

Anionic Polymerization of Butadiene Using Lithium/Potassium Multi-metallic Systems: Influence on Polymerization Control and Polybutadiene Microstructure

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 Electronic Supplementary Information

Abstract Thermal, mechanical, and viscoelastic properties of polybutadiene-based rubber materials are highly dependent on polybutadiene microstructure. The use of polar modifier in association with alkyllithium is a well-known method to obtain polybutadiene with a high vinyl content. Another approach is to use bimetallic initiating species such as alkyllithium combined to heavier alkali metal alkoxide (RONa, ROK...). The polymerization control is nevertheless not achieved and several parameters were found to influence it. Using bimetallic initiating systems based on alkyllithium and a potassium alkoxide, alkyllithium structure, initiator preformation time, and initiator composition were identified as parameters influencing the anionic polymerization process of butadiene and/or polybutadiene microstructure. In addition, the use of trimetallic systems based on alkyllithium, potassium alkoxide, and alkylaluminum was investigated in order to prevent side reactions regardless of the [K]/[Li] ratio and of the initiator preformation time.

Keywords Polybutadiene; Anionic polymerization; Microstructure; (Multi)metallic systems; Lithium/potassium-based systems

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INTRODUCTION

Butadiene polymerizes with three different isomeric units along the polymer chain (namely 1,4-*cis*, 1,4-*trans*, and 1,2). Each one of these polymeric structures has its own physical properties and controlling polybutadiene microstructure allows a fine tuning of its mechanical and thermal properties.^[1] For instance, polybutadiene with a high 1,4 content tends to have a glass transition temperature about –110 °C while polybutadiene with a high 1,2 content exhibits a glass transition temperature about –10 °C.^[2] Accordingly, polybutadiene microstructure and in particular the control of the 1,4/1,2 ratio can be seen as a useful tool to tune polybutadiene properties similarly to what can be achieved by copolymerization of butadiene with styrene.

A method to tune the microstructure consists of using polar modifiers^[3–7] or polar solvents^[8–10] during the polymerization process. Another approach is to use multi-metallic systems.

The reaction products between alkyllithium and alkali metal alkoxides referred as “super-base” or Lochmann-Schlosser base are used to metalate a wide range of organic substrates

(e.g. benzene, toluene, ethylbenzene...),^[11–14] Such systems were also proven to be able to polymerize styrene and butadiene,^[15–18] and the one-pot/one-step copolymerization of styrene and butadiene initiated by *n*-BuLi + ROMt (Mt = Na, K, Rb, Cs) was reported to produce random copolymers without block segregation.^[19] In terms of microstructure, the general trend for heavy alkali metal alkoxides in association with *n*-butyllithium is an increase of vinyl content with the ratio [ROMt]/[RLi]. When this ratio is equal to or higher than 1, polybutadiene microstructure tends to be the same one as for polybutadiene made with the corresponding alkyl metal initiator (< 10% for Li, 68% vinyl for Na, 50% for K, 55% for Rb, and 51% for Cs).^[15]

Applying the ratio [potassium *tert*-pentoxide]/[*n*-butyllithium] > 1, Halasa and coworkers reported the formation of polybutadiene with a hexane soluble fraction and a hexane insoluble one; the soluble fraction was identified as polybutadiene with 50% vinyl units and a broad dispersity ($\bar{M}_w/\bar{M}_n > 1.3$) while the insoluble one was said to be high 1,4-*trans* polybutadiene.^[17] Using toluene with similar ratios, Yakubovich reported the formation of soluble polybutadiene with a high vinyl content (40%), and a small insoluble fraction was also observed but not analyzed.^[18]

In this research work we focused on multi-metallic initiating species based on a potassium alkoxide and alkyllithium in

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apolar media with the objective to identify the experimental parameters that can achieve polymerization control with a high vinyl content microstructure. To better understand the initiation mechanisms, styrene was used when needed as a model monomer.

