molecular structure is depicted on scheme 1; the neodymium atom is surrounded by two terminal BH$_4$ groups (Nd(BH$_4$)$_3$(THF)$_3$ is a monomer in the solid state) [21] and the third one bridging to the Mg-R moiety, leading to a ^{1}H NMR spectrum showing average BH$_4$ resonance

(Figure 3, b). No coalescence could be observed at low temperature, indicating fast exchange at NMR time scale.

(Scheme 1)

Similar experiments were carried out with half-neodymocene $Cp^*Nd(BH_4)_2(THF)_2$ (**3**), ($Cp^* = C_5Me_5$, giving only one signal for the Me groups, the electron donating ability being similar to that of **2**)**.** 1 equivalent of butylethylmagnesium (BEM, 20 % in hexanes) is added and a blue precipitate partially soluble is formed. Figure 4 displays ^1H NMR spectrum of **3** (a), and that of the same complex after addition of BEM (b). Initial BH_4 signal (δ = 96 ppm, (a)) is shifted to ca 43 ppm at 293 K, which is an uncommonly low value for a borohydrido half-neodymocene ($(C_5{}^iPr_4H)Nd(BH_4)_2(THF)$: δ = 114 ppm[18]). As same as for **1**, the BH_4 resonance is very broad, typical of a dynamic exchange between different borohydride groups. A variable temperature NMR study was undertaken (Fig. 4, b); this time coalescence occurs, at 253 K, and one BH_4 resonance is clearly depicted since 213 K (the second one is probably masked in the diamagnetic zone). Dynamic exchange between BH_4 groups, slower than with **1**, arises from the presence of the bulky Cp* in the coordination sphere of neodymium atom.

(Figure 4)

On scheme 2 is depicted a possible bimetallic $Nd(\mu\text{-}BH_4)Mg$ compound resulting from the reaction of **3**, represented under associated form, [42] with 1 equivalent of dialkylmagnesium. The Nd atom bears two different BH_4 ligands: a pure $Nd(BH_4)$ one, and the other one bridging to the Mg moiety. Association of that Nd/Mg compound, likely in an oligomeric form, may account for the poor solubility observed in NMR solvent. Note however that in isoprene medium, the *in situ* formed Nd/Mg catalyst is perfectly soluble.

(Scheme 2)

Comparison with similar dual component catalysts. In table 3 are compared the performances of catalysts prepared from **1** and **2**, to the results obtained with $NdCl_3(THF)_3$, $Cp^*Nd(BH_4)_2(THF)_2$ (**3**), heteroleptic $\{Cp^{*\prime}[C(p\text{-tol})NMe]_2Nd(BH_4)\}_2$ (**4**),[43] and $(C_5{}^iPr_4H)Sm(BH_4)_2(THF)$ (**5**) [18] in analogous conditions.

(Table 3)

All complexes show a high rate of *trans*-specificity. Catalyst prepared from **2** remains the most active and is the most *trans*-stereospecific, closely followed by **4**, the latter showing only a moderate activity, correlated with the high steric hindrance due to the diketiminate ligand. [44] We could not obtain, with **3**, a conversion and an activity as high as with **2**, though the latter provides also more than 98 % *trans*-regular polymer. It is noteworthy that the hyper bulky C_5iPr_4H ligand in **5** is not as efficient as C_5Me_4nPr to ensure the steric hindrance allowing the *trans*-stereospecificity. But in the case of **5**, the co-catalyst used was *n*BuLi.

We observed that combination of $NdCl_3(THF)_3$ with 1 equivalent of $Mg(nBu)_2$ affords a quite *trans*-stereospecific catalyst of low activity. Similar behavior was previously reported for $NdCl_3(TBP)_3/MgR_2$ system (TBP = tributylphosphate). [13,15] To improve the activity of $NdCl_3$-based catalysts, Porri added (allyl)MgCl to $NdCl_3(THF)_3$ -he obtained *in situ* prepared allyllanthanide complexes- arguing that σ Ln-C compounds were too unstable. [45] The enhancement of activity observed for $Nd(BH_4)_3(THF)_3/Mg(nBu)_2$ against $NdCl_3(THF)_3/Mg(nBu)_2$ may be here attributed to the higher solubility of the trisborohydride. $Nd(BH_4)_3(THF)_3$, much more easily available and handled, appears then as a valuable alternative to alkyl- and allyllanthanide catalysts. The use of MgR_2 as alkylating reagent is required to afford *trans*-polyisoprene, whereas in combination with *n*BuLi or $AlEt_3$, $Nd(BH_4)_3(THF)_3$ gives rise to the formation of irregular polyisoprene. [24]

The low activity of **4**/$Mg(nBu)_2$ might be ascribed to the high steric environment around the metal, [44] leading to a probable competition between internal and monomer coordination. Also, molecular weight distribution (2.01) shows that the process is not as controlled as with **2**/$Mg(nBu)_2$.

