



Tuning polybutadiene microstructure using multi-metallic initiation systems by anionic polymerization

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Par Pierre-Antoine FORENS

**Tuning polybutadiene microstructure using multi-metallic initiation
systems by anionic polymerization**

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Antoine.

Résumé en français

Utilisation de systèmes d'amorçage multi-métalliques pour la polymérisation anionique du butadiène et le contrôle de sa microstructure.

1. Introduction

Le caoutchouc naturel est historiquement le premier élastomère utilisé dans le domaine des pneumatiques. Il est notamment issu de la culture de l'arbre *Hevea brasiliensis*, et il est décrit comme étant composé à 100% d'unités 1,4-cis polyisoprène [1]. Ses propriétés d'intérêt sont notamment la cristallisation sous contrainte, sa faible génération de chaleur lors de la déformation, et sa bonne résistance à la déchirure. Cependant ces propriétés sont sujettes à fluctuation en fonction du climat, de la qualité des sols, et de l'âge de l'arbre. La culture de l'hévéa et la ressource caoutchouc naturel sont également confrontées aux changements climatiques, au risque fongique, et à la compétition avec d'autres cultures comme celle de l'huile de palme, ainsi qu'à la volatilité des prix. Le caoutchouc naturel est notamment utilisé pour les bandes de roulement des pneumatiques pour les poids lourds et les engins de génie civil.

Les caoutchoucs synthétiques sont pétro-sourcés, et sont notamment représentés par le polybutadiène et les copolymères statistiques styrène / butadiène. Ils sont notamment utilisés pour les bandes de roulement des voitures et des motos, en raison des propriétés d'adhérence qu'ils permettent d'obtenir. Leur intérêt réside dans leurs propriétés qui peuvent être ajustées, au moyen de la chimie, afin d'obtenir de nouveaux compromis entre la résistance au roulement et l'adhérence [2], [3]. La résistance au roulement est décrite comme l'écrasement de la bande de roulement du pneumatique à chaque rotation, tandis que l'adhérence provient de la déformation du pneu au contact des rugosités de la route.

La résistance au roulement est une dissipation d'énergie, lors de la déformation, qui n'est pas utile au véhicule. Cette énergie inutilement dissipée sous forme de chaleur, correspond à 20% de la consommation en carburant du véhicule. Ce phénomène doit donc être minimisé [2], [3]. A l'opposé, l'adhérence conduit également à une dissipation d'énergie lors de la déformation qui doit être maximisée car directement corrélée à la performance sécurité du pneumatique et du véhicule. Bien qu'à priori contradictoire, la recherche de compromis entre adhérence et résistance au roulement est possible car les fréquences de sollicitation sont très différentes. En effet, les fréquences de sollicitations liées à la résistance au roulement sont de l'ordre de 100 Hz, alors que celles liées à l'adhérence sont de l'ordre de 10^6 Hz. En vertu de l'équivalence temps – température cela revient à ajuster la température de transition vitreuse des élastomères. Par exemple la macrostructure (distribution des masses molaires, architecture des chaînes et fonctionnalisation) et la microstructure des chaînes polymères sont des leviers pour ajuster la

résistance au roulement, tandis que le taux de styrène (dans le cas de copolymères statistiques styrène / butadiène) et la microstructure du polybutadiène ont un impact sur les propriétés d'adhérence [4]. Dans le cas du polybutadiène, la température de transition vitreuse est de -110°C pour un polybutadiène 100% 1,4-cis, -100°C pour un polymère 100% 1,4-trans et -7°C pour un polymère 100% 1,2 [5].

La polymérisation anionique du butadiène, du fait de son caractère contrôlé et vivant permet l'obtention d'architectures macromoléculaires définies, le contrôle des masses molaires, l'obtention de faibles dispersités, la synthèse de copolymères, ainsi que la fonctionnalisation des bouts de chaînes [6]. Contrairement aux chimies de coordination, la polymérisation anionique ne permet pas l'obtention de polymères avec une microstructure pure. En d'autres termes, la polymérisation anionique du butadiène conduit à des polymères présentant des unités à isoméries variables le long de la chaîne (nommément 1,4-cis, 1,4-trans et 1,2), ce qui permet de contrôler la température de transition vitreuse du matériau obtenu. Ce contrôle de la microstructure s'effectue au moment de la synthèse notamment en ajustant la polarité du milieu réactionnel ou en additionnant des dérivés de métaux alcalins ou alcalino-terreux à un alkyllithium dans les solvants apolaires [7]. L'addition de dérivés de métaux alcalins permet de contrôler le rapport 1,4 / 1,2, tandis que l'addition de dérivés alcalino-terreux permet de faire varier le rapport 1,4-cis / 1,4-trans. Les microstructures du polybutadiène obtenues en polymérisation anionique, et décrites dans la littérature, sont présentées sur la Figure 1.

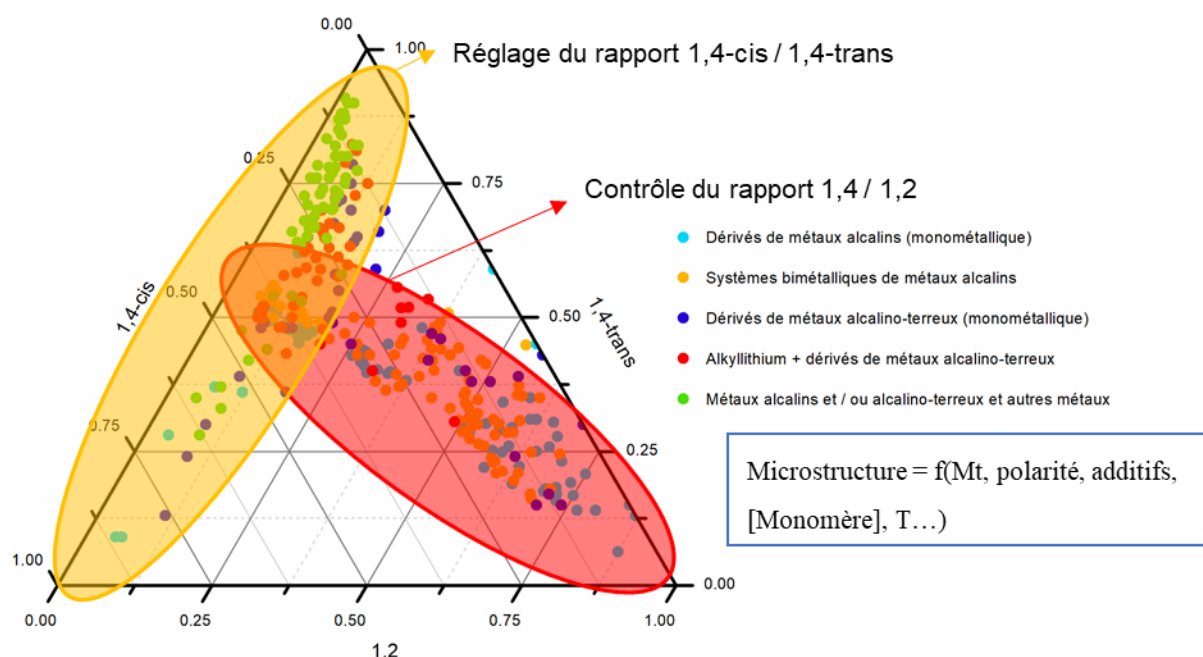


Figure 1. Microstructures du polybutadiène accessibles par polymérisation anionique du butadiène [7]

L'objet de ces travaux de thèse est d'étudier la synthèse de polybutadiène au moyen de systèmes multi-métalliques. Dans un premier temps, les systèmes à base de lithium et de potassium ont été étudiés pour l'obtention de polybutadiène avec 50% d'unités vinyliques, le challenge étant d'obtenir ces polymères de façon contrôlée. Dans un second temps, l'utilisation de composés de métaux alcalino-terreux en association avec des composés alkylolithium a été étudiée pour la synthèse de polybutadiène à fort taux d'unités 1,4-trans. Un composé organocalcique a été envisagé pour répondre à cet objectif. La troisième et dernière partie de ces travaux s'applique à étudier des systèmes d'amorçage sans lithium pour la polymérisation anionique du butadiène et leurs effets sur la microstructure du polybutadiène.

2. Polymérisation anionique du butadiène avec des systèmes d'amorçage à base d'alcoolates de potassium et d'alkyllithium.

L'objet de ce chapitre est d'étudier la polymérisation anionique du butadiène sous l'influence de systèmes alkyllithium + x eq. de *tert*-pentanolate de potassium ($0 < x < 5$).

Lorsque le butadiène est polymérisé dans le cyclohexane avec un système alkyllithium / *tert*-pentanolate de potassium ($[K] / [Li] \leq 1$, sans temps de préformation), on obtient des polymères ayant des masses molaires proches de celle visées. Quand $[K] / [Li] > 0,35$, les microstructures obtenues sont typiques des systèmes à base de potassium (Tableau 1, Figure 2). Le centre actif est un complexe composé d'alkyllithium et d'alkylpotassium (Schéma 1).

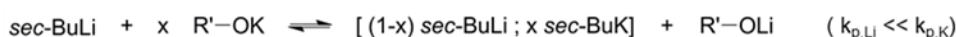


Schéma 1. Structure possible de l'amorceur bimétallique composé de *sec*-butyllithium et de *tert*-pentanolate de potassium pour $[K] / [Li] < 1$

Pour $[K] / [Li] = 5$, les polymères obtenus présentent une dispersité élevée ($\bar{D} = 2,21$). Ce résultat peut être expliqué par une réaction de transfert des centres actifs à la chaîne polymère. La microstructure obtenue est typique des systèmes à base de potassium avec 49% d'unités vinyliques. Pour $[K] / [Li] > 1$, le centre actif correspond soit à un alkylpotassium libre (hypothèse 1) ou à un complexe composé de l'alkyllithium et de l'alcoolate de potassium avec une liaison alkylpotassium active (hypothèse 2) comme représenté sur le Schéma 2. L'excès de d'alcoolate de potassium reste en solution et peut conduire à des complexes de plus haute stoechiométrie dont il est difficile d'écrire les structures précises. Le Schéma 2 représente l'écriture la plus simple possible.

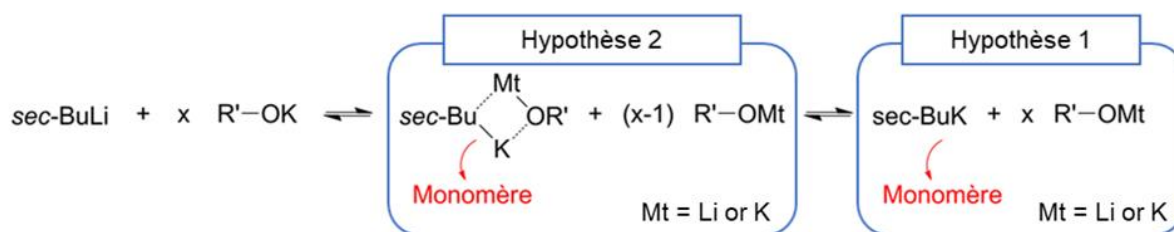


Schéma 2. Structure possible de l'amorceur bimétallique composé de *sec*-butyllithium et de *tert*-pentanolate de potassium pour $[K] / [Li] \geq 1$

Tableau 1. Polymérisation du butadiène amorcée par un système bimétallique *sec*-butyllithium + x eq. de *tert*-pentanolate de potassium ($0 \leq x \leq 5$, $\bar{M}_{nth} = 10,000 \text{ g.mol}^{-1}$, [butadiène] = 2 mol.L^{-1} , [*sec*-BuLi] = $10^{-2} \text{ mol.L}^{-1}$, cyclohexane, 20°C , 16h, rendement = 100%)

[K] / [Li]	$\bar{M}_n \text{ exp}$ (g.mol^{-1})	$\bar{D}$	1,2 (%)	1,4-cis (%)	1,4-trans (%)
0	11 000	1,02	7	41	52
0,1	11 000	1,02	14	37	49
0,35	12 000	1,02	44	19	35
0,7	12 000	1,03	41	21	38
1	12 000	1,03	42	18	40
5	6 500	2,21	49	14	37

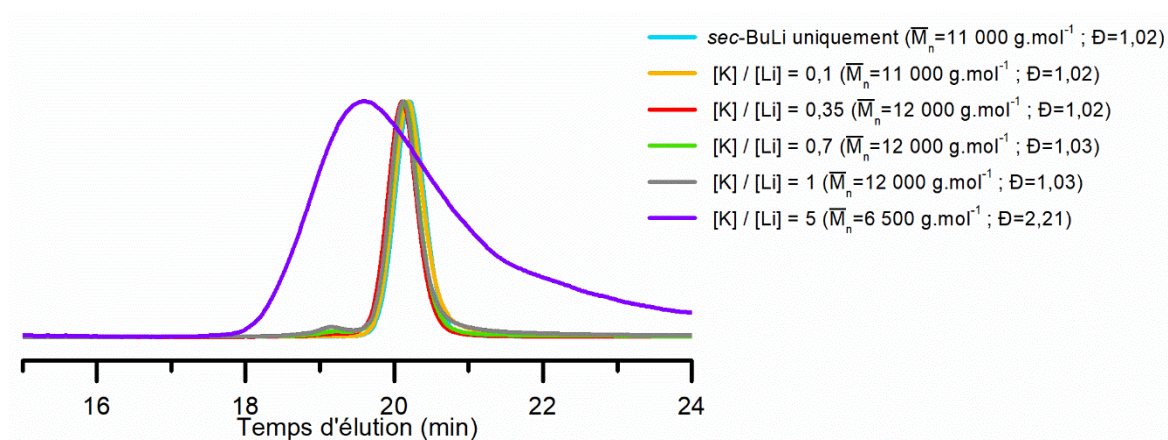


Figure 2. Chromatogrammes SEC des polybutadiènes obtenus en utilisant un système d'amorçage *sec*-butyllithium + x eq. de *tert*-pentanolate de potassium ($0 \leq x \leq 5$, $\bar{M}_{nth} = 10,000 \text{ g.mol}^{-1}$, [butadiène] = 2 mol.L^{-1} , [*sec*-BuLi] = $10^{-2} \text{ mol.L}^{-1}$, cyclohexane, 20°C , 16 h, rendement = 100 %)

L'amélioration du contrôle de la polymérisation des systèmes composés de *sec*-butyllithium + 5 eq. de *tert*-pentanolate de potassium a été démontré possible par l'ajout de triisobutylaluminium. Un contrôle de la polymérisation a été observé avec des masses molaires expérimentales proches de celles visées ainsi que des dispersités proche de 1 (Figure 3). Ces améliorations semblent être la conséquence de la formation d'un complexe aluminate de basicité plus réduite en bout de chaînes qui permet de minimiser les réactions secondaires. Les microstructures des polybutadiènes ainsi obtenues restent typiques de celles que l'on obtient avec des systèmes au potassium (50 – 60% 1,2). Un mécanisme de formation de l'amorceur est proposé dans le Schéma 3, comme précédemment l'excès d'alcoolate de potassium peut conduire à des complexes de plus haute stoechiométrie la structure présentée au Schéma 3 est donc l'écriture la plus simple possible.

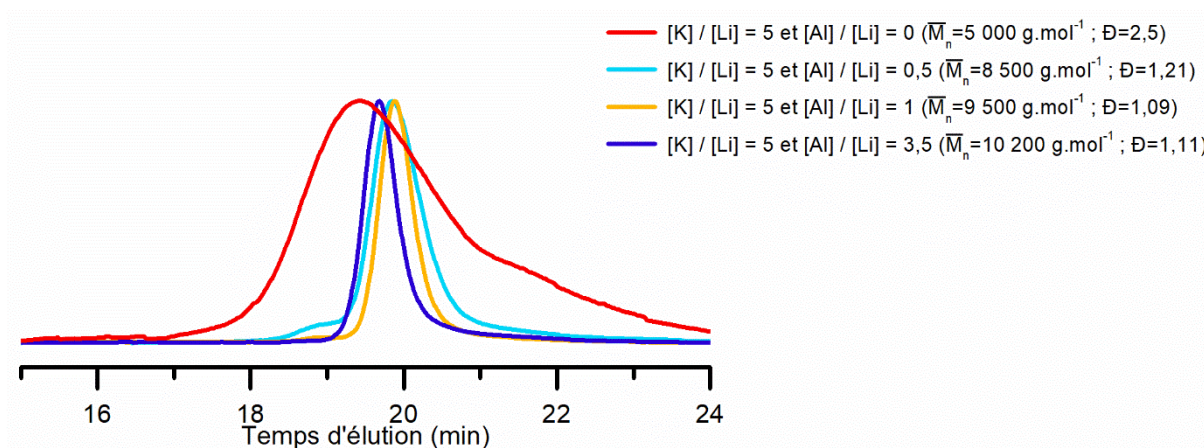


Figure 3. Chromatogrammes SEC des polybutadiènes obtenus en utilisant un système d'amorçage trimétallique *sec*-butyllithium + 5 eq. de *tert*-pentanolate de potassium + x eq. triisobutylaluminium ($0 \leq x \leq 3,5$, $\bar{M}_{nth} = 10,000$ g.mol⁻¹, [butadiène] = 2 mol.L⁻¹, [sec-BuLi] = 10⁻² mol.L⁻¹, cyclohexane, 20°C, 16 h, rendement = 100 %)

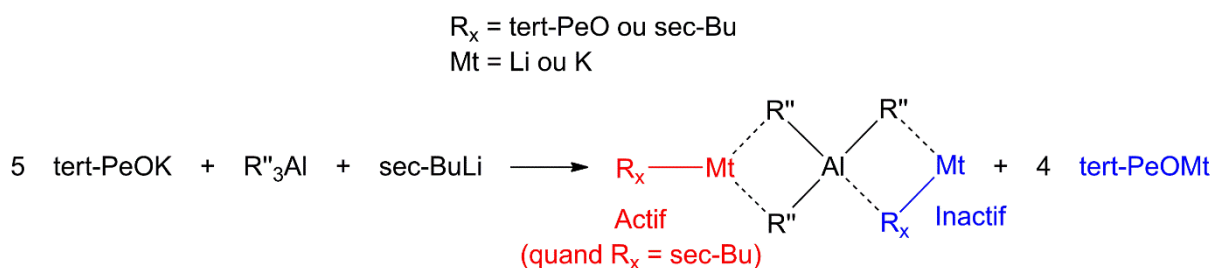


Schéma 3. Formation du complexe d'amorçage trimétallique à partir *sec*-butyllithium, *tert*-pentanolate de potassium et de triisobutylaluminium ([K] / [Li] = 5 et [Al] / [Li] = 1)

3. Polymérisation anionique du butadiène avec des systèmes d'amorçage à base de dérivés alcalino-terreux et d'alkyllithium.

L'obtention de polybutadiène à fort taux d'unités 1,4-trans nécessite généralement l'utilisation de systèmes trimétalliques associant alkyllithium, alcoolate de baryum et un trialkylaluminium. Partant de ce constat, l'objectif de ce chapitre était de développer un système bimétallique, plus simple et à base de calcium, toujours dans le but de produire des polybutadiènes avec des forts taux d'unités 1,4-trans et de façon contrôlée. Pour cela, la synthèse de bis(triméthylsilyl)amidure de calcium ($\text{Ca}(\text{HMDS})_2$) a été entreprise avec un rendement global de 22% (Schéma 4).

