

# Neodymium alk(aryl)oxides–dialkylmagnesium systems for butadiene polymerization and copolymerization with styrene and glycidyl methacrylate

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Received 7 March 2003; received in revised form 28 April 2003; accepted 29 April 2003

## Abstract

The application of well-defined neodymium alkoxides/aryloxides in combination with dialkylmagnesium reagents for 1,3-butadiene (BD) polymerization and copolymerization with styrene (St) and glycidyl methacrylate (GMA) has been investigated. The trinuclear complex  $\text{Nd}_3(\text{Ot-Bu})_9(\text{THF})_2$  (**1**) provided a low-activity system for BD polymerization, even at high temperature, but with a high *trans*-1,4 stereospecificity (*trans*-1,4  $\approx$  95%). Aryloxy complexes  $\text{Nd}(\text{O}-2,6-t\text{-Bu}_2-4\text{-Me-Ph})_3(\text{THF})$  (**2**) and  $\text{Nd}(\text{O}-2,6-t\text{-Bu}_2-4\text{-Me-Ph})_3$  (**3**) were found to give more active systems. The polymerization displayed a controlled character, i.e. a precise control of the molecular weight and a low polydispersity ( $M_w/M_n < 1.30$ ) for high catalyst concentration, keeping the same level of stereocontrol over the polymerization course. The statistical copolymerization of BD and styrene with those systems was successful. High-molecular weight copolymers ( $M_n$  up to 50 000  $\text{g mol}^{-1}$ ) with noticeable styrene content (3–15 mol%) were synthesized. Determination of the microstructure by  $^{13}\text{C}$ -NMR showed exclusively *trans*-1,4-BD–St sequences. The livingness of BD polymerization encouraged attempts of diblock copolymerization with GMA. In this case, low-molecular weight polymers with variable polydispersities were obtained ( $M_n < 20\,000\ \text{g mol}^{-1}$ ;  $M_w/M_n = 1.4\text{--}5.0$ ). The composition of the copolymers was analyzed by  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR and IR spectroscopies. SEC analyses confirmed the true nature of the diblock copolymer. The influence of the alkylating agent on those (co)-polymerizations was briefly studied. Finally, the mechanism of polymerization is also discussed.

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**Keywords:** Allyl complexes; Neodymium; Alkylmagnesium; Diene polymerization; Block copolymers

## 1. Introduction

Synthesis of highly stereospecific polybutadiene (PBD) is a major goal for elastomer industry, since the resulting polymers can find wide applications as synthetic rubbers [1]. Among the variety of organometallic or metalorganic complexes used for this purpose, rare earth metal-based compounds are most effective and

attractive candidates [2]. In binary or ternary systems associated to aluminum alkyls and/or alkyl halides, these precursors enable the synthesis of *cis*-1,4-PBD with high selectivity (> 98%) [2,3]. *trans*-1,4-PBD has been obtained with rare earth allyl compounds [4] or by replacing alkylaluminum with dialkylmagnesium reagents [5]. Oxygen-based ligands have been largely associated to rare earth metals for butadiene polymerization. The most common catalyst precursors are long-chain, hindered carboxylates  $\text{Ln}(\text{carboxylate})_3/\text{AlR}_3/\text{AlR}_{3-n}\text{X}_n$  [6]. Alcohols proved also to be efficient ligands when associated to the binary system  $\text{LnCl}_3/\text{AlR}_3$  [7]. It has been reported that lanthanide alkoxides “ $\text{Ln}(\text{OR})_3$ ”, especially those with linear alkoxy radicals rather than corresponding branched isomers, led to

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active triple component systems due to the higher degree of covalency of the Ln–O bonds [8].

Despite the high activity and stereoregularity so far achieved in 1,3-butadiene (BD) polymerization, in particular with neodymium-based systems [9], development of new catalysts is still under way to improve control over the polymerization [10]. Indeed, it is of interest to prepare new materials based on stereoregular PBD such as block copolymers. In this respect, highly stereospecific living polymerizations of BD and isoprene have been achieved recently with lanthanocene-based systems, enabling their block copolymerizations with styrene [11] and  $\epsilon$ -caprolactone [12], respectively.

We have recently reported a unique polymerization system composed of a neodymium alkoxide,  $\text{Nd}_3(\text{O}t\text{-Bu})_9(\text{THF})_2$  (**1**), and a dialkylmagnesium reagent, which has proven to be efficient for ethylene polymerization and its block copolymerization with methyl methacrylate (MMA) [13]. Syndiotactic poly(methyl methacrylate) (sPMMA) with low polydispersity was also obtained using this initiating system [14]. It was shown that alkyl-lanthanide species are formed in situ from this binary system, acting as polymerization initiator with lanthanocene-like properties [13]. In this paper, we report on the use of such systems for BD polymerization and also its statistical copolymerization with styrene (St) and block copolymerization with glycidyl methacrylate (GMA) to prepare potential compatibilizing agents. The polymerizations were carried out using binary systems based on a neodymium alkoxide/aryloxide and a dialkylmagnesium reagent. As neodymium precursors, we employed the well-defined trinuclear complex  $\text{Nd}_3(\text{O}t\text{-Bu})_9(\text{THF})_2$  (**1**) [13], and mononuclear complexes  $\text{Nd}(\text{O}-2,6-t\text{-Bu}_2-4\text{-Me-Ph})_3(\text{THF})$  (**2**) and  $\text{Nd}(\text{O}-2,6-t\text{-Bu}_2-4\text{-Me-Ph})_3$  (**3**) [15].

## 2. Experimental

### 2.1. General remarks

All operations were performed under dry argon using standard Schlenk techniques or in a glove box under nitrogen. Butadiene (air-liquid, N25) was used as received. GMA (99%, Aldrich) and styrene (St) (99%, Aldrich) were vacuum-distilled over  $\text{CaH}_2$  and stored at  $-20^\circ\text{C}$  under argon. Solvents (hexane, toluene) and deuterated solvents were freshly distilled from sodium/potassium amalgam under argon and degassed prior to use. Di(*n*-hexyl)magnesium (DHM) (20 wt.% in heptane; Akzo Nobel) and *n*-butylethylmagnesium (BEM) (1.33 M in heptane; Texas Alkyl), anhydrous neodymium chloride (99.9%; Strem) and  $\text{NdCl}_3(\text{THF})_2$  (99.9%+; Rhodia) were used as received.  $\text{Na}(\text{O}-2,6-t\text{-Bu}_2-4\text{-Me-Ph})(\text{THF})$  was prepared by reaction of the corresponding phenol, 2,6-*t*-Bu<sub>2</sub>-4-Me-PhOH, pre-pur-

ified by sublimation with metallic sodium in THF solution at room temperature (r.t.) for 24 h. Neodymium *tert*-butoxide (**1**) and aryloxide (**3**) were synthesized according to literature procedures [13,15,16] or using a modified procedure as follows.

### 2.2. Synthesis of $\text{Nd}(\text{O}-2,6-t\text{-Bu}_2-4\text{-Me-Ph})_3(\text{THF})$ (**2**)

$\text{Na}(\text{O}-2,6-t\text{-Bu}_2-4\text{-Me-Ph})(\text{THF})$  (24.15 g, 77.0 mmol) and  $\text{NdCl}_3(\text{THF})_2$  (10.11 g, 25.6 mmol) were weighed and placed in the same Schlenk flask in the glove box. Hexane (125 ml) was added to the mixture and the suspension was stirred for 20 h at r.t. The mixture was filtered over celite, resulting in a limpid violet solution. After removal of the solvent under vacuum at  $25^\circ\text{C}$ , a deep blue powder was obtained (18.50 g, 90%). Analytical data for Nd and Cl and  $^1\text{H-NMR}$  spectroscopy agreed with the formation of  $\text{Nd}(\text{O}-2,6-t\text{-Bu}_2-4\text{-Me-Ph})_3(\text{THF})$  (**2**).  $^1\text{H-NMR}$  (200 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  ( $23^\circ\text{C}$ ): 15.29 (s, 2H, Ar), 7.37 (s, 3H, Me),  $-2.36$  (brs, 18H, *t*-Bu),  $-16.88$  (s, 4H, THF),  $-35.84$  (s, 4H, THF).