EXPERIMENTAL

Materials

sec-Butyllithium (1.4 mol·L⁻¹ in cyclohexane), triisobutylaluminum (25 wt% in toluene), and *n,s*-dibutylmagnesium (0.7 mol·L⁻¹ in hexane) were obtained from Aldrich and used as received. 2-Methyl-2-butanol (99%, Aldrich) was dried over freshly crushed CaH₂ and distilled off prior to use. Potassium chunks (98% in mineral oil, Aldrich) were stored in an argon filled glovebox, and mineral oil was removed through cyclohexane washing prior to use. Styrene (99%, Fisher) was dried over calcium hydride, stored over *n,s*-dibutylmagnesium, and freshly distilled prior to use. Butadiene (99.6%, Aldrich) was dried over CaH₂ for 1 h, distilled off, and stored in a high-pressure glass burette. Cyclohexane (VWR) was dried over freshly crushed calcium hydride (Acros, 93%) and stored over polystyryllithium seeds.

Potassium *tert*-pentoxide (*tert*-PeOK), also called *tert*-amyl-oxide (*t*-AmOK), was obtained through the reaction of dry 2-methyl-2-butanol (1 mL) and an excess of potassium metal 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). Concentration was assessed by hydrolysis of an aliquot (1 mL) followed by titration with HCl using phenolphthalein as an indicator. Potassium *tert*-pentoxide solutions were stored at room temperature over a chunk of potassium (remaining from the initial excess of potassium).

Polymerizations

For all experiments the targeted molar mass was calculated as follow: $\bar{M}_{n,th} = m_{monomer}/n_{RLi} = (C_{monomer} \times M_{butadiene})/C_{BuLi}$.

A typical experimental process to obtain polybutadiene with an initiator composed of *sec*-butyllithium and 1 equiv. 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 (9.5 mL), under vacuum, through connected glass tubes. Potassium *tert*-pentoxide solution (580 µL of a 0.18 mol·L⁻¹ solution in cyclohexane) was added *via* a syringe under an argon flow. Butadiene (1.04 g, 1.92×10^{-2} mol) was then vacuum distilled into the reaction apparatus. *sec*-Butyllithium (75 µL of a 1.4 mol·L⁻¹ solution in cyclohexane) was then added *via* a syringe under an argon flow into the reaction apparatus. Reaction was allowed to proceed for 16 h 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 overnight. The polymer was then weighed to determine the yield and analyzed ($\bar{M}_{n,theo} = 1.0 \times 10^4$ g·mol⁻¹, yield = 100%, $\bar{M}_{n,exp} = 1.2 \times 10^4$ g·mol⁻¹ from polystyrene calibration after application of a corrective factor equal to 0.52, $\bar{D} = 1.03$, 42% vinyl content, 40% 1,4-*trans* content, and 18% 1,4-*cis*

content). The SEC chromatogram is presented in Fig. S1 (in the electronic supplementary information, ESI, grey plot) and obtained ¹H- and ¹³C-NMR spectra are presented in Figs. S3 and S4 (in ESI).

A typical experimental process to obtain polystyrene with an initiator composed of *sec*-butyllithium and 0.5 equiv. of potassium *tert*-pentoxide with 1 h of 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. Then, 7 mL of dry cyclohexane was added under vacuum through connected glass tubes. Potassium *tert*-pentoxide solution (211 µL of a 0.18 mol·L⁻¹ solution in cyclohexane) and *sec*-butyllithium (55 µL of a 1.4 mol·L⁻¹ solution in cyclohexane) were added *via* a syringe under an argon flow into the reaction apparatus. This solution was kept at 20 °C for 1 h before vacuum distillation of styrene (0.76 g, 7.3×10^{-3} mol) into the reaction apparatus. Polymerization was allowed to proceed for 16 h 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 before being weighed and analyzed ($\bar{M}_{n,theo} = 1.0 \times 10^4$ g·mol⁻¹, yield = 100%, $\bar{M}_{n,exp} = 1.4 \times 10^4$ g·mol⁻¹ from polystyrene calibration, $\bar{D} = 1.3$). The SEC chromatogram is presented in Fig. 1 (green plot).

