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**Anionic polymerization of butadiene by dialkylmagnesium / alkali metal alkoxide systems in apolar medium: Polybutadiene microstructure and polymerization control.**

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**ABSTRACT**

Lithium based anionic polymerization of butadiene in apolar media allows the obtention of polybutadiene with a high vinyl content by using polar modifier or alkali metal alkoxide. For instance, butadiene polymerization with alkyllithium and potassium *tert*-pentoxide produces polybutadiene with 50% of vinyl content. The aim of this paper is to develop an approach without any alkyllithium moieties in order to synthesize polybutadiene with a high vinyl content (50% - 70%) in a controlled way. To do so bi-metallic systems based on di-*n*-butylmagnesium in association with potassium or sodium *tert*-pentoxide were studied in apolar medium. The influence of parameters such as the initiator preformation time and the [Mt] / [Mg] ratio were assessed (Mt = K, Na). The potassium *tert*-pentoxide-based system was found to produce polybutadienes in a controlled way with 50 % of vinyl content, while polybutadienes with up to 70% of vinyl content were obtained in a controlled way with Na based systems.

## 1. Introduction

Lithium-based anionic polymerization is a well-established route for the synthesis of polybutadiene in a controlled way. Mechanical and thermal properties of polybutadiene can be tuned by adjusting molar masses, dispersity, chain end functionalization, architecture, styrene content in the case of styrene-butadiene rubber and through varying polybutadiene microstructure [1]. Microstructure can be modulated by adjusting the reaction media polarity (solvent, addition of polar modifier in apolar media) [2-6] or by the addition of alkali metal or alkaline earth metals derivatives in apolar media. Alkali metal derivatives are known to vary the 1,4 / 1,2 content of the obtained polybutadiene, meanwhile addition of alkaline earth metal derivatives (Ca, Sr, and Ba) enables tuning of 1,4-cis / 1,4-trans ratio keeping a vinyl content below 10% [7].

Even though lithium-based anionic polymerization is well established to achieve microstructure tuning, initiating systems based on heavier alkali metal or alkaline earth metal are also reported. In hydrocarbon media, alkylsodium are reported to produce polybutadiene with 60 – 80% vinyl content with molar masses close to the theoretical ones with dispersities ranging from 1.2 to 1.5 [8], [9]. Such polymerization reactions are said to be subjected to chain termination and to chain transfer to the polymer backbone. In addition, organosodium compounds are not stable in apolar media and stabilization requires a reaction with diphenylethylene. Potassium as a counterion is reported to produce polybutadiene with about 50% vinyl content [10], but synthesis and storage of alkylpotassium derivatives is challenging since a rapid deactivation occurs [11], [12]. Like in the case of **organosodium**, storage of organopotassium moieties requires the addition of diphenylethylene. In terms of butadiene polymerization control, little informations were found and one can assume side reactions similar to the one reported for organosodium-initiated polymerization. The use of alkylcalcium ([8]-[15]), strontium [15] and barium ([15]-[17]) derivatives are reported to produce polybutadiene with a low vinyl content (10 – 25%) and a 1,4-cis / 1,4-trans ratio ranging from 0.16 to 7 in apolar media. Such alkaline earth based initiators are not readily available and metal activation is often required through the use of amalgam or electronic transfer in THF [18]. Recently, Ma and Li reported on the regulation of cis and trans microstructures of isoprene units in alternated copolymers using sodium or potassium alkoxides as regulators [19].

