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1 CALCIUM-MAGNESIUM SYSTEMS AS LITHIUM-FREE INITIATORS  
2 FOR THE ANIONIC POLYMERIZATION OF BUTADIENE

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10  
11 **Abstract:**

12 Lithium-based initiators are commonly used for the polymerization of aromatic vinylic  
13 monomers and conjugated dienes. The corresponding polymers and copolymers are of huge  
14 importance in particular in the field of tire industry. Nevertheless, lithium is nowadays  
15 increasingly used for energy-related applications and alternatives has to be proposed in the  
16 field of anionic polymerization. A lithium-free anionic polymerization of butadiene using a  
17 new bimetallic initiator based on two alkaline earth metals, calcium and magnesium, is  
18 proposed and discussed. From two inactive initiators for butadiene polymerization, i.e  
19 [(THF)<sub>2</sub>Ca{N(SiMe<sub>3</sub>)<sub>2</sub>}<sub>2</sub>] and [(n,s)Bu<sub>2</sub>Mg], an active bimetallic initiator complex is prepared  
20 by mixing the two in apolar medium at 40 or 60°C. Polybutadienes are synthesized with  
21 controlled molar masses, a low dispersity, and a living character. Interestingly, unusual  
22 microstructure of 75% of 1,4-trans units with low vinyl content (< 10%) could be reached.

## 24 **Introduction**

25 In 1956, Szwarc<sup>1,2</sup>, relying on his work and other researchers like Ziegler<sup>3-5</sup>, Abkkin and  
26 Medvedev<sup>6</sup>, demonstrated and named the living character of anionic polymerization using high  
27 vacuum techniques and permit to fully appreciate the potentiality of those systems. The rise of  
28 anionic polymerization and the main discoveries began from this date. Alkyl lithium derivatives  
29 are mostly used as initiators for the anionic polymerization of vinyl aromatic and conjugated  
30 dienic monomers<sup>7-9</sup>. Due to the growth of lithium batteries and the lithium demand worldwide,  
31 there is an interest in finding alternatives to this alkali metal to anticipate its scarcity, its  
32 increasing cost and the increasing complexity of the supply chain. Looking at the use of other  
33 alkali and alkaline earth metal derivatives as anionic initiators, ring-opening polymerizations  
34 of cyclic esters are predominantly reported<sup>10</sup>. In particular calcium derivatives can be  
35 employed<sup>11-15</sup>. However, they are much less used for conjugated dienes and styrene  
36 polymerization. Magnesium derivatives are commonly used and usually combined with  
37 lanthanides, like neodymium. Researchers such as Visseaux, Zinck and coll. developed  
38 dialkylmagnesium:lanthanide systems for styrene<sup>16-19</sup> polymerization and conjugated  
39 dienes<sup>20,21</sup>. The dialkylmagnesium was used as a chain transfer agent to a lanthanide as a single  
40 site catalyst to conduct the coordinative chain transfer polymerization. The amounts of  
41 magnesium have an influence on molar masses, dispersities and catalytic activities. These  
42 systems were used in particular for the synthesis of stereospecific polydienes<sup>22,23</sup>. Focused on  
43 1,4-trans dienes microstructure, Visseaux and coll. were pioneers for the synthesis of 1,4-trans  
44 polyisoprene using the combination of borohydride neodymium complexes with  
45 dialkylmagnesium in good yields<sup>24,25</sup> and more generally with polydienes like myrcene<sup>26,27</sup> or  
46 butadiene<sup>28</sup>. Looking at an anionic mechanism, only a few reports refer to the use of  
47 dialkylmagnesium as initiator/co-initiator for the polymerization of conjugated dienes.  
48 Dibutylmagnesium alone cannot initiate the butadiene or styrene polymerization, but,

49 combined with an alkyllithium, initiation and polymerization occur<sup>29-31</sup>. It is observed,  
50 depending on [Mg]/[Li] ratios and the polarity of the medium, that the rate of the  
51 polymerization is decreased, as a proof of the formation of magnesiate complexes which reduce  
52 the reactivity of the active chain ends. Interestingly, in the case of secondary  
53 dialkylmagnesium, the molar masses of a polybutadiene obtained is lower than the expected  
54 one due to a co-initiation coming from the dialkylmagnesium. The bimetallic initiator does not  
55 affect the stereochemistry generally obtained with an alkyllithium. We have also shown  
56 recently that the association of calcium and lithium derivatives can promote the synthesis of  
57 high 1,4-trans polybutadienes with controlled molar masses, narrow dispersities, and living  
58 character<sup>32,33</sup>.

59 The use of lithium-free initiator for anionic polymerization of styrene and conjugated dienes is  
60 even more challenging. A few reports mention possible solutions. As an example sodium-  
61 tributylmagnesiate complex is prepared from butylsodium and dibutylmagnesium<sup>34</sup>. Thanks to  
62 the dialkylmagnesium, the complex is soluble and stable enough to initiate the polymerization  
63 of isoprene. The polymerization appears to be not controlled with broad dispersities due to  
64 chain transfer and chain branching reactions. Heavier alkaline earth metals such as calcium-,  
65 strontium-, or barium-based complexes were proposed for the polymerization of styrene and  
66 dienes. The synthesis of [bis(phenyldimethylcarbonyl)barium]<sup>35</sup> and dibenzylbarium<sup>36</sup> are  
67 reported, and can be used as an anionic initiator for the polymerization of styrene. A barium-  
68 alkoxide with dialkylmagnesium is reported to produce polybutadiene with poor yields<sup>37</sup>.  
69 Adding 1,1-diphenylethylene (DPE) permits to generate an active barium complex allowing  
70 the preparation of polybutadienes with better yields. As an example, a polybutadiene with 72%  
71 of 1,4-trans, 9% of 1,2 and 19% of 1,4-cis units with a yield of 100% is obtained. Strontium  
72 and calcium chemistry have also been explored by Feil and Harder with the synthesis of [(2-  
73 *Me*<sub>2</sub>*N*-*α*-*Me*<sub>3</sub>*Si*-benzyl)Ae·(THF)<sub>2</sub>] (Ae : Ca or Sr)<sup>38,39</sup>. The strontium analog shows a better