Experiments conducted with $Sm(BH_4)_3(THF)_3$ were totally unsuccessful irrespective of the alkylating agent used. This is a rare difference of catalytic behavior between Nd and Sm, both belonging to the same early lanthanides group. Complex **5** is however an example of borohydrido complex of samarium (and the sole one reported) that provides as well good activity and 95 % *trans*-content.

Finally, **2**/$Mg(nBu)_2$ is clearly the first catalytic system to simultaneously satisfy high conversion, well-controlled and narrow distribution of macromolecular weights, together with high 1,4-*trans* content. The half-lanthanidocene framework appears as particularly well-suited for the efficient *trans*-polymerization of conjugated dienes.

Conclusion

Borohydrido complexes of neodymium have been found very efficient toward isoprene polymerization catalysis in the presence of equimolar amounts of dialkylmagnesium co-catalyst. Cp*'$Nd(BH_4)_2(THF)_2$/$Mg(n\text{Bu})_2$ and $Nd(BH_4)_3(THF)_3$/$Mg(n\text{Bu})_2$ are both *trans*-stereospecific, up to 98.5 % with the former catalyst. As far as we know, this is the best result yet obtained with an organometallic catalyst. Quasi-living character is observed, with extremely narrow polydispersity and formation of polymers whose molecular weight corresponds well to the monomer/catalyst ratios. Monomodal distribution is typical of a single-site character. *Trans*-stereospecific character of these catalysts is tentatively attributed to the formation of $Nd(\mu\text{-}BH_4)Mg$ bridging active species on the basis of ^{1}H NMR experiments. Further studies are in progress.

Acknowledgements: the authors wish to thank C. Meliet (UMR 8010 CNRS) for recording variable temperature NMR spectra.

Experimental section

Materials. The solvents were dried on sodium-benzophenone ketyl and deoxygenated by distillation immediately before use. All solids were handled in an argon-filled glove-box (Jacomex)). Isoprene (99 %, Aldrich) was dried first on calcium hydride, then on 3A molecular sieve and distilled just before use. BuLi (1.6 M, hexane) and $Mg(nBu)_2$ (1.0 M, heptane) were purchased from Aldrich. BEM (20 %, hexanes) was purchased from Texas Alkyl. $Nd(BH_4)_3(THF)_3$, [21] $Cp^*Nd(BH_4)_2(THF)_2$ [19] and $Cp^{*'}Nd(BH_4)_2(THF)_2$, [20] were synthesized from $NdCl_3(THF)_3$ [21] as reported in the literature.

Polymerization procedure. In a typical polymerization (run 5 is given as an example), 20 mg (0.041 mmol) of catalyst precursor **2** was weighed in a glove box, in a 20 mL flask. Dry toluene (0.5 mL), $Mg(n\text{Bu})_2$ (0.036 mL, as a 1.0 M solution in heptane), and freshly distilled isoprene (0.5 mL, 5 mmol), were added in this order via syringes into the flask. The reaction mixture was magnetically stirred at 50 °C for 2 h 45 min. The polymerization reaction was terminated as follows: the viscous mixture was diluted in standard toluene (1 mL) and the resulting solution was poured into ethanol. The white polymer was filtered out, and dried under vacuum for 24 h. Yield: 338 mg (99.3 %); SEC: M_n = 9500, PDI = 1.15; ^{1}H NMR: 98.5 % *trans*-1,4, 1.5 % 3,4.

Measurements. ^{1}H and ^{13}C NMR were recorded on a Bruker Avance 300 at 300 K in $CDCl_3$ solutions. Steric Exclusion Chromatography analyses were carried out in THF as eluent at 20 °C (1 mL/min) using a Gynkotek P580A apparatus equipped with two PLgel 5μm MIXED-C 300x7.5 mm Polymer-Labs divinylbenzene columns (range 200 – 200,000,000) and with a PLgel 5μm 300x7.5 mm Guard column, and an IOTA2 refractive index detector. Absolute values of molecular weights were calculated against polystyrene standards, without correction due to the lack of Mark-Houwink constants for *trans*-regular polyisoprene in the literature. Differential Scanning Calorimetry (DSC)

measurements were performed on a TA Instruments 2920 DSC. An indium standard was used for calibration. Samples of *c.a.* 10 mg were scanned under nitrogen flow (60 $mL.min^{-1}$; ramp rate 10 $°C.min^{-1}$). Temperatures were determined on the second scan to ensure identical thermal histories, as the inflection point of the corresponding heat capacity jump (Tg), and as the endothermic maximum (Tm).

***NMR experiments*.** In a typical experiment, pre-catalyst **1** (10 mg) was weight inside the glove-box, in an NMR tube equipped with a stop-cock (Young). The solvent was added (C_6D_6 or C_7D_8 for variable temperature analysis), and then the desired amount of dialkylmagnesium (heptane or hexanes solution). The blue solution turned to yellow-green and then yellow-brown within 30 min. A small amount (less than 10 %) of olefin was present in the ^1H NMR spectrum. After 24 h at room temperature, the tube's content was brownish, and NMR analysis showed olefins as major products. In the case of pre-catalyst **2**, progressive formation of a slightly soluble blue compound was observed. No olefins were detected in the spectrum, even after several hours.