Several multi-metallic systems (typically based on sodium, potassium, magnesium, or aluminum derivatives) are described in the literature to polymerize dienes and styrene. These systems are commonly based on alkylsodium / trialkylaluminum (for butadiene polymerization) [20], [21], potassium hydride / alkali metal alkoxide / trialkylaluminum (for isoprene and butadiene polymerization [22]), alkylmagnesium / alkali or alkaline earth derivatives (for butadiene polymerization) [23]-[26], and metal-zinc tetraalkyl (metal = Ca, Sr or Ba), for dienes / styrene copolymerization [27]. Looking at Mg-based systems, bimetallic systems based on  $R_3MgK$  ( $[tert\text{-}PeOK] / [R_3MgK] = 1.5 - 2.3$ ) were developed by Halasa and coworkers [23]. After polymerization, two polybutadiene fractions were observed. A first hexane-soluble fraction (2 – 31%,  $\bar{D} \geq 1.6$ ) is described to be polybutadiene with a vinyl content equal to 50%. A second fraction ( $\geq 76\%$ ), non-soluble in hexane, is reported as an insoluble 1,4-trans polybutadiene resin. A trimetallic system based on di-*n*-butylmagnesium, barium alkoxide hydroxide, and triethylaluminum was developed by Hargis and coworkers [24]. With such a system, butadiene polymerization is said to be living and produces polybutadiene with up to 90% 1,4-trans content. Polybutadiene microstructure can be varied by adjusting the ratio  $[Ba] / [Mg]$  from 63% ( $[Ba] / [Mg] = 1$ ) up to 87% 1,4-trans content ( $[Ba] / [Mg] = 0.2$ ) while keeping a vinyl content below 10%. These magnesium-based systems are allowing polybutadiene polymerization with various microstructures simply by changing the nature of the alkoxide. This observation drives us to study such magnesium-based systems to synthesize in a controlled way polybutadiene with a high vinyl content. To do so, potassium *tert*-pentoxide was first selected as the alkoxide moieties and associated with di-*n*-butylmagnesium. Parameters such as the initiator preformation time and  $[K] / [Mg]$  ratio were investigated. The use of sodium *tert*-pentoxide + di-*n*-butylmagnesium was then studied to produce polybutadiene in a controlled way with a high vinyl content.

## 2. Experimental

### 2.1. Materials

Di-*n*-butylmagnesium (1M in hexane) was purchased from Sigma-Aldrich and used as received. 2-Methyl-2-butanol (99%, Sigma-Aldrich) was dried over freshly crushed  $CaH_2$  and distilled off prior to use. Potassium chunks (98% in mineral oil, Sigma-Aldrich) were stored in an argon filled glovebox, mineral oil was removed through cyclohexane washing prior to

use. Butadiene (99.6%, Sigma-Aldrich) was dried over CaH<sub>2</sub> for an hour, distilled off and stored in a pressure resistant glass burette. Cyclohexane (99.5%, VWR) was dried over freshly crushed calcium hydride (Acros, 93%) and stored over polystyryllithium seeds. Potassium *tert*-pentoxide was obtained by the reaction of dry 2-methyl-2-butanol (1 mL) with potassium metal (0.5 g) dispersed in dry cyclohexane (51 mL). Reaction was allowed to proceed at 20°C overnight followed by 3-5 days at 80°C (until complete dissolution of the initially forming gel). Sodium *tert*-pentoxide was obtained following the same experimental procedure by reacting 2-methyl-2-butanol (1 mL) with sodium (0.3 g) in cyclohexane (51 mL). Concentrations were assessed by hydrolysis of an aliquot (1 mL) followed by titration with HCl using phenolphthalein as an indicator. Potassium *tert*-pentoxide and sodium *tert*-pentoxide solutions were stored at 20°C over a chunk of metal (remaining from the initial amount of alkali metal).

## 2.2. Polymerizations

For all experiments the targeted molar mass was calculated as follow:  $\bar{M}_{n\ th, Mg} = m_{monomer} / n_{R_2Mg} = (C_{monomer} \times M_{butadiene}) / C_{R_2Mg}$  while  $\bar{M}_{n\ th, ROMt} = m_{monomer} / n_{ROMt} = (C_{monomer} \times M_{butadiene}) / C_{ROMt}$  with molar masses in g.mol<sup>-1</sup>, concentration in mol.L<sup>-1</sup>, masses in g and number of moles in mol.