Sublimation of **2** at  $220^\circ\text{C}$  under  $10^{-3}$  mmHg yielded THF-free complex **3**.  $^1\text{H-NMR}$  (200 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  ( $23^\circ\text{C}$ ): 16.32 (s, 2H, Ar), 8.32 (s, 3H, Me),  $-8.53$  (brs, 18H, *t*-Bu).

### 2.3. Homopolymerization of butadiene

The initiator was prepared by reacting a neodymium alkoxide (**1–3**) and a dialkylmagnesium reagent (typically 1.0 mmol of each) in hexane or toluene for 1 h under magnetic stirring at  $0^\circ\text{C}$ . The neodymium salt and dialkylmagnesium derivative were weighed in the glove box and placed in two separate Schlenk tubes. The latter were each filled in on the Schlenk line with hexane or toluene (12.5 ml) and the solutions were cooled to  $0^\circ\text{C}$ ; the neodymium solution was then transferred via canula into the dialkylmagnesium solution and the mixture was stirred for 1 h. The catalytic solution was placed at  $-30^\circ\text{C}$  and butadiene (8.5 ml, 100 mmol) added via canula. Polymerization was carried out for 1–17 h under stirring at the desired temperature and then stopped by adding methanol (ca. 2 ml). The polymer was recovered by extraction with chloroform and dried at  $60^\circ\text{C}$  until constant weight.

### 2.4. Butadiene–styrene copolymerization

The neodymium salt and dialkylmagnesium derivative were weighed in the glove box and placed in two separate Schlenk tubes. The latter were each filled in on the Schlenk line with styrene (6.0 ml, 50 mmol) and the solutions were cooled to  $-30^\circ\text{C}$ . The neodymium solution was transferred via canula into the dialkylmagnesium solution, and butadiene (typically 8.5 ml, 100 mmol) was added via canula. Polymerization was

carried out for 1–17 h under magnetic stirring at the desired temperature and then stopped by adding methanol (ca. 2 ml). The polymer was recovered by extraction with chloroform and dried at 60 °C until constant weight.

### 2.5. Butadiene–GMA diblock copolymerization

Butadiene homopolymerization was performed as described above. Before quenching, at a desired reaction time, the reaction mixture was vented, refilled with argon and cooled down at 0 °C. GMA (2.0 ml, 15 mmol) was added dropwise over 1 min and the resulting solution was warmed up to r.t. for additional 2 h. The polymerization was quenched by addition of aqueous THF (1% water). Volatile solvents were removed at r.t. and the resultant polymer was dissolved in dry THF, then filtered over celite. Removal of the solvent yielded the block copolymer as a white powder.  $^1\text{H-NMR}$  (200 MHz,  $\text{CDCl}_3$ ) (see also Fig. 5)  $\delta$ : 5.40 (1,4-PBD, =CH), 4.95 (1,2-PBD, =CH<sub>2</sub>), 4.32 (PGMA, CH<sub>2</sub>–O), 3.78 (PGMA, CH<sub>2</sub>–O), 3.23 (PGMA, CH–CH<sub>2</sub>), 2.84 (PGMA, CH<sub>2</sub>–CH), 2.63 (PGMA, CH<sub>2</sub>–CH), 2.02 (1,4-PBD, CH<sub>2</sub>), 1.90 (PGMA, CH<sub>2</sub>), 1.51 (1,2-PBD, CH<sub>2</sub>), 1.26 (PGMA, CH<sub>3</sub>), 1.10 (PGMA, CH<sub>3</sub>), 0.92 (PGMA, CH<sub>3</sub>).  $^{13}\text{C}\{^1\text{H}\}\text{-NMR}$  (50 MHz,  $\text{CDCl}_3$ ) (data in italics refer to PBD resonances)  $\delta$ : 67.90, 65.88, 65.65, 54.27, 51.64, 49.08, 49.94, 48.76, 45.60, 45.09, 44.76, 44.53, 43.40, 38.09, 34.64, 34.17, 33.88, 32.66, 31.82, 30.28, 30.05, 29.58, 29.14, 29.06, 27.35, 25.55, 22.62, 21.13, 19.61, 17.86, 14.05. For IR data, see text.

### 2.6. Polymer characterization

Size exclusion chromatography (SEC) was performed in THF at 20 °C using a Waters SIS HPLC-pump, a Waters 410 refractometer, a DAD-UV detector and Waters styragel columns (HR2, HR3, HR4, HR5E) or PL-GEL Mixte B and 100A columns. The number-average molecular masses ( $M_n$ ) and polydispersity index ( $M_w/M_n$ ) of the resultant polymers were calculated with reference to a polystyrene calibration. Polymers' microstructure and composition were measured by both NMR and FTIR spectroscopies. NMR spectra were recorded on Bruker AC-200 and AC-300 spectrometers at 23 °C in  $\text{CDCl}_3$ .  $^1\text{H}$  (200 and 300 MHz) and  $^{13}\text{C}$  (50 and 75 MHz) chemical shifts are reported vs.  $\text{SiMe}_4$  and were determined by reference to the residual solvent peaks. IR spectra were recorded on a Nicolet 510 FTIR spectrophotometer in KBr pellets and are expressed by wave number ( $\text{cm}^{-1}$ ).

## 3. Results and discussion

### 3.1. Homopolymerization of butadiene

#### 3.1.1. With $\text{Nd}_3(\text{Ot-Bu})_9(\text{THF})_2$

In light of literature (vide supra) [8], we did not expect a high polymerization activity from the system formed by  $\text{Nd}_3(\text{Ot-Bu})_9\text{THF}_2$  (**1**) and  $\text{Mg}(n\text{-Hex})_2$  (DHM). The reaction was first performed at room temperature in hexane solution with  $[\text{Nd}]_0 = [\text{Mg}]_0 = 3.5 \times 10^{-2}$  M and  $[\text{BD}]_0 = 3.5$  M for 17 h (run 1). The results are reported in Table 1. Indeed, both the conversion and initiation efficiencies (based on the formation of two polymer chains per  $\text{MgR}_2$ ) are very low, leading to a low-molecular weight PBD ( $M_n = 1900$  g mol<sup>-1</sup>) with a quite broad molecular weight distribution (MWD) ( $M_w/M_n = 1.77$ ). The stereospecificity of the polymerization under those conditions was checked by  $^{13}\text{C-NMR}$  (Fig. 1). The latter reveals a high *trans*-1,4 content (ca. 95%) along with small amounts of 1,2-PBD. When the reaction was performed at higher temperature (60 °C), the conversion increased because of both the increase of the propagation rate constant and initiation efficiency (from 7 to 22%) (run 1 vs. 2, 4, 6). The effect of the nature of the dialkylmagnesium was studied. DHM was replaced by BEM, resulting in a low-molecular weight PBD, which corresponds to an increase in the initiation efficiency from 22 to 68%. The same decrease in the polymer molecular weight on using BEM instead of DHM was noticed previously in ethylene polymerization [13]. The effect of an alkyl halide in the polymerization medium was evaluated using *tert*-butyl chloride ( $[\text{Nd}]_0 = 3.5 \times 10^{-2}$  M;  $[\text{Nd}]_0/[\text{Cl}]_0 = 0.33$ ). The addition of halide donors in Ziegler-Natta-type catalytic systems is known to be essential for the synthesis of *cis*-1,4-rich PBD [17]. Also, the synthesis of *cis*-1,4-PBD was reported with the ternary system  $\text{Nd}(\text{P}_{507})_3/\text{Mg}(n\text{-Bu})_2/\text{CHCl}_3$  [18]. With our system, a higher initiation efficiency along with a broad MWD were observed (run 5). *t*-BuCl probably favored the formation of supplementary active sites through the creation of Ln–X bonds. The presence of *t*-BuCl had no influence on the *trans*-1,4 content of the polymer; however, a *cis*-1,4-rich PBD could be prepared using the same catalytic precursor upon addition of *t*-BuCl with di(isobutyl)aluminumhydride (DIBAL-H) instead of DHM [19].