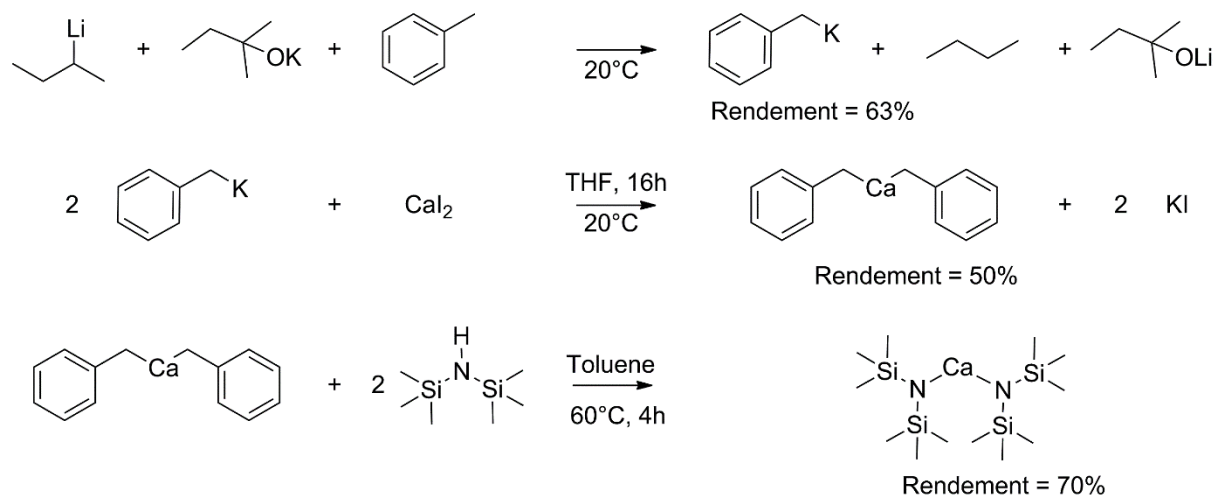


Schéma 4. Synthèse du bis(triméthylsilyl)amidure de calcium

L'utilisation de $\text{Ca}(\text{HMDS})_2$ en association avec du *sec*-butyllithium comme système d'amorçage, pour la polymérisation anionique du butadiène, permet d'obtenir 70 % d'unités 1,4-trans pour $[\text{Ca}] / [\text{Li}] = 0,4$ (Tableau 2). Au-delà de cette valeur, le taux d'unités 1,4-trans monte pour atteindre 76 % pour $[\text{Ca}] / [\text{Li}] = 1$. Le taux d'unités vinyliques est peu affecté et reste sous la barre des 10 %. La modulation de la composition de l'amorceur permet donc un réel contrôle du rapport 1,4-cis / 1,4-trans. Enfin, les analyses SEC montrent que les polymères obtenus ont des masses molaires proche de celles visées avec des dispersités faibles (Figure 4). La liaison carbone – calcium, au sein d'un complexe, est envisagée comme étant responsable de la polymérisation du butadiène.

Résumé en français

Tableau 2. Polymérisation du butadiène amorcée par un système bimétallique *sec*-butyllithium + x eq. de bis(triméthylsilyl)amidure de calcium ($0 \leq x \leq 1$, cyclohexane, 20°C, [butadiène] = 2 mol.L⁻¹, [sec-BuLi] = 10⁻² mol.L⁻¹, $\bar{M}_{n\ th} = 10,000$ g.mol⁻¹)

[Ca] / [Li]	Temps (Jours)	Rendement (%)	$\bar{M}_n\ exp$ (g.mol ⁻¹)	$\bar{D}$	1,2 (%)	1,4-cis (%)	1,4-trans (%)
0	1	100	11 000	1,02	7	41	52
0,1	7	100	11 000	1,02	10	40	49
0,4	7	100	14 000	1,02	9	22	69
0,7	7	100	11 400	1,06	8	17	75
1	3	80	8 000	1,04	9	15	76

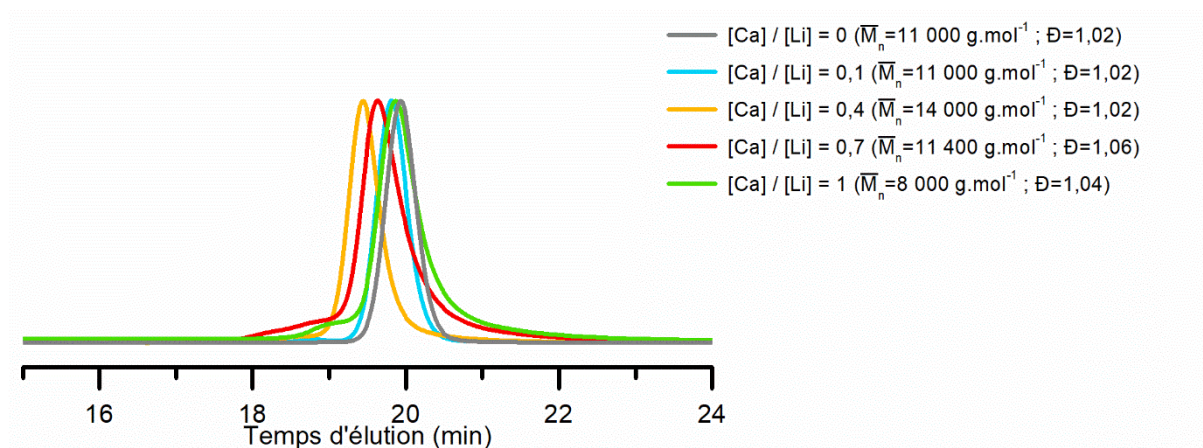


Figure 4. Chromatogrammes SEC des polybutadiènes obtenus en utilisant un système d'amorçage bimétallique *sec*-butyllithium + x eq. de bis(triméthylsilyl)amidure de calcium ($0 \leq x \leq 1$, cyclohexane, 20°C, [butadiène] = 2 mol.L⁻¹, [sec-BuLi] = 10⁻² mol.L⁻¹, $\bar{M}_{n\ th} = 10,000$ g.mol⁻¹)

4. Polymérisation anionique du butadiène avec des systèmes d'amorçage sans lithium

Ce chapitre a pour objectif d'étudier des systèmes multi-métalliques sans lithium en termes de contrôle de la polymérisation du butadiène et de la microstructure des polymères formés.

1.1. Système d'amorçage di-*n*-butylmagnesium / tert-pentanolate de potassium pour la synthèse de polybutadiène à fort taux d'unités 1,2.

L'influence du rapport $[K] / [Mg]$ sur la microstructure du polybutadiène et sur le contrôle de la polymérisation a été étudiée dans un premier temps (Tableau 3, Figure 5). Lorsque $[K] / [Mg] \leq 1$, deux populations de polymères sont observées, la polymérisation n'est pas contrôlée et les microstructures sont similaires à celles obtenues avec des systèmes bimétalliques Li / K. Pour $[K] / [Mg] = 5$, la masse molaire obtenue est proche de celle visée avec une dispersité élevée ($D=1,42$). Un mécanisme de formation de l'espèce amorçante est proposé au Schéma 5. Les centres actifs sont proposés comme étant soit des butadienylpotassium libres ou au sein de complexés par l'alcoolate alkyl de magnesium.

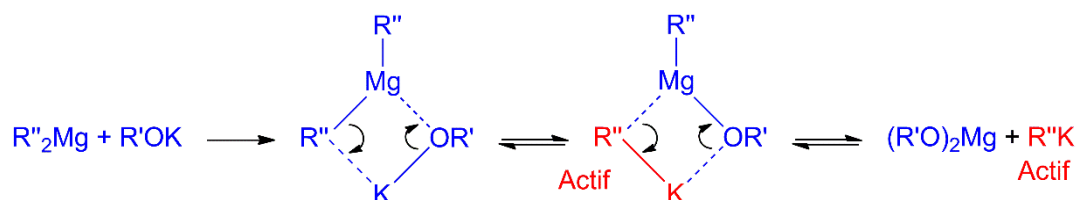


Schéma 5. Formation de l'espèce active dans les systèmes bimétalliques di-*n*-butylmagnesium / tert-pentanolate de potassium ($[K] / [Mg] = 1$)

Tableau 3. Polymérisation du butadiène amorcée par un système bimétallique di-*n*-butylmagnesium + *x* eq. de *tert*-pentanolate de potassium ($0,75 < x < 5$, cyclohexane, 20°C, [butadiène] = 2 mol.L⁻¹, [(*n*-Bu)₂Mg] = 10⁻² mol.L⁻¹, $\bar{M}_{n\ th} = 10,000$ g.mol⁻¹*)

[K] / [Mg]	$\bar{M}_n\ exp^a$ (g.mol ⁻¹)	$\bar{D}^a$	1,2 (%)	1,4-cis (%)	1,4-trans (%)
0,75	26 000	1,25	48	18	32
1	23 000	1,21	50	18	32
5	11 000	1,42	54	15	31

* Hypothèse de calcul : une chaîne polymère par molécule de di-*n*-butylmagnesium. ^a Calculé pour la population principale.

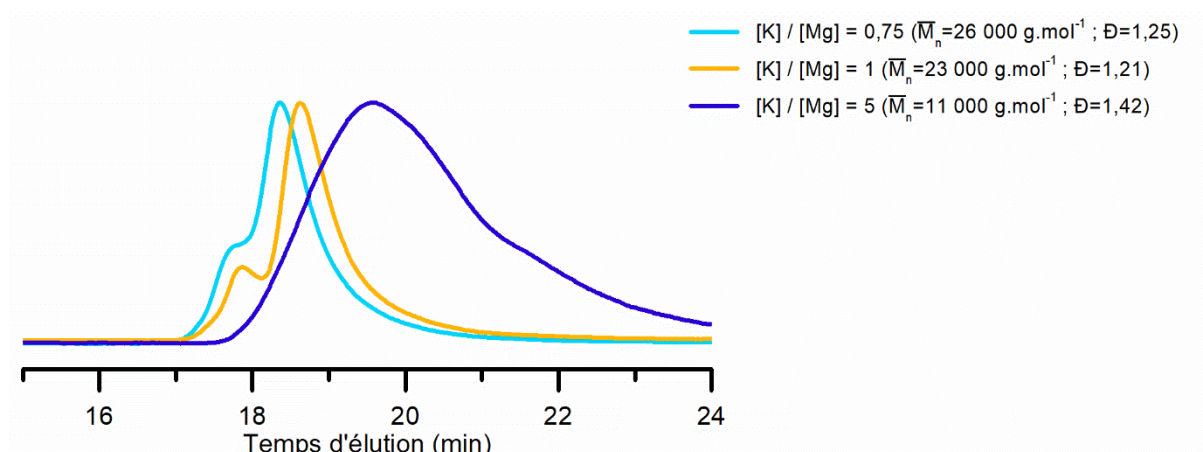


Figure 5. Chromatogrammes SEC des polybutadiènes obtenus en utilisant un système d'amorçage di-*n*-butylmagnesium + *x* eq. de *tert*-pentanolate de potassium ($0,75 < x < 5$, cyclohexane, 20°C, [butadiène] = 2 mol.L⁻¹, [(*n*-Bu)₂Mg] = 10⁻² mol.L⁻¹, $\bar{M}_{n\ th} = 10,000$ g.mol⁻¹)

Comme dans le cas des systèmes au lithium, l'ajout de triisobutylaluminium permet de réduire la dispersité quand [K] / [Mg] = 5 et [Al] / [Mg] = 0.5 ou 1. Ces systèmes trimétalliques permettent d'obtenir des polymères avec des masses molaires proches de celles visées, bien que les chromatogrammes SEC restent bimodaux.

5. Système d'amorçage hydrure de sodium / 2-ethylhexanolate de baryum pour la synthèse de polybutadiène à fort taux d'unités 1,4-trans.

Un complexe KH :*i*-Bu₃Al + ϵ ROK a été décrit pour la synthèse de polybutadiène avec un taux d'unités vinyliques compris entre 40 et 50% [8]. D'un point de vue mécanistique KH :*i*-Bu₃Al est un complexe soluble dans les composés apolaires mais inactif en polymérisation. L'ajout d'un alcoolate de potassium permet de générer un centre actif au sein du complexe aluminique comme présenté sur le Schéma 6.

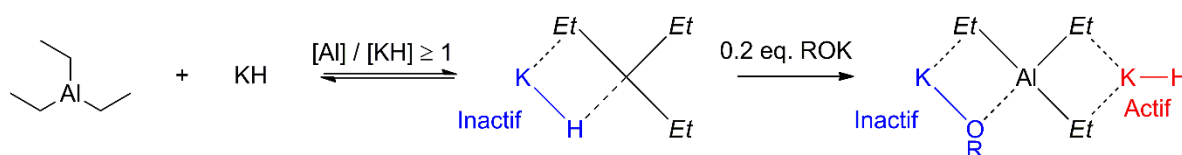


Schéma 6. Mécanisme proposé pour la formation de l'amorceur KH : R₃Al + 0.2 eq. de ROK

Dans cette étude préliminaire, un complexe soluble sodium hydride / triisobutylaluminium a été généré. Il est lui aussi inactif pour la polymérisation anionique du styrène et du butadiène. Cependant, au lieu de déplacer ce complexe avec un alcoolate de métal alcalin, 0,2 équivalent d'un alcoolate de baryum ont été ajoutés. Des polymères avec un taux de 1,4-trans entre 50 et 78% ont été obtenus laissant supposer la formation d'une liaison baryum – carbone responsable de la polymérisation du butadiène.

6. Bibliographie

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Introduction

From an historical point of view, natural rubber is the first elastomer used in the tire rubber industry, it is mainly obtained from *Hevea brasiliensis* as a latex and is composed of 1,4-cis polyisoprene. The interest of natural rubber lies in its properties such as strain induced crystallization, cut growth resistance, fatigue resistance and a reduced internal heat generation related to low rolling resistance. Natural rubber properties are subjected to fluctuation depending on the recovery process and to the area of production (age of the tree, climate, soil composition, and hevea species...) [1]. In 2017, the worldwide production of natural rubber was 13.5 million tons, against 15 million tons for synthetic rubber [2]. Natural rubber supplies are threatened by climate change, competition with other cultivation such as palm tree, and finally price volatility. Nowadays natural rubber is mainly used for truck and earthmover tire tread, while synthetic rubbers are mainly used in passenger car and motorcycle tire tread for their improved grip performance.

Butadiene rubber (BR) and Styrene Butadiene Rubber (SBR) are widely used synthetic rubbers in the tire industry because their properties can be tuned to vary tire performances such as safety through wear resistance, wet and dry grip or vehicle fuel efficiency by reducing the rolling resistance [3]. Rolling resistance is related to the crushing of tire at each rotation, the deformation leads to useless energy dissipation and consequently for the vehicle to higher fuel consumption. Accordingly, rolling resistance had to be minimize. Grip performance is related to the ability of the tire to deform against road roughness, this deformation also leads to energy dissipation, but it had to be maximized since it is directly related to tire safety performance. Those two objectives may seem contradictory, but solicitation frequencies are quite different, about 100 Hz (corresponding to high temperature accordingly to time – temperature superposition) for rolling resistance and about 10^6 Hz (corresponding to low temperature) for grip performance (Figure 1).

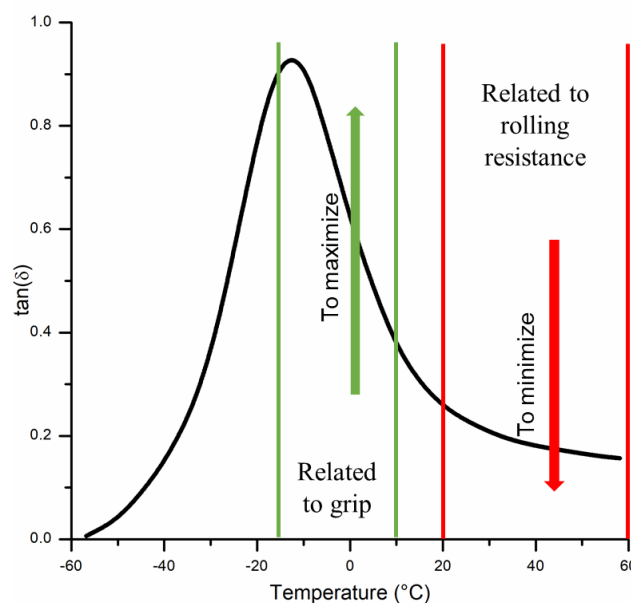


Figure 1. Variation of the loss factor ($\tan \delta$) as a function of temperature [3], [4]

Viscoelastic properties of polydiene can be tuned using several levers as monomer nature, molar mass, dispersity, microstructure, macromolecule architecture (*e.g.* linear, branched, star...) and chain end functionalization [5]–[8]. For instance, macrostructure and microstructure parameters allows to adjust rolling resistance, while styrene content and microstructure are useful tools to adjust tire grip performance [3], [9]. In the case of polybutadiene, glass transition temperatures are about -110°C for 1,4-cis polybutadiene, -100°C for 1,4-trans, and -7°C for 1,2 allowing glass transition temperature modulation with the objective of reaching new compromise between grip and rolling resistance.

Synthetic rubbers are commonly synthetized at the industrial scale using a radical process or anionic polymerization. The obtained polymers exhibit different properties depending on the process used. Emulsion-SBR (e-SBR) and e-BR are produced in a water-born emulsion of monomers with free radical mechanism. Radical initiation of new polymer chain occurs all along the process, these propagating centers have a short life span during which a large amount of monomer is consumed leading to high molar mass rubber. Obtained dispersity are broad, macromolecule architectures cannot be achieved and polydiene microstructure is not controlled, even though free radical polymerization is known to produce polybutadiene with 15 - 20% vinyl content and a 1,4-cis / 1,4-trans ratio dependent on the polymerization temperature [10], [11].

Solution-SBR (s-SBR) progressively displace e-SBR in tire application because of the greater tunability of rubber properties thanks to anionic polymerization and to the stability of the active

center all along the polymerization process [12]. When alkylolithium derivatives are used as initiator in apolar media, anionic polymerization is known to be a living and controlled polymerization allowing chain end-functionalization, copolymerization and macromolecular architecture along with a low vinyl content (below 10%) [13]. This low vinyl content leads to a lower glass transition temperature for s-SBR than the one observed for their e-SBR (20% vinyl content) counterparts with the same styrene content [12]. A lower glass transition temperature allows the addition of higher amount of carbon black and oil extender in tire formulation, and finally leads to cost reduction. In addition, improved compromise between grip and rolling resistance along with improved abrasion resistance are reachable which was not possible with e-SBR [12].

Butadiene can also be polymerized with cationic polymerization, which is reported to produce polybutadiene with about 87% 1,4-trans and 13% 1,2 contents [11], [14]. Obtained polybutadienes exhibit low molar masses and broad dispersities, which might be a consequence of chain transfer leading to branching and / or cyclization. Butadiene polymerization with Ziegler-Natta catalysts lead to the formation of highly stereoregular polymers for each one of the three structural units [11], [15]. For example, 98-99% 1,4-cis content is obtained when butadiene is polymerized with a system based on neodymium trichloride / tributyl phosphate and triisobutylaluminum [16]. High 1,4-cis polybutadiene is used for their improved fatigue resistance, and improved abrasion performance along with a low heat generation. Catalysts based on neodymium borohydride and dialkylmagnesium were reported to produced polybutadiene with a high 1,4-trans content (up to 96.7%) [17]. Polybutadiene with a high 1,4-trans are said to present a low rolling resistance, a low heat buildup, a good green strength and low abrasion loss [18], [19].