A typical experimental process to obtain polybutadiene with an initiator composed of di-*n*-butylmagnesium and 2.5 eq. of potassium *tert*-pentoxide, with no initiator preformation, can be described as follow: A glass reactor of 50 mL, equipped with a magnetic stirrer, and fitted with PTFE stopcocks was flame-dried under vacuum before addition of dry cyclohexane (13 mL) through connected glass tubes. Potassium *tert*-pentoxide solution (1.8 mL of a 0.18 M solution in cyclohexane) was added via a syringe under an argon flow. Butadiene (1.3 g, 2.4 x 10<sup>-2</sup> mol) was vacuum-distilled into the reaction apparatus. Di-*n*-butylmagnesium (130 µL of a 1.0 M solution in hexane) was then added via a syringe under an argon flow into the reaction apparatus. Reaction was allowed to proceed for 16 hours at 20°C, after which degassed methanol (0.5 mL) was introduced into the reaction mixture via a syringe under an argon flow. The obtained solution was recovered with THF and dried under vacuum. The polymer was then weighted to determine the yield and analyzed ( $\bar{M}_{n\ th, Mg} = 10,000$  g.mol<sup>-1</sup>, Yield = 100%,  $\bar{M}_n\ exp = 10,000$  g.mol<sup>-1</sup>,  $\bar{D} = 1.14$ , 50% vinyl content, 33% 1,4-trans content and 17% 1,4-cis content). The SEC chromatogram is presented on Figure 1 (red plot).

A typical experimental process to obtain polybutadiene with an initiator composed of di-*n*-butylmagnesium and 2.5 eq. of sodium *tert*-pentoxide can be described as follow: A glass reactor of 50 mL, equipped with a magnetic stirrer, and fitted with PTFE stopcocks was flame-dried under vacuum before addition of dry cyclohexane (9 mL) through connected glass tubes. Sodium *tert*-pentoxide solution (1.4 mL of a 0.18 M solution in cyclohexane) was added via a syringe under an argon flow followed by di-*n*-butylmagnesium (102  $\mu$ L of a 1.0 M solution in hexane). The obtained solution was kept at 40°C for 1h before addition of butadiene (1.02 g,  $1.8 \times 10^{-2}$  mol) into the reaction apparatus. Reaction was allowed to proceed for 48 hours at 40°C, after which degassed methanol (0.5 mL) was introduced into the reaction mixture via a syringe under an argon flow. The obtained solution was recovered with THF and dried under vacuum overnight. The polymer was then weighted to determine the yield and analyzed ( $\bar{M}_{n\ th,Mg} = 10,000$  g.mol<sup>-1</sup>, Yield = 100%,  $\bar{M}_n\ exp = 11,500$  g.mol<sup>-1</sup>,  $\bar{D} = 1.06$ , 67% vinyl content, 20% 1,4-trans content and 13% 1,4-cis content). The SEC chromatogram is presented on Figure 2 (red plot).

### 2.3.Polymer characterizations

Polymer molar masses were determined by Size Exclusion Chromatography (SEC) using tetrahydrofuran (THF) as the eluent. Measurements in THF were performed on an Ultimate 3000 system from Thermoscientific equipped with diode array detector DAD. The system also includes a multi-angles light scattering detector MALS and differential refractive index detector dRI from Wyatt technology. Polymers were separated on three G2000, G3000 and G4000 TOSOH HXL gel columns (300 x 7.8 mm) (exclusion limits from 1000 Da to 400 000 Da) at a flow rate of 1 mL/min. Columns temperature was held at 40°C. Presented SEC chromatograms were obtained from the RI detector. For polybutadiene samples, molar masses were determined with the SEC-Multi-Angle Light Scattering using the dn/dc value of polybutadiene equal to 0.124  $\text{ml.g}^{-1}$ .

Liquid-state <sup>1</sup>H NMR (400.2MHz) and <sup>13</sup>C NMR (Inversed gated decoupling, 100.6 MHz, D1 = 10 sec, 4096 scans) spectra were recorded at 298 K on a Bruker Avance 400 spectrometer in CDCl<sub>3</sub>. A detailed description of the method used to determine polybutadiene microstructure is presented on the ESI with an example of typical spectra (Figures S1 and S2).