The variation of the Nd/Mg ratio was also investigated. With  $[\text{Nd}]_0/[\text{Mg}]_0 = 0.2$ , the monomer conversion after 17 h was nearly complete (run 4). Despite a high polydispersity, the molecular weight was in agreement with the calculated one, considering the initial ratio of monomer to magnesium concentrations, monomer conversion and the initiation efficiency of run 2. This shows clearly that one can control the molecular weight of PBD by adjusting the ratio  $[\text{BD}]_0/[\text{Mg}]_0$  as it can be done in “living”/controlled polymerizations. Here, the dia-

Table 1  
Butadiene polymerizations promoted by  $\text{Nd}_3(\text{Ot-Bu})_9(\text{THF})_2/\text{Mg}(n\text{-Hex})_2$ <sup>a</sup>

Run	Nd/Mg	BD/Mg	<i>t</i> -BuCl/Nd	<i>T</i> (°C)	<i>t</i> (h)	Yield (%)	$M_n$ (g mol <sup>-1</sup> )	$M_{n,\text{th}}$ (g mol <sup>-1</sup> )	Initiation efficiency <sup>b</sup>	$M_w/M_n$
1	1.0	100	–	20	17	5	1900	135	0.07	1.77
2	1.0	100	–	60	17	22	2700	595	0.22	2.40
3 <sup>c</sup>	1.0	100	–	60	17	24	950	650	0.68	2.90
4	0.2	20	–	60	17	95	1700	370	0.22	4.40
5	1.0	100	3.0	60	17	68	3050	1840	0.60	4.20
6	0.2	200	–	60	17	47	10300	2540	0.24	5.10
7	0.2	200	3.0	60	17	91	6100	4920	–	24

<sup>a</sup>  $[\text{BD}]_0 = 3$  M in hexane;  $M_{n,\text{th}} = ([\text{BD}]_0/2[\text{Mg}]_0) \times (\text{yield}/100) \times 54$ .

<sup>b</sup> Initiation efficiency as estimated from the ratio  $M_{n,\text{th}}/M_{n,\text{exp}}$ ; these values cannot be considered as accurate due to high PDI values.

<sup>c</sup> BEM was used.

lkylmagnesium acts as a preliminary alkylating reagent and then as a reversible transfer agent, while the rare earth metal acts as a catalyst. In ethylene and MMA polymerizations, the latter played a role of initiator and an excess of  $\text{MgR}_2$  led respectively to a loss of activity or of the living character [13,14]. However, we cannot ascribe a living nature to BD polymerizations promoted by  $1/\text{MgR}_2$  combinations given the high polydispersity values ( $M_w/M_n = 1.80\text{--}4.40$ ) under these reaction conditions. Slow initiation and significant transfer and/or termination reactions might be the causes of such values. Decreasing the catalyst concentration to  $3.5 \times 10^{-3}$  M had no particular influence on the polymerization (run

6). The experimental molecular weight matched with the calculated one and the percentage of 1,4-*trans* units was not modified. Thus, the 1/DHM system exhibits a moderate activity for stereospecific *trans*-1,4-BD polymerization with control over the molecular weight. Unfortunately, the initiation efficiency remains low (<25%) but can be improved by addition of an alkyl halide or with other magnesium reagents.

### 3.1.2. With neodymium aryloxides

Neodymium aryloxides showed a much more interesting activity. The precursor  $\text{Nd}(\text{O}-2,6\text{-}i\text{-Bu}_2\text{-4-Me-Ph})_3(\text{THF})$  (**2**), prepared by ionic metathesis and that

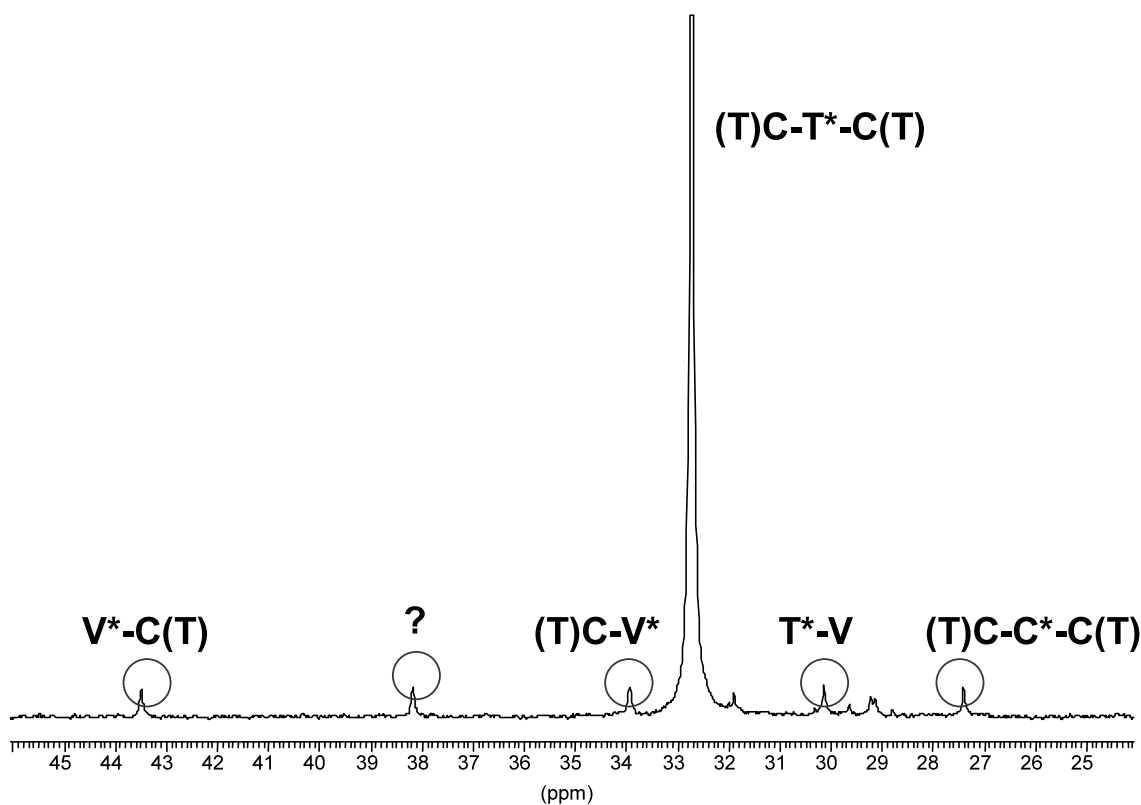


Fig. 1. <sup>13</sup>C-NMR spectrum ( $\text{CDCl}_3$ ) of homo-PBD synthesized from  $\text{Nd}_3(\text{Ot-Bu})_9(\text{THF})_2/\text{Mg}(n\text{-Hex})_2$  (run 2) (T, C and V stand respectively for *trans*-1,4, *cis*-1,4 and 1,2-butadiene units).