References and Notes

[1] Thiele, S. K. H.; Wilson, D. R. *J. Macromol. Sci. Part C Polym. Rev.* **2003**, *43*, 581-628.

[2] Hou, Z.; Wakatsuki, Y. *J. Organomet. Chem.* **2002**, *647*, 61-70.

[3] Shen, Z. *Inorg. Chim. Act.* **1987**, *140*, 7-14.

[4] Mazzei, A. *Makromol. Chem. Phys. Suppl.* **1981**, *4*, 61-72.

[5] Natta, G.; Porri, L.; Corradini, P.; Morero, D. *Chim. Ind. (Milano)* **1958**, *40*, 362-371.

[6] Halasa, A. F.; Hsu, W. L.; Austin, L. E.; Jasiunas, C. A.: US-Pat. (Goodyear) 183469, **2002** [*Chem. Abstr.* **2002**, 138, 14610].

[7] Song, J. S.; Huang, B. C.; Yu, D. S. *J. Appl. Pol. Sci.* **2001**, *82*, 81-89.

[8] Visseaux, M.; Barbier-Baudry, D.; Bonnet, F.; Dormond, A. *Macromol. Chem. Phys.* **2001**, *202*, 2485-2488.

[9] Bonnet, F.; Visseaux, M.; Barbier-Baudry, D.; Dormond, A. *Macromolecules* **2002**, *35*, 1143-1145.

[10] Boisson, C.; Monteil, V.; Ribour, D.; Spitz, R.; Barbotin, F. *Macromol. Chem. Phys.* **2003**, *204*, 1747-1754.

[11] Wilson, D. J. *Polym. Int.* **1996**, *39*, 235-242.

[12] Evans, W. J.; Giarikos, D. G.; Allen, N. T. *Macromolecules* **2003**, *36*, 4256-4257.

[13] Yang, J. H.; Tsutsui, M.; Chen, Z.; Bergbreiter, D. E. *Macromolecules* **1982**, *15*, 230.

[14] Dong, W.; Masuda, T. *J. Pol. Sci. Part A: Pol. Chem.* **2002**, 1838-1844.

[15] Monakov, Y. B.; Sabirov, Z. M.; Urazbaev, V. N.; Efimov, V. P. *Kinet. Catal.* **2001**, *42*, 310.

[16] Jenkins, D. K. *Polymer* **1985**, *26*, 147-151.

[17] Barbier-Baudry, D.; Bonnet, F.; Domenichini, B.; Dormond, A.; Visseaux, M. *J. Organomet. Chem.* **2002**, *647*, 167-179.

[18] Barbier-Baudry, D.; Blacque, O.; Hafid, A.; Nyassi, A.; Sitzmann, H.; Visseaux, M. *Eur. J. Inorg. Chem.* **2000**, 2333-2336.

[19] Cendrowski-Guillaume, S.; Le Gland, G.; Nierlich, M.; Ephritikhine, M. *Organometallics* **2000**, *19*, 5654-5660.

[20] Bonnet, F.; Visseaux, M.; Hafid, A.; Barbier-Baudry, D.; Vigier, E.; Kubicki, M. M. *Inorg. Chem.* **2004**, *43*, 3682-3690.

[21] Mirsaidov, U.; Shaimuradov, I. B.; Khikmatov, M. *Russ. J. Inorg. Chem.* **1986**, *31*, 753-754.

[22] Guillaume, S. M.; Schappacher, M.; Soum, A. *Macromolecules* **2003**, *36*, 54-60.

[23] Nakayama, Y. *Organomet. News* **2003**, *4*, 150.

[24] Bonnet, F.; Visseaux, M.; Pereira, A.; Barbier-Baudry, D. *Macromol. Rapid Commun.* **2004**, *25*, 873-877.

[25] Arndt, S.; Okuda, J. *Chem. Rev.* **2002**, *102*, 1953-1976 and refs therein.

[26] In our conditions, we observed that $NdCl_3(THF)_3/Mg(n\text{Bu})_2$ yields 23 % of polymer only in 21 h: see ref 24.

[27] Peluso, A.; Improta, R.; Zambelli, A. *Organometallics* **2000**, *19*, 411-419.

[28] Duvakina, N. V.; Monakov, Y. B. *Dokl. Chem.* **2002**, *384*, 129-131.

[29] Visseaux, M.; Andre, N.; Baudry, D.; Dormond, A.; Pardes, C. *J. All. Comp.* **1998**, *275-277*, 891-893.

[30] Bonnet, F.; Visseaux, M.; Barbier-Baudry, D. *J. Organomet. Chem.* **2004**, *689*, 264-269.

[31] Gromada, J.; Carpentier, J. F.; Mortreux, A. *Coord. Chem. Rev.* **2004**, *248*, 397-410.

[32] Mark-Houwink corrections were not performed, as the constant values available in the literature concern irregular polyisoprene only: see ref 24.