### 3. Results and discussion

In the first part of this work, butadiene polymerization experiments initiated by a mixture of di-*n*-butylmagnesium and 1 eq. of potassium *tert*-pentoxide were carried out in cyclohexane at 20°C with targeted molar masses equal to  $\bar{M}_{n\ th, Mg} = \bar{M}_{n\ th, ROK} = 10,000\ \text{g}\cdot\text{mol}^{-1}$ .

We have shown in a previous study, for systems based on *sec*-butyllithium / potassium *tert*-pentoxide, that increasing the initiator preformation time (*i.e.* time between active species synthesis and monomer addition) led to reduced initiation efficiency [28]. Accordingly, the influence of this parameter was first investigated for a system di-*n*-butylmagnesium / potassium *tert*-pentoxide ([K] / [Mg] = 1). Polymerization reactions described as experiments with no initiator preformation time were achieved by introducing butadiene in the reaction medium between potassium *tert*-pentoxide and di-*n*-butylmagnesium. Results are presented in Table 1 and [ESI Figure S3](#).

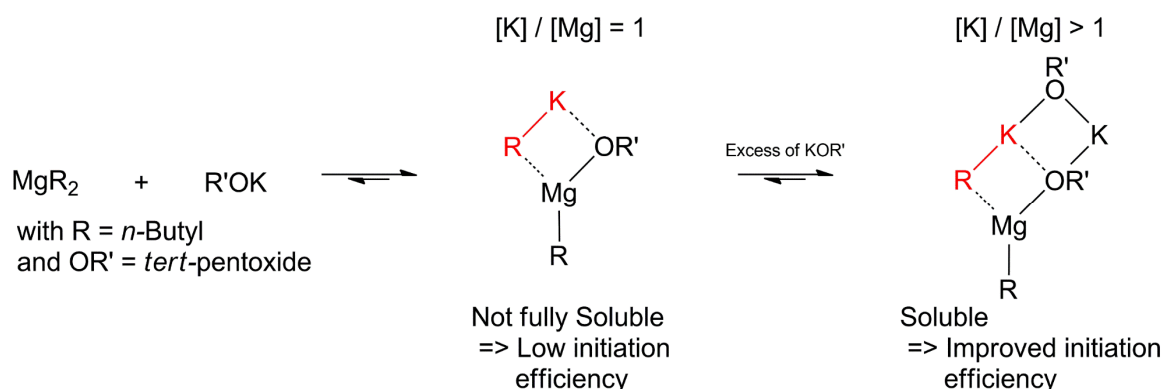
Obtained yields for this system were found to be quantitative within 16 hours. In all cases, obtained molar masses were found to be higher than expected and the calculated initiation efficiency was observed to be ranging from 22 to 30 %. Increasing the initiator preformation time was found to have no influence on initiation efficiency nor polybutadiene microstructure. Such a low initiation efficiency might be related to the lack of solubility of the initiating system in cyclohexane. Obtained polybutadiene microstructures (Table 1), with 50% vinyl content and a 1,4-*cis* / 1,4-*trans* ratio equal to 0.5, are typical of initiation systems based on potassium alone [10] and fairly similar to the one obtained when the initiating system is based on butyllithium + potassium alkoxide ([K] / [Li] = 1) [28], [29].

**Table 1. Influence of the initiator preformation time and of the ratio [K] / [Mg] on butadiene polymerization using di-*n*-butylmagnesium + x eq. of potassium *tert*-pentoxide (1 < x < 4, [butadiene] = 2 mol.L<sup>-1</sup>, [(*n*-Bu)<sub>2</sub>Mg] = 10<sup>-2</sup> mol.L<sup>-1</sup>, cyclohexane, 20°C, 16h, yield = 100%)**

[K] / [Mg]	Preformation time	$\bar{M}_{n\ th,Mg}$ (g.mol <sup>-1</sup> )	$\bar{M}_{n\ th,ROK}$ (g.mol <sup>-1</sup> )	$\bar{M}_n\ exp$ (g.mol <sup>-1</sup> )	$\bar{D}$	1,2 (%)	1,4-cis (%)	1,4-trans (%)
1	None	10,000	10,000	45,000	1.18	50	18	32
1	24h	10,000	10,000	44,000	1.24	48	18	34
1	48h	10,000	10,000	35,000	1.26	50	17	33
2	None	10,000	5,000	9,500	1.20	50	18	32
2.5	None	10,000	4,000	10,000	1.14	50	17	33
4	None	10,000	2,500	9,900	1.18	52	13	37