Since polybutadiene microstructures have an impact both on rolling resistance and grip performances of rubber, a good control of microstructure without threatening polymerization control seems to be preferable. In addition, lithium-based anionic polymerization allows the obtention of polymers with a well-defined chain architecture, controlled molar masses, low dispersities, and allows chain end functionalization, which are important levers to reach improved tire performance.

The goal of this research work was to gain in comprehension of multi-metallic initiation systems for the control of butadiene polymerization with defined microstructure.

To achieve this objective, the first part of this report is a bibliographic study with the purpose of presenting an overview of reachable polybutadiene microstructure through anionic polymerization. The influence of solvent, concentration, temperature, and active center nature / structure is discussed.

The aim of the first experimental chapter was to obtain polybutadiene with a medium vinyl content, the challenge being to do so in a controlled way. To achieve this objective, bimetallic systems based on alkyllithium / potassium alkoxide were studied and the influence of parameters such as the ratio $[K] / [Li]$, the initiator preformation time, the structure of the alkyllithium and of the potassium alkoxide were varied. The role of trialkylaluminum, as a third component, was also investigated and the influence of initiator preparation and composition were investigated to assess their influence on polybutadiene microstructure and polymerization control.

The objective of the second experimental chapter was to obtain polybutadienes with a high 1,4-trans content and in a controlled way. The use of trimetallic systems based on barium alkoxide, alkyllithium and trialkylaluminum are well known to achieve such an objective. Nevertheless, the use of a two-component initiation system based on calcium derivatives in association with alkyllithium was studied in this objective. Calcium bis(trimethylsilyl)amide was synthesized and investigated as a potential co-initiator for butadiene anionic polymerization. Parameters like the initiator preformation time and the $[Ca] / [Li]$ ratio were investigated to determine their influence on polymerization control and polybutadiene microstructure.

The third experimental chapter presents the prospection of multimetallic systems allowing obtention of either medium vinyl content polybutadiene or high 1,4-trans polybutadiene with a lithium free approach and using readily available compounds for the initiating systems. To achieve this objective, systems based on potassium (medium vinyl content) or barium alkoxide (high 1,4-trans content) in association with dialkylmagnesium moieties were studied in order to achieve polybutadiene synthesis. A second system based on sodium hydride / trialkylaluminum / barium alkoxide was also proposed. Parameters such as the initiator preparation and composition were varied to assess their influence on butadiene polymerization.

This manuscript will end up with a general conclusion and perspectives for future work.

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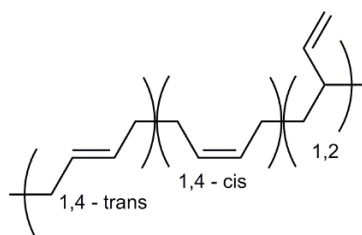
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Chapter I. Bibliography

**Accessible microstructures of polybutadiene by anionic
polymerization**

1. Introduction

Butadiene polymerizes with three different isomeric structures along the polymer chain (ignoring chirality). These isomeric units are presented on Scheme 1, the proportion between those structures is usually referred as polybutadiene microstructure [1]. As mentioned in the general introduction, microstructure is a key parameter to tune polybutadiene mechanical and thermal properties, and polymerization chemistry allows control of this parameter through initiator / catalyst design.



Scheme 1. Polybutadiene structural units

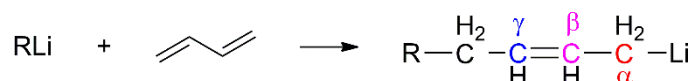
Butadiene monomer can be polymerized using polymerization methods such as anionic, cationic, radical, or coordination – insertion polymerization mechanism. Cationic polymerization is reported to produce polybutadiene with about 87% 1,4-trans and 13% 1,2 contents [2], [3]. Free radical polymerization allows the obtention of polybutadiene with 20% 1,2 content, and the 1,4-cis / 1,4-trans ratio can be adjusted by changing the polymerization temperature [2], [4]. Coordination – insertion catalysts are known to produce polybutadiene with an almost pure microstructure up to 98% 1,4-cis polybutadiene using a catalyst based on neodymium trichloride / tributyl phosphate and triisobutylaluminum [5] and up to 97% 1,4-trans content for a catalyst composed of neodymium borohydride and dialkylmagnesium [6].

Anionic polymerization provides an access to a wide range of microstructure by varying parameters such as the monomer or initiator concentration, the nature of the counter-ion, or solvent polarity. The purpose of this bibliographic part is to present the influence of such parameters, with a special emphasis on the use of alkali metals, alkaline earth metals and multimetallic initiation systems. When data are available, polymerization rate, copolymerization with styrene, initiation efficiency and side reaction linked to counter-ion nature will be discussed.

2. Alkali metals monometallic systems

2.1. Polar solvent

The anionic polymerization of butadiene in polar solvent with alkali metal as counter-ion produces polybutadiene with a high vinyl content [7], [8]. In polar solvent, the negative charge was shown by NMR spectroscopy, to be localized both on the α and γ position explaining the formation of polybutadiene with high vinyl content (see Scheme 2 for carbon denomination on the last unit of polybutadienyllithium) [1]. The aim of this section is to describe the influence of parameters such as the solvent polarity, the polymerization temperature, and the nature of the counter-ion on polybutadiene microstructure.



Scheme 2. Carbon denomination of the last unit of polybutadienyllithium

As the size of the counter-ion involved in the polymerization process increases, the vinyl content of the resulting polybutadiene decreases from 87.5% for lithium-initiated polymerization in THF to 67% for potassium. Meanwhile, the 1,4-trans content increases from 6% for lithium counter-ion to 27% for potassium (Figure 1) [7], [8]. Increasing solvent polarity by using THF rather than diethyl ether seems to favor the vinyl insertion, for instance at 0°C and with lithium as a counter-ion, the vinyl content is increased from 75% in diethyl ether to 88% in THF. Similar behaviors are observed for sodium (70% in diethyl ether to 80% in THF) and potassium (55% in diethyl ether to 67% in THF). Temperature is also reported to have an influence on polybutadiene microstructure since vinyl content are reported to decrease with increasing temperature. For example, sodium counter-ion in diethyl ether at -40°C leads to the formation of polybutadiene with 75% vinyl content whereas at 0°C this content is reported to be 70%, similar phenomenon is presented in Figure 1 with potassium counter-ion in diethyl ether with 65% vinyl units at -40°C against 55% at 0°C[7].

The size of the alkali metal counter-ion in 1,4-dioxane has a similar influence on polybutadiene microstructure and leads to vinyl content ranging from 87% for lithium to 41% for cesium, while the 1,4-trans content increases from 13% to 59% [9]. Meanwhile, the reported 1,4-cis content is 0% [9]. The absence of 1,4-cis seems to be specific of butadiene anionic polymerization in 1,4-dioxane. It can be a consequence of the solvent polarity which allows polymerization by contact ion pairs rather than dissociated ion pairs.

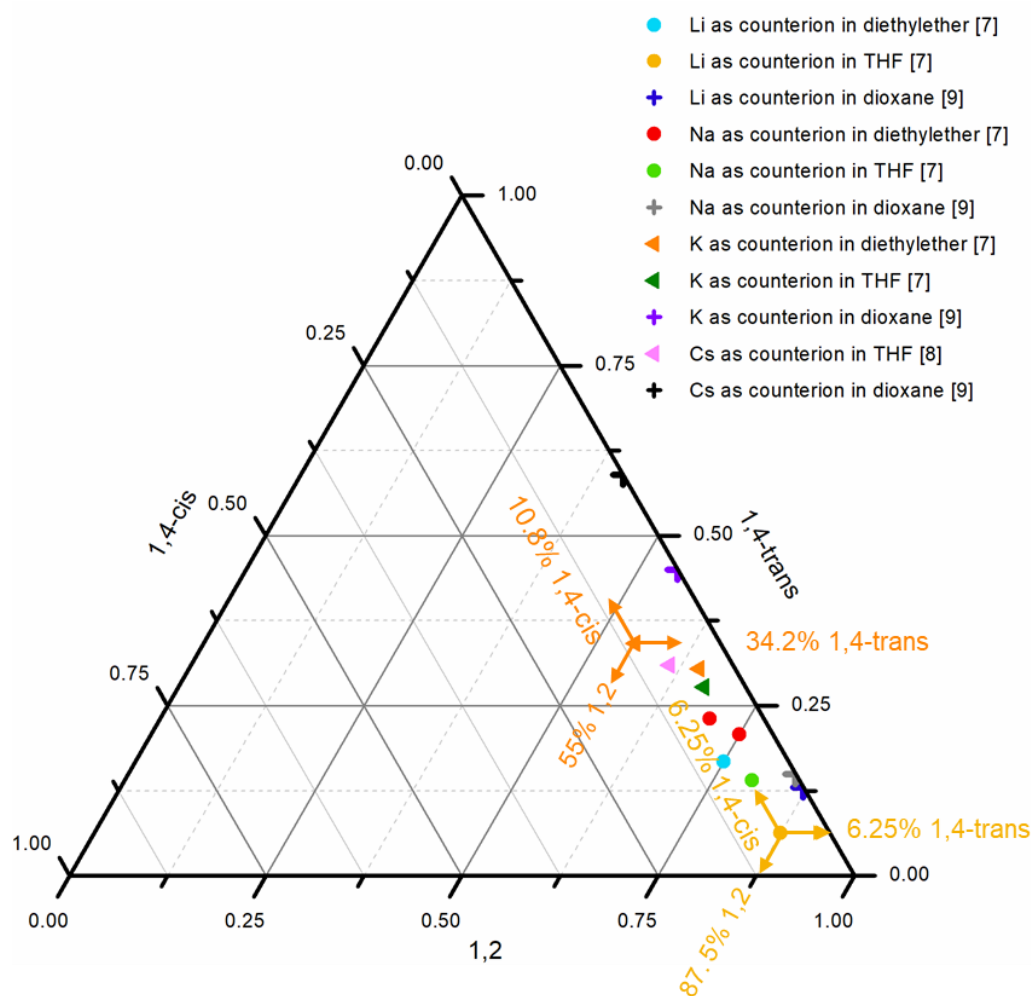


Figure 1. Influence of polar solvent and counter-ion on polybutadiene microstructure [7]–[9]

The addition of polar modifier on butadiene anionic polymerization in hydrocarbon solvent was studied by Kozak and coworker [10], [11]. The general trend for such system is an increase of the vinyl content from 10% (typical of Li as a counter-ion in apolar media) up to 75% along with a decrease 1,4-cis / 1,4-trans (Figure 2).

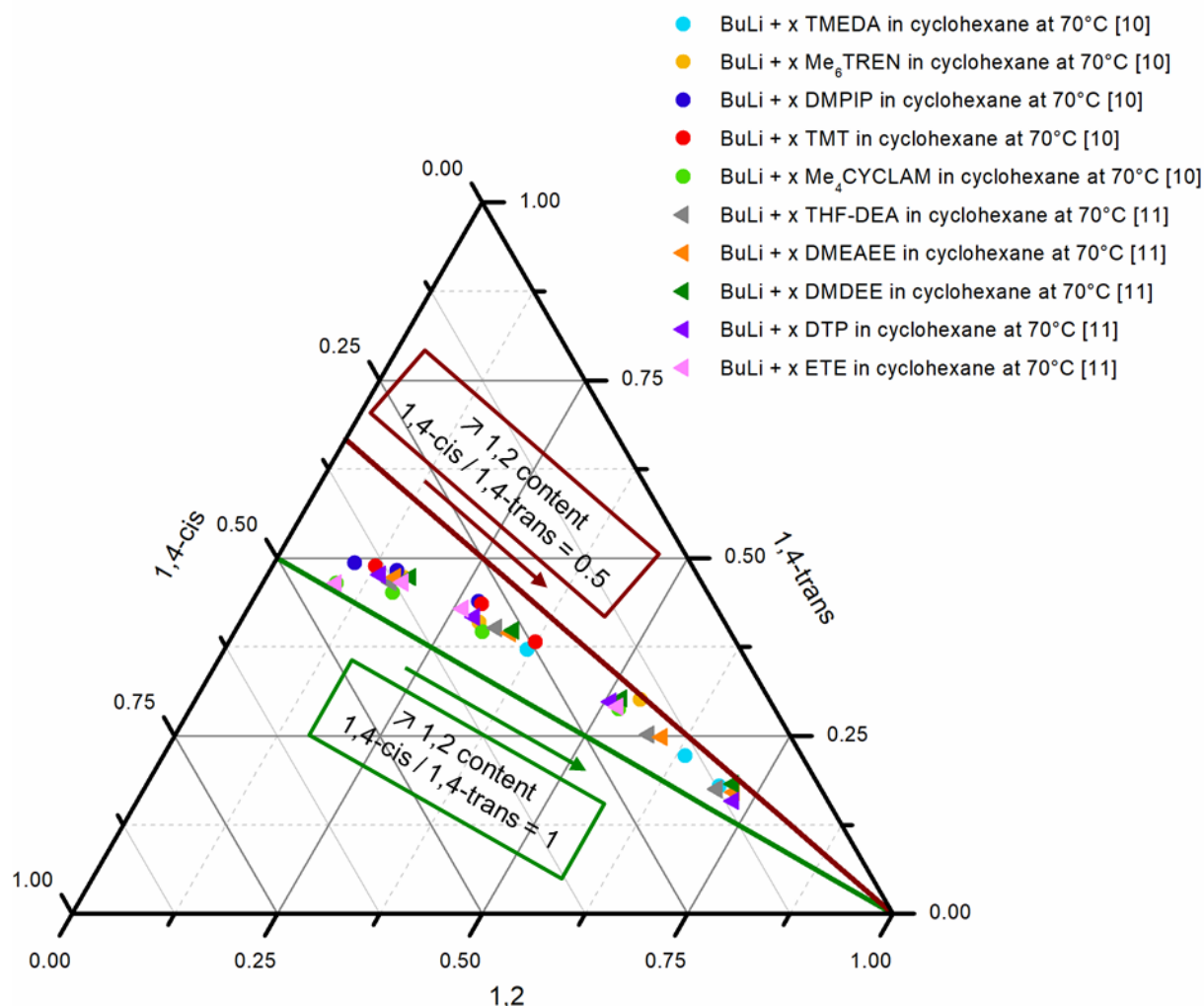


Figure 2. Influence of polar modifier on polybutadiene microstructure [10], [11]. (TMEDA = N,N,N',N'-tetramethylethylenediamine, TMT = 1,3,5-trimethylhexahydro-1,3,5-triazine, Me₆TREN = tris[2-(dimethylamino)ethyl]amine, Me₄CYCLAM = 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane, DMPiP = 1,4-dimethylpiperazine, DMEAAE = bis[2-(N,N-dimethylamino)ethyl] ether, THF-DEA = tetrahydrofurfuryl-N,N-dimethylamine, ETE = ethyl tetrahydrofurfuryl ether, DTP = 2,2-di(tetrahydrofuryl)propane, DMDEE = 2,2-dimorpholinodiethylether)

2.2. Apolar solvent

Polymerization of butadiene with lithium as counter-ion in apolar solvent is producing polybutadiene with about 10% vinyl units. The 1,4-cis / 1,4-trans is affected by the initiator concentration and the solvent nature [12] (Figure 3). For example, lowering the initiator concentration, meaning increasing theoretical molar masses, results into a higher 1,4-cis content (from 39% up to 86%) when varying $[RLi]$ from 3×10^{-3} to 7×10^{-6} mol.L⁻¹ for butadiene neat polymerization [1], [12]. At low concentration, the use of aliphatic solvent favors the formation of polybutadiene with a lower vinyl content (below 10% in aliphatic solvent, $[RLi] = 10^{-5}$ - 10^{-6} mol.L⁻¹) with respect to their aromatic counterpart (12% in benzene, $[RLi] = 8 \times 10^{-5}$ mol.L⁻¹) [1]. At higher concentration, and from this set of data, nature of the apolar solvent does not seem to have an influence on polybutadiene microstructure. Meanwhile, temperature has a minor influence on polybutadiene microstructure in hydrocarbon media when alkyllithium is used as an initiator. For butadiene polymerization in cyclohexane at 5°C the reported polybutadiene microstructure is 43% 1,4-cis, 52% 1,4-trans and 5% vinyl, whereas at 196°C, microstructure is 40% 1,4-cis, 48% 1,4-trans and 12% 1,2 [13].

The dependence of polybutadiene microstructure to the targeted molar mass was also reported by Makowsky *et al.* [14]. The 1,2 content of alkyllithium-initiated butadiene polymerization was up to 45% for $\bar{M}_n = 400$ g.mol⁻¹ and was shown to decrease below 10% for $\bar{M}_n = 5,600$ g.mol⁻¹ in heptane at 25°C (Figure 3).