Experiments involving triisobutylaluminum were conducted in a similar way. For instance, the experimental process with trimetallic initiators composed of *sec*-butyllithium, 5 equiv. of potassium *tert*-pentoxide, and 1 equiv. of triisobutylaluminum can be depicted as follow. A glass reactor of 50 mL, equipped with a magnetic stirrer and fitted with PTFE stopcocks, was flame dried under vacuum. Then, 13 mL of dry cyclohexane was added under vacuum through connected glass tubes. Potassium *tert*-pentoxide solution (3.5 mL of a 0.18 mol·L⁻¹ solution in cyclohexane), triisobutylaluminum (125 µL of a 25 wt% solution in toluene), and *sec*-butyllithium (90 µL of a 1.4 mol·L⁻¹ solution in cyclohexane) were added to

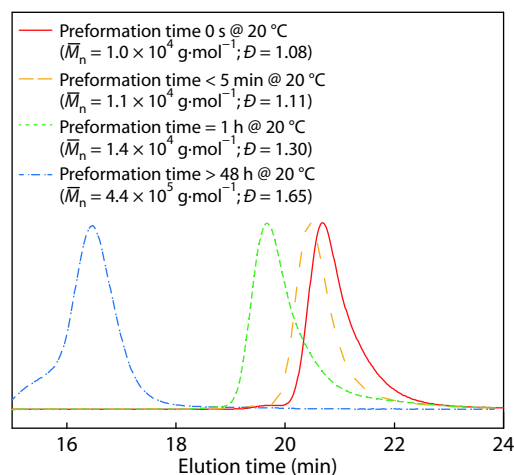


Fig. 1 SEC chromatograms of polystyrene synthesized using *sec*-butyllithium plus 0.5 equiv. of potassium *tert*-pentoxide with various initiator preformation time in cyclohexane at 20 °C ([styrene] = 1 mol·L⁻¹, [sec-BuLi] = 10^{-2} mol·L⁻¹, $\bar{M}_{n,theo} = 1.0 \times 10^4$ g·mol⁻¹, 16 h, yield = 100%).

the reaction medium *via* syringes under an argon flow. This solution was kept at 20 °C for 24 h before vacuum distillation of butadiene (1.18 g, 2.18×10^{-2} mol) into the reaction apparatus. Polymerization was allowed to proceed for 16 h 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 before being weighed to determine yield and analyzed ($\bar{M}_{n,theo} = 9300 \text{ g}\cdot\text{mol}^{-1}$, yield = 100%, $\bar{M}_{n,exp} = 9500 \text{ g}\cdot\text{mol}^{-1}$ from polystyrene calibration after application of a corrective factor equal to 0.52, $\bar{D} = 1.09$, 56% vinyl content, 32% 1,4-*trans* content, and 13% 1,4-*cis* content). The SEC chromatogram is presented in Fig. S2 (in ESI, orange plot).

Polymer Characterization

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 a 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 ($300 \times 7.8 \text{ mm}$) (exclusion limits from 1000 Da to $4.0 \times 10^5 \text{ Da}$) at a flow rate of $1 \text{ mL}\cdot\text{min}^{-1}$. Column temperature was held at 40 °C. Presented SEC chromatograms in this paper and in ESI were obtained from the RI detector. In the case of polystyrene samples, molar masses were determined using polystyrene calibration. For polybutadiene samples, molar masses were determined using polystyrene calibration with application of a corrective factor equal to 0.52. Obtained molar masses with this method were found to be consistent with the ones obtained with the SEC-Multi-Angle Light Scattering using the dn/dc value of polybutadiene equal to 0.124.

Liquid-state ^1H -NMR (400.2 MHz) and ^{13}C -NMR (Inversed gated decoupling, 100.6 MHz, $D_1 = 10 \text{ s}$, 4096 scans) spectra were recorded at 298 K on a Bruker Avance 400 spectrometer in CDCl_3 . A detailed description of the method used to determine polybutadiene microstructure is presented in ESI with an example of typical spectra (Figs. S3 and S4 in ESI).

RESULTS AND DISCUSSION

Since the formation of active species requires the reaction between two organometallic compounds, and to assess the possibility of the initiator solution storage, the influence of the preformation time on polymerization control was first investigated (time between active species synthesis and monomer addition, *i.e.* initiator ageing at 20 °C before the polymerization). As shown in the literature, the reaction between different compounds may take several hours before formation of a complex at the equilibrium. As an example, Desbois and coworkers showed that a system composed of polystyryllithium plus 0.9 equiv. of triisobutylaluminum needs