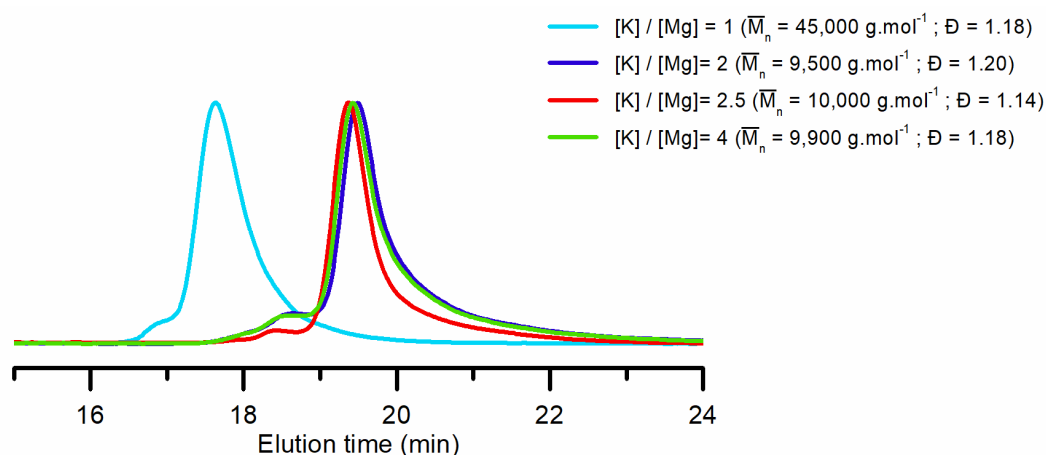
Di-*n*-butylmagnesium alone, as well as potassium *tert*-pentoxide alone, are known to be inactive toward anionic polymerization of styrene or diene. Consequently, it can be assumed that the initiation reaction occurs through ligand exchange between di-*n*-butylmagnesium and potassium *tert*-pentoxide leading to the formation of *n*-butylpotassium moieties. The precise nature of the initiating species is not studied in this experimental work. Nevertheless, one can assume the formation of bi-metallic “ate” complex between potassium alkoxide and dialkylmagnesium (Scheme 1) or the formation of free alkylpotassium moieties. In a previous work, we have demonstrated that in the case of butyllithium + potassium *tert*-pentoxide, the increase of the initiator preformation time decreases the initiation efficiency [28]. This phenomenon was explained through the rapid deactivation of the active species through a hydride elimination leading to potassium hydride moieties (not soluble in cyclohexane and therefore not active in anionic polymerization). Experiments conducted with dialkylmagnesium rather than alkyllithium showed a different behavior, since obtained molar masses are not affected by the initiator preformation time. To explain such a different behavior we can postulate that the “ate” complex formed by R<sub>2</sub>Mg + ROK is a lower basicity complex, with respect to the one formed by RLi + ROK, and consequently more efficient to stabilize the newly formed alkyl potassium moieties and preventing its deactivation. Polymerization control is not achieved, and such a low initiation efficiency is believed to be related the lack of solubility of the initiating “ate” complex at [K] / [Mg] = 1.