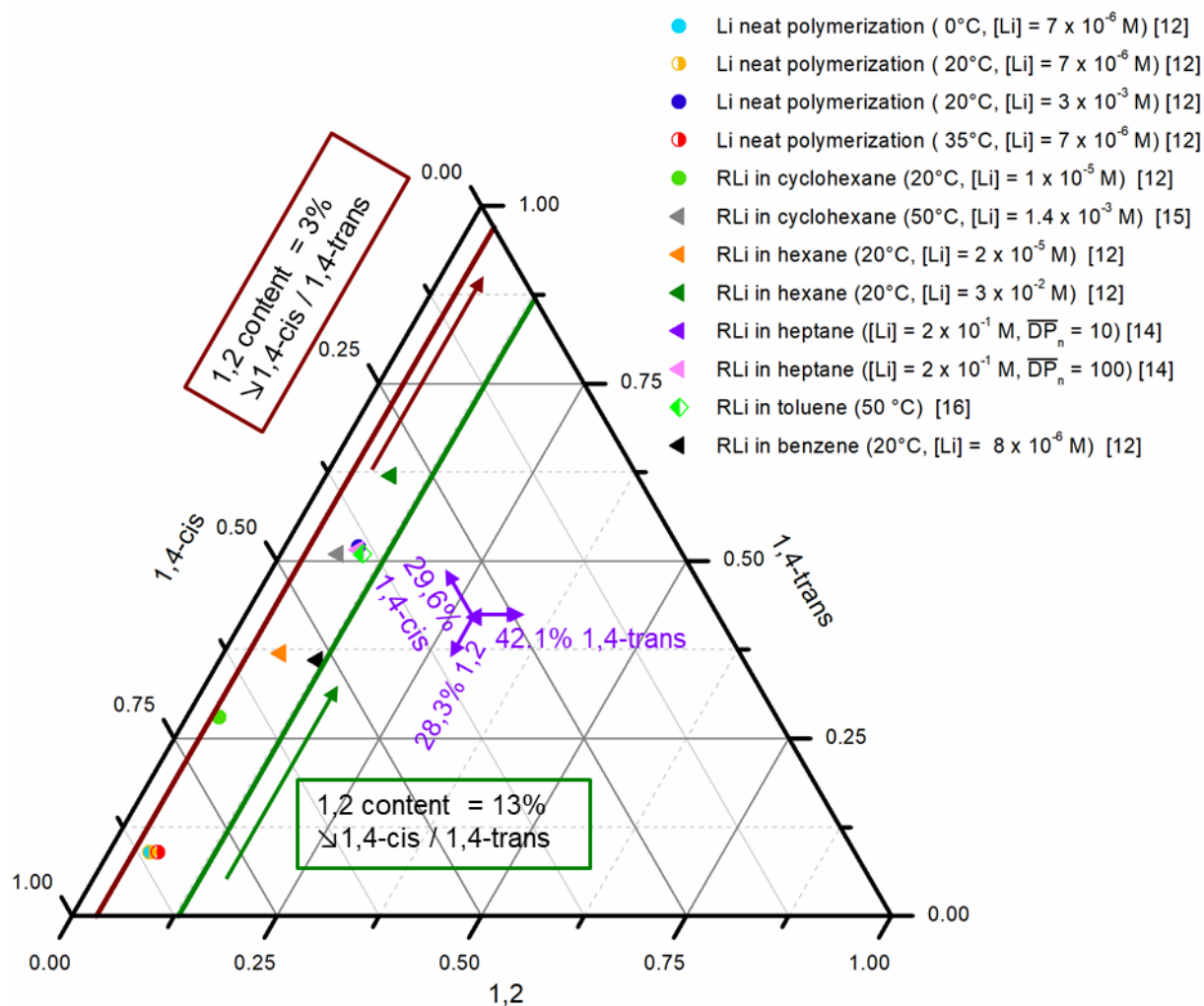
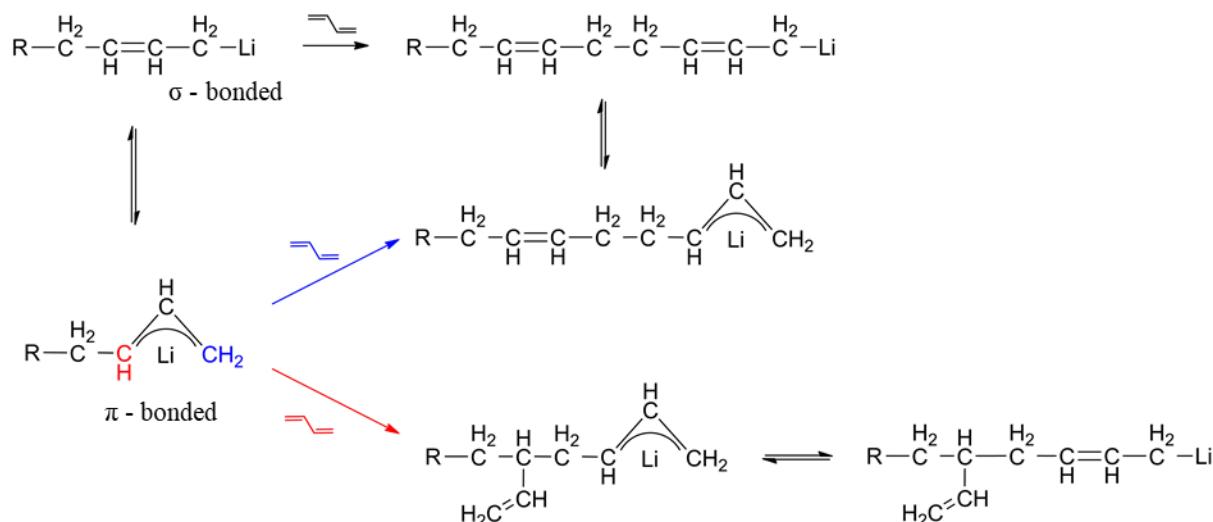


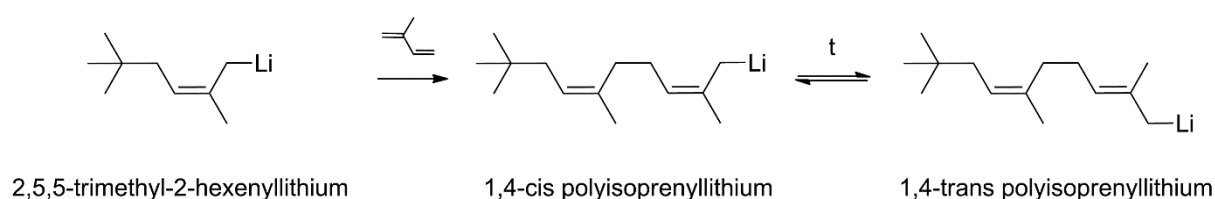
Figure 3. Influence of apolar solvent, temperature and chain end concentration on Li initiated polymerization [12], [14]–[16]

Upon addition of butadiene to alkyllithium initiator in apolar media, NMR spectroscopy of the living polymer showed only 1,4 configurations for the last unit of polybutadienyllithium with a σ -bond between carbon and lithium [17]. To explain the occurrence of vinyl units, it was postulated an equilibrium between a σ – bonded and a π – bonded lithium species producing either vinyl units or 1,4 units. A proposed mechanism is presented on Scheme 3.



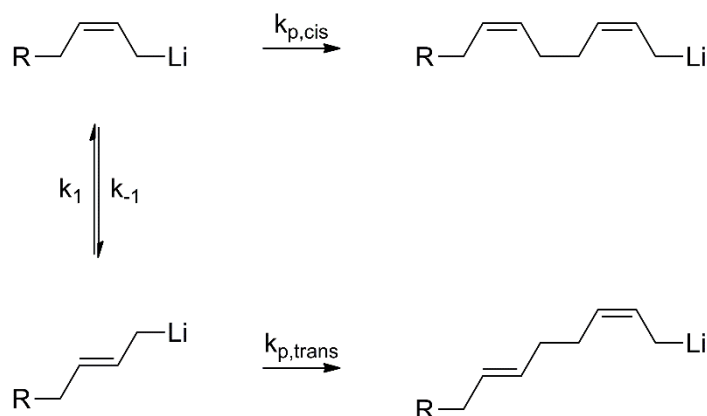
Scheme 3. Proposed mechanism for the propagation of butadiene polymerization using alkyllithium derivatives as initiator [17]

A model compound, namely 2,5,5-trimethyl-2-hexenyllithium, was used to mimic the living polyisoprenyllithium chain end and to study its behavior toward monomer addition [18]. Immediately after addition of isoprene to this model compound, essentially 1,4-cis polyisoprenyllithium chain ends were observed. Upon ageing, an increasing amount of living chain end are observed with a 1,4-trans configuration (Scheme 4). This phenomenon leads then to suggest that an isomerization reaction is possible between 1,4-cis and 1,4-trans chain end configurations and the isomerization rate was found to be competitive with the polymerization one.



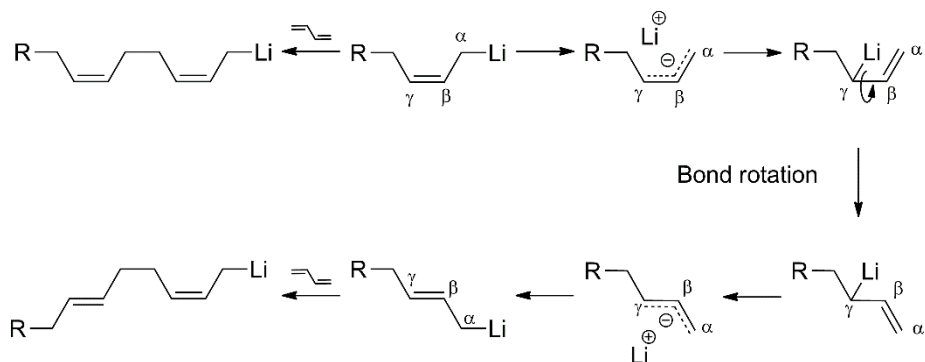
Scheme 4. Monomer addition to model compound for polyisoprenyllithium chain end, followed by an isomerization reaction (observed in heptane at -20°C) [18]

Accordingly, butadiene anionic polymerization can be presented as shown on Scheme 5 [1], [18]. Nucleophilic attack of an alkyllithium derivative on a butadiene monomer leads to the formation of a 1,4-cis butadienyllithium living center. This last unit can isomerize until the following nucleophilic attack on butadiene occurs. Depending on experimental parameters such as monomer concentration and chain end concentration, the isomerization rate is more or less competitive with the propagation rate, and consequently the polybutadiene microstructure is affected. For instance, if the chain end concentration is reduced by a factor 10^4 , the propagation rate ($R_p \propto [PBLi]^{1/4}$) will be reduced by a factor 10, while the isomerization rate ($R_{isomerization} \propto [PBLi]$) will be reduced by a factor 10^4 , preventing isomerization and leading to the formation of polybutadiene with a high 1,4-cis content [1]. Such theory allows to explain the observed influence of chain end concentration on polybutadiene microstructure as presented on Figure 3 (*i.e.* lowering the initiator concentration tends to produce polybutadiene with higher 1,4-cis content).



Scheme 5. Proposed mechanism for the chain propagation of polybutadienyllithium [1], [18]

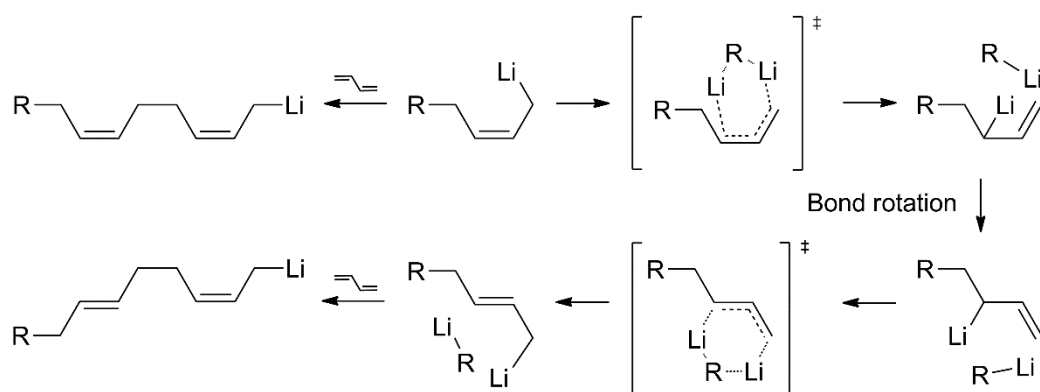
Two mechanisms for the isomerization reaction can be drawn according to scientific literature. A first proposed mechanism, presented on Scheme 6, implies the formation of π -allylic delocalized bond between lithium counter-ion and the last unit of the chain, followed by lithium migration on the γ position, bond rotation, reformation of a π -allylic delocalized species, and back on σ bond on the α position with a reversed isomeric situation [1].



Scheme 6. Proposed mechanism for the chain end isomerization of polybutadienyllithium through the formation of a π -allylic intermediate [1]

A second suggested mechanism for the chain-end isomerization involved counter-ion exchange in chain ends aggregates as presented on Scheme 7 [1].

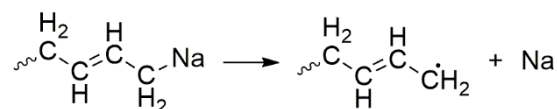
In both scenario, lithium is localized on the γ position during the isomerization process and it can be envisaged that monomer insertion at this stage of the isomerization reaction is responsible of the low amount of vinyl units in the polymer chain when synthesized in apolar media with lithium as the counter-ion.



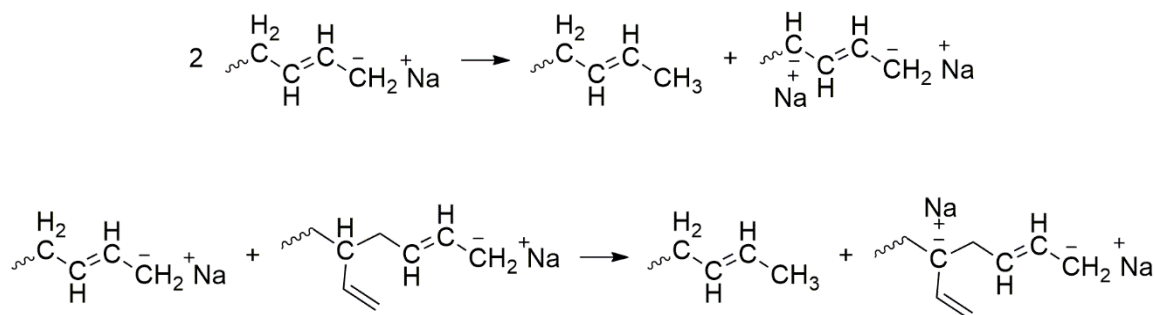
Scheme 7. Proposed mechanism for the isomerization of polybutadienyllithium chain end in aggregates [1]

Sodium counter-ion allows the highest vinyl content for the anionic polymerization of butadiene in apolar media. Molar masses and monomers conversions were reported to be highly dependent on the initiating systems. It was reported by Halasa that sodium metal initiated polymerization produces a low molar mass polybutadiene with 62% of vinyl units and low monomer conversion in hexane at 30°C [19]. For butylsodium / sodium chloride systems a polybutadiene with 80% of vinyl units was obtained in a low yield (50% in hexane at 26.5°C after 4 days), with a high dispersity and a low molar mass. Low yield was explained through living chain end loss followed by radical disproportionation (72% of living species are lost after

16h, Scheme 8), and the broad dispersity and low molar mass through chain transfer to polymer chain (Scheme 9) [19]–[21].



Scheme 8. Proposed mechanism for radical formation at the chain end followed by radical disproportionation chain termination [20]



Scheme 9. Proposed mechanism for chain transfer to the polymer [20]

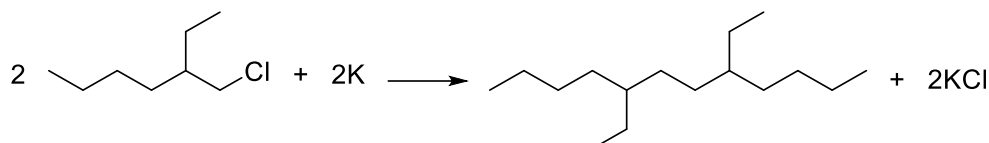
Meanwhile, Basova *et al.* reported the ability of sodium / anthracene system or 1,1-diphenylhexylsodium (+ sodium chloride) to produce polybutadiene with a good yield in cyclohexane, benzene, toluene and ethylbenzene at room temperature. Reported microstructures for those systems are ranging from 64% to 70% 1,2 content [22].

The ability of 1,1,3-triphenylpropylsodium and 2-ethylhexylsodium to produce polybutadiene at 100% monomer conversion in aliphatic solvent was reported by Yakubovich and coworkers. In aliphatic solvents, molar masses were said close to the targeted ones but with broadened distribution attributed to chain transfer to polymer (*D* ranging from 1.2 to 1.5). The vinyl content was 60 – 65%, 1,4-cis was 15% and 1,4-trans was 20-25% [23].

The ratio of chain transfer to chain propagation rate was calculated to be 3.7×10^{-2} for sodium - based systems, whereas it is below 10^{-6} for lithium, 7×10^{-4} for potassium and 3.3×10^{-3} for cesium. The expected order for this ratio, $\text{Li} < \text{Na} < \text{K} < \text{Cs}$, is observed when toluene is diluted with 40 vol% of THF. Another factor affecting this ratio is the initiator concentration: this ratio decreases from 3.7×10^{-2} when $[\text{RNa}] = 7.5 \times 10^{-3} \text{ mol.L}^{-1}$ to 2.8×10^{-3} for $[\text{RNa}] = 2.4 \times 10^{-4} \text{ mol.L}^{-1}$ [23]. This behavior, with respect to chain transfer to toluene, and in addition to sodium initiator being able to produce the highest vinyl content with respect to other alkali metals, tends

to suggest that the main active species is a dimeric active center rather than unassociated propagating centers [23].

Little information can be found on organopotassium-initiated polymerization. As reported by Lochmann, 2-ethylhexylpotassium decomposition can be detected in hexane after only 15 min at room temperature [24]. Maréchal suggested the formation of 5,8-diethyldodecane as the result of the coupling of 2-ethylhexylchloride following a Wurtz reaction (Scheme 10) [25].



Scheme 10. Proposed reaction for the coupling reaction of 2-ethylhexylchloride in presence of potassium [25]

Nakhmanovich *et al.* reported the stabilization of organopotassium species through reaction of 2-ethylhexylpotassium with 1,1-diphenylethylene to produce stable dispersion of 1,1-diphenyl-4-ethyloctylpotassium over at least a year [26]. Reported monomer conversions are in the range from 10% to 15% [26].

Polymerization with cesium and rubidium as counter-ion leads to the formation of polybutadiene with a high 1,2 content, up to 60%, with a 1,4-cis content below 10% in apolar media [1].

As discussed above, lithium-based initiators are quite unique among the alkali metal series as lithium is the only one to produce polybutadiene with a vinyl content as low as 10%. The use of heavier alkali metals leads to the formation of polybutadiene with a 1,2 content between 50% and 75%. A summary of polybutadiene microstructure with alkali metal as initiator is given on Figure 3 (for Li), Figure 4 and Figure 5 (for Na, K, Cs and Rb).