Table 2  
Butadiene polymerizations promoted by  $\text{Nd}(\text{O}-2,6\text{-}t\text{-Bu}_2\text{-4-Me-Ph})_3(\text{THF})/\text{Mg}(n\text{-Hex})_2^a$

Run	Nd/Mg	BD/Mg	$T$ ( $^\circ\text{C}$ )	$t$ (h)	Yield (%)	$M_n$ ( $\text{g mol}^{-1}$ )	$M_{n,\text{th}}$ ( $\text{g mol}^{-1}$ )	Initiation efficiency	$M_w/M_n$
2 <sup>b</sup>	1.0	100	20	17	5	1900	135	0.07	1.77
8	1.0	100	20	17	99	5800	2700	0.46	1.26
9	0.2	20	20	17	98	1100	540	0.49	1.15
10	1.0	200	20	2	60	6300	3250	0.51	1.18
11	1.0	1000	20	17	99	49900	26800	0.53	1.86
12 <sup>c</sup>	1.0	100	20	17	99	2700	2680	0.99	1.53
13 <sup>c</sup>	1.0	1000	20	17	99	28700	26800	0.93	2.07

<sup>a</sup>  $[\text{BD}]_0 = 3 \text{ M}$  in hexane;  $M_{n,\text{th}} = ([\text{BD}]_0/2[\text{Mg}]_0) \times (\text{yield}/100) \times 54$ .

<sup>b</sup> *tert*-Butoxide (**1**) was used as precursor.

<sup>c</sup>  $\text{Nd}(\text{O}-2,6\text{-}t\text{-Bu}_2\text{-4-Me-Ph})_3$  was used.

contains one THF-coordinated molecule, was evaluated under similar conditions as for **1** (Table 2, run 8). Complete monomer conversion was reached at room temperature within 17 h, although it must be noticed that the reaction times were not optimized. The main feature of the PBD produced under those conditions is its quite low polydispersity ( $M_w/M_n = 1.26$ ). The initiation efficiency is now close to 50%. This increase in efficiency and activity could be explained by the mononuclearity of the complex, enabling a better interaction between the dialkylmagnesium reagent and the aryloxy ligand in the lanthanide salt, and/or to the higher acidity of this ligand conferring to the metal center a higher intrinsic activity (vide infra). The stereospecificity of the polymerization was unchanged, suggesting that BD polymerization using **1** and **2** proceeds via the same mechanism despite a different precursor structure. The molecular weight is roughly determined by the  $[\text{BD}]_0/[\text{Mg}]_0$  ratio as suggested by the results obtained in run 9. Modification of this ratio showed that the higher the magnesium concentration, the lower the polydispersity (compare runs 9 and 11). For low  $M_n$  values ( $M_n < 10000 \text{ g mol}^{-1}$ ), the polymerization can be considered as “living/controlled” since we have control over both molecular weights and low polydispersities. When higher molecular weights were targeted, a deviation from these living characteristics was noticed. A kinetics experiment was performed with  $[\text{Nd}]_0/[\text{Mg}]_0 = 0.5$  and  $[\text{BD}]_0/[\text{Mg}]_0 = 100$ . Fig. 2 shows that the experimental molecular weights increased linearly with conversion up to ca. 20%, then a deviation from this straight line occurred, along with an increase of the polydispersity. A linear first-order kinetic plot was obtained under these conditions, which suggests a constant number of active species throughout the polymerization course (Fig. 3). These results, i.e. progressive broadening of MWD and linear first-order kinetic plot, are consistent with transfer reactions. The latter, insignificant for low molecular weights, i.e. short reaction times, cannot be neglected for high  $M_n$  values.

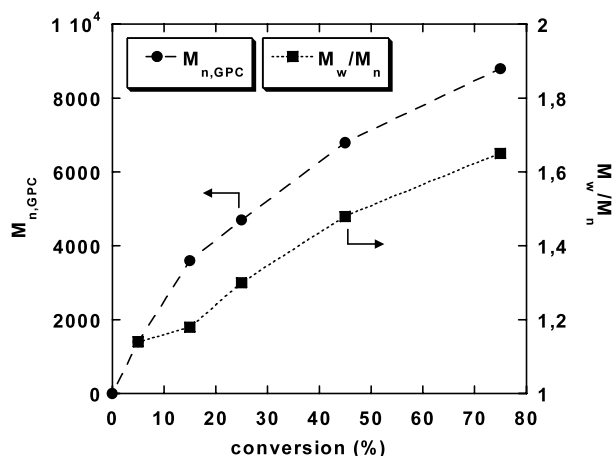


Fig. 2. Evolution of molecular weight and polydispersity as a function of conversion for butadiene polymerization promoted by  $\text{Nd}(\text{O}-2,6\text{-}t\text{-Bu}_2\text{-4-Me-Ph})_3(\text{THF})/\text{Mg}(n\text{-Hex})_2$  (conditions:  $[\text{Nd}]_0 = 3.5 \times 10^{-3} \text{ M}$ ;  $[\text{Mg}]_0 = 7.0 \times 10^{-3} \text{ M}$  and  $[\text{BD}]_0/[\text{Mg}]_0 = 100$ ,  $25^\circ\text{C}$ , in hexane).

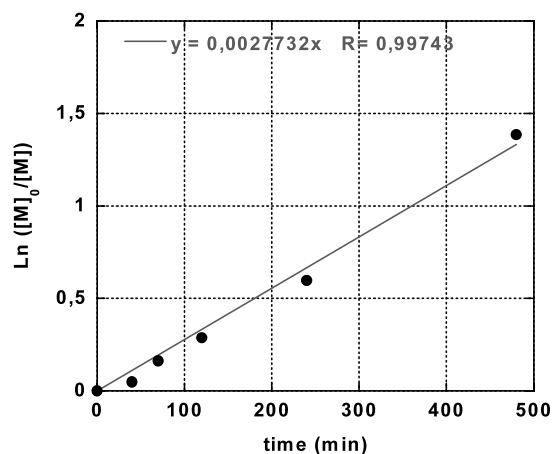


Fig. 3. First-order kinetic plot of butadiene polymerization promoted by  $\text{Nd}(\text{O}-2,6\text{-}t\text{-Bu}_2\text{-4-Me-Ph})_3(\text{THF})/\text{Mg}(n\text{-Hex})_2$  (conditions:  $[\text{Nd}]_0 = 3.5 \times 10^{-3} \text{ M}$ ;  $[\text{Mg}]_0 = 7.0 \times 10^{-3} \text{ M}$  and  $[\text{BD}]_0/[\text{Mg}]_0 = 100$ ,  $25^\circ\text{C}$ , in hexane).

The activity of **2** associated to other alkylating agents was evaluated. Usual aluminum derivatives, i.e.  $\text{Al}(n\text{-Oct})_3$ , DIBAL-H, DIBAL-H/ $\text{AlEt}_2\text{Cl}$  as well as  $\text{BEt}_3$ ,

were found to lead to inactive systems for BD polymerization. On the other hand, two equivalents of *n*-HexMgBr or *n*-BuLi vs. Nd enabled the sluggish formation of *trans*-1,4-PBD with  $M_n = 1600$  and  $M_w/M_n = 1.40$  (8% yield), and  $M_n = 5300$  and  $M_w/M_n = 1.35$  (21% yield), respectively, when the reaction was performed for 2 h at room temperature. An interesting feature to be noticed here is again a strong difference in the  $M_n$  value, consistent with a transfer reaction in the former case. Diene polymerization appears thus less sensitive to the nature of the alkylating agent as it was noticed for ethylene polymerization [13].