74 reactivity and a lower dispersity than the calcium derivative. To enhance the reactivity and  
75 stability of calcium derivatives, a ligand exchange was applied to modify the steric hindrance.  
76 These new calcium complexes are active for the anionic polymerization of styrene and showed  
77 that the syndiotacticity is increased with the steric hindrance of the ligand<sup>40</sup>. Broad dispersities  
78 are generally obtained no matter the calcium derivatives used. Looking at the polymerization  
79 of butadiene initiated by calcium derivatives, Lindsell et al.<sup>41</sup> published Grignard-like  
80 initiators, i.e.  $\text{Ph}_3\text{CCaCl}(\text{THF})_2$  and  $\text{Ph}_3\text{CCaBr}(\text{THF})_4$ , which were shown to initiate butadiene  
81 polymerization in THF at low temperature ( $-10^\circ\text{C}$ ), yielding polybutadienes with molar masses  
82 around  $10,000 \text{ g}\cdot\text{mol}^{-1}$ , and dispersities around 2.

83 It is worth mentioning that alkali metal derivatives, in particular alkyllithium, are used to  
84 polymerize conjugated dienes, but also to synthesize the alkaline earth-based initiators. Herein,  
85 we report an innovative anionic alkali-free system, based on an unexpected synergy between  
86 calcium and magnesium derivatives for butadiene polymerization until full conversion. The  
87 control and livingness of the anionic polymerization of butadiene, and unusual microstructure  
88 of the resulting polybutadienes, is discussed.

89

## 90 **Experimental section**

91 **Materials.**

92 Butadiene (99.5% from Shell Chemicals), distilled under vacuum and stored under vacuum at  
93 room temperature in graduated glass tubes until use. Hexamethyldisilazane (HMDS, 99%),  
94 calcium granular (99%) and n,s-dibutylmagnesium ((n,s)Bu<sub>2</sub>Mg) solution in hexane (0.7  
95 mol.L<sup>-1</sup>) were purchased from Sigma Aldrich and used without further purification.  
96 Cyclohexane (99%, J.T. Baker) was purified by polystyryllithium seeds, distilled under  
97 vacuum, and then stored in graduated glass tubes under vacuum until use. Deuterated benzene

98 (Sigma Aldrich) was dried over sodium/benzophenone and freshly distilled directly in a Young  
99 tube for NMR purpose. THF (Sigma Aldrich, 99.9%) was dried over sodium/benzophenone,  
100 distilled under vacuum and stored under vacuum at room temperature in graduated glass tubes  
101 until use. Calcium bis[bis(trimethylsilyl)amide] ( $[(\text{THF})_2\text{Ca}\{\text{N}(\text{SiMe}_3)_2\}_2]$ ) was synthesized  
102 according to literature<sup>32</sup>.

103 ( $[(\text{THF})_2\text{Ca}\{\text{N}(\text{SiMe}_3)_2\}_2]$ ): <sup>1</sup>H NMR (400MHz, C<sub>6</sub>D<sub>6</sub>, 25°C): δ 3.54ppm (t, 8H, THF), δ  
104 1.21ppm (t, 8H, THF), δ 0.37 ppm (s, 36H, N(SiMe<sub>3</sub>)<sub>2</sub>). <sup>13</sup>C NMR (400MHz, C<sub>6</sub>D<sub>6</sub>, 25°C): δ  
105 69.7, 24.9 ppm (THF), δ 5.87 ppm (N(SiMe<sub>3</sub>)<sub>2</sub>)

106

107 Procedures.

108 All polymerizations were performed at 40°C or 60°C under argon in a high-pressure glass  
109 reactor equipped with a magnetic stirrer and fitted with PTFE stopcocks previously flamed  
110 under vacuum. The calcium complex ( $[(\text{THF})_2\text{Ca}\{\text{N}(\text{SiMe}_3)_2\}_2]$ ) was weighed under glovebox,  
111 then added in a schlenk previously flamed under vacuum. Cyclohexane can be introduced  
112 under vacuum through connected glass tubes to obtain a solution at the desired concentration.  
113 A desired amount of calcium was injected in a schlenk previously flamed under vacuum  
114 followed by (n,s)Bu<sub>2</sub>Mg in hexane via a syringe under argon flow. Cyclohexane was added  
115 under vacuum through connected glass tubes to obtain the desired concentration. And finally,  
116 butadiene was introduced under vacuum through connected glass tubes to start the  
117 polymerization. After the desired reaction time, degassed methanol was added to stop the  
118 reaction, and the possible remaining butadiene and cyclohexane were stripped off under  
119 vacuum. Conversions were determined using <sup>1</sup>H NMR (integration of butadiene vs.  
120 polybutadiene) with an aliquot taken during the run of polymerization (Figure S1 for details).