[33] Pelletier, J. F.; Mortreux, A.; Olonde, X.; Bujadoux, K. *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 16.

[34] Friebe, L.; Nuyken, O.; Windisch, H.; Obrecht, W. *Macromol. Chem. Phys.* **2002**, *203*, 1055-1064.

[35] Taube, R.; Maiwald, S.; Sieler, J. *J. Organomet. Chem.* **2001**, *621*, 327-336.

[36] Kaita, S.; Koga, N.; Hou, Z.; Doi, Y.; Wakatsuki, Y. *Organometallics* **2003**, *22*, 3077-3082.

[37] Barbottin, F.; Monteil, V.; Llauro, M. F.; Boisson, C.; Spitz, R. *Macromolecules* **2000**, *23*, 8521-8523.

[38] Gromada, J.; Mortreux, A.; Nowogrocki, G.; Leising, F.; Mathivet, T.; Carpentier, J. F. *Eur. J. Inorg. Chem.* **2004**, *16*, 3247-3253.

[39] Wu, W.; Chen, M.; Zhou, P. *Organometallics* **1991**, *10*, 98-104.

[40] Sun, C.; Wei, G.; Jin, Z.; Chen, W. *J. Organomet. Chem* **1993**, *453*, 61-64.

[41] Gromada, J.; Le Pichon, L.; Mortreux, A.; Leising, F.; Carpentier, J. F. *J. Organomet. Chem.* **2003**, *683*, 44-55.

[42] Guillaume, S. M.; Le Gland, G.; Nierlich, M.; Ephritikhine, M. *Organometallics* **2000**, *19*, 5654-5660.

[43] Bonnet, F.; Visseaux, M.; Barbier-Baudry, D.; Vigier, E.; Kubicki, M. M. *Chem. Eur. J.* **2004**, *10*, 2428-2434.

[44] X Ray structure of the samarium analogue of **4** revealed an interaction between the methyne carbon of the diketiminate ligand and the metal: see ref 43.

[45] Porri, L.; Shubin, N.: PCT (Basell Technology Co BV) WO0187991, **2001** [*Chem. Abstr.* **2001**, 136, 7504].

Tables

Table 1. Selected experiments of isoprene polymerization with borohydride complexes activated with $Mg(n\text{Bu})_2$.

run[a]	precatalyst	[Mg]/[Nd]	[I]/[Nd]	Time (h)	Yield (%)	Activity[b] ($g_{pol}/mol_{Nd}/h$)	$M_{n(exp)}$[c]	MWD[d]	$M_{n(calcd)}$[e]
1[f]	**1**	1	600	2h45	69	10200	27600	1.57	28100
2[f]	**1**	1	1000	2h45	63	15600	43000	1.79	42800
3[f]	**1**	2	600	2h45	95	14100	23600	1.14	19400
4[f]	**1**	3	1000	20	91	3100	15000	1.50	20600
5	**2**	0.9	120	2h45	>99	2900	9500	1.15	9100
6	**2**	0.9	520	2h45	75	9600	26400	1.26	29400
7	**2**	0.9	870	2	73	21600	56700	1.18	48000
8	**2**	1.2	1180	2	93	37300	50500	1.16	62100
9	**2**	1.2	520	2h45	89	11400	29100	1.21	26200
10	**2**	1.7	120	2h45	91	2700	6600	1.27	4400
11	**2**	52	120	20	60	250	-[h]	-	-
12[g]	**2**	0.9	120	20	>99	400	13400	1.54	9100
13	-	$Mg(n\text{Bu})_2$	135	20	0	-	-	-	-

[a] Toluene 0.5 ml; T = 50 °C. $Mg(n\text{Bu})_2$ (1.0 M, heptane solution). [b] Calculated with {[monomer]/[Nd]} x Yield x 68 x $(time)^{-1}$. [c] Average number molecular weight, determined par Steric Exclusion Chromatography (THF, polystyrene standards). [d] M_w/M_n. [e] Calculated with {[monomer]/[Mg]} x Yield x 68. [f] Preliminary results, already published.[24] [g]Isoprene/1-hexene: 1/1. [h] Poorly soluble.

Table 2. Microstructure of polyisoprenes synthesized with borohydrido catalysts

run	precatalyst[a]	[Mg]/[Nd]	*trans*-1,4[b] (%)	*cis*-1,4[b] (%)	3,4[b] (%)
1[c]	**1**	1	95.1	3.2	1.7
2[c]	**1**	1	95.3	3.1	1.6
3[c]	**1**	2	96.2	1.8	2.0
4[c]	**1**	3	95.5	2.4	2.1
5	**2**	0.9	98.5	-	1.5
6	**2**	0.9	98.4	-	1.6
7	**2**	0.9	98.3	-	1.7
8	**2**	1.2	98.1	-	1.9
9	**2**	1.2	98.0	-	2.0
10	**2**	1.7	96.2	1.0	2.8
11	**2**	52	57.7	1.0	41.3
12	**2**	0.9	97.2	1.4	1.4