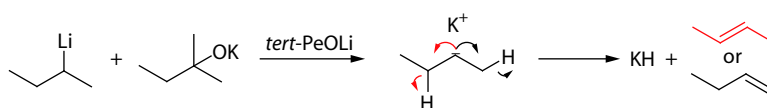
up to 15 h at 50 °C in cyclohexane to afford the bimetallic complex.^[20] Preliminary experiments with butadiene initiated by *sec*-butyllithium plus 0.5 equiv. of potassium *tert*-pentoxide led to the formation of uncontrolled high molar mass polybutadienes, with evidences of side reactions. Since styrene polymerization was found to be not subjected to side reactions, this monomer was chosen as a model compound to assess the influence of the initiator preformation time/ageing on polymerization control. For this set of experiments, styrene was used as the monomer, cyclohexane as the solvent, and a mixture of *sec*-butyllithium and 0.5 equiv. of potassium *tert*-pentoxide (*tert*-PeOK) was used as initiator (mixed *in situ* for each experiment since the so-formed organometallic system is poorly soluble in cyclohexane). Experiments with no preformation time were performed by introducing the monomer between the addition of potassium *tert*-pentoxide and *sec*-butyllithium. In all cases, styrene polymerization experiments were carried out with a targeted molar mass of $1.0 \times 10^4 \text{ g}\cdot\text{mol}^{-1}$ with the hypothesis of one polymer chain per alkyl lithium molecule.

As shown in Fig. 1, molar masses are in good agreement with the targeted ones when the initiator preformation time is below 1 h showing that the initial amount of *sec*-butyllithium controls the polymer chain length. However, for longer preformation time, increased molar mass and broader distributions are observed, and polymerization control is not achieved anymore. This may be due to the loss of active centers and slow initiation rate with respect to the propagation one.

The reaction between potassium *tert*-butoxide and *n*-butyllithium ($[\textit{t}\text{-BuOK}]/[\textit{n}\text{-BuLi}] < 1$) is reported in the scientific literature to produce a precipitate composed of *n*-butyllithium-*n*-butylpotassium adducts, free of so-formed lithium alkoxide moieties (which remain in solution).^[21] A tail is generally observed on the low molar mass region and can be attributed to a slow initiation step from *sec*-butyllithium with respect to the initiation by *sec*-butylpotassium moieties. As only one polystyrene population is observed, a fast counterion exchange between polystyrylpotassium and polystyryllithium chain ends can be suggested.

As said before, when potassium *tert*-pentoxide and *sec*-butyllithium are let to react together before addition of styrene, molar mass control is not achieved anymore. This is believed to be linked to a progressive deactivation of the active species resulting in a molar mass increase. It might be related to the reported side reaction specific to superbases leading to the formation of potassium hydride, which is not soluble in cyclohexane and therefore not active in anionic polymerization (Scheme 1).^[21]

A set of experiments conducted in similar conditions with $[\text{K}]/[\text{Li}] = 5$ show the same behavior regarding the loss of initiation efficiency when the initiator preformation time is long. As for the initiation and propagation mechanisms, one can assume the formation of a bimetallic complex composed of *sec*-



Scheme 1 Hypothetic mechanism for the formation of potassium hydride upon degradation of *sec*-butylpotassium.

butyllithium and *sec*-butylpotassium moieties or the formation of multi-metallic adduct involving alkali metal alkoxide along with alkyllithium and alkylpotassium.

Knowing that initiator preformation disrupts polymerization control, the influence of the ratio $[K]/[Li]$ on butadiene polymerization was assessed without initiator preformation time. In each case, the theoretical molar mass was calculated with the hypothesis of one polymer chain per alkyllithium moiety.

In all cases for $[K]/[Li] \leq 1$, polymerization occurs and obtained molar masses are in good agreement with the targeted ones and the initial amount of alkyllithium controls the polymer chain length. For $[K]/[Li] = 0.1$, polybutadiene vinyl content is slightly increased (14%) with respect to polybutadiene obtained with alkyllithium alone (7%) (Table 1 and Fig. S1 in ESI). When $0.25 \leq [K]/[Li] \leq 1$, the vinyl content ranges from 40% to 50%, which is typical for potassium-based systems in apolar media.^[22] Meanwhile, the 1,4-*cis*/1,4-*trans* ratio decreases while increasing $[K]/[Li]$ ratio in the initiator, meaning that the formation of 1,4-*trans* units is favored with respect to the formation of 1,4-*cis* content (keeping a high vinyl content). In the case of alkyllithium in apolar media, obtained 1,4-*cis*/1,4-*trans* ratio mainly depends on the competition between the isomerization rate (between the 1,4-*cis* and the 1,4-*trans* chain end configuration) and the propagation rate.^[22,23] Based on the collected data in this work, we cannot go further in that direction.