121 Polybutadiene:  $^1\text{H}$  NMR (400MHz,  $\text{CDCl}_3$ ,  $25^\circ\text{C}$ ):  $\delta$  5.57ppm (m, 1H, vinyl proton from 1,2  
122 unit),  $\delta$  5.43ppm (s, 2H, vinyl protons from 1,4-trans unit),  $\delta$  5.39ppm (s, 2H, vinyl protons  
123 from 1,4-cis unit),  $\delta$  4.96ppm (m, 2H, vinyl protons from 1,2 unit),  $\delta$  2.05-2.08ppm (2s, 8H,  
124 protons from 1,4 unit),  $\delta$  0.8ppm (m, 3H, protons from 1,2 unit)

125 As an example, for  $[\text{Ca}]/[\text{Mg}] = 0.75$  (molar ratio), 53mg of  $[(\text{THF})_2\text{Ca}\{\text{N}(\text{SiMe}_3)_2\}_2]$   
126 (105 $\mu\text{mol}$ ) was introduced into the glass reactor followed by 9mL of cyclohexane. 200 $\mu\text{L}$  of  
127 (n,s) $\text{Bu}_2\text{Mg}$  (140 $\mu\text{mol}$ ) solution in hexane (0.7M) was then added via a syringe under argon  
128 flow followed by 2mL of liquid butadiene (22.8mmol) to run the polymerization, then heated  
129 at  $60^\circ\text{C}$  (run 11 Table 1).

130 The analysis of the calcium:magnesium complex at  $[\text{Ca}]/[\text{Mg}] = 0.75$  ratio in cyclohexane  
131 solution (5-10mL) was carried out by  $^1\text{H}$  and  $^{13}\text{C}$  NMR in deuterated benzene. An aliquot of  
132 the complex solution was first dried in a Young tube under vacuum to remove all volatiles  
133 before adding the deuterated solvent under vacuum (spectra are given in ESI Figures S5 and  
134 S6).

135 Analysis.

136 Polymer molar masses were determined by Size Exclusion Chromatography (SEC) using  
137 tetrahydrofuran (THF) as the eluent. Measurements in THF were performed on an Ultimate  
138 3000 system equipped with differential refractive index detector dRI from Wyatt Technology.  
139 Polymers were separated on three G2000, G3000 and G4000 TOSOH HXL gel columns (300  
140 x 7.8 mm) (exclusion limits from 1000 Da to 400 000 Da) at a flowrate of 1 mL/min. Columns  
141 temperature was held at  $40^\circ\text{C}$ . Polybutadiene molar masses were determined using polystyrene  
142 standards and application of a corrective factor equal to 0.6 for low molar masses ( $<$   
143 30,000 $\text{g}\cdot\text{mol}^{-1}$ ) or 0.52 for high molar masses determined elsewhere.

144 Liquid-state  $^1\text{H}$ -NMR (400.2 MHz) and  $^{13}\text{C}$ -NMR (Inversed gated decoupling, 100.6 MHz, D1  
145 = 10 s, 4,096 scans) spectra were recorded at 298 K on a Bruker Avance 400 spectrometer in  
146  $\text{CDCl}_3$  or in  $\text{C}_6\text{D}_6$ . A detailed description of the method used to determine polybutadiene  
147 microstructure is presented in ESI Figure S2.

148 MALDI-MS spectra were performed by the CESAMO (Bordeaux, France) on a Autoflex maX  
149 TOF mass spectrometer (Bruker Daltonics, Bremen, Germany) equipped with a frequency  
150 tripled Nd:YAG laser emitting at 355 nm. Spectra were recorded in the positive-ion mode with  
151 an accelerating voltage of 19 kV. Samples were dissolved in THF at 10 mg/ml. The 9-  
152 nitroanthracen matrix solution was prepared by dissolving 10 mg in 1 ml of THF. A THF  
153 solution of cationization agent (silver trifluoroacetate, 10 mg/ml) was also prepared. The  
154 solutions were combined in a 10:1:1 volume ratio of matrix to sample to cationization agent.  
155 One to two microliters of the solution obtained were deposited onto the sample target.

156 Inductively Coupled Plasma analysis was performed by the Laboratoire de Chimie de  
157 Coordination (Toulouse, France) on ICP-OES ICAP 6300 Duo Thermo. Wavelength range:  
158 166-847 nm; detector: high performance CID86 chip; RF source: 27.12MHz solid state, 750-  
159 1500 W; plasma gas: fixed  $12\text{L}\cdot\text{min}^{-1}$ , argon; nebulizer gas: pressure control from 0 to 0.4 MPa.

160

## 161 **Results and discussions**

162 Based on the work of Krieck et al.<sup>42</sup>,  $[(\text{THF})_2\text{Ca}\{\text{N}(\text{SiMe}_3)_2\}_2]$  complex was first synthesized  
163 and characterized by  $^1\text{H}$  NMR in  $\text{C}_6\text{D}_6$  (Figure S3). Inductively Coupled Plasma analysis  
164 showed the presence of a tiny number of impurities, mainly calcium dibromide (Table S1).  
165 This complex was then used without further purification as this impurity is not expected to  
166 terminate the butadienyl active centers. This was confirmed by preliminary experiments.

167 Butadiene polymerization was then studied using  $[(\text{THF})_2\text{Ca}\{\text{N}(\text{SiMe}_3)_2\}_2]$  with  $(n,s)\text{Bu}_2\text{Mg}$   
 168 as initiator in different proportions. Results are given in Table 1.