[a] $Nd(BH_4)_3(THF)_3$ (**1**), Cp*'$Nd(BH_4)_2(THF)_2$ (**2**). [b]Determined by ^1H NMR. [c] Preliminary results, already published. [24]

Table 3. Influence of the molecular structure of the catalyst for isoprene *trans*-polymerization

Catalytic system[a]	[I]/[Nd]	Activity ($g_{pol}/mol_{Nd}/h$)	M_n	MWD	*trans*-specificity (%)	reference
1/1 Mg(*n*Bu)$_2$	600	15600	43000	1.79	95.3	[24]
2/1.2 Mg(*n*Bu)$_2$	1180	37300	50500	1.16	98.1	this work
2/0.9 Mg(*n*Bu)$_2$	120	2900	9500	1.15	98.5	this work
3/1.2 Mg(*n*Bu)$_2$	160	700	9700	1.22	98.2	this work
4/1 Mg(*n*Bu)$_2$	600	1100	15400	2.01	98.4	[43]
5/1.5 *n*BuLi	1000	13000	90000	1.5	95.0	[18]
$NdCl_3(THF)_3$/1 Mg(*n*Bu)$_2$	460	340	-	-	89.5	[24]

[a] $Nd(BH_4)_3(THF)_3$ (**1**), Cp*'$Nd(BH_4)_2(THF)_2$ (**2**), Cp*$Nd(BH_4)_2(THF)_2$ (**3**), {Cp*'[C(*p*-tol)NMe]$_2$$Nd(BH_4)$}$_2$ (**4**), ($C_5{}^iPr_4H$)$Sm(BH_4)_2(THF)$ (**5**).

Figures captions

Equation 1. Synthesis of half-neodymocene **2**.

Scheme 1: Formation of the active bimetallic species Nd(μ-BH_4)Mg upon addition of dialkylmagnesium to $Nd(BH_4)_3(THF)_3$ (solvent molecules are omitted for clarity).

Scheme 2: Formation of the active bimetallic species Cp*Nd(μ-BH_4)Mg upon addition of dialkylmagnesium to $Cp^*Nd(BH_4)_2(THF)_2$ (solvent molecules are omitted for clarity).

Figure 1: Steric Exclusion Chromatography trace showing the monomodal character of polyisoprene obtained with Cp*'$Nd(BH_4)_2(THF)_2$/Mg(*n*Bu)$_2$ (run 5).

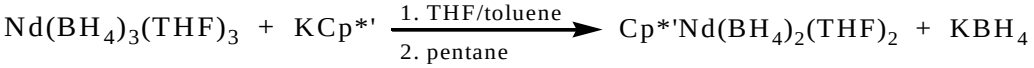
Figure 2: ^{1}H NMR ($CDCl_3$) spectrum of 98.5% *trans*-polyisoprene, aliphatic region (a), olefinic region (b), showing traces of *cis*-polyisoprene (∗) and 3,4-polyisoprene defects (◊) (run 6).

Figure 3: ^{1}H NMR (C_6D_6, 300 K) spectrum of $Nd(BH_4)_3(THF)_3$ (a) and after addition of 1 equivalent of Mg(*n*Bu)$_2$ (b) (s = C_6D_5H, ∗ = heptane).

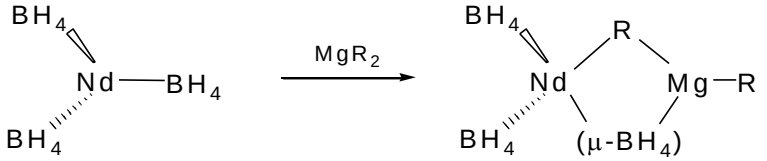
Figure 4: ^{1}H NMR (C_7D_8) spectrum of $Cp^*Nd(BH_4)_2(THF)_2$ (a, 300 K), and after addition of 1 equivalent of BEM, recorded at different temperatures (b, range 193 – 293 K, ∗ = hexanes).

Schemes and figures

Equation 1.



Scheme 1.



Scheme 2.

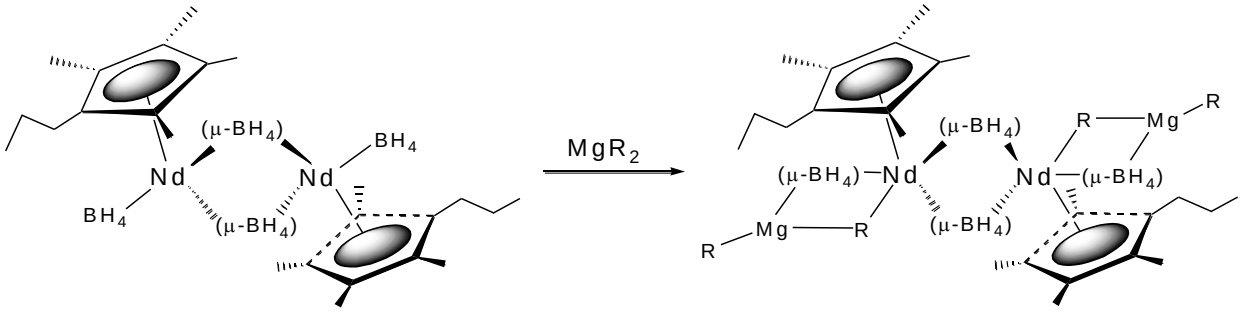


Figure 1.