It was also interesting to carry out BD polymerizations with the THF-free analogue precursor Nd(O-2,6-*t*-Bu<sub>2</sub>-4-Me-Ph)<sub>3</sub> (**3**). It is known that the addition of a small amount of THF in Nd(Versatate)<sub>3</sub>/MgR<sub>2</sub> systems enhances the *trans* content of PBD [5] and the presence of an additional vacancy on the metal could modify the stereospecificity of the polymerization [2]. A set of experiments were performed with  $[Nd]_0/[Mg]_0 = 1.0$  (runs 12 and 13) and can be directly compared to runs 8 and 11. For a similar monomer conversion, the molecular weights are twice lower (2700 vs. 5800 and 28 700 vs. 49 900) with a minor broadening of MWD. The efficiency of initiation is now over 95%. Also, the <sup>13</sup>C-NMR spectrum showed that the PBD microstructure is not affected. Consequently, the absence of coordinated THF did not lead to the bidentate coordination of the monomer, known to produce *cis*-1,4-PBD with rare earth metal-based catalysts. The steric hindrance of the aryloxy groups and the possible presence of the magnesium derivative in the coordination sphere of Nd probably may prevent such coordination (vide infra).

### 3.2. Statistical butadiene–styrene copolymerization

Styrene–butadiene copolymers (SBR) have a great importance in the elastomer industry. Prepared by anionic or radical polymerizations, the polymers do not exhibit the perfect SBR profile, i.e. high *cis*-1,4 content, high molecular weight and more than 20% of incorporation of styrene. To fulfill these requirements, many catalysts based on Ni, Co, Ti and lanthanides have been developed [20]. Even if “Nd(OR)<sub>3</sub>/MgR<sub>2</sub> systems did not produce rich *cis*-1,4-polybutadiene, we judged interesting to consider the statistical copolymerization of butadiene and styrene.

A preliminary experiment was carried out with pure styrene and complex **2** as catalyst precursors (Table 3, run 14). Under the typical polymerization conditions, 30% conversion and a low-molecular weight PSt was obtained. SEC analysis showed a monomodal chromatogram with  $M_w/M_n = 1.45$ . As revealed by <sup>13</sup>C-NMR, the polymerization did not show any kind of stereospecificity.

The BD–St copolymerizations were performed in bulk. At room temperature, for 2 h, an overall monomer conversion of 45% was reached (run 15). This value corresponds to complete BD conversion and 13% conversion of St, which is in agreement with the estimation made from the integrals ratio in the <sup>1</sup>H-NMR spectrum of the polymer recovered. MWD is quite large and bimodal. To establish the true nature of the copolymer, the microstructure was studied by <sup>13</sup>C-NMR spectroscopy (Fig. 4). In addition to the signals observed for homo-PBD (Fig. 1), a new set of peaks was noticed, with resonances at  $\delta$  45.68 and 35.61 ppm corresponding to the St units of a *trans*-1,4-BD–St diad, and at  $\delta$  40.08 and 30.41 ppm corresponding to the BD units of the same sequence [21]. The copolymer recovered is therefore best described as PBD sequences separated by single St units. The *trans*-1,4 content of the polymer remained unchanged since only *trans*-1,4-BD–styrene sequences were observed. That behavior differs from *cis*-1,4 stereospecific BD polymerizations. In these cases, the insertion of styrene induced a decrease of the *cis*-1,4 content attributed to the back-biting reaction, i.e. the coordination of the penultimate monomer unit onto the catalyst [20]. Thus, each styrene insertion is followed by a *trans*-BD unit. When the catalyst concentration was reduced to  $[Nd]_0 = 3.5 \times 10^{-3}$  M, the monomer conversion after 2 h dropped to 20% and the amount of St incorporated was low (3.5%) (run 16). Again, the molecular weight was roughly determined by the  $[BD]_0/[MgR_2]_0$  ratio. Prolonging the reaction from 2 to 20 h enabled a higher monomer conversion and the styrene content jumped from 3.5 to 13.5% (run 17). Unfortunately, the molecular weight did not increase proportionally with the latter. The late formation of a low-molecular weight copolymer with a high styrene content cannot be discarded.

The effect of temperature was evaluated in order to increase the styrene content into the copolymer. In bulk conditions, above 50 °C, the polymers obtained after purification were insoluble in toluene, THF or CHCl<sub>3</sub>. When the polymerization was conducted at 50 °C in toluene solution, comparable results to those observed at room temperature in bulk were obtained but in a reduced reaction time (1 h). The styrene content remained low for all the experimental conditions. This can be ascribed to its strong coordination to the metal due to the nature of the ligand, as it has been already reported [9].

None of the copolymerizations presented a living character. However, <sup>13</sup>C-NMR spectra showed, for all the conditions, the sole presence of BD–St sequences and no signals characteristic of homo-PSt.

Table 3

Styrene–butadiene statistical copolymerization promoted by  $\text{Nd}(\text{O}-2,6-t\text{-Bu}_2\text{-4-Me-Ph})_3(\text{THF})/\text{Mg}(n\text{-Hex})_2$ <sup>a</sup>

Run	Nd/Mg	BD (eq.)	St (eq.)	<i>T</i> (°C)	<i>t</i> (h)	Yield (%)	<i>M<sub>n</sub></i> (g mol <sup>-1</sup> )	<i>M<sub>w</sub></i> / <i>M<sub>n</sub></i>	St (mol%)
14	1/1	–	100	20	17	30	2400	1.45	–
15	1/2	200	200	20	2	45	5200	2.42	13
16	1/2	1000	1000	20	2	21	20200	1.72	3.5
17	1/2	1000	1000	20	20	41	25200	2.13	13.5
18	1/1	1000	1000	20	20	41	42800	2.25	8.5
19 <sup>b</sup>	1/1	1000	1000	50	1	39	35100	1.90	10

<sup>a</sup>  $[\text{BD}]_0 = [\text{St}]_0 = 4.9$  M in hexane.<sup>b</sup> Polymerization carried out in toluene solution:  $[\text{BD}]_0 = [\text{St}]_0 = 3$  M;  $[\text{Nd}]_0 = 3 \times 10^{-3}$  M.

### 3.3. Butadiene–GMA diblock copolymerization

As stated in Section 1, the synthesis of new materials based on stereospecific PBDs is of high interest, especially block copolymers with polar monomers [12]. We were particularly focused on GMA as a co-monomer given its reactive epoxide function. It can react with both electrophiles and nucleophiles providing versatility in compatibilization. Thus, GMA has been used as a grafting monomer onto polyolefins but also more recently onto St–BD–St rubbers [22]. In tire industry, these materials could be applied as reinforcement agent for mineral charges (e.g.  $\text{SiO}_2$ ) [23]. Poly(GMA-*b*-BD-*b*-GMA) triblock copolymer was synthesized by living anionic polymerization facing drastic experimental conditions [24]. Grubbs et al. [25] used nitroxide-mediated polymerization to prepare related copolymers. Both

techniques led to well-defined block copolymers but without any stereospecificity of the PBD block. To our knowledge, no report mentioned so far the use of rare earth catalyst for this application. Given the ability of our catalytic systems to polymerize stereospecifically butadiene and methacrylates in a “living”/controlled fashion, we investigated the synthesis of poly(BD-*b*-GMA) diblock copolymers.