169 *Table 1. Butadiene polymerization initiated by  $(n,s)\text{Bu}_2\text{Mg}$  in the presence of different*  
 170 *amounts of  $[(\text{THF})_2\text{Ca}(\text{HMDS})_2]$  in cyclohexane*

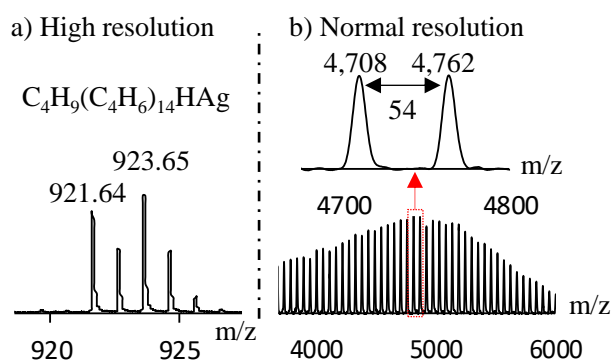
Run	$\frac{[\text{Ca}]}{[\text{Mg}]}$	$\frac{[\text{M}]}{[\text{I}]}$	T (°C)	Time	Conv. <sup>a</sup> (%)	$\bar{M}_{n,\text{th}}^b$ ( $\text{g}\cdot\text{mol}^{-1}$ )	$\bar{M}_{n,\text{exp}}^c$ ( $\text{g}\cdot\text{mol}^{-1}$ )	Đ	1,2 (%)	1,4-trans (%)	1,4-cis (%)
1	0.5	181	40	24h	68	6,600	4,600	1.07	11	75	14
2			60	24h	99	9,700	5,700	1.22	10	73	17
3	0.75	181	40	24h	78	7,600	5,200	1.05	10	75	15
4			60	24h	100	9,800	7,000	1.10	10	74	16
5	1	181	40	24h	80	7,800	6,900	1.08	11	75	14
6			60	24h	98	9,600	7,300	1.21	10	73	17
7	1.25	181	40	24h	80	7,800	7,300	1.13	11	75	14
8			60	24h	99	9,700	8,300	1.15	10	73	17
9	1.5	181	40	24h	84	8,200	8,000	1.15	10	74	16
10			60	24h	99	9,700	9,200	1.21	10	73	17
11		163	60	4d	100	8,800	8,100	1.11	10	74	16
12	0.75 <sup>d</sup>	481	60	4d	100	26,000	23,300	1.18	8	75	17
13		1945	60	6d	97	105,000	90,000	1.44	7	68	25

<sup>a</sup>Determined by <sup>1</sup>H NMR regarding butadiene vs. polybutadiene. <sup>b</sup>Calculated with one polymer chain per Mg at the given conversion. <sup>c</sup>Number-average molar mass estimated by SEC based on polystyrene standards applying a corrective factor (0.6 for low molar masses and 0.52 for high molar masses [last experiment]). <sup>d</sup>Polymerization run in closed reactor without withdrawal until quenched

171  
 172  
 173 As shown, butadiene polymerized using different ratios of  $[\text{Ca}]/[\text{Mg}]$ , ranging from 0.5 to 1.5,  
 174 with narrow or quite narrow chain distributions depending on this ratio. The lowest dispersity  
 175 was obtained for  $[\text{Ca}]/[\text{Mg}] = 0.75$  at 40 or 60°C, and it tends generally to increase when  
 176 temperature increases from 40 to 60°C. One can note that molar masses are for most samples  
 177 lower than the expected ones due to repetitive opening of the reactor for aliquot withdrawals  
 178 used for kinetics following and causing a loss of butadiene. Polymerizations carried out in  
 179 closed reactors at 60°C confirms that molar masses can be closer to the theoretical values as  
 180 shown in run 11 and 12. They are still lower, possibly due to an initiation by the second alkyl  
 181 group of the Mg derivative giving more than 1 chain per “ate” complex. Looking at the  
 182 dispersities, a slow initiation of the complex, as compared to the propagation step, might be  
 183 also considered when increasing the reaction temperature or when a high molar mass is

184 targeted. Those experiments also confirmed that full conversion can be reached, and high molar  
185 mass as well with run 13.

186 As known in anionic polymerization, the 1,4-trans microstructure is reduced when the  
187 concentration of active species is reduced<sup>43</sup>, due to different rates of chain ends conformations  
188 of active species (Figure S4) with  $k_{cis}/k_{trans} = 2$  for butadiene<sup>44</sup>. Indeed, in these conditions, the  
189 propagation rate is favored as compared to the isomerization rate, yielding to an increasing  
190 amount of 1,4-cis units. The decrease of the  $[Ca]/[Mg]$  initiator concentration by 10 as  
191 compared to the other experiments confirms that observation (Table 1, run 13). High resolution  
192 MALDI-TOF MS analysis showed that a  $C_4H_9$  group initiated the polymerization and a H  
193 ended it. As shown in Figure 1a), molar masses obtained for  $\overline{DP}_n = 14$  agree with theoretical  
194 ones simulated by an isotopic pattern (monoisotopic mass equal to  $921.64 \text{ g}\cdot\text{mol}^{-1}$  and an  
195 average of  $923.65 \text{ g}\cdot\text{mol}^{-1}$ ). A butyl group provided by the dialkylmagnesium initiates the  
196 polymerization and the theoretical molar masses were calculated according to the amount of  
197 dialkylmagnesium with 1 chain per magnesium. Moreover, one population of polymer is  
198 observed and confirmed that no transfer reaction to the complexed THF occurs (Figure 1b)).