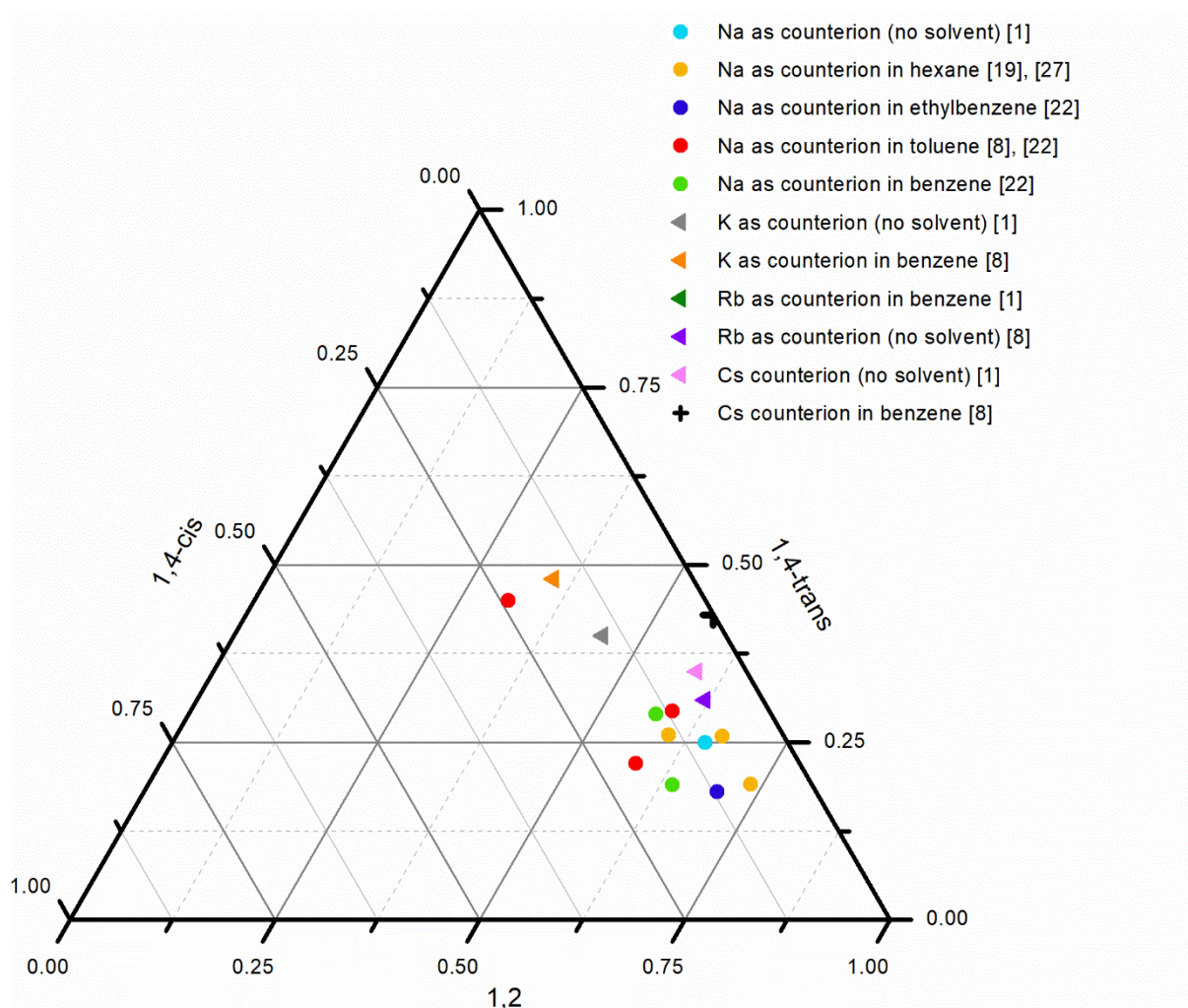


Figure 4. Influence of apolar solvents and nature of the counter-ion for Na, K, Cs and Rb [1], [8], [19], [22], [27]

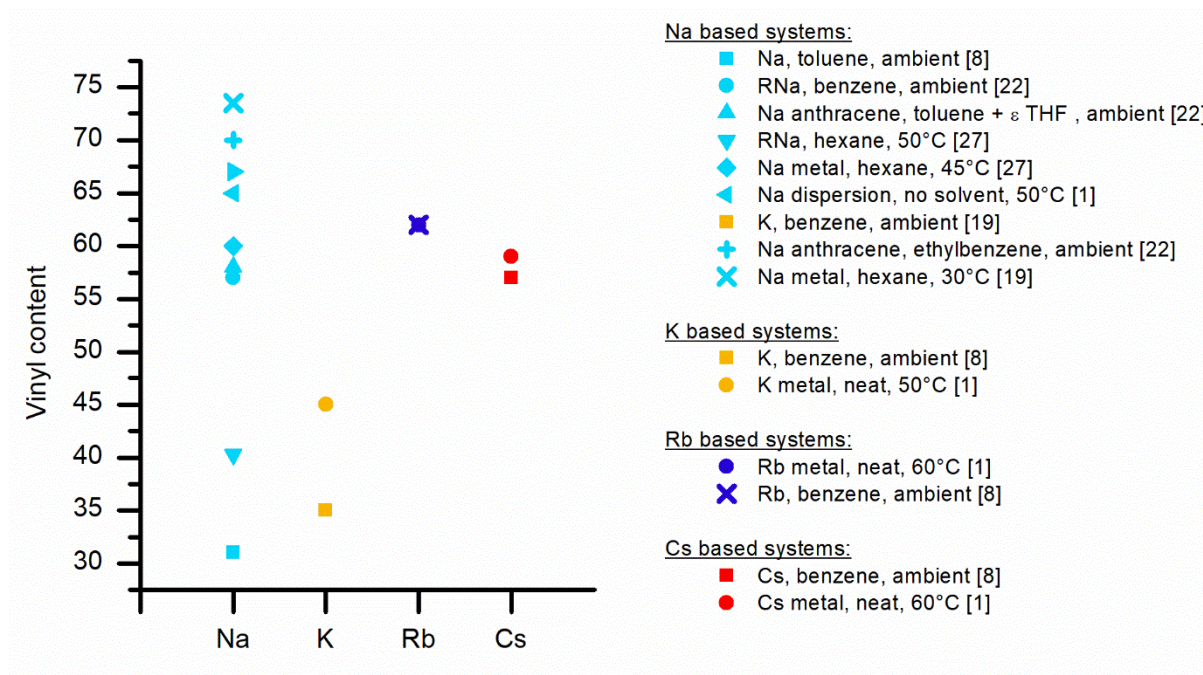


Figure 5. Influence of the alkali metal counter-ion on polybutadiene vinyl content [1], [8], [19], [22], [27]

3. Alkali metal bimetallic systems

3.1. Alkyl lithium / lithium alkoxide systems

According to Hsieh, increasing amounts of lithium *tert*-butoxide in toluene will lead to a continuous decrease of both the initiation and polymerization rates [28]. Polybutadiene vinyl content increases from 10% to 30% when $[tert\text{-BuOLi}] / [\text{BuLi}]$ ratio increases from 0 to 6 in toluene at 30°C. A much lower effect was observed at 70°C in toluene, as the vinyl content increased from 13% ($[tert\text{-BuOLi}] / [\text{BuLi}] = 0$) to 17% ($[tert\text{-BuOLi}] / [\text{BuLi}] = 6$) [28] (Figure 6).

In cyclohexane, the initiation rate reaches a maximum for a ratio $[tert\text{-BuOLi}] / [\text{BuLi}] = 0.4$ and decreases continuously beyond that point. As in toluene, the propagation rate continuously decreases whatever the amount of *tert*-BuOLi. The hypothesis behind the initiation rate increase in cyclohexane (below 0.4 eq.) is that a relatively small amount of lithium *tert*-butoxide helps to dissociate *n*-butyllithium hexamers to form highly reactive species. When more alkoxide is added, complexation of alkyl lithium with lithium *tert*-butoxide occurs and reduces the overall reactivity. In aromatic solvent, the amount of dissociated species is already important and the addition of alkoxide does not allow much more dissociation [28]. In terms of polybutadiene microstructure, the effect of lithium *tert*-butoxide is quite low since 6 eq. shifts the 1,2 content from 6% to 11% at 30°C, and from 8% to 10% at 70°C (Figure 6) [28].

The vinyl content is reported by Makowsky to increase with the ratio $[tert\text{-BuOLi}] / [\text{BuLi}]$ [14]. For low molar mass polybutadiene ($\overline{DP}_n = 10$), the addition of 4 eq. of lithium *tert*-butoxide shifts the 1,2 content from 30% to 60% when polymerization is performed in heptane at 25°C. For higher molar mass ($\overline{DP}_n = 46$) and under the same conditions, the vinyl content is equal to 36% [14]. A summary of their results is presented in Figure 6.

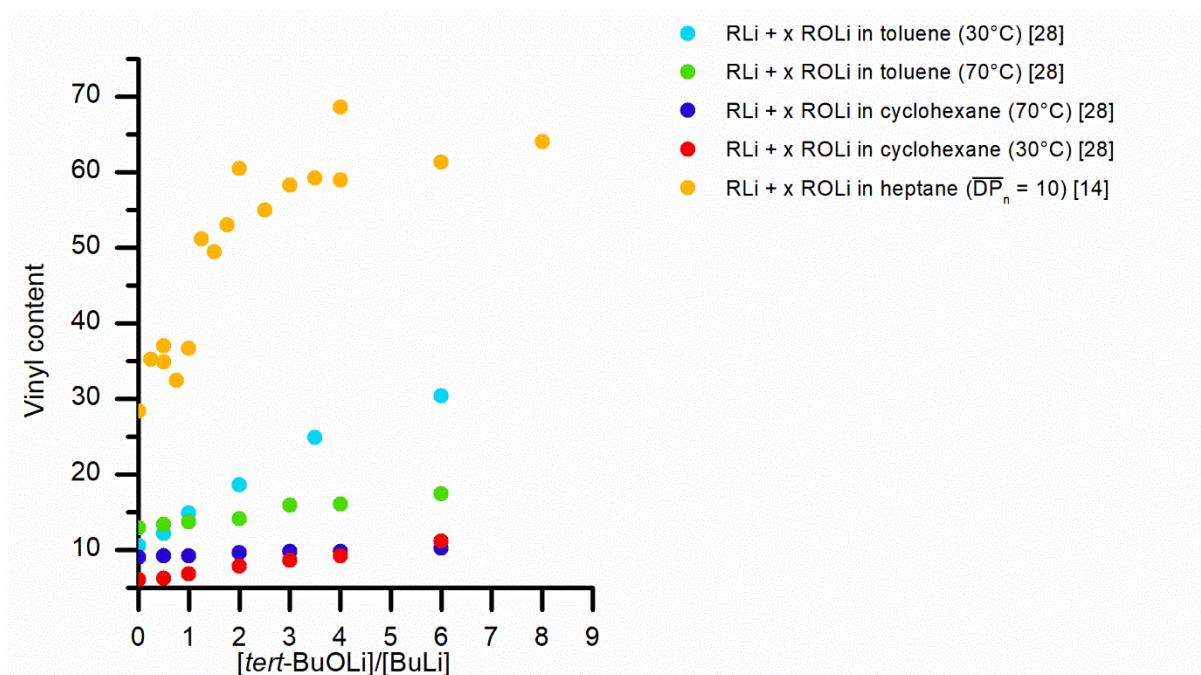


Figure 6. Influence of the ratio [*tert*-BuOLi] / [BuLi] on polybutadiene vinyl content [14], [28]

3.2. Alkyl lithium / heavier alkali metals

When applied to butadiene polymerization, the general trend for those systems is an increase of the number of vinyl unsaturation when the ratio [*tert*-BuOMt] / [BuLi] is increased with Mt = Na, K, Rb, Cs (Figure 7, Figure 8). When [*tert*-BuOMt] / [BuLi] is close to one, the microstructure of the resulting polybutadiene tends to be the same one as for polybutadiene made with the corresponding alkyl metal initiator as presented in Figure 7. In all cases the propagation rate was increased with respect to alkyl lithium initiated ones [29].

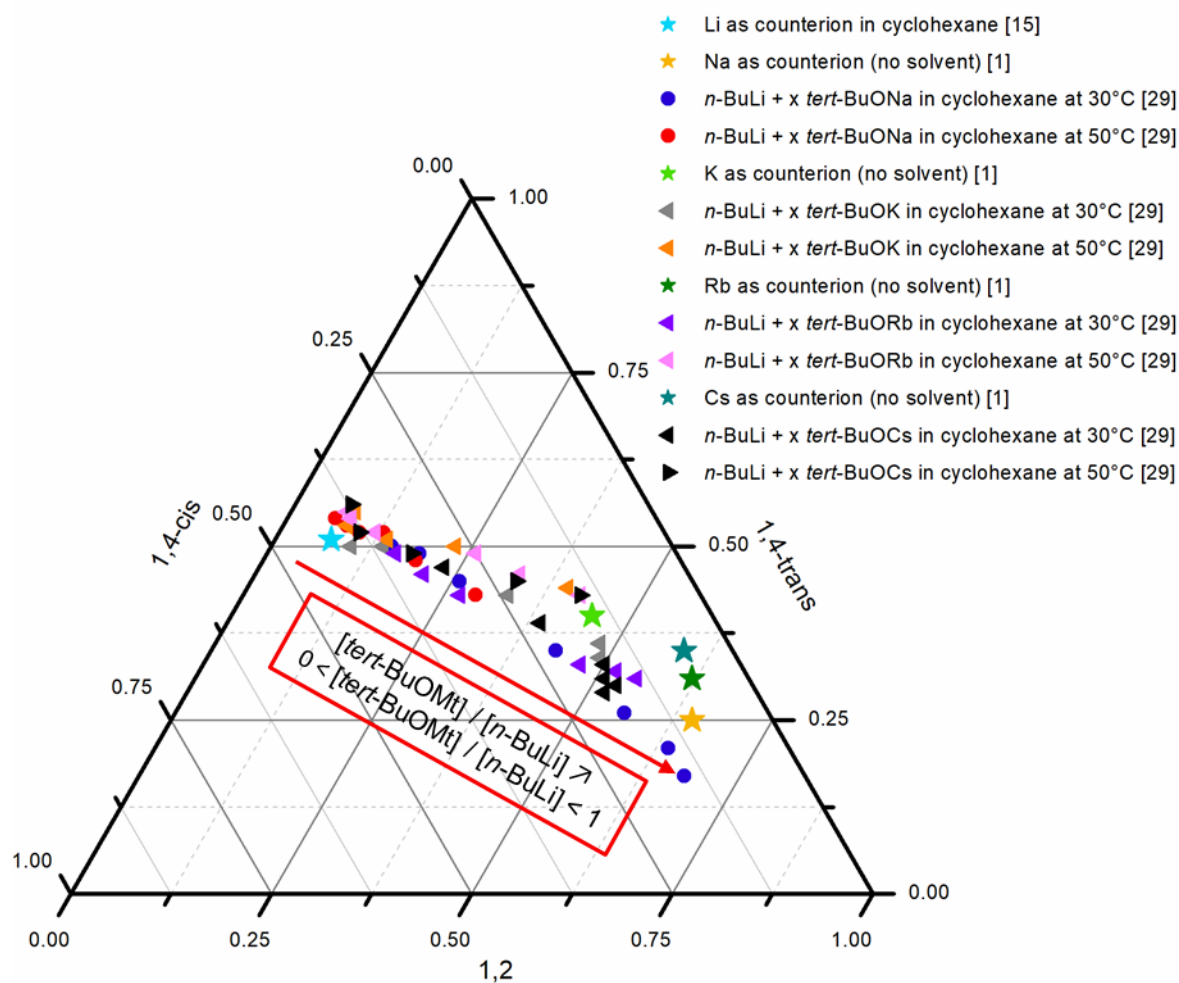


Figure 7. Influence of heavy alkali metals on alkyl Li initiated polymerization of butadiene in cyclohexane (T = 30°C or 50°C, $0 < [\text{ROMt}] / [\text{RLi}] < 1$) [1], [15], [29]

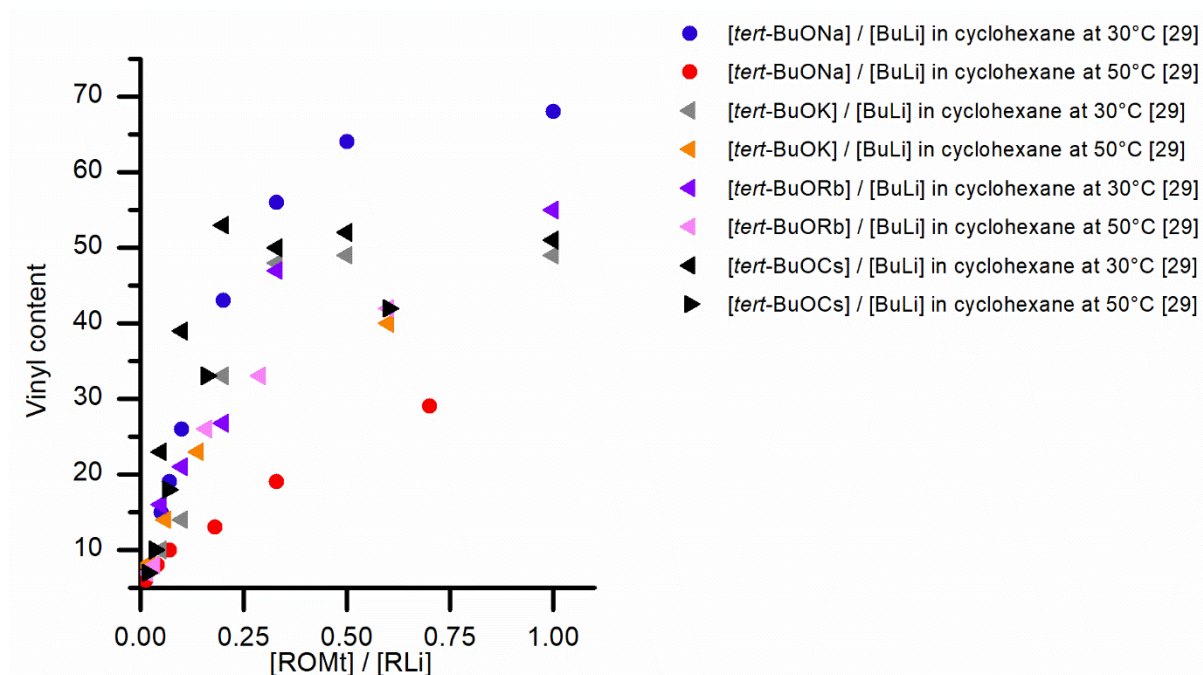
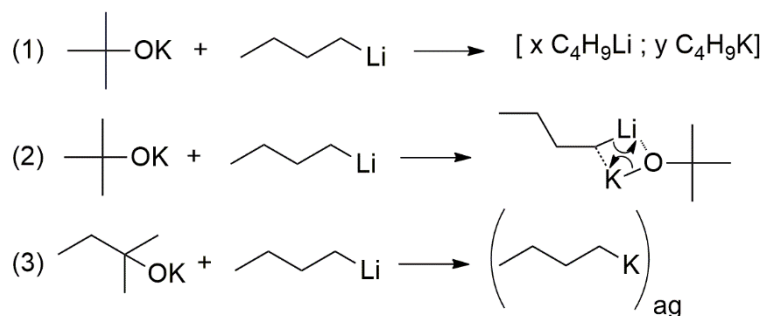


Figure 8. Influence of the ratio $[tert\text{-BuOMt}] / [RLi]$ on polybutadiene vinyl content [29]

Lochmann stated that the addition of potassium alkoxide to butyllithium leads to the formation of alkylpotassium moieties in various aggregated forms. The summary of their work might be drawn as in Scheme 11. If close to the stoichiometry with *n*-butyllithium, the precipitate contains roughly one alkoxide per one organometallic compound and almost 70% of the initial amount of potassium can be found in the precipitate. In addition, the presence of alkyl potassium was proven by the ability of the product to metalate organic compounds.

When $[tert\text{-BuOK}] / [n\text{-BuLi}] < 1$, the product was shown to be almost free of alkoxide moieties. The ratio potassium to lithium in the product was reported to be dependent on the ratio $[t\text{-BuOK}] / [BuLi]$ and the formation of an adduct *n*-butyllithium – *n*-butylpotassium was suggested [30].

For $1 < [tert\text{-PeOK}] / [n\text{-BuLi}] < 3$, Lochmann [31] stated, that superbases made from *n*-BuLi and potassium *tert*-pentoxide lead to the formation of *n*-butylpotassium in aggregated form [31] (Scheme 11).

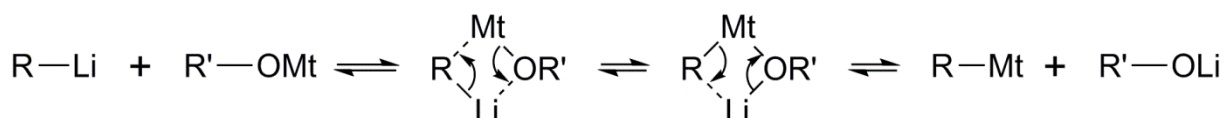


Scheme 11. Reaction of potassium alkoxide with *n*-butyllithium in hydrocarbon media: influence of the ratio $[\text{R}'\text{OK}] / [\text{RLi}]$. (1) $[\text{tert-BuOK}] / [\text{n-BuLi}] < 1$, (2) $[\text{tert-BuOK}] \approx [\text{n-BuLi}]$, (3) $1 < [\text{tert-PeOK}] / [\text{n-BuLi}] < 3$

For initiating systems based on *n*-BuLi + *tert*-BuOK, the initiator preformation time (time left to *n*-BuLi and *tert*-BuOK to react before the addition of monomers) was said to be critical since increasing preformation time leads to a reduced initiation efficiency and to increased molar masses [33]. This phenomenon might be a consequence of a secondary reaction of *n*-BuLi and *tert*-BuOK leading to the formation of metal hydride and alkene [32].