The block copolymers were obtained by pre-polymerization of BD followed by sequential addition of GMA. Both precursors **1** and **2** associated with various alkylating reagents were tested (Table 4). The resulting polymers were analyzed by NMR and IR spectroscopies. Fig. 5 shows significant details of the <sup>1</sup>H-NMR spectrum of a copolymer synthesized using the 2/DHM system. Resonances at  $\delta$  5.40 (>95%) and 4.95 (<5%) ppm correspond to the 1,4-BD and 1,2-BD

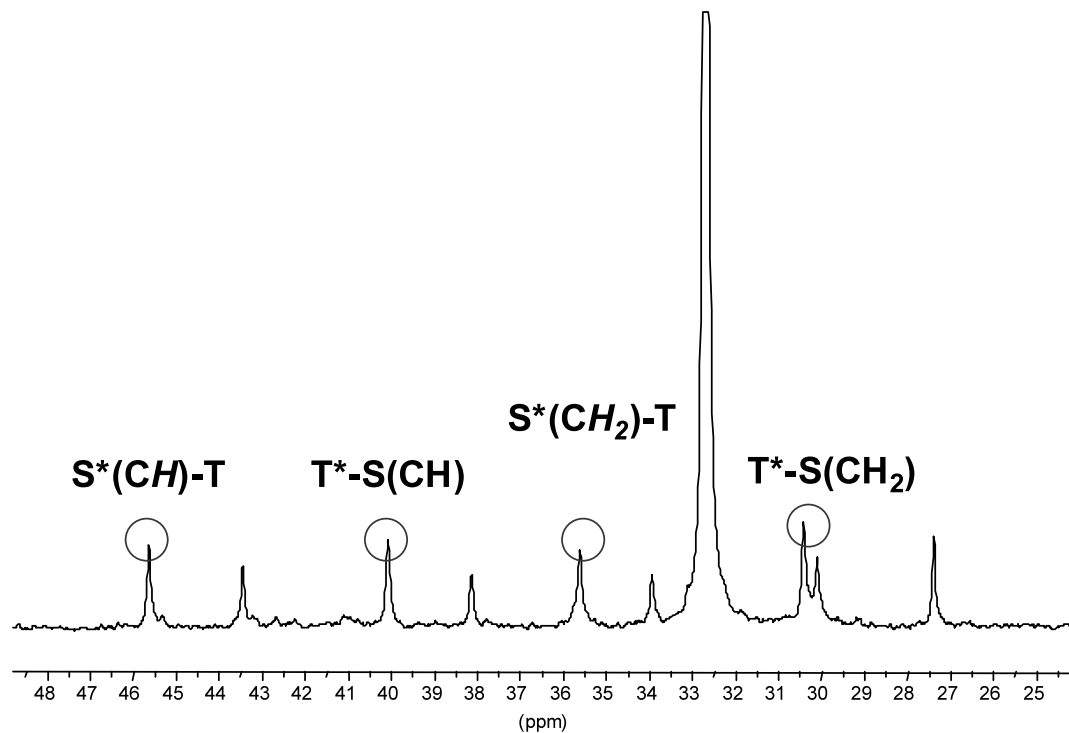


Fig. 4. <sup>13</sup>C-NMR spectrum ( $\text{CDCl}_3$ ) of poly(butadiene-*co*-styrene) obtained from  $\text{Nd}(\text{O}-2,6-t\text{-Bu}_2\text{-4-Me-Ph})_3(\text{THF})/\text{Mg}(n\text{-Hex})_2$  (run 8) (circled peaks refer to resonances specific to BD–St diads; non-circled peaks refer to resonances for PBD).

Table 4  
Results of the sequential diblock copolymerization of butadiene and GMA<sup>a</sup>

Run	«Nd(OR) <sub>3</sub> » (eq.)	Alkyl reagent (eq. vs. Nd)	BD (eq.) (t, T)	GMA (eq.) (t, T)	Yield (%)	M <sub>n</sub> (g mol <sup>-1</sup> )	M <sub>w</sub> /M <sub>n</sub>	BD/GMA
20	1 (0.5)	Mg( <i>n</i> -Hex) <sub>2</sub> (1)	100 (18 h, 60 °C)	15 (1.5 h, 25 °C)	43	23800	1.84	1.9
21	2 (0.5)	Mg( <i>n</i> -Hex) <sub>2</sub> (1)	100 (2 h, 25 °C)	15 (3 h, 25 °C)	60	11900	1.40	10
22	2 (0.5)	Mg( <i>n</i> -Hex) <sub>2</sub> (1)	100 (4 h, 25 °C)	15 (18 h, 25 °C)	60	11600	1.40	10
23	2 (0.5)	Mg( <i>n</i> -Hex) <sub>2</sub> (1)	100 (2 h, 25 °C)	15 (3 h, 0 °C)	43	7100	2.0	12
24	1+2 (0.5+0.5)	Mg( <i>n</i> -Hex) <sub>2</sub> (1)	100 (2 h, 25 °C)	15 (3 h, 25 °C)	47	9500	1.92	4.4
25	2 (0.5)	<i>n</i> -BuLi (2)	100 (2 h, 25 °C)	15 (3 h, 25 °C)	20	10000	2.67	7
26	2 (0.5)	<i>n</i> -HexMgBr (2)	100 (2 h, 25 °C)	15 (3 h, 25 °C)	23	3900	2.10	n.d.
27	2 (0.5)	Al( <i>n</i> -Oct) <sub>3</sub> (1)	100 (2 h, 25 °C)	15 (3 h, 25 °C)	0	–	–	–
28	2 (0.5)	Dibal-H/BuLi (0.5/0.5)	100 (2 h, 25 °C)	15 (3 h, 25 °C)	63	11900	1.40	Homo-PBD
29	Versatate (0.5)	Mg( <i>n</i> -Hex) <sub>2</sub> (1)	100 (2 h, 25 °C)	15 (15 h, 25 °C)	27	22800	4.8	0.25

<sup>a</sup> [BD]<sub>0</sub> = 3 M in hexane.

units, respectively. The characteristic signals of PGMA were found at  $\delta$  4.32, 3.78, 3.23, 2.84 and 2.03 ppm, indicating that the oxirane functionality was not affected during the polymerization. Integration of the different signals provides the BD/GMA ratio, which is ca. 8 in this case. IR spectroscopy confirmed these results with bands at 967 (very strong, 1,4-*trans*-PBD) and 910 cm<sup>-1</sup> (weak, 1,2-PBD), consistent with a *trans*-1,4-rich content, and PGMA was characterized with bands at 1733, 1260, 1150, 849 and 760 cm<sup>-1</sup>. Still, these results were insufficient to confirm the true nature of the block copolymer. <sup>13</sup>C-NMR proved uninformative as

linking carbons of BD–GMA sequences, estimated to be at  $\delta$  29–30 ppm and 32–35 ppm, could not be unambiguously detected, which was not unexpected considering their low concentration. SEC analyses with UV detection were more enlightening. For this purpose, the selective incorporation of a typical phenyl chromophore by ring-opening of the pending oxirane functions with PhSH was performed. The UV spectra of the modified copolymer, recorded at characteristic wavelengths (254 and 219 nm), showed the presence of GMA and BD, respectively, on the entire range of molar mass. In addition to SEC data (*vide infra*), this proves that