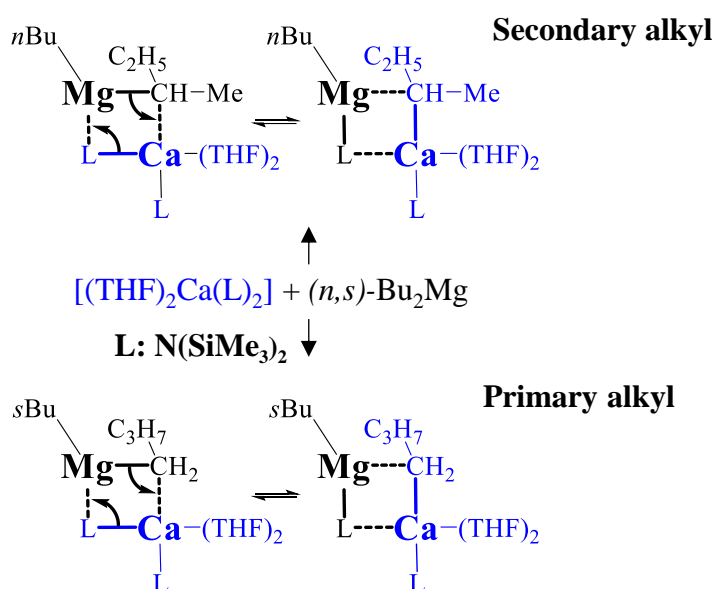
199

200 *Figure 1. MALDI-TOF MS of polybutadiene obtained with*  
201  *$[(THF)_2Ca\{N(SiMe_3)_2\}_2]:(n,s)Bu_2Mg$  ( $[Ca]/[Mg] = 0.75$ ,  $60^\circ C$ , cyclohexane)*

202

203 To understand and represent the structure of the initiating complex,  $^1H$  NMR was first carried  
204 out (Figure S5). The spectrum of the Ca:Mg complex showed that most of the peaks present in

205 the initial (n,s)Bu<sub>2</sub>Mg are shifted meaning that the magnesium derivative has reacted with the  
 206 calcium one to form a bimetallic complex. However, the exact structure is unclear. As shown  
 207 in HSQC experiment (Figure S6), the amide ligand from calcium gives several singlets between  
 208 0 to 0.6 ppm which agrees that calcium is involved in bimetallic complexes. This can be  
 209 interpreted by different calcium-magnesium stoichiometries and by different geometries  
 210 between amide-calcium and amide-magnesium derivatives. Based on some literature on “ate”  
 211 complexes<sup>30,31</sup>, it is proposed that the initiator is formed via a 4-membered ring as described in  
 212 Scheme 1.



213

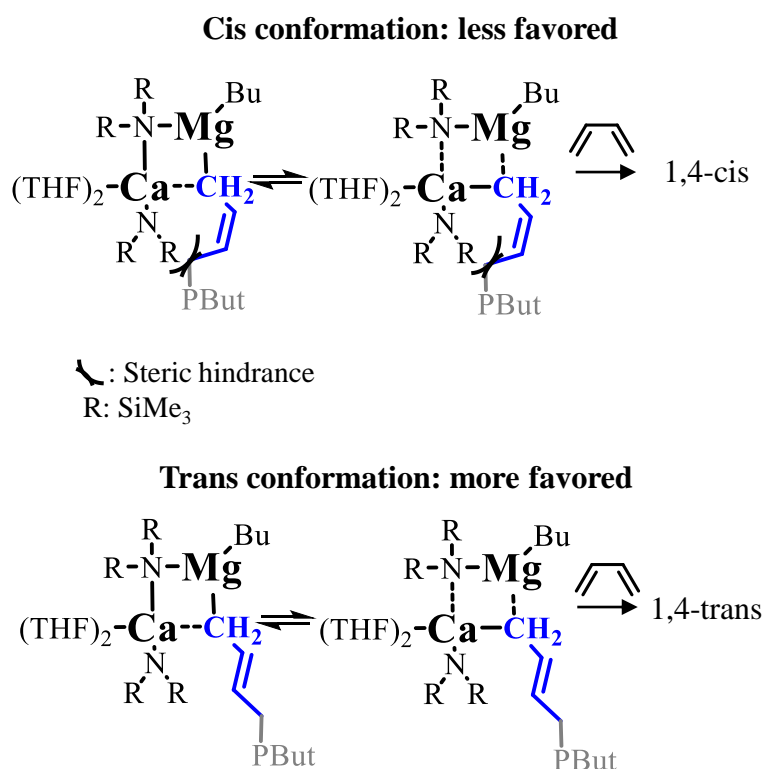
214 *Scheme 1. Proposed mechanism for the formation of an active butyl-calcium bond within the*  
 215 *Ca:Mg complex*

216

217 Interestingly, the microstructure of the prepared polybutadiene from Ca:Mg systems is mainly  
 218 1,4 units with low 1,2 units (Table 1), similarly as a polybutadiene obtained with an  
 219 alkyllithium in apolar condition<sup>45</sup>. As a difference, monometallic alkyllithium allows to reach  
 220 up to 55% of 1,4-trans units, when 73-75% are obtained with this bimetallic system whatever  
 221 the ratio between calcium and magnesium. Such values are in agreement with the  
 222 microstructure observed with a Ca:Li system previously published<sup>32,33</sup>. C-Ca bonds, in situ

223 generated, act as propagative species, yielding to high 1,4-trans units (Scheme 2). The  
 224 equilibrium between syn- and anti-conformation of an active chain ends is shifted to syn-  
 225 conformation due to the steric hindrance induced by bis-trimethylsilyl-amide ligands.