Other side reactions were reported for systems based on *n*-BuLi + *tert*-BuONa, including metalation of the polymer chain, possibly leading to branched polybutadiene [34]. It seems reasonable to assume that similar behavior can occur with heavier alkali metals as it was reported the ability of ROK / RLi systems to create anions on polybutadiene backbone and to initiate styrene polymerization from these anions [35] or on polystyrene one to functionalize it [36].

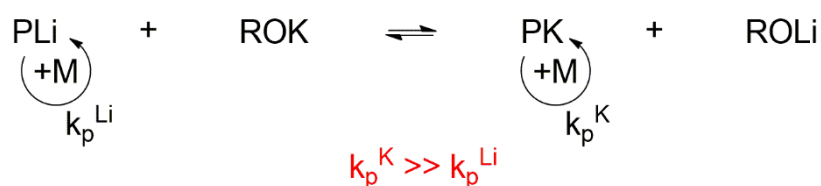
Two explanations can be drawn from this behavior (Scheme 12). The first one explain the microstructure change by the formation of an alkyl of the heavier alkali metal, the second as the formation of a mixed metal complex with an equilibrium allowing both lithium and the other metal to act as the counter-ion (Scheme 12) [37].



Scheme 12. Suggested equilibrium allowing metal – metal interexchange between alkyllithium and alkali metal alkoxide [37]

Knowing that organo-sodium initiated polymerizations are not able to produce high molar mass polybutadiene, whereas RLi / RNa initiated polymerizations are. In addition to, the chain transfer constant to toluene being reported to be three orders of magnitude lower for [RLi] / [RNa] = 1 with respect to the one observed with RNa alone. And since the polymer microstructure was typical of sodium-initiated polymerization for both systems, it was suggested that multimetallic active centers were involved in chains propagation in the case of RLi / RNa systems [37].

Nakhmanovich and coworkers studied the influence of potassium alkoxide on alkyllithium initiated polymerization over a wide range of concentration and they suggested three different types of active centers depending on the initiator composition. In the sub-stoichiometric region ($[K] / [Li] \in [0;1]$), when increasing the amount of potassium *tert*-pentoxide, the polymerization rate increases quite monotonously with $[tert\text{-}PeOK] / [n\text{-}BuLi]$, the rate of chain transfer to toluene increases, and the 1,2 content of the resulting polybutadiene increases. This behavior is in line with a fast exchange between potassium and lithium counter-ions as presented in Scheme 13 [38].



Scheme 13. Polymerization mechanism for $[tert\text{-}PeOK] / [n\text{-}BuLi] < 1$ [38]

When $1 < [tert\text{-}PeOK] / [n\text{-}BuLi] < 3$, the polymerization rate drops down and the chain transfer rate increases resulting in a low molar mass polybutadiene. Knowing that the chain transfer rate depends only on the nature of the propagating species, it was stated that the active species is different from the ones in the sub-stoichiometric region [38]. It was reported by Halasa and coworkers the formation of high 1,4-trans polybutadiene with such systems in hexane when $[tert\text{-}PeOK] / [n\text{-}BuLi] = 4$, this unexpected behavior might be attributed to multimetallic polymerization center [38], [39]. Similar behavior was also reported for systems based on alkylmagnesium and potassium alkoxide in hexane [40].

When $[tert\text{-}PeOK] / [n\text{-}BuLi] > 3$, the molar mass gets even higher than the theoretical one, with a high dispersity (up to 52 when $[ROK] / [RLi] = 6$). Due to the high molar mass obtained, it was stated that the active center was again different and was supposed to be rather active in propagation but not in chain transfer [38].

3.3. Organo sodium / alkali metal alkoxide

As presented in the first section, organo-sodium or sodium metal based systems are reported to not be able to produce high molar mass polybutadiene, because of the poor stability of the living chain ends. In order to increase their stability, and to reach full monomer conversion, it was proposed to add alkali metal alkoxide to those sodium based systems [19]–[21]. No chain end loss over time was observed when 0.7 eq. of $ROLi$ were added to RNa , or when 2 eq. of ROK were added to RNa . Using such conditions full monomer conversion was achieved after less than 24 hours at room temperature, however experimental molar masses remain below the targeted ones and high dispersities were obtained [20]. Microstructure is sensitive to different parameters, like the temperature ($T \nearrow \Rightarrow$ 1,2 content $\searrow$, Figure 9) or the initiator composition (from 70% to 40% 1,2 when $[tert\text{-}BuOK] / [RNa]$ varies from 0 to 0.5, then up to 50% 1,2 units when $[tert\text{-}BuOK] / [RNa] > 2$ in hexane at 30°C) [21]. According to these observations, the formation of a complexed chain end was suggested. However, it should be noted that $RONa$ does not improve the living chain end stability (even at $[RNa] / [RONa] = 2$).

In the case of Na dispersion + $ROLi$, the ratio $[Na] / [Li]$ was reported to have a minor influence on polybutadiene microstructure (from 56.4% to 60.4% 1,2 units when $[Na] / [Li]$ varies from 2 to 15) [19]. Meanwhile, increasing the polymerization temperature was reported to reduce the vinyl content from 69% at 5°C to 38% at 110°C. Temperature is reported to have a similar effect on Na dispersion + ROK based initiating systems, similar behavior was reported for K dispersion + $ROLi$. Na dispersion + $RONa$ systems do not reach full conversion and low molar mass polymers are obtained (Figure 9) [19].

Reported and discussed microstructures with such systems are presented in Figure 10.

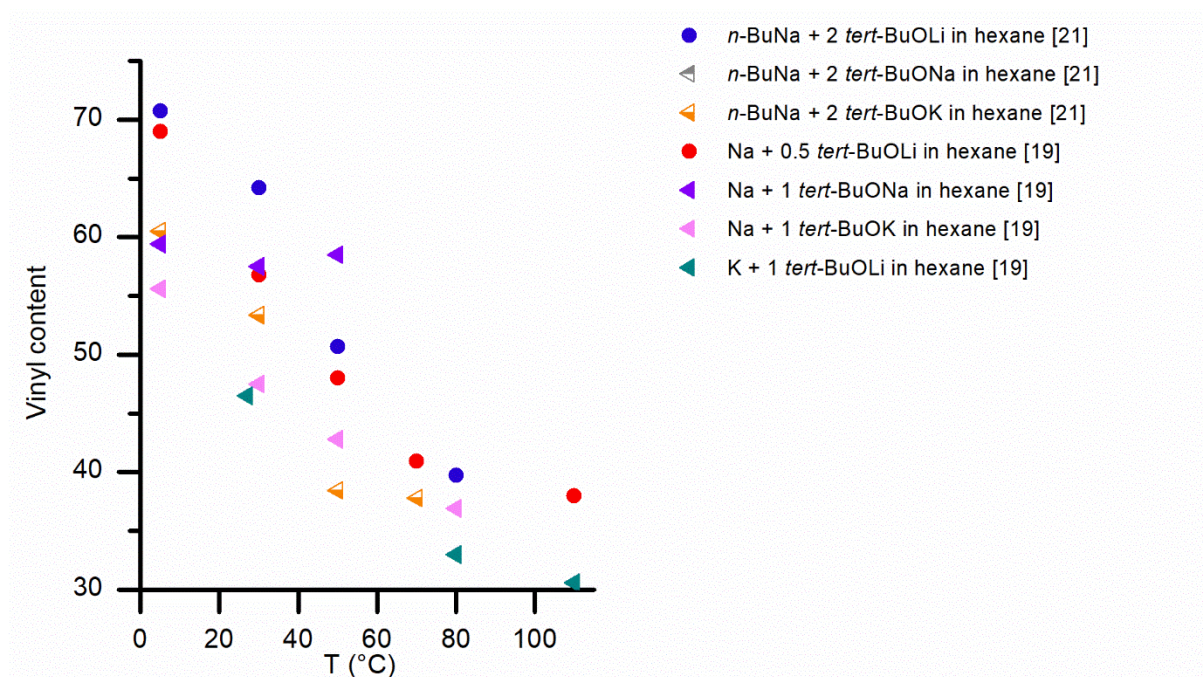


Figure 9. Influence of the temperature on polybutadiene vinyl content obtained with heavy alkali metal derivatives + alkali metal alkoxide [19], [21]

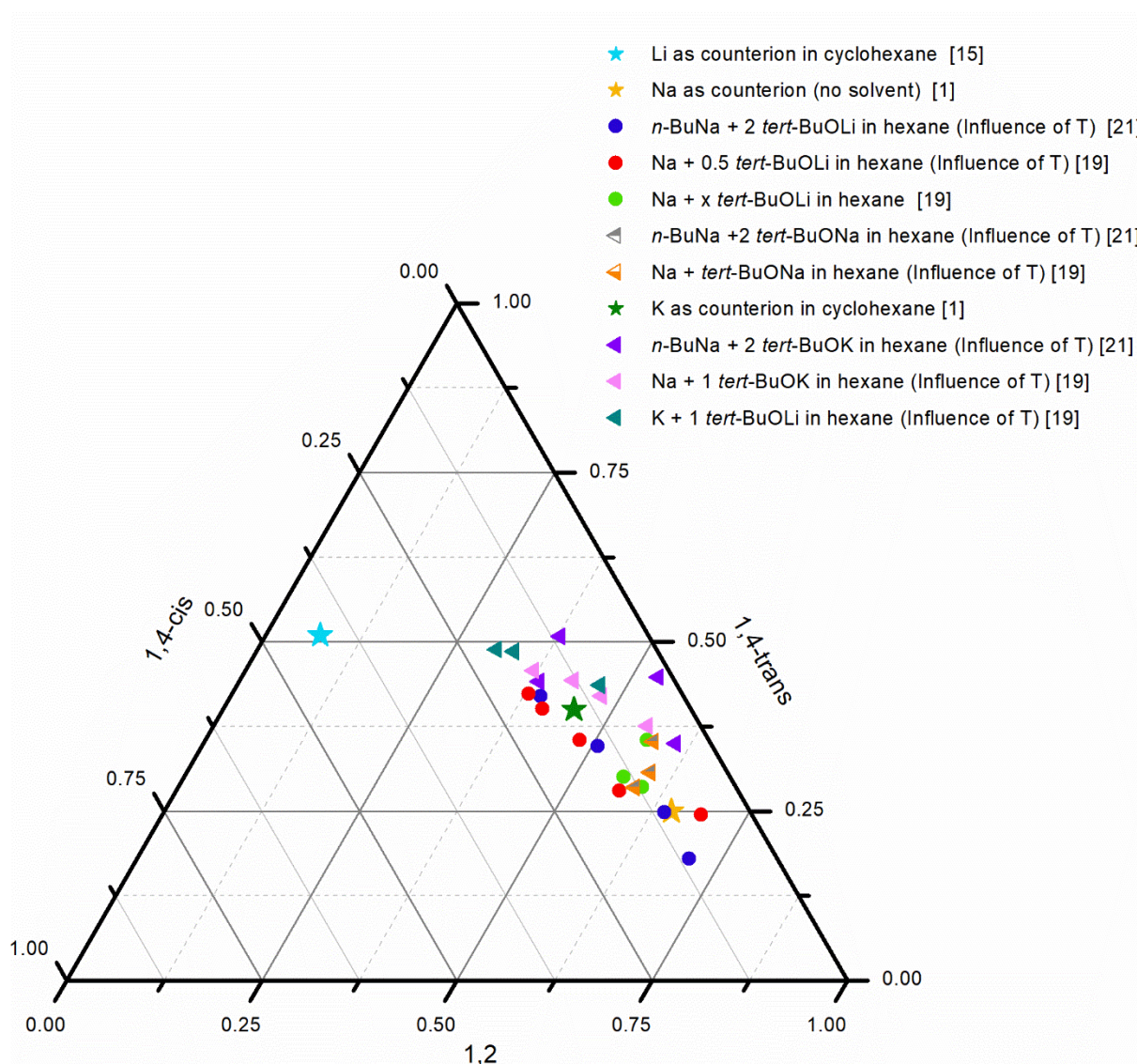
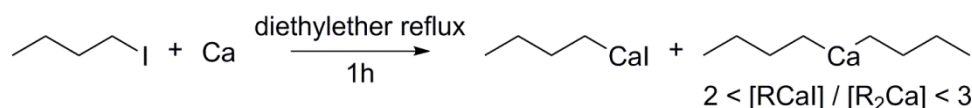


Figure 10. Polybutadiene microstructures using heavy alkali metal + alkali metal alkoxide based systems [1], [15], [19], [21]

4. Alkaline earth metal monometallic systems

Grignard reagents are not able to initiate the anionic polymerization of diene monomers under usual condition. However, it was reported the ability of such compounds to initiate butadiene polymerization in polar media at 100 – 150°C. Such systems produce polybutadiene with 30% 1,4-cis, 45% 1,4-trans and 25% 1,2 [41] (Figure 11, squares).

Organo-calcium compounds were reported to initiate butadiene polymerization with a living character showing a linear increase of molar mass with conversion but obtained molar masses were said to be higher than expected. In THF, the polybutadiene microstructure obtained is 71% 1,2 and 12% 1,4-cis and 17% 1,4-trans (Figure 11) [42]. Neat polymerization and apolar solvent provides polybutadiene with a high 1,4-trans content (up to 78.5%) [43]. The reaction used to produce *n*-butylcalcium iodide is presented on Scheme 14, di-*n*-butylcalcium was reported to be a side product with $2 < [n\text{-BuCaI}] / [(n\text{-Bu})_2\text{Ca}] < 3$ [43].



Scheme 14. Formation of *n*-butylcalcium iodide in diethylether [43]

For systems based on $\text{Ph}_3\text{CMtX}(\text{THF})_y$, Lindsell *et al.* reported low polymerization rates either in THF or for neat polymerization ($\text{Mt} = \text{Ca}, \text{Sr}, \text{Ba}$ and $\text{X} = \text{Cl}, \text{Br}$) [44]. The nature of the halogen and the initiator concentration were said to have only a little influence on polybutadiene microstructure. However, in THF at -10°C, polybutadiene microstructure was shifted from 50% vinyl content when using organo-calcium compounds to 20% for organo-barium compounds. For neat polymerization at 15°C, the 1,4-trans content reaches 66% (81% of 1,4 units) for calcium compounds against 48% for barium ones (86% of 1,4 units). Those initiators were synthesized in THF, by the reaction of Ph_3CX with an amalgam of the corresponding metal [45]. The results for organo-calcium, strontium, and barium are presented in Figure 11, Figure 12 and Figure 13.

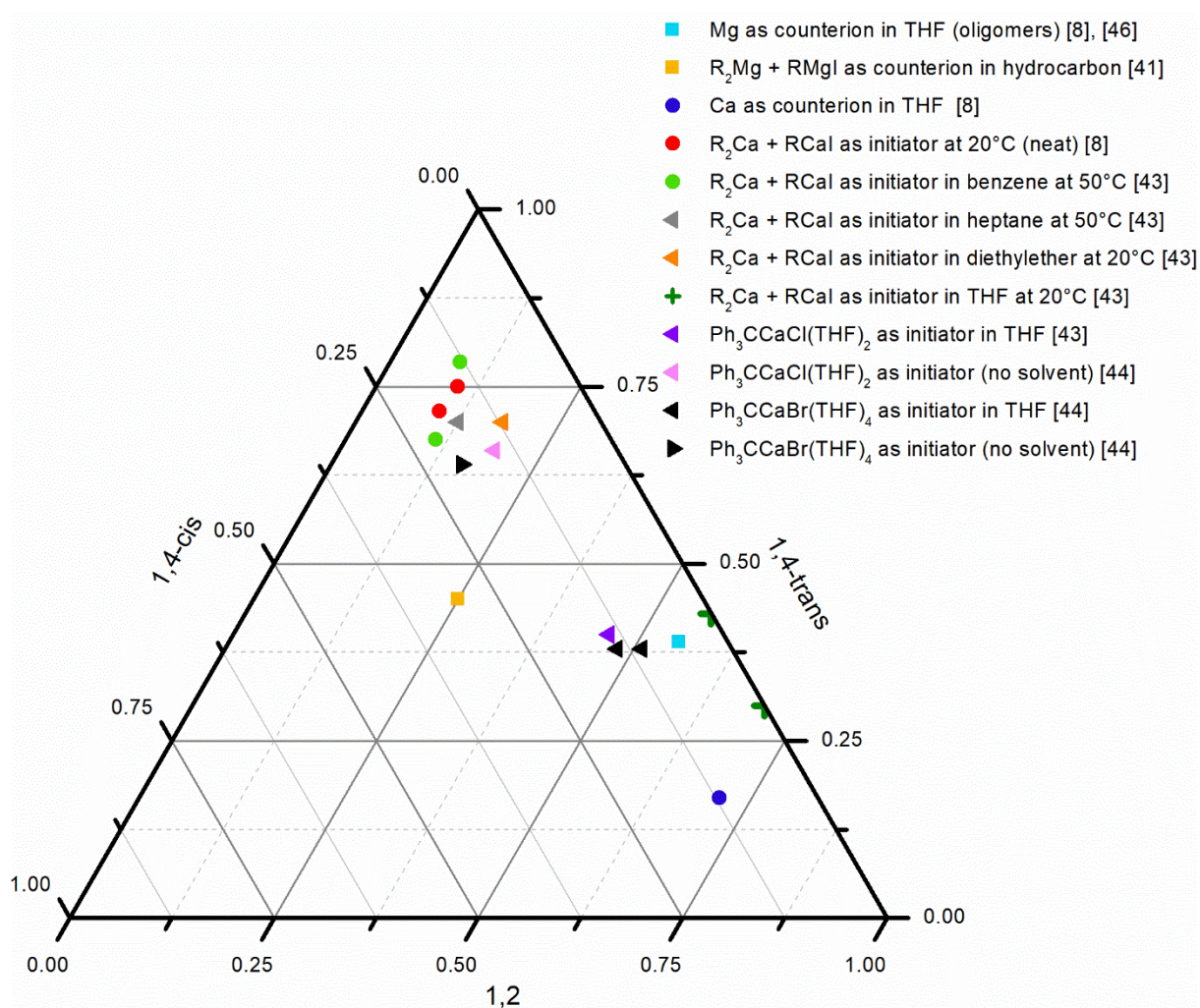


Figure 11. Polybutadiene microstructure for organo-magnesium and -calcium compounds as initiators of butadiene polymerization [8], [41], [43], [44], [46]