Table 1 Polymerization of butadiene using *sec*-butyllithium and *x* equiv. of potassium *tert*-pentoxide ($0 \leq x \leq 5$, no initiator preformation, $M_{n,theo} = 1.0 \times 10^4$ g·mol⁻¹, [butadiene] = 2 mol·L⁻¹, [sec-BuLi] = 10^{-2} mol·L⁻¹, cyclohexane, 20 °C, 16 h, yield = 100%).

$[K]/[Li]$	$\bar{M}_{n,exp}^a \times 10^{-4}$ (g·mol ⁻¹)	$\bar{D}$	1,2 Content (%)	1,4- <i>cis</i> Content (%)	1,4- <i>trans</i> Content (%)
0	1.2	1.05	7	41	52
0.1	1.1	1.02	14	37	49
0.35	1.1	1.01	44	19	35
0.7	1.2	1.03	41	21	38
1	1.2	1.03	42	18	40
5	0.65	2.21	49	14	37

^a Determined by SEC after application of the following equation: $\bar{M}_{n,exp} = \bar{M}_{n,RI} \times 0.52$ where $\bar{M}_{n,RI}$ is obtained from a polystyrene calibration.

Systems based on *n*-butyllithium associated with *x* equiv. potassium *tert*-pentoxide ($x > 1$) were reported to metalate polybutadiene backbone and then to initiate anionic polymerization from it.^[24] When potassium alkoxide is used in large excess ($[K]/[Li] = 5$), a broad polymer chain distribution ($\bar{D} = 2.21$) is obtained, and accordingly, we can make the assumption that it is the consequence of chain transfer to the polymer backbone due to the high reactivity of K moieties. Terminated chains and branched polymers can be the consequence of the metalation reaction.

A set of experiments using polystyryllithium seeds rather than *sec*-butyllithium in association with potassium *tert*-pentoxide was then performed in cyclohexane at 20 °C. Changing the alkyllithium nature was expected to improve the solubility of initiating species and/or to prevent its deactivation upon standing.

For initiating systems based on polystyryllithium seeds plus

5 equiv. of potassium *tert*-pentoxide, the bimetallic initiator remains soluble even if it is kept for 16 h at 20 °C. Styrene polymerization control is achieved and is not susceptible to the initiator preformation time (Fig. 2). Deactivation of the initiator does not occur unlike in the case of alkyllithium/potassium *tert*-pentoxide based systems. The concentration of active species remains constant with time and can be the consequence of initiator stabilization through mesomeric effect on the last unit and/or by the solubility of the initiating species.

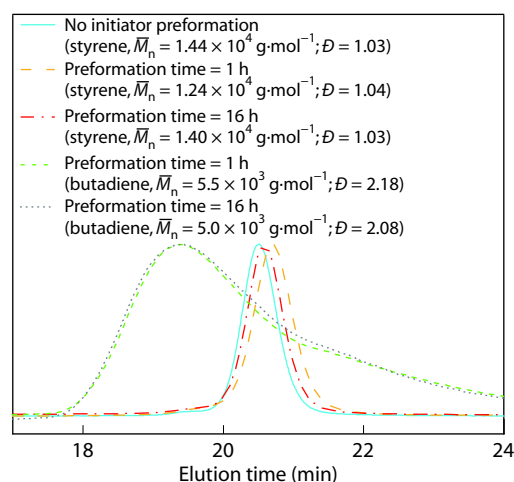


Fig. 2 SEC chromatograms of polymers synthesized using PSLi seeds plus 5 equiv. potassium *tert*-pentoxide with various preformation time in cyclohexane at 20 °C ([PSLi] = 10^{-2} mol·L⁻¹, 16 h, yield = 100%).

On the contrary, experiments conducted on butadiene polymerization with polystyryllithium seeds in association with 5 equiv. of potassium *tert*-pentoxide show a monomodal and broad distribution with $\bar{D} > 2$ (Fig. 2). The initiator preformation time does not have any influence on the polymerization control. However, a tail can be observed in the low molar mass region in all cases, as also observed for polybutadiene produced with *sec*-butyllithium plus 5 equiv. of potassium *tert*-pentoxide. Obtained microstructures are typical for potassium-based initiation systems with 54% vinyl content, which suggests that the carbon-potassium species is responsible for the polymerization. Like in the case of *sec*-butyllithium associated with 5 equiv. of potassium *tert*-pentoxide, large dispersity tends to suggest that chain transfer to the polymer backbone occurred, leading to branching through metalation of the polymer backbone and subsequent reactions.