226



227

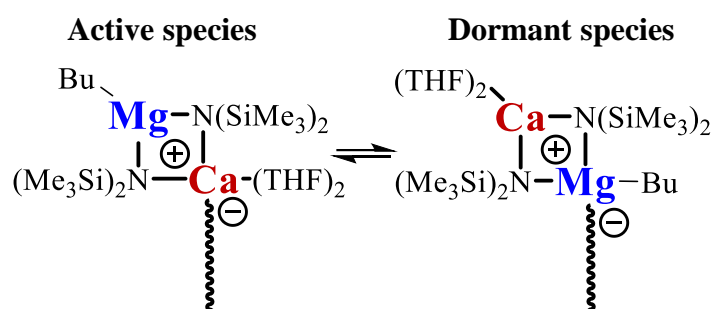
228 *Scheme 2. Structures of polybutadiene propagating species yielding 1,4-trans units*

229

230 It is worth adding that an equilibrium between active C-Ca bonds and dormant C-Mg ones can  
 231 also exist (Scheme 3), which explain the limited possibility to modulate the 1,4-cis / 1,4-trans  
 232 ratio (Table 1). This can be related to the possibility to increase the 1,4-cis, or decrease the 1,4-  
 233 trans units, when Ca:Li systems are used. Indeed, both C-Ca and C-Li bonds are active meaning  
 234 that, when [Ca]/[Li] ratios decrease, C-Li bonds are predominant yielding to a decrease of the  
 235 1,4-trans content.

236 Isoprene was also polymerized with the Ca:Mg system to confirm the nature of the active  
 237 species yielding mostly 1,4-trans units (Table S2). As compared to the 10-30% (depending on  
 238 [M]/[I] ratios) of 1,4-trans units obtained from n-BuLi initiation<sup>46</sup>, polyisoprenes obtained from  
 239 the Ca:Mg initiator are mainly composed of 1,4-trans units (55-58%). These results agree with  
 240 the proposed mechanism based on an active C-Ca bond.

241



242

243 *Scheme 3. Equilibrium between active C-Ca bond and non-active C-Mg bond*

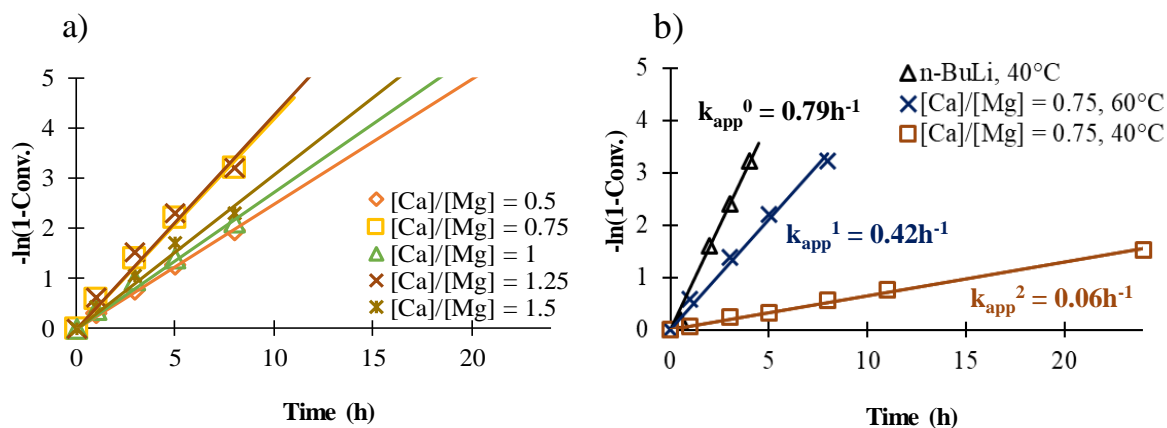
244

245 Polymerization kinetics were also determined using  $-d[\text{But}]/dt = R_p = k_p[\text{Ca:Mg}]_0[\text{But}] =$   
 246  $k_{\text{app}}[\text{But}]$ , with  $k_{\text{app}}$  the slope of the fitted curves given by the equation  $-\ln(1-\text{Conv.}) = k_{\text{app}} t$ .  
 247 The influence of [Ca]/[Mg] ratios between 0.5 and 1.5 on the propagation rate was first studied  
 248 at 60°C (Figure 2a)). The sub-stoichiometry of one metal (i.e. [Ca]/[Mg] = 0.75 or 1.25) allows  
 249 the propagation rate to increase slightly. This was not observed at 40°C (Figure S7). Now,  
 250 comparing the kinetics, it can be noted that  $k_{\text{app}}^1$  is almost divided by 2 at 60°C, and more than  
 251 10 at 40°C ( $k_{\text{app}}^2$ ) using [Ca]/[Mg] = 0.75 as compared to the n-BuLi reference  $k_{\text{app}}^0$  at 40°C  
 252 (Figure 2b)). The new Ca:Mg active species are less reactive than alkyl lithium derivatives used  
 253 alone due to the delocalization of the anionic charge within the Ca:Mg complex. This supports  
 254 the presented equilibrium between active and dormant species.