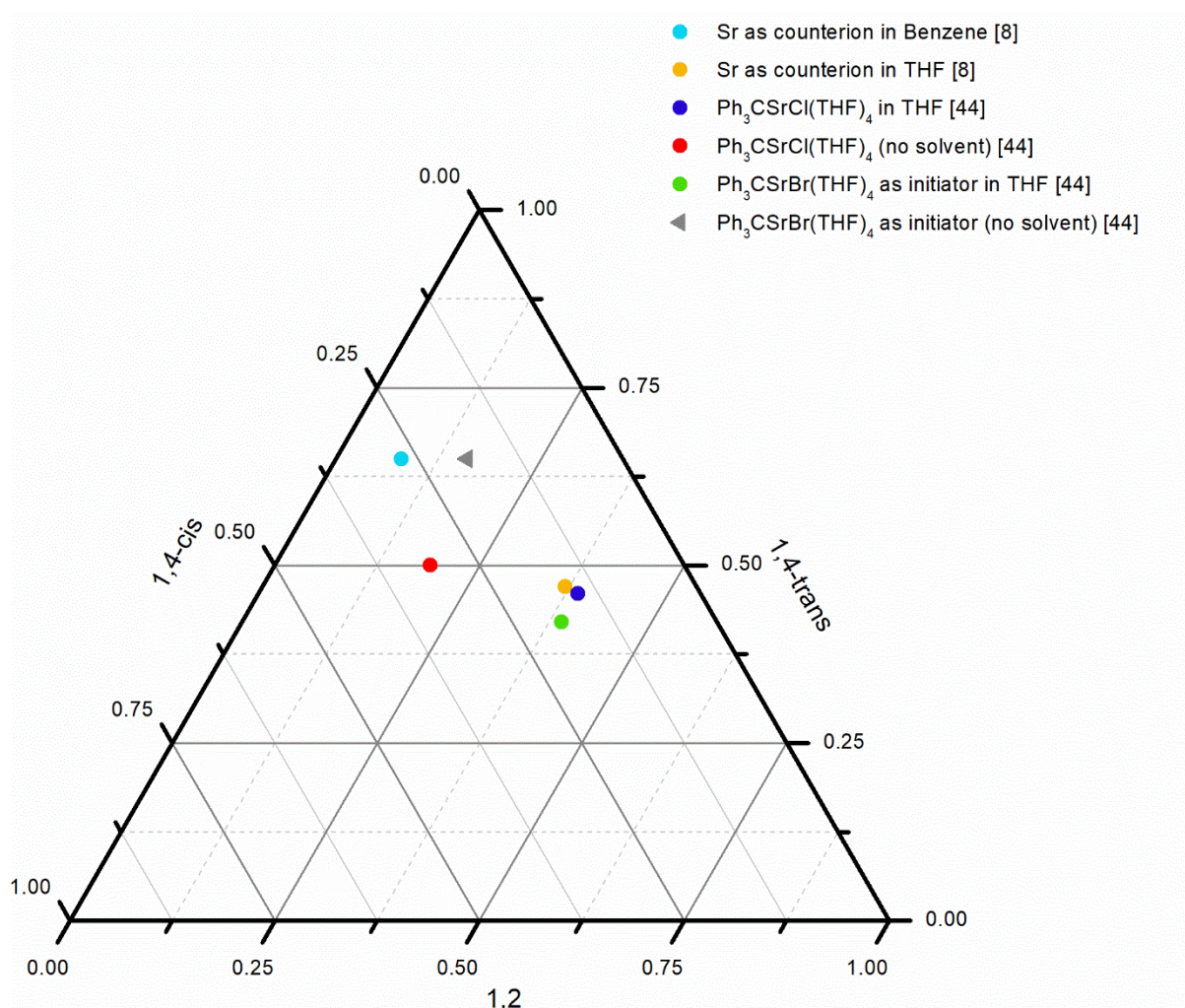


Figure 12. Polybutadiene microstructure for organo-strontium compounds as initiators of butadiene polymerization [8], [44]

Another way to obtain barium-based initiator is through the reaction of metallic barium with 1,1-diphenylethylene or α -methylstyrene, or through the reaction of dibenzylmercury with barium metal. Polybutadiene microstructure (Figure 13) with such initiators fall in the same range in THF at 25°C (49% of 1,4-trans, 31% of 1,4-cis and 20% of 1,2) [8], [47], [48]. In dimethoxyethane (DME), barium salt of 1,1-diphenylethylene was reported to produce polybutadiene with a high 1,2 content (74% at 25°C) decreasing when used at higher temperature (62% at 90°C).

In the case of barium salt of diphenylethylene as polymerization initiator in apolar solvent, the 1,4-cis content ranges from 60% to 70%. It does not reach 76% of 1,4-cis content reported for a metallic barium initiation, and it was suggested to be a consequence of THF moieties complexed to the initiator. Increasing the polymerization temperature in benzene helps to improve the yield (57% after 28h at 25°C vs. 100% in 4 hours at 95°C) but 1,4-cis content drops down from 61% to 42% while 1,4-trans content increases from 30% to 49% (Figure 13) [48]. The influence of the solvent and polymerization temperature are reported on Figure 14.

The structure of the counter-ion was reported to have an influence on the anionic polymerization of styrene (M_1) and butadiene (M_2). In THF, it was shown that bis-triphenylmethylbarium induces the polymerization as an asymmetrical ion pair, because of its low initiation rate, unlike dibenzylbarium which polymerizes the monomers as free ions. For example, in THF, the reactivity ratios for a dibenzylbarium initiator are $r_1 = 8$ and $r_2 = 0.1$ whereas for bis-triphenylmethylbarium initiator they are $r_1 \approx r_2 \approx 1$ [8]. Differences can also be noticed on polybutadiene microstructure during copolymerization with styrene as for dibenzylbarium increasing conversion favors 1,2 addition rather than 1,4-cis whereas bis-triphenylmethylbarium favors 1,4-trans [8]. These differences were attributed to steric hindrance of a triphenylmethyl group, as it was demonstrated that the reactive center is asymmetric. However, for higher conversion, a small fraction of active center with both triphenyl groups was reported [47] (Figure 13).

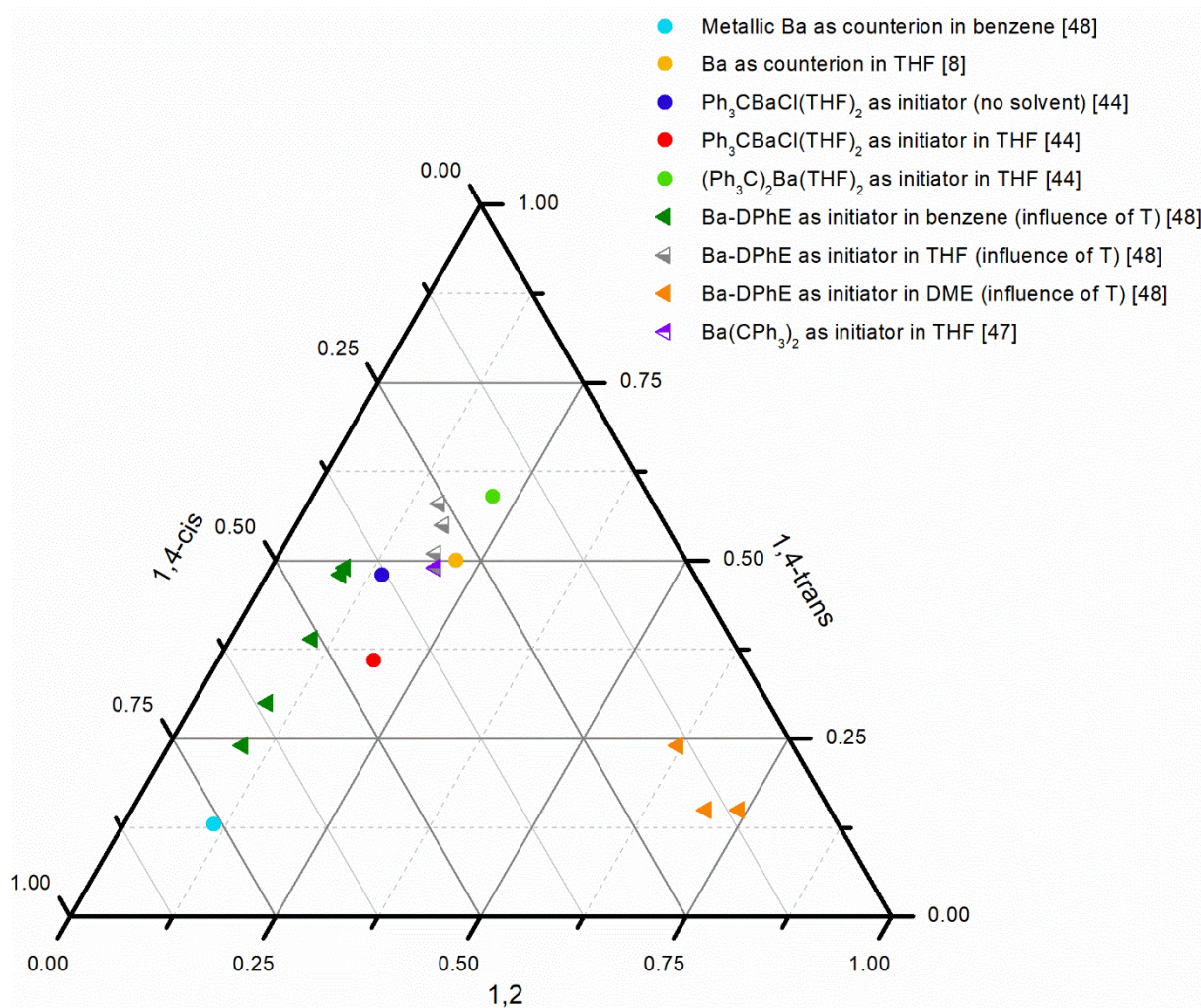


Figure 13. Microstructure of polybutadiene synthesized with barium-based initiators [8], [44], [47], [48]
(DME = dimethoxyethane)

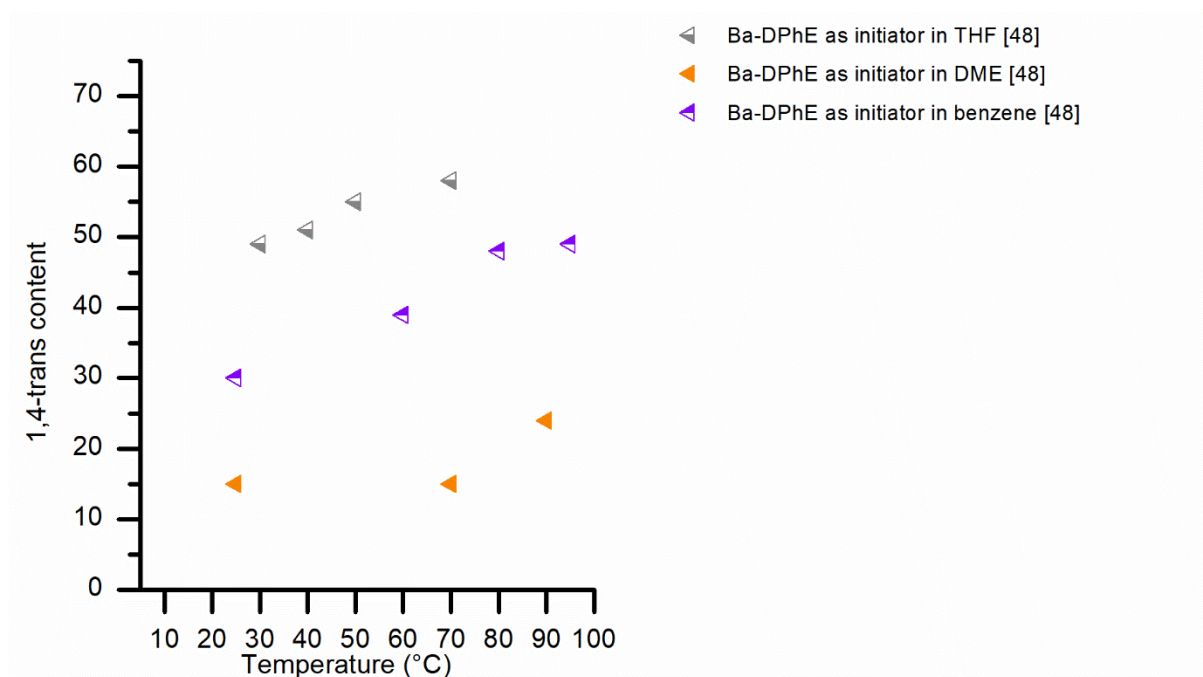
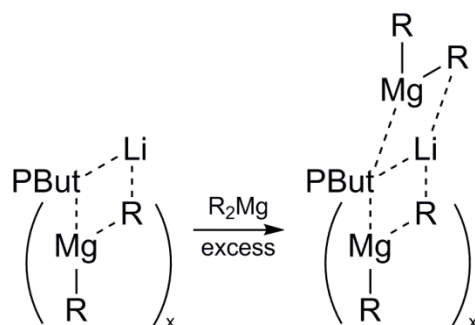


Figure 14. Influence of the solvent and polymerization temperature on polybutadiene 1,4-trans content obtained with barium salt of diphenylethylene [48]

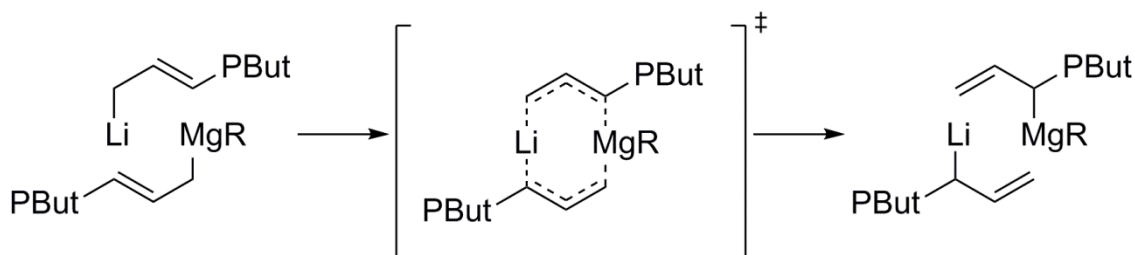
5. Alkyl lithium and alkaline earth bimetallic systems

In this section the addition of alkaline earth compounds to alkyl lithium is discussed toward the regulation of the polymerization rate and the microstructure. Reported systems in the literature deals with $\text{RLi} + \text{R}_2\text{Mg}$, $\text{RLi} + (\text{RO})_2\text{Ca}$, $\text{RLi} + (\text{RO})_2\text{Sr}$ and $\text{RLi} + (\text{RO})_2\text{Ba}$. It should be noted that none of these organo-alkaline earth compounds alone are active in anionic polymerization of diene or styrene in apolar media.

It was observed by Hsieh the ability of *n,s*-dibutylmagnesium to form complexes with either associated or non-associated alkyl lithium, without any induction period leading to the reduction of the polymerization rate for both styrene and butadiene [15]. The copolymerization reaction with such a system produces tapered poly(butadiene-*co*-styrene) in cyclohexane. Within the range $0 < [\text{R}_2\text{Mg}] / [\text{RLi}] < 1$, the addition of R_2Mg was reported to not influence polybutadiene microstructure [15] (Figure 15). For higher R_2Mg content ($1 < [\text{R}_2\text{Mg}] / [\text{RLi}] < 10$), it was shown by Carlotti and Deffieux a reduction of the polymerization rate along with an increase of the vinyl unsaturation from 13% when $[\text{R}_2\text{Mg}] / [\text{RLi}] = 1$ in cyclohexane at 40°C to 49% when $[\text{R}_2\text{Mg}] / [\text{RLi}] = 10$ (Figure 15). This phenomenon might be the result of highly complexed living chain end and / or isomerization of the last unit inside the $\text{PBLi} / \text{R}_2\text{Mg}$ in the complex responsible of chain propagation (Scheme 15 and Scheme 16) [49].



Scheme 15. Suggested additional complexation of living chain-end under the influence of R_2Mg in excess [49]



Scheme 16. Suggested mechanism for chain-end isomerization inside magnesiate complex [49]

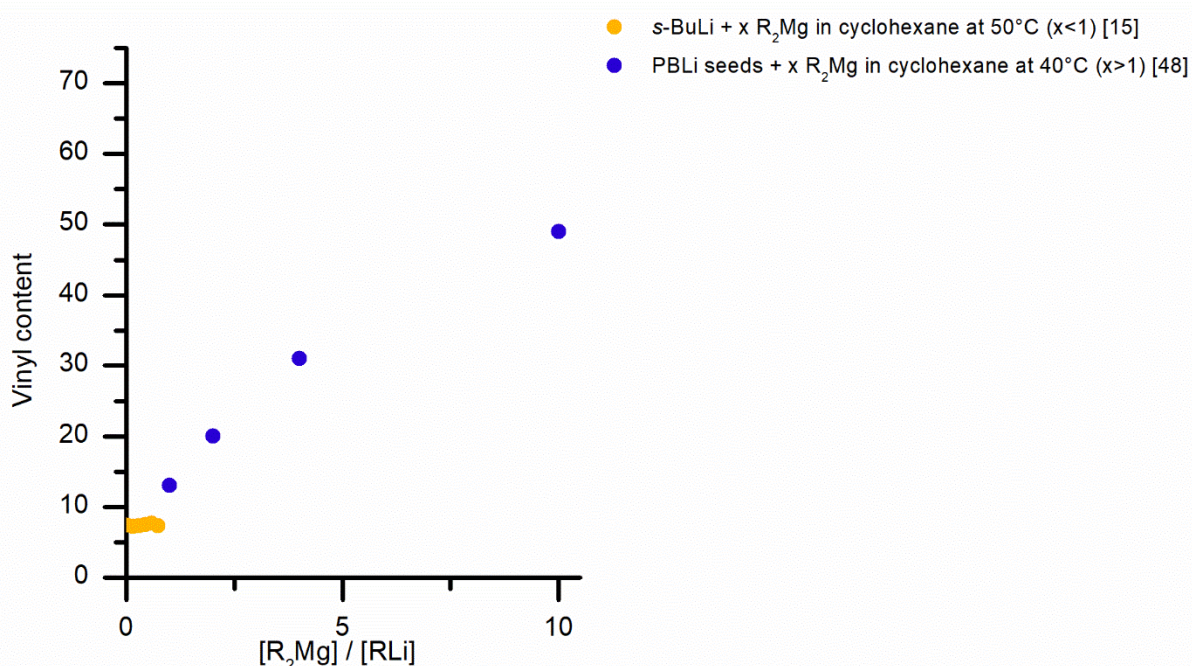


Figure 15. Influence of the ratio $[R_2Mg] / [RLi]$ on polybutadiene vinyl content [15], [49]

Copolymerization of butadiene and styrene, under the influence of calcium di-alkoxide (or calcium di-carboxylate) was shown by Fujio to reduce the rate of polymerization and to have a little influence on copolymers microstructure (For instance 36 - 40% 1,4-cis, 48 - 52% 1,4-trans and 12% 1,2 for $0.1 < [Ca] / [Li] < 1$ in toluene) [16] (Figure 16). The use of strontium *tert*-butoxide increases the styrene content of copolymers and tends to increase the 1,4-trans content of polybutadiene (up to 61.3% 1,4-trans in toluene $[Sr] / [Li] = 0.5$). Barium *tert*-butoxide has a similar impact but with an increased magnitude (e.g. 68% 1,4-trans in cyclohexane for $[Ba] / [Li] = 0.2$) (Figure 17). With barium *tert*-butoxide in toluene at 80°C , there is an optimum catalyst composition around $[Ba] / [Li] = 0.2$, obtaining a microstructure of 70% 1,4-trans, 20% 1,4-cis and 10% 1,2. In hexane, the optimum composition at 80°C is about $[Ba] / [Li] = 0.8$, obtaining a microstructure of 60% 1,4-trans, 20% 1,4-cis and 13% 1,2 (Figure 18).

Alkyl lithium / barium *tert*-butoxide initiating styrene / butadiene copolymerization was reported to produce copolymers with a random distribution. Fujio and coworkers suggested the formation of alkylbarium moieties to explain the behavior of $\text{RLi} + (\text{RO})_2\text{Ba}$ as initiating system [16].