**Scheme 1. Suggested mechanism for the initiator formation from di-*n*-butylmagnesium and potassium *tert*-pentoxide.**

To better understand factors having an influence on polymer chain length and polybutadiene microstructure, the influence of  $[\text{K}] / [\text{Mg}]$  (ranging from 1 to 4) was assessed. As discussed before, the initiator preformation time was observed to have no influence on polymerization control nor on polybutadiene microstructure. Following experiments were made without initiator preformation. Obtained results are presented in Table 1 and Figure 1. A shoulder can be observed on the high molar mass side which can be related to oxygen coupling during the termination step [10]. When the ratio  $[\text{K}] / [\text{Mg}] = 2$ , the experimental molar mass is close to the targeted one with the hypothesis of one polymer chain per dialkylmagnesium moieties. Increasing the amount of potassium alkoxide was found to have no further influence on polymerization control indicating that the amount of dialkylmagnesium moieties define the polymer chain length. Similar results were observed and same conclusions were made for  $[\text{K}] / [\text{Mg}] = 2.5$  and 4. All dispersities were ranging from 1.14 to 1.20. This set of experiments tend to demonstrate that polymerization control is achieved when  $[\text{K}] / [\text{Mg}] \geq 2$ , with a polymer chain length defined by the initial amount of dialkylmagnesium moieties. Additional complexation of the so-formed “ate” complex with potassium *tert*-pentoxide is believed to enhance the solubility of the initiating species and consequently the initiation efficiency (Scheme 1). Obtained polymer at  $[\text{K}] / [\text{Mg}] \geq 2$  were found to have a vinyl content equal to 50% and a 1,4-cis / 1,4-trans ratio around 0.5.  $[\text{K}] / [\text{Mg}]$  has a minor influence on polybutadiene microstructure, since the nature of the counterion remains potassium (carbon – magnesium bonds are not active toward anionic polymerization of butadiene).



**Figure 1.** SEC chromatograms of polybutadienes obtained using various [*tert*-PeOK] / [(*n*-Bu)<sub>2</sub>Mg], (No preformation time, cyclohexane, 20°C,  $\bar{M}_{nth} = 10,000 \text{ g.mol}^{-1}$ ).

A straightforward way to further increase the vinyl content of the obtained polymer is by using sodium *tert*-pentoxide rather than potassium *tert*-pentoxide. In apolar media, the ability of sodium-based systems to provide polybutadiene with a higher 1,2 content than potassium based one is reported for many initiation systems. For instance, butadiene polymerization initiated by metallic sodium (bulk) is reported to produce a polymer with 62% 1,2 content, while potassium metal produced polymers with 45% vinyl content [30]. A bimetallic system based on *n*-butyllithium + 1 eq. of sodium *tert*-butoxide in cyclohexane at 30°C is reported to produce polybutadiene with 68% vinyl content, while using potassium *tert*-butoxide (same conditions) led to polybutadiene with 50% vinyl unsaturation [23]. To explain the behavior of organosodium compounds in apolar media, Arest-Yakubovich suggested that the main propagating species is aggregated rather than unassociated [9].

Like in the case of potassium alkoxide-based system, the bi-metallic initiator was generated *in situ* for this study starting from di-*n*-butylmagnesium and sodium *tert*-pentoxide. Experiments conducted at 20°C with no preformation time were found to produce polybutadiene with a low yield (< 10 %) and obtained samples were not further analyzed. Such a low yield is believed to be the consequence of a slow propagation rate. Looking at systems based on BuLi + *x* eq. *t*-BuOMt (Mt = Na, K, Rb, Cs and  $0 \leq x \leq 1$ ) studied by Hsieh and Wofford [31] and applied to butadiene polymerization in cyclohexane at 30°C, propagation rate were shown to depend on the nature of the metal (alkoxide) added. Polymerization rate using BuLi + 1 eq. *t*-BuONa is increased by a factor 8 with respect to BuLi alone, and a factor 20 when using BuLi