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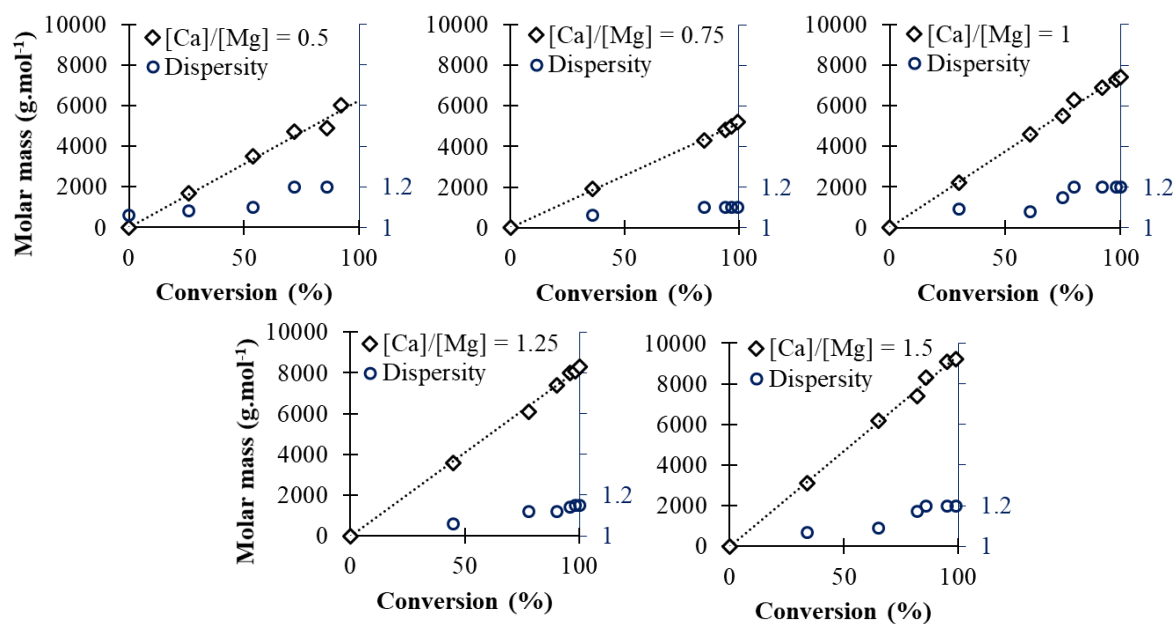


258

259 *Figure 2. (a)  $\ln[M]/[M]_0$  vs time plots for the polymerization of butadiene initiated by bimetallic*  
 260 *Ca:Mg systems at 60°C, (b) Comparison of  $k_{app}$  of butadiene polymerization initiated by  $n\text{-BuLi}$*   
 261 *( $[n\text{-BuLi}]_0 = 13.8\text{mmol.L}^{-1}$ ) vs. Ca:Mg systems ( $[Mg]_0 = 13.8\text{ mmol.L}^{-1}$ ,  $[Ca]/[Mg] = 0.75$ )*  
 262 *(cyclohexane,  $[But]_0 = 2.5\text{mol.L}^{-1}$ ,  $\bar{M}_{n,th} = 9,800\text{ g.mol}^{-1}$ )*  
 263

264 The evolution of molar masses with conversion and dispersities was plotted for [Ca]/[Mg] =  
 265 0.5, 0.75, 1, 1.25 and 1.5 at 60°C. The absence of transfer and termination reactions is  
 266 confirmed by the linear evolution for all systems. As illustrated in Figure 3 (and Figure S8 at  
 267 40°C), the evolution of molar masses with conversion are quite linear no matter the [Ca]/[Mg]  
 268 ratios, which agrees with the absence of side reactions. It is confirmed by MALDI-TOF (Figure  
 269 1) and SEC (Figure S9) with only 1 population of polymers observed. One can note that the  
 270 dispersities increase up to 1.2 after 50% of conversion, except for a small sub-stoichiometric  
 271 amount of calcium, i.e. [Ca]/[Mg] = 0.75 (Figure 3) and is explained by aggregation issues.

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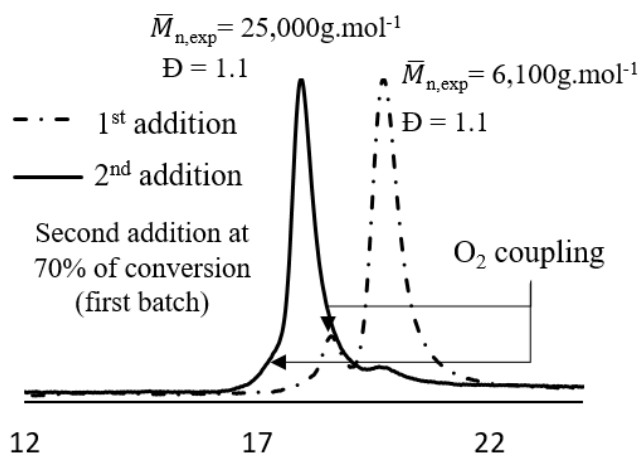
273

274 *Figure 3. Molar mass and dispersity vs. conversion plots with fitted curve for the*  
 275 *polymerization of butadiene initiated by bimetallic Ca:Mg systems ( $\bar{M}_{n,th} = 9,800\text{g.mol}^{-1}$ ,*  
 276 *cyclohexane, 60°C)*

277

278 The livingness of Ca:Mg initiated polymerization of butadiene was investigated by a sequential  
279 addition of butadiene at 60°C with the most efficient system, i.e. for a [Ca]/[Mg] ratio equal to  
280 0.75. As shown in Figure S10, when butadiene is added to the medium after full conversion of  
281 the first batch, not all chains could be re-initiated. However, if the second addition of butadiene  
282 is added during the polymerization process of the first batch, i.e. before reaching full  
283 conversion, almost all chains could be re-initiated as shown in Figure 4. The same phenomenon  
284 was observed in our previous work using Ca:Li systems<sup>32</sup>. As described with these calcium-  
285 lithium systems, similar aggregation issues can explain this phenomenon due to dormant chain  
286 ends hypothesis.