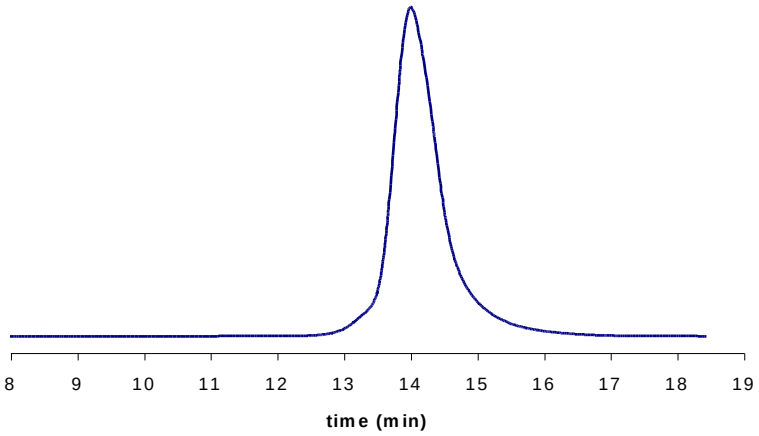
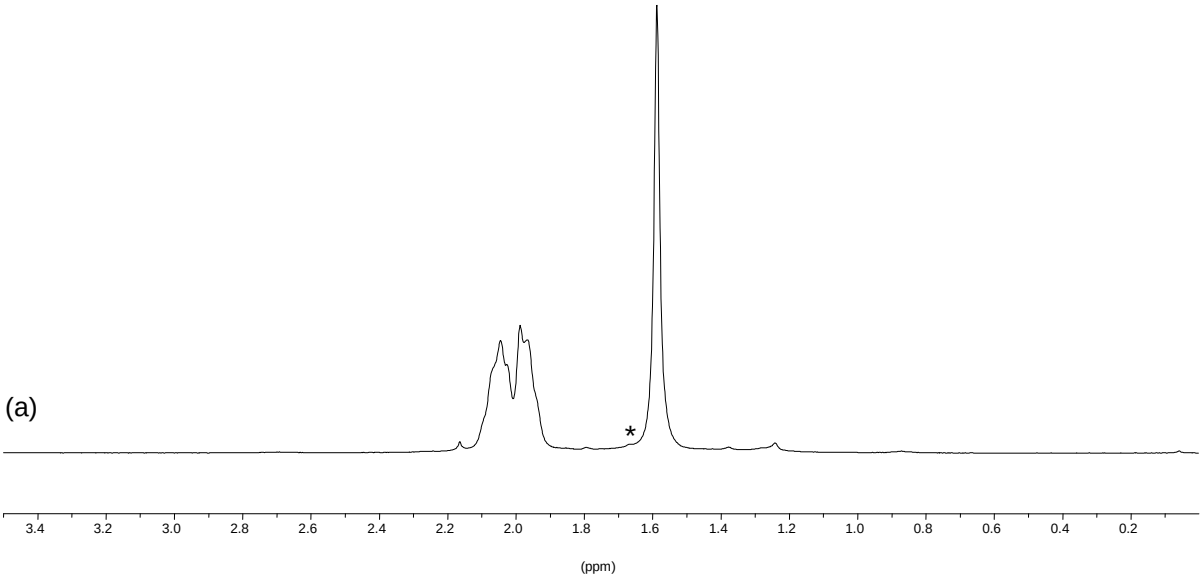


Figure 2.


(a)
*
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
(ppm)