Even if the nature of the chain end remains unclear, polybutadiene microstructure with bimetallic systems is typical for potassium-based systems, and a potassium-carbon bond seems to be responsible for the propagation step. Two hypotheses can be envisaged to explain this increasing amount of 1,2-units. (i) While the carbon-lithium bond is usually considered as localized on the α position of the last unit favoring the obtention of low vinyl content polybutadiene in apolar media,^[22] the carbon-potassium bond is considered as a dissociated ion-pair due to the larger ionic radius of potassium. Accordingly, it can be assumed that potassium counter-ion is

preferentially π -bonded to the last unit of polybutadienylpotassium and consequently favors the formation of 1,2 units. Even if butadienylpotassium is aggregated or complexed (by alkali metal alkoxide), the dissociating character of the ion-pair seems to be preserved. (ii) Coordination of the monomer by potassium alone or complexed could also be envisaged and might play a role in monomer position before the nucleophilic attack and consequently affect polybutadiene microstructure.

Another way to prevent side reactions and molar mass broadening was studied by using a tri-metallic initiating system. The addition of triisobutylaluminum to *sec*-butyllithium/potassium *tert*-pentoxide initiating systems was attempted for butadiene polymerization. The objective is the formation of aluminate complexes at the chain end might modify the electronic environment of the propagating center and reduce its reactivity.

For this set of experiments, the influence of the initiator preformation time was first investigated with the system $[K]/[Li] = 5$ and $[Al]/[Li] = 0.5$ in cyclohexane at 20 °C. Potassium *tert*-pentoxide was added first to the reaction medium, followed by triisobutylaluminum and then *sec*-butyllithium. Unlike for bimetallic systems where no preformation time is mandatory to achieve polymerization control, this set of experiments with a trimetallic system shows that a long preformation is required to achieve polymerization control (Fig. 3). A shoulder can be observed in the high molar mass region, and can be attributed to oxygen coupling.

A second set of butadiene polymerizations was performed with $[tert\text{-}PeOK]/[sec\text{-}BuLi] = 5$ while $[i\text{-}Bu_3Al]/[sec\text{-}BuLi] = 0.5$, 1, or 3.5 in cyclohexane with 24 h preformation time to assess the influence of $[Al]/[Li]$ on polymerization control and polybutadiene microstructure. One can note that $[Al]/([K] + [Li])$ is always below 1, and accordingly, the formation of 1:1 inactive aluminate complex is not expected.^[25] Increasing the triisobutylaluminum content in this trimetallic systems for butadiene polymerization clearly improves the polymerization control and much lower dispersities are obtained in particular when compared to bimetallic systems with $[K]/[Li] = 5$ (Table 2 and Fig. S2 in ESI). No shoulder is observed when $[Al]/[Li] = 1$ or 3.5. Microstructure remains typical of potassi-

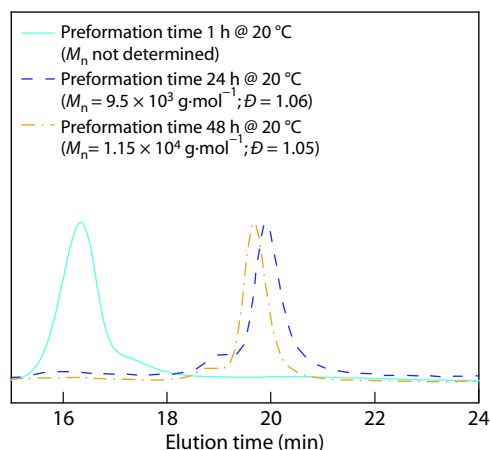


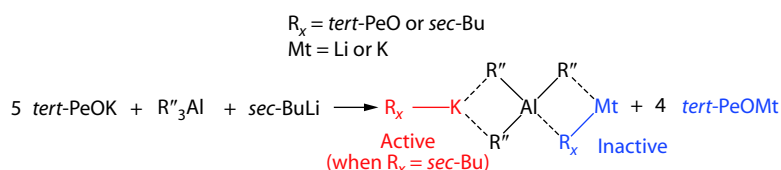
Fig. 3 Influence of the initiator preformation time on SEC chromatograms of polybutadiene synthesized using $[tert\text{-}PeOK]/[sec\text{-}BuLi] = 5$ and $[i\text{-}Bu_3Al]/[sec\text{-}BuLi] = 0.5$ ($[butadiene] = 2 \text{ mol}\cdot\text{L}^{-1}$, $[sec\text{-}BuLi] = 10^{-2} \text{ mol}\cdot\text{L}^{-1}$, $\bar{M}_{n,th} = 1.0 \times 10^4 \text{ g}\cdot\text{mol}^{-1}$, cyclohexane, 20 °C, 16 h, yield = 100%).