287



288

289 *Figure 4. SEC of a polybutadiene initiated by [(THF)<sub>2</sub>Ca{N(SiMe<sub>3</sub>)<sub>2</sub>}<sub>2</sub>]:(n,s)Bu<sub>2</sub>Mg system*  
290 *([Ca]/[Mg] = 0.75, cyclohexane, 60°C). Butadiene was added two times, first addition with*  
291  *$\bar{M}_{n,th} = 9,000 \text{ g.mol}^{-1}$  as targeted mass, then a second addition to reach  $\bar{M}_{n,th} = 18,000 \text{ g.mol}^{-1}$*

292

293 The nature of alkyl group from magnesium derivatives was also investigated using (n,s)Bu<sub>2</sub>Mg,  
294 (n,n)Bu<sub>2</sub>Mg and n-Bu,n-OctMg (Table 2). As expected, all systems reached full conversion  
295 with a similar reaction time and with controlled molar masses. Looking at the dispersities of

296 the polybutadienes obtained, (n,s)Bu<sub>2</sub>Mg-based initiating complexes yield the lowest ones. The  
 297 secondary alkyl of the magnesium derivative seems to allow an easier ligand exchange into to  
 298 the Ca:Mg complex for the formation of C-Ca bond.

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305 *Table 2. Butadiene polymerization initiated by different dialkylmagnesium derivatives in the*  
 306 *presence of various amounts of [(THF)<sub>2</sub>Ca{N(SiMe<sub>3</sub>)<sub>2</sub>}<sub>2</sub>] in cyclohexane at 60°C during 24h*

[Ca] [Mg]	Alkylmagnesium	Conv. <sup>a</sup> (%)	$\bar{M}_{n,th}^b$ (g.mol <sup>-1</sup> )	$\bar{M}_{n,exp}^c$ (g.mol <sup>-1</sup> )	$\bar{D}$
0.5	(n,s)Bu <sub>2</sub> Mg	100	11000	8500	1.1
	(n,n)Bu <sub>2</sub> Mg	100	12,300	11,400	1.4
	n-Bu-n-OctMg	100	12,300	13,200	1.4
0.75	(n,s)Bu <sub>2</sub> Mg	100	11,000	9900	1.1
	(n,n)Bu <sub>2</sub> Mg	100	12,300	11,000	1.4
	n-Bu-n-OctMg	100	12,300	11,000	1.4
1	(n,s)Bu <sub>2</sub> Mg	100	11,000	9,900	1.1
	(n,n)Bu <sub>2</sub> Mg	100	12,300	11,400	1.3
	n-Bu-n-OctMg	100	12,300	11,400	1.4
1.25	(n,s)Bu <sub>2</sub> Mg	100	11,000	9600	1.1
	(n,n)Bu <sub>2</sub> Mg	100	12,300	11,200	1.4
	n-Bu-n-OctMg	100	12,300	12,600	1.2
1.5	(n,s)Bu <sub>2</sub> Mg	100	11,000	9700	1.2
	(n,n)Bu <sub>2</sub> Mg	100	12,300	11,400	1.3
	n-Bu-n-OctMg	100	12,300	13,800	1.3

317 <sup>a</sup>Determined by <sup>1</sup>H NMR regarding butadiene vs. polybutadiene. <sup>b</sup>Calculated with one polymer  
 318 chain per Mg. <sup>c</sup>Number-average molar mass estimated by SEC on the basis of polystyrene  
 319 standards applying x0.6 corrective factor

## 319 Conclusion

320 The combination of calcium and magnesium derivatives is an efficient route to create lithium-  
321 free initiating systems for the anionic polymerization of butadiene. The polybutadienes are  
322 obtained with controlled molar masses, narrow dispersities and low 1,2 units content ( $\leq 10\%$ ).  
323 Interestingly, unusual high 1,4-trans microstructure (75%) was reached whatever the [Ca]/[Mg]  
324 ratio used. Those results confirm the role of the calcium compound within the “ate” complex  
325 with the formation of an active C-Ca bond. Furthermore, it is important to highlight that no  
326 alkali metal was required as an alkyl donor, the magnesium derivative supplying the alkyl  
327 group.

328 The best [Ca]/[Mg] ratio appeared to be 0.75 as a good compromise can be obtained with full  
329 conversion, controlled molar masses by the amount of (n,s)Bu<sub>2</sub>Mg introduced, low dispersity  
330 (D=1.1), a living character of the butadiene polymerization and a relative fast polymerization  
331 at 60°C. This calcium:magnesium system is still lower as compared to alkyllithium initiators  
332 in terms of polymerization rate of butadiene but, opens a new era in the field of lithium-free  
333 anionic initiators for conjugated dienes and copolymers.

334

### 335 **Data availability**

336 Complementary data required to reproduce these findings are present in the Supplementary  
337 Information file linked to this manuscript.

338

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