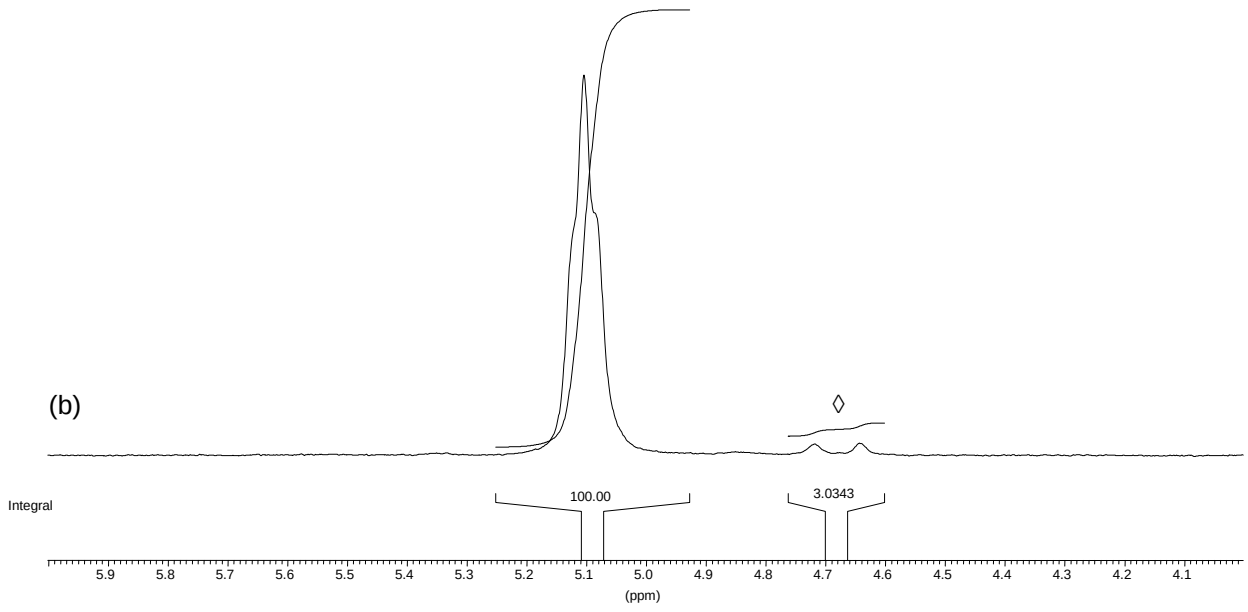

(b)
◊
Integral
100.00
3.0343
5.9
5.8
5.7
5.6
5.5
5.4
5.3
5.2
5.1
5.0
4.9
4.8
4.7
4.6
4.5
4.4
4.3
4.2
4.1
(ppm)

Figure 3.