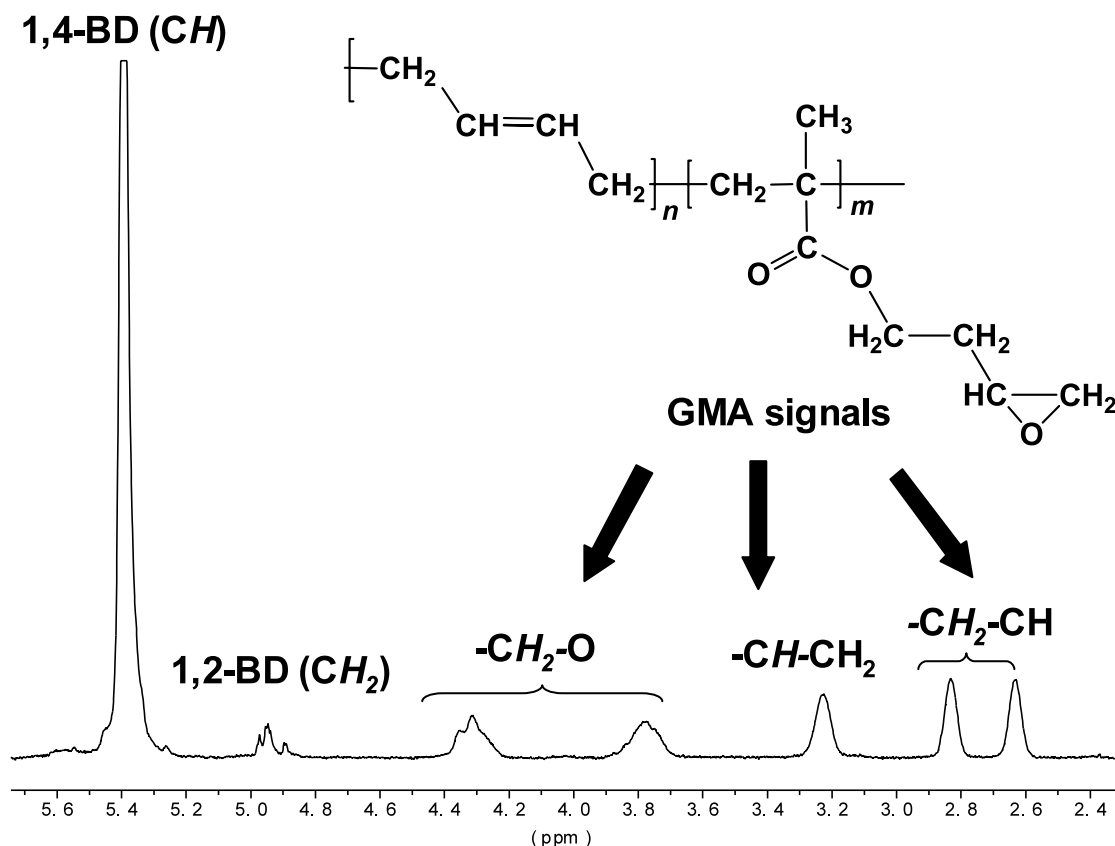


Fig. 5. Detail of the <sup>1</sup>H-NMR spectrum (CDCl<sub>3</sub>) of poly(butadiene)-*b*-poly(glycidyl methacrylate) diblock copolymer (run 21).



PGMA blocks are linked to PBD blocks and therefore the diblock nature of the copolymer.

With 1/DHM, a polymer with quite high  $M_n$  and polydispersity was recovered (run 20). A broad MWD was already observed for BD homopolymerization with this system. The GMA content (BD/GMA  $\approx$  2) is in agreement with the high reactivity towards methacrylates of initiating systems based on neodymium *tert*-butoxide (1) [14]. The use of the 2/Mg(*n*-Hex)<sub>2</sub> combination was next investigated (runs 21–23). The SEC traces display the evolution of the molecular weight after addition of GMA to the “living” PBD chains obtained with this system (Fig. 6). As expected for a diblock copolymer, the initial symmetrical trace of the homo-PBD block moved to higher molecular weights to give a monomodal trace, still with a minor tailing on low molecular masses. This tailing can be ascribed to a slow initiation and/or termination reactions, although MWD remained narrow. The BD/GMA ratio obtained with this system is rather low (BD/GMA = 10) and likely accounts for the lower activity of neodymium aryloxide/MgR<sub>2</sub> systems towards methacrylates [26]. Longer reaction times did not allow higher monomer conversion or a higher GMA content in the copolymer. When GMA polymerization was carried out at 0 °C, the molecular weight decreased while the polydispersity increased due to the slower initiation of the methacrylate polymerization. The GMA content in the bulk could be improved on using simultaneously a mixture of *tert*-butoxide and aryloxide complexes as catalyst precursors (run 24). The difference of activity of the two distinct catalysts resulted in a slightly larger MWD due to the mixture of copolymers with different GMA contents.

The use of alternative alkylating agents was investigated with precursor 2 (runs 25–28). *n*-BuLi was found to be somewhat effective for Li/Nd = 2.0; lower ratios led only to BD homopolymerization. With *n*-hexylmagnesium bromide, the copolymerization took place only with a low activity. In both cases, the *trans*-1,4 stereospecificity of the diene polymerization and a significant broadening of MWD were noticed. Alkylaluminum and aluminate (formed in situ by reaction of DIBAL-H and *n*-BuLi) were inefficient. The former did not polymerize butadiene and side reactions (ring-opening) occurred with GMA. The latter did not incorporate GMA, leaving pure PBD. It is noteworthy that diblock copolymers with a rich GMA content could be prepared with Nd(Versatate)<sub>3</sub>/Mg(*n*-Hex)<sub>2</sub>, though this system induced a large MWD (run 29).

#### 3.4. Mechanistic considerations

The assumed mechanism for stereospecific 1,4-polymerization of dienes has been reported for years. For Natta and Soga [27], the coordination mode of the monomer is essential. *trans*-1,4 polymer is formed from unidentately coordinated monomer while bidentate coordination leads to *cis*-1,4 polymer. Dolgoplosk [28] proposed a stereoregulation based on the structure of the last monomer unit (chain control mechanism). The anti- $\pi$ -allylic structure favors the *cis* units whereas the *syn* one favors the formation of the *trans* units.

In “Nd(OR)<sub>3</sub>/MgR<sub>2</sub> systems, the in situ formation of alkyl lanthanide species has been evidenced [13,29]. Recent results suggest that these species may have a mononuclear lanthanide structure irrespective of the starting lanthanide alkoxide [29]. However, interaction

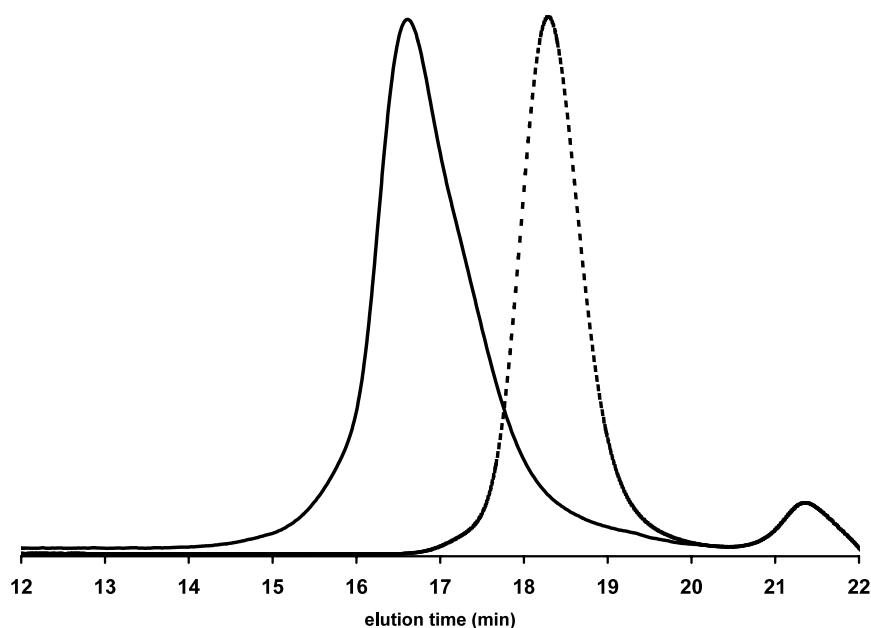


Fig. 6. SEC traces of homo-PBD (---) and diblock copolymer PBD-*b*-PGMA (—) (run 21).

of the resulting alkylanthanide species with the magnesium derivative, e.g. via alkyl  $\mu$ -bridging, to form a bimetallic Nd–Mg species active in polymerization cannot be discarded. Existence of  $\mu$ -alkyl(allyl)-bridged bimetallic Nd–Mg species, in fast dissociation equilibrium with mononuclear alkyl(allyl)–Nd species and with fast reversible transfer of alkyl(allyl) chains between the Nd and Mg centers, is the most likely hypothesis to account for the pseudo-living character of BD polymerization, as it has been shown before for olefin polymerization with chlorolanthanocene–dialkylmagnesium systems [30]. Based on the existing literature, *trans*-selective BD polymerization with the present systems is assumed to proceed through initial BD insertion into a Nd–R bond and then monodentate monomer coordination followed by 1,3-insertion into the *syn*- $\pi$ -allyl bond; the bulkiness of the ligands shifting the equilibrium between *anti* and *syn* configurations towards the *syn* structure (Fig. 7). Since *cis*-1,4 polymers are usually observed with weakly coordinating ligands, it is coherent to have *trans*-1,4 stereospecificity with such strongly coordinated ligands that are aryloxides and THF.