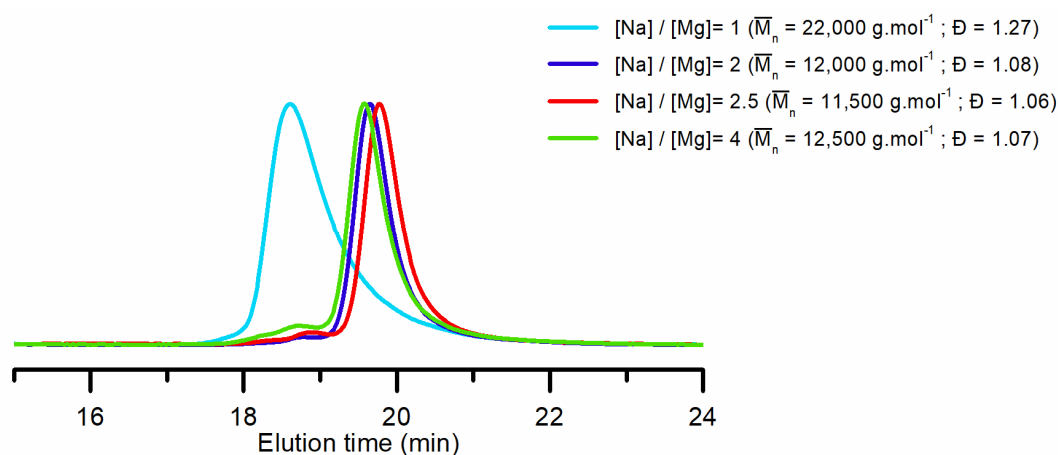
+ 1 eq. *t*-BuOK. This phenomenon was attributed to counterion shifting from Li ( $x = 0$ ) to heavier alkali metal counterion ( $x > 0.5$ ). Since the propagation rate is believed to increase with the ionic character of the C-Mt bond, the expected order of counter-ions reactivity is believed to be  $\text{Li} < \text{Na} < \text{K}$  as the ionic character of C-Mt bond increases. Consequently, following polymerization experiments were conducted at 40°C in cyclohexane with  $[\text{Na}] / [\text{Mg}]$  ratios ranging from 1 to 4. For practical ease, the initiator preformation time was brought up to 1h at 40°C. As the initiation efficiency for potassium-based systems was not shown to depend on time and temperature, this parameter was not investigated. Polymerization reactions were allowed to proceed during 2 days at 40°C, before the addition of degassed methanol. Obtained results are presented on Table 2 and Figure 2.

**Table 1. Influence of the ratio  $[\text{Na}] / [\text{Mg}]$  on butadiene polymerization using di-*n*-butylmagnesium +  $x$  eq. of sodium *tert*-pentoxide ( $1 < x < 4$ , preformation time = 1 h at 40°C,  $[\text{butadiene}] = 2 \text{ mol.L}^{-1}$ ,  $[(n\text{-Bu})_2\text{Mg}] = 10^{-2} \text{ mol.L}^{-1}$ , cyclohexane, 40°C, 48h, yield = 100%)**

$[\text{Na}] / [\text{Mg}]$	$\bar{M}_{n\text{ th,Mg}}$ (g.mol <sup>-1</sup> )	$\bar{M}_{n\text{ th,RONa}}$ (g.mol <sup>-1</sup> )	$\bar{M}_n\text{ exp}$ (g.mol <sup>-1</sup> )	$\bar{D}$	1,2 (%)	1,4-cis (%)	1,4-trans (%)
1	10,000	10,000	22,000	1.27	60	19	21
2	10,000	5,000	12,000	1.08	62	16	23
2.5	10,000	4,000	11,500	1.06	67	13	20
4	10,000	2,500	12,500	1.07	69	11	20

Yields were found to be quantitative after 48h at 40°C, suggesting a slower propagation rate for Mg / Na systems as compared to Mg / K ones. This might be related to the formation of a lower basicity/nucleophilicity complex with a sodium additive. When  $[\text{Na}] / [\text{Mg}] = 1$ , the obtained polymer was found to have a molar mass twice higher than the expected one, and the initiation efficiency was calculated to be equal to 45%. When  $[\text{Na}] / [\text{Mg}] \geq 2$ , obtained polymers were observed with molar masses close to the targeted one with narrow molar mass distributions. Such a behavior indicates that the amount of di-*n*-butylmagnesium involved in the polymerization reaction determine again the polymer chain length. In terms of polybutadiene microstructure, obtained polymers had a vinyl content ranging from 60% to 69% and a 1,4-cis / 1,4-trans content ranging from 1 to 0.5, which is similar to reported