um-based initiators with high vinyl content, indicating that polymerization is still occurring inside a carbon-potassium bond. These observations can be explained through complete complexation of alkylpotassium moieties in a lower basicity complex thanks to the trialkylaluminum compound preventing side reactions. A mechanism pathway for the formation of the initiating complex is proposed in Scheme 2. An increased value of 1,2 vinyl content from 56% to 67% is also noticed when the $[Al]/[Li]$ ratio goes from 1 to 3.5. The stoichiometry of aluminum-complexed alkylpotassium appears as a tool to modify the 1,4/*cis*/1,4-*trans* ratio of the obtained polybutadiene. One can also note that the addition of the aluminum compound has no effect on the 1,4-*cis*/1,4-*trans* ratio ($0.38 < 1,4\text{-}cis/1,4\text{-}trans < 0.44$) which remains similar to the one obtained for the bimetallic system (0.38 when $[K]/[Li] = 5$). The increase of vinyl content when triisobutylaluminum is used might be the consequence of a new electronic environment and/or steric hindrance due to the complexation of living chain end.

Table 2 Polymerization of butadiene using *sec*-butyllithium associated with 5 equiv. of potassium *tert*-pentoxide and x equiv. of triisobutylaluminum ($0 \leq x \leq 3.5$, preformation time = 24 h, $[butadiene] = 2 \text{ mol}\cdot\text{L}^{-1}$, $[sec\text{-}BuLi] = 10^{-2} \text{ mol}\cdot\text{L}^{-1}$, cyclohexane, 20 °C, 16 h).

$[K]/[Li]$	$[Al]/[Li]$	$\bar{M}_{n,theo} \times 10^{-4} (\text{g}\cdot\text{mol}^{-1})$	$\bar{M}_{n,exp}^a \times 10^{-4} (\text{g}\cdot\text{mol}^{-1})$	$\bar{D}$	1,2 Content (%)	1,4- <i>cis</i> Content (%)	1,4- <i>trans</i> Content (%)
5	0	1.0	0.50	2.5	54	14	32
5	0.5	0.90	0.85	1.21	53	14	33
5	1	0.93	0.95	1.09	56	13	32
5	3.5	1.0	1.02	1.11	67	9	24

^a Determined by SEC after application of the following equation: $\bar{M}_{n,exp} = \bar{M}_{n,RI} \times 0.52$ where $\bar{M}_{n,RI}$ is obtained from a polystyrene calibration.



Scheme 2 Proposed mechanism for the formation of the initiating complex with *sec*-butyllithium, potassium *tert*-pentoxide, and triisobutylaluminum ($[K]/[Li] = 5$ and $[Al]/[Li] = 1$).

CONCLUSIONS

Bimetallic systems composed of lithium derivatives and a potassium alkoxide were studied and parameters such as $[K]/[Li]$ ratios, preformation time of the initiator, and structure of alkyllithium derivatives were first investigated. Butadiene polymerization control was achieved when no preformation time is allowed and for $[K]/[Li] \leq 1$. The control was lost when increasing K content. To reach again a control, addition of triisobutylaluminum to the bimetallic system was shown effective, even with a large excess of potassium alkoxide, and with a microstructure typical for potassium-based systems. Improvements in terms of polymerization control with respect to bimetallic systems were explained through the formation of a lower basicity complex that lowers the reactivity of the active chain end and prevents side reactions. For all cases, addition of potassium alkoxide to alkyllithium initiation systems was found to produce polybutadiene with a high vinyl content (50%). Butadienylpotassium moieties (free or within a complex with alkali metal alkoxide) are believed to be responsible for the nucleophilic attack on butadiene monomers.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <http://dx.doi.org/10.1007/s10118-020-2355-4>.

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