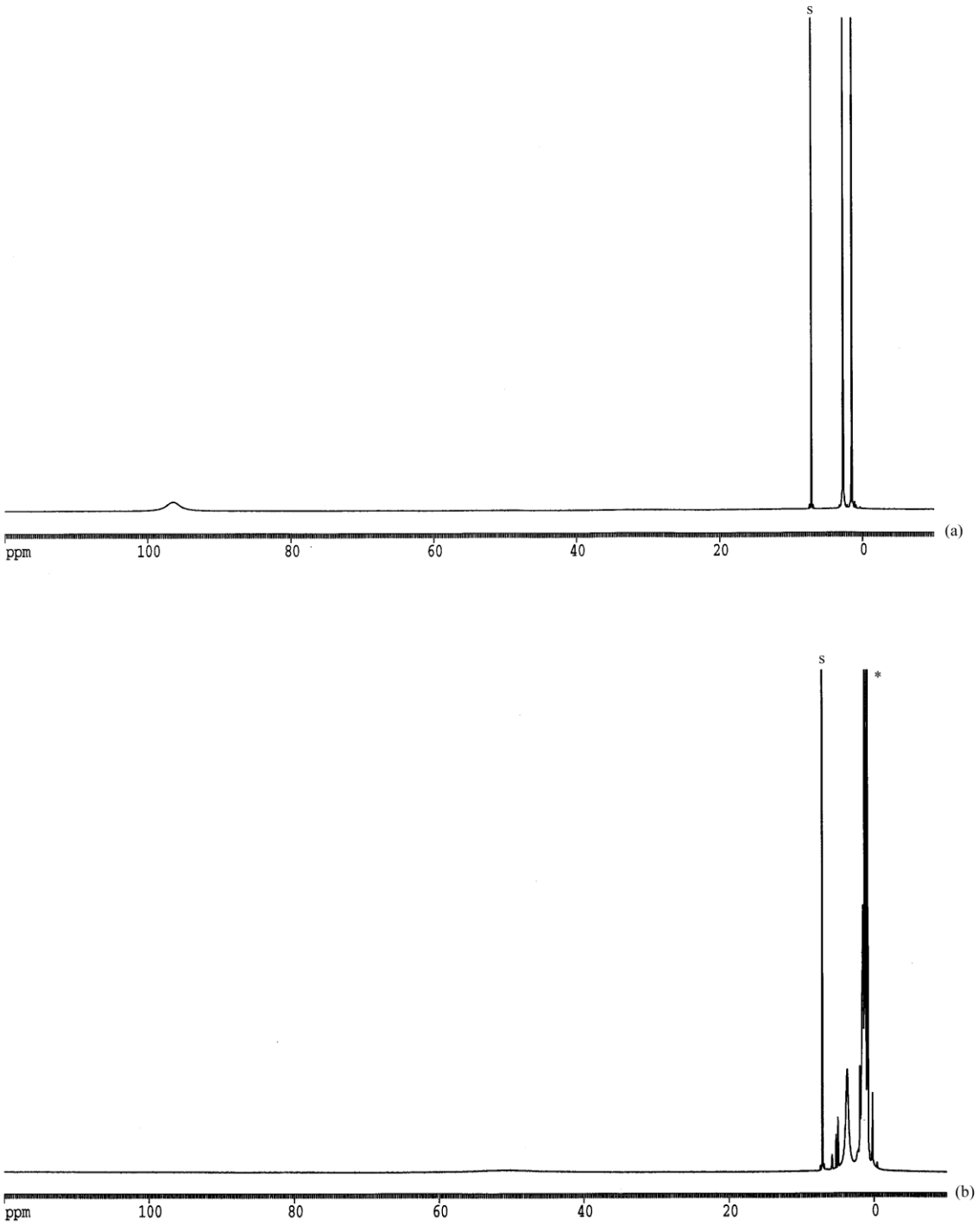
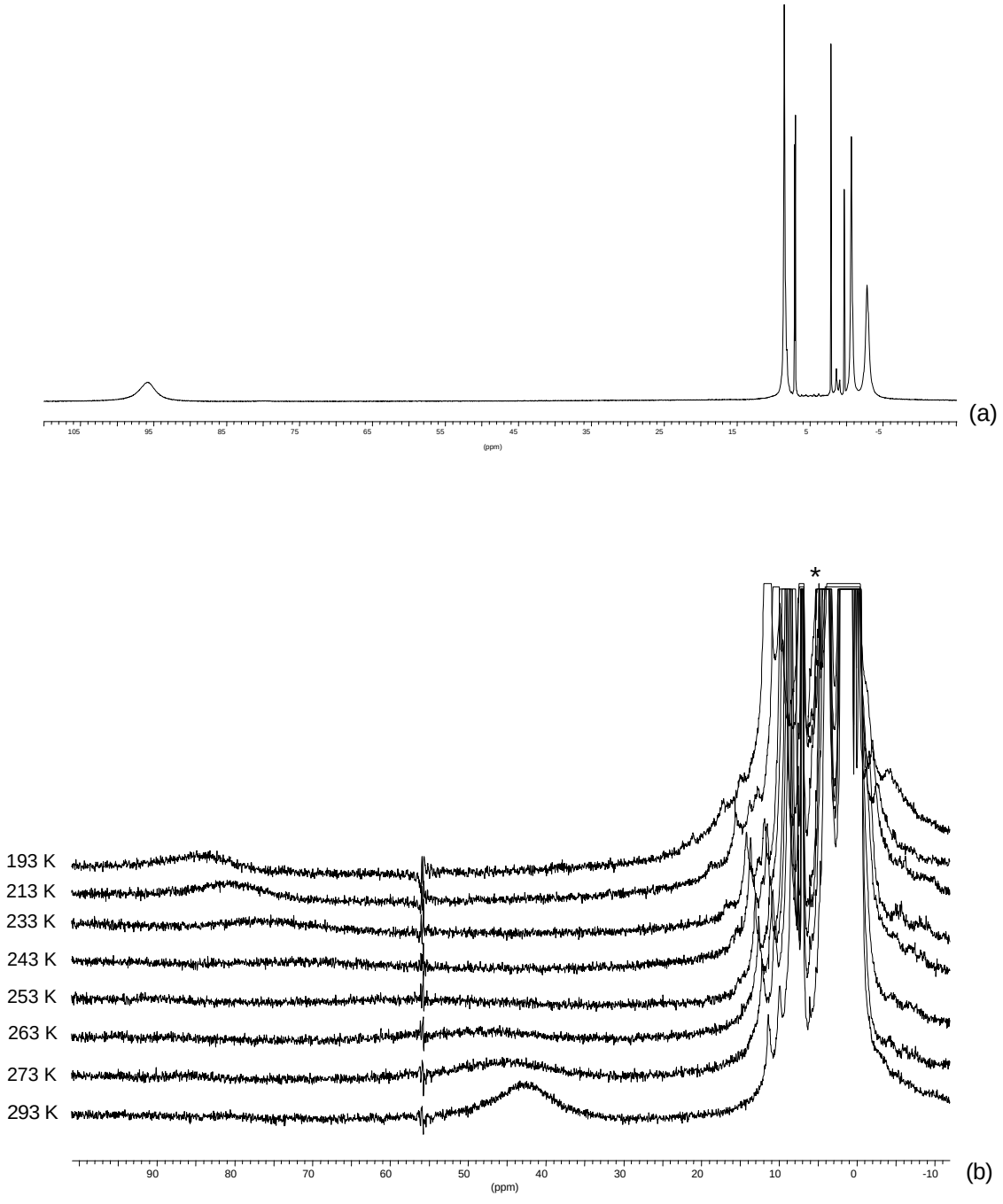


Figure 4.


105
95
85
75
65
55
45
35
25
15
5
-5
(ppm)
(a)
*
193 K
213 K
233 K
243 K
253 K
263 K
273 K
293 K
90
80
70
60
50
40
30
20
10
0
-10
(ppm)
(b)

Graphical abstract:

Borohydrido complexes of neodymium afford efficient and highly *trans*-stereospecific catalysts toward isoprene polymerization in the presence of dialkylmagnesium co-catalyst. The whole process is quasi-living as shown by well-controlled molecular weights and distribution.