polybutadiene microstructure with sodium as the counterion [7], [10]. Like in the case of Mg / K based systems, polybutadiene microstructure is found to depend on the nature of the counterion of the alkoxide moieties. Increasing the amount of sodium *tert*-pentoxide was observed to increase the vinyl content of the obtained polymer; the 1,4-trans content was barely affected and the 1,4-cis / 1,4-trans ratio dropped down from 1 to 0.5. Increasing [Na] / [Mg] ratio is believed to increase aggregation number of the propagating centers which might be the consequence of the observed influence of [Na] / [Mg] on the vinyl content and on the 1,4-cis / 1,4-trans ratio. The observed behavior is quite different from the one observed with potassium *tert*-pentoxide, where [K] / [Mg] was observed to have no influence on the obtained microstructure. This difference is probably related to a lower ionic radius of sodium counterion enabling a higher aggregation number of the propagation chain end. This increased bulkiness of the propagation chain end may influence the conformation of the last unit of the growing chain, until the following nucleophilic attack, favoring the formation of polymer with a higher vinyl content. In other words, magnesium-based systems allow to yield controlled polybutadienes with specific vinyl contents simply by changing the nature of the alkoxide moieties and without using alkyllithium derivatives.



**Figure 2.** SEC chromatograms of polybutadienes obtained using various [*tert*-PeONa] / [(*n*-Bu)<sub>2</sub>Mg], (Preformation time = 1h at 40°C, cyclohexane, 40°C,  $\bar{M}_{n\text{ th}}$ ,  $M_g = 10,000 \text{ g.mol}^{-1}$ ).

## 4. Conclusion

In hydrocarbon media, an initiating system based on di-*n*-butylmagnesium + 1 eq. of potassium *tert*-pentoxide was found to be able to produce a polybutadiene with 50% vinyl content with a low initiation efficiency (30 – 40%). When the ratio  $[K] / [Mg] \geq 2$ , polymerization control is achieved in all cases with a dispersity ranging from 1.14 and 1.2. Obtained polybutadiene microstructures are typical of systems with potassium as the counterion (50% vinyl, 1,4-cis / 1,4-trans  $\approx 0.5$ ) and the ratio  $[K] / [Mg]$  was found to have no influence on it. By using such an initiating species, the formation of a carbon – potassium bound is believed to be responsible of the anionic polymerization. Substituting potassium alkoxide by sodium alkoxide was also found to achieve polymerization control for  $[Na] / [Mg] \geq 2$ . To some extent, the ratio  $[Na] / [Mg]$  was found to have an influence on polybutadiene microstructure, since increasing this ratio from 1 to 4 leads to an increased vinyl content from 60% to 69 %.

Bi-metallic initiating systems, based on readily available compounds and without using alkyllithium, allow butadiene anionic polymerization in apolar media in a controlled way (unlike polymerization directly initiated by organosodium or organopotassium derivatives) with a vinyl content ranging from 50 to 69 %.

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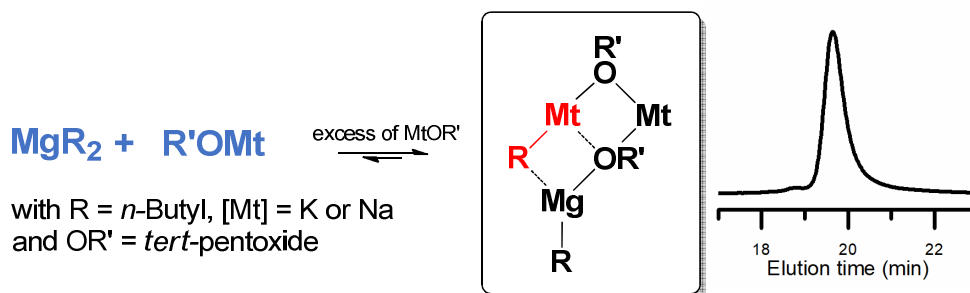
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## GRAPHICAL ABSTRACT

### BUTADIENE ANIONIC POLYMERIZATION (apolar solvent)



- Polymerization control
- 1,2 content controlled by the counter-ion
- 50% < 1,2 content < 70%
- AlkylLi initiator- free