The difference in reactivity noticed between the systems based on  $\text{Nd}_3(\text{O}t\text{-Bu})_9(\text{THF})_2$  (**1**) and  $\text{Nd}(\text{O}$ -

*2,6-t*-Bu<sub>2</sub>-4-Me-Ph)<sub>3</sub>(THF) (**2**) or its THF-free analogue (**3**) can arise from their different intrinsic activity but also their difference in stability. Since aryloxides are more acidic ligands than *tert*-butoxide, the Nd center in systems based on **2** or **3** is expected to be more electrophilic and thus more active than those based on **1**. Also, the bulkiness of the aryloxy ligand may prevent decomposition of the corresponding alkyl(allyl)–Nd species and further contribute to the overall higher reactivity of those systems. Consistent with those trends, mononuclear alkyl complexes  $(\text{ArO})_2\text{NdR}$  could be selectively isolated from in situ **3**/MgR<sub>2</sub> combinations [29]. Variable temperature <sup>1</sup>H-NMR monitoring of “Nd(OR)<sub>3</sub>/Mg(CH<sub>2</sub>CH<sub>2</sub>R)<sub>2</sub> combinations, in the absence of monomer, showed a much easier  $\beta$ -H elimination for *tert*-butoxide than aryloxy systems yielding a more unstable metal hydride (and RCH=CH<sub>2</sub>) [13].  $\beta$ -H elimination proceeded from –60 °C for *tert*-butoxide–Nd–R systems, while it required about 20 °C with the aryloxy–Nd–R. Nonetheless, the present results in diblock copolymerization with **1** established the presence of some active species even after 18 h at 60 °C; obviously, monomer coordination might stabilize these alkyl(allyl)–Nd species. The pseudo-living nature of diene polymerization, evidenced by the true diblock

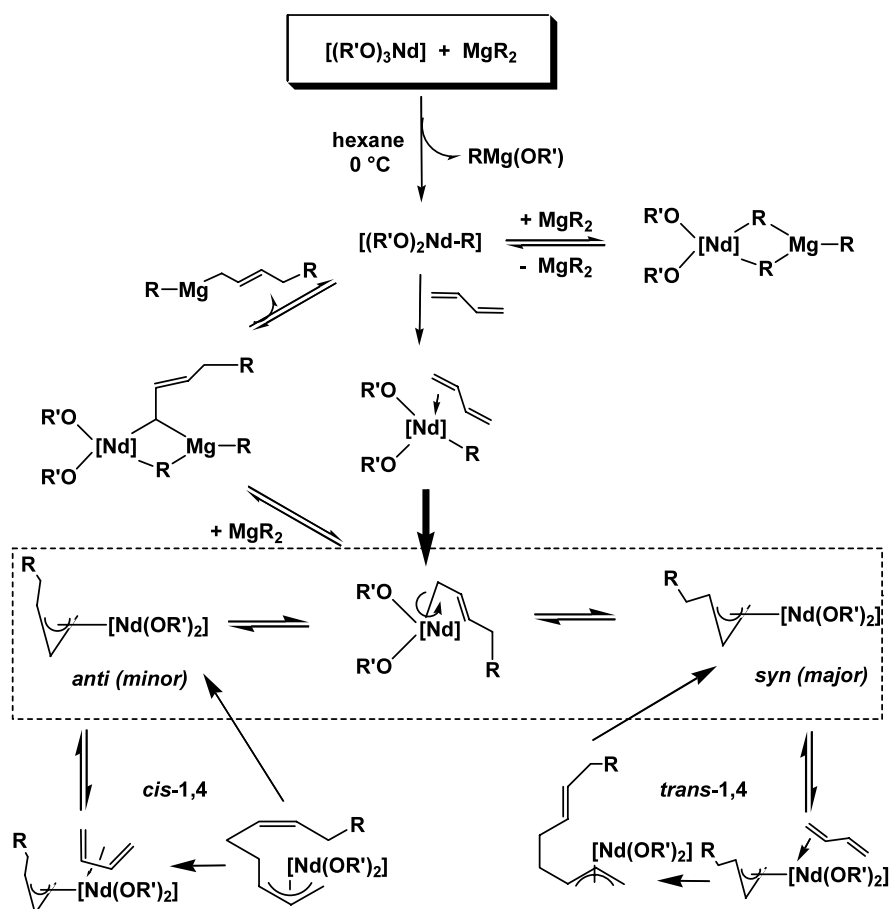


Fig. 7. Assumed mechanism of diene polymerization promoted by “Nd(OR)<sub>3</sub>/MgR<sub>2</sub> systems.

nature of poly(BD-*b*-GMA) copolymers and their low polydispersities, is another indicator of the robustness of the alkyl/allyl–Nd species generated from Nd(OAr)<sub>3</sub>(THF). We can reasonably assume that the polymerization mechanism of GMA is identical to the coordinative anionic mechanism reported by Yasuda et al. [31] for MMA polymerization initiated by alkyl-lanthanocenes.

#### 4. Conclusion

Binary combinations of neodymium alkoxide/aryloxide precursors with dialkylmagnesium reagents lead to the formation of active systems for the controlled stereospecific *trans*-1,4 polymerization of BD in hexane solution. The exact nature of the active species is not established but experimental results agree with the in situ formation of a bis(alkoxy)monoalkyl neodymium species. Best results were observed with neodymium aryloxides. Under specific conditions, these allow a precise control of the polymer molecular weight along with a low polydispersity. Experimental  $M_n$  values approach the ones calculated by  $([BD]_0 \times \text{Eff})/[Mg]_0$ , irrespective of the Nd/Mg ratio, which is consistent with a dynamic equilibrium between growing polymer chains on Nd and dormant chains on Mg centers, i.e. fast reversible transfer. It was taken advantage of the livingness of the system and its reactivity towards methacrylates to achieve efficiently the original stereospecific diblock copolymerization of butadiene with GMA. In addition, the statistical copolymerization of butadiene and styrene was successfully conducted. Copolymers with controlled molecular weight and moderate styrene content were obtained. <sup>13</sup>C-NMR spectra revealed that styrene incorporation did not modify the stereoregularity of PBD unlike the observation made in *cis*-1,4 polymerizations. Binary combinations “Nd(OR)<sub>3</sub>/MgR<sub>2</sub> appear as versatile systems. Efficient for ethylene polymerization and its copolymerizations with MMA, they are also active for butadiene co-polymerization with styrene and GMA. Identification of the active species and determination of their formation mechanism are still under investigation and will be reported in due course.

#### Acknowledgements

We gratefully thank Rhodia Electronics and Catalysis for financial support (Ph.D. grant to J.G. and post-doctoral fellowship to L.L.P.). We thank Dr. T. Mathivet (Rhodia E&C) for helpful discussions and Mrs. A.-M. Caze (University of Lille) and the analytical service of Rhodia Research (Aubervilliers) for SEC measurements.

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