Similar results in terms of microstructure were obtained by Hargis and coworkers with $[(\text{tert-BuO})_2\text{Ba}] / [\text{RLi}]$ in toluene at 30°C (63% 1,4-trans, 27% 1,4-cis and 10% 1,2) [50] (Figure 17). They also reported that the use of dissymmetric barium salt $((\text{tert-BuO})_{1.82}(\text{OH})_{0.18}\text{Ba})$, in association with alkyl lithium, allows the formation of polybutadiene with up to 79% 1,4-trans. As the ratio $[(\text{tert-BuO})_{1.82}(\text{OH})_{0.18}\text{Ba}] / [\text{BuLi}]$ increases from 0 to 0.5, the 1,4-cis content drops down from 38% to 18%, while 1,4-trans increases from 55% to 75%. When $[(\text{tert-BuO})_{1.82}(\text{OH})_{0.18}\text{Ba}] / [\text{BuLi}] > 0.5$, the 1,4-trans content drops down from 75% to 48% for $[(\text{tert-BuO})_{1.82}(\text{OH})_{0.18}\text{Ba}] / [\text{BuLi}] = 1$ while the 1,2 content increases from 7% to 30% (Figure 18). Meanwhile, increasing monomer to initiator ratio results in a decrease of 1,4-trans content from 78% to 67% when the $[\text{butadiene}] / [\text{BuLi}]$ ratio increases from 0.5×10^{-3} to 4×10^{-3} . As the polymerization temperature is increased from 5°C to 80°C, the 1,4 trans content drops from 80% to 60%. Polybutadiene synthesized with such a system exhibits a broad dispersity and copolymerization of styrene and butadiene was producing a random copolymer [50].

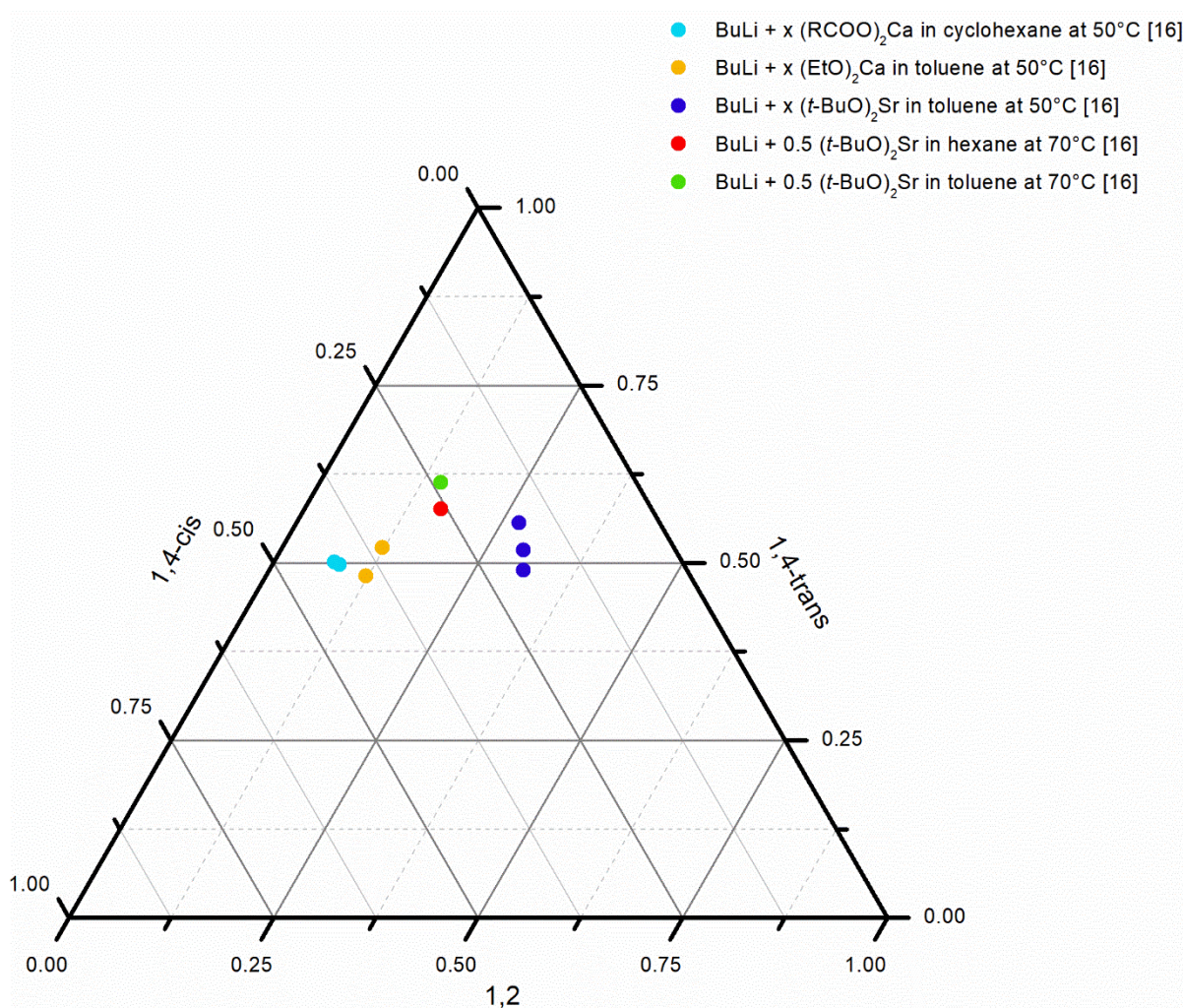


Figure 16. Influence of alkyllithium / alkaline earth metals derivatives (alkoxide or carboxylate) initiating systems on the microstructure of polybutadiene [16]. Data with a 1,2-content above 25% were measured at low yield (below 10%), which may explain their microstructure. (RCOO)₂Ca = calcium stearate

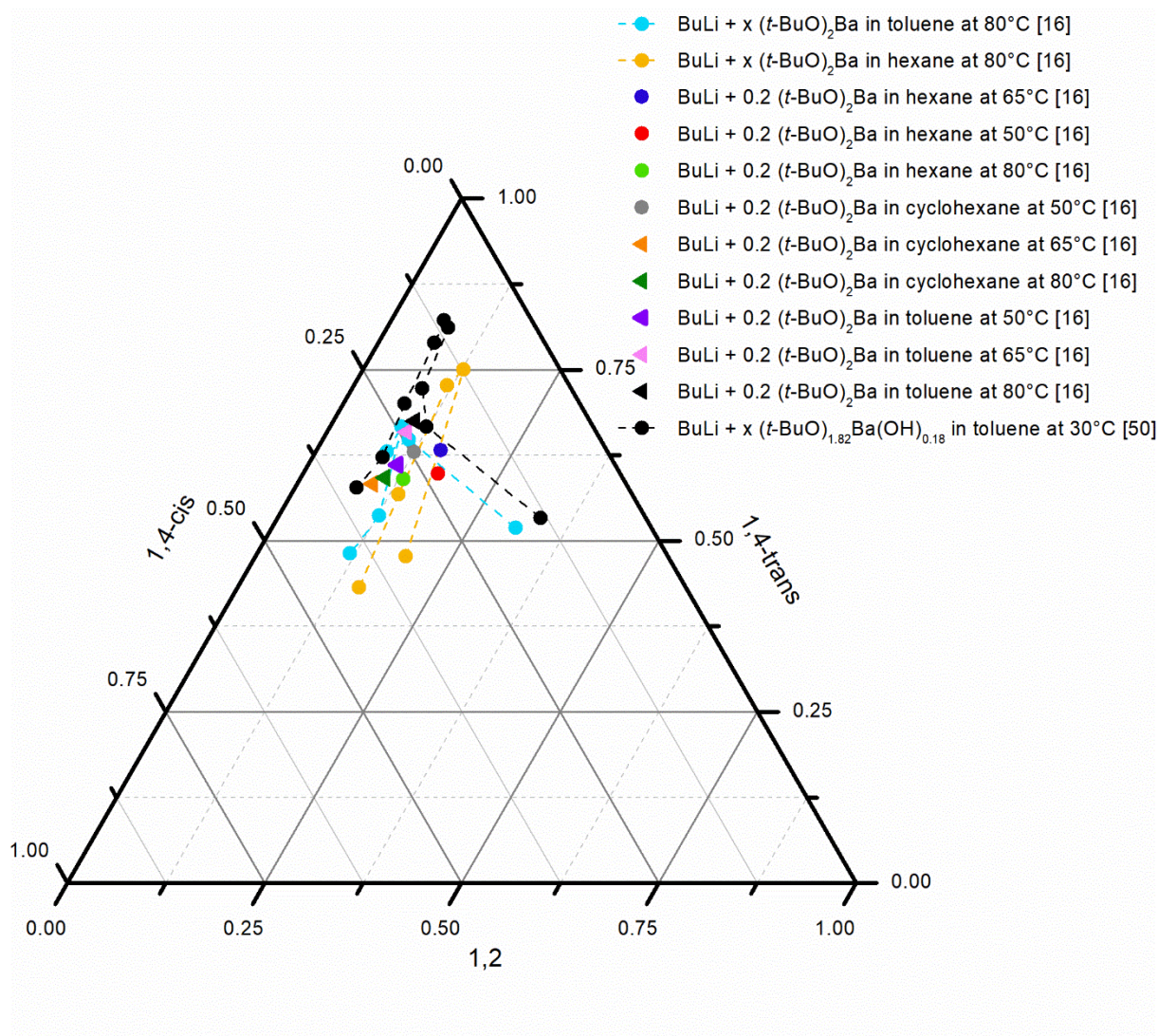


Figure 17. Influence of alkyllithium / Ba alkoxide initiating systems on the microstructure of polybutadiene [16], [50]

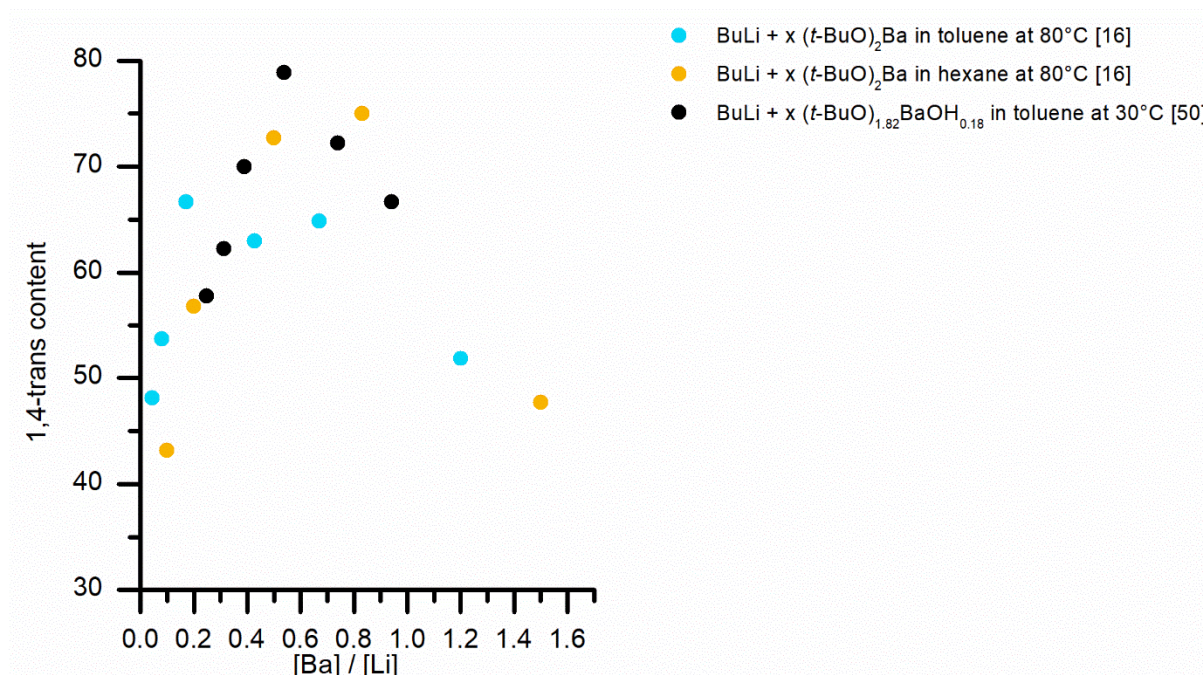
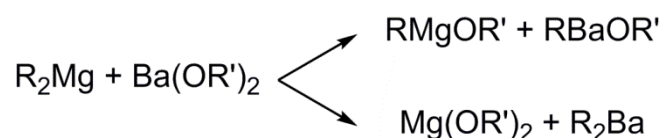


Figure 18. Influence of the ratio [Ba] / [Li] on polybutadiene 1,4-trans content obtained with Ba + Li based systems [16], [50]

6. Alkali metals and / or alkaline earth metals and other metals

It was reported by Baidakova *et al.* the ability of magnesium derivatives and barium alkoxides to polymerize butadiene either in benzene or in THF [46]. In THF, a system based on Mg + Ba(OEt)₂ is reported to produce polybutadiene with a 58% 1,4 trans content, 25% 1,4-cis and 17% 1,2 (Figure 19). The reaction of organo-magnesium with barium alkoxide and 1,1-diphenylethylene was described to produce a colored solution. Since after the initiator formation, analysis has showed that only Ba salts remain in solution, it was suggested the formation of both Ba(OR')R and BaR₂, which are supposed to be responsible for butadiene polymerization (Scheme 17) [46].



Scheme 17. Formation of alkyl barium and di-alkyl barium from di-alkyl magnesium and barium di-alkoxide [46]

The general trend for polybutadienes produced with this kind of system in benzene is a low amount of 1,2 unit (between 6% and 13%). The 1,4-cis / 1,4-trans ratio seems to be dependent on the solvent used during the initiator formation [46]. When the initiator is produced in benzene, reported 1,4-trans content is above 70%, and the 1,4-cis content is between 16% and 19%. Meanwhile, if the initiator synthesis was performed in polar solvent, the 1,4-trans content is between 28% and 54% and the 1,4-cis content is ranging from 34% to 63% [46]. Knowing that the amount of alkoxide moieties present in solution was reported to be dependent on the solvent used for the initiator formation (higher in benzene with respect to THF) and dependent on the ratio $[Mg] / [Ba]$, it was suggested that $Ba(OR')R$ active centers are responsible for the formation of 1,4-trans units and BaR_2 for the 1,4-cis units [46]. Obtained microstructures are reported in Figure 19.

A tri-component system based on barium alkoxide-hydroxide, dialkylmagnesium and trialkylaluminum was described by Hargis and coworkers [50]. When polymerization was performed in cyclohexane at 50°C and with $[Mg] / [Al] = 6$, an increasing amount of barium salt resulted in a decrease of the 1,4-trans content from 90% ($[Ba] / [Mg] = 0.2$) to 65% ($[Ba] / [Mg] = 1$) while the 1,2 content increases from 2% to 7% (Figure 19, Figure 20). Increasing polymerization temperature was also reported to decrease the 1,4-trans content from 90% (at 30°C) to 79% (at 80°C). Meanwhile, increasing monomer to initiator ratio resulted in a decrease of 1,4-trans content from 88% to 76% when $[butadiene] / [Mg]$ ratio increases from 0.4×10^{-3} to 3.2×10^{-3} . For copolymerization of a styrene / butadiene mixture, the styrene content was reported to be higher at low conversion with respect to RLi initiated polymerization. Both butadiene polymerization and butadiene / styrene copolymerization exhibit a living character allowing block copolymerization and chain end functionalization. Obtained polymers have a unimodal population [50].

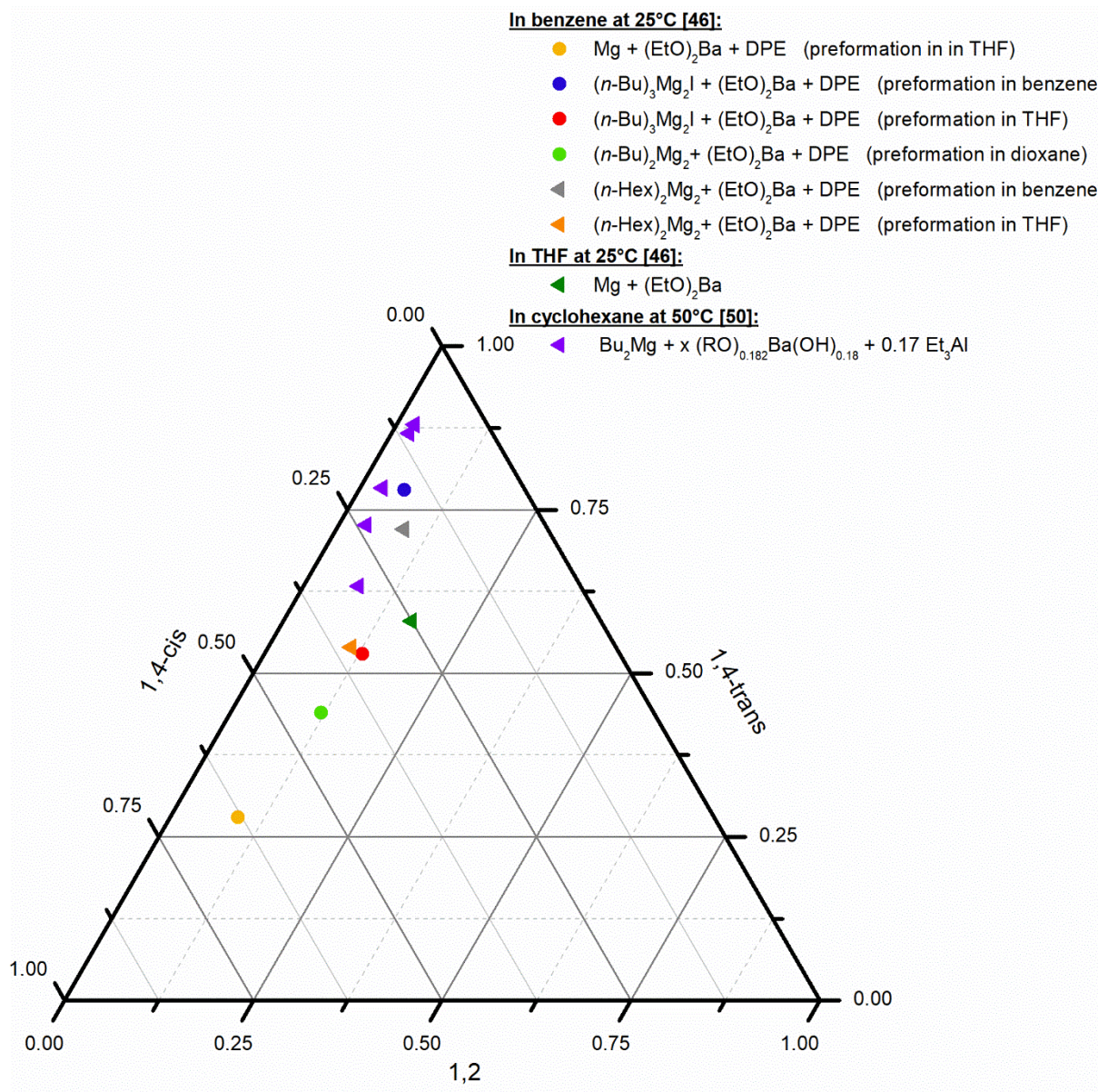


Figure 19. Polybutadiene microstructure obtained from Mg / Ba and Mg/Ba/Al based systems [46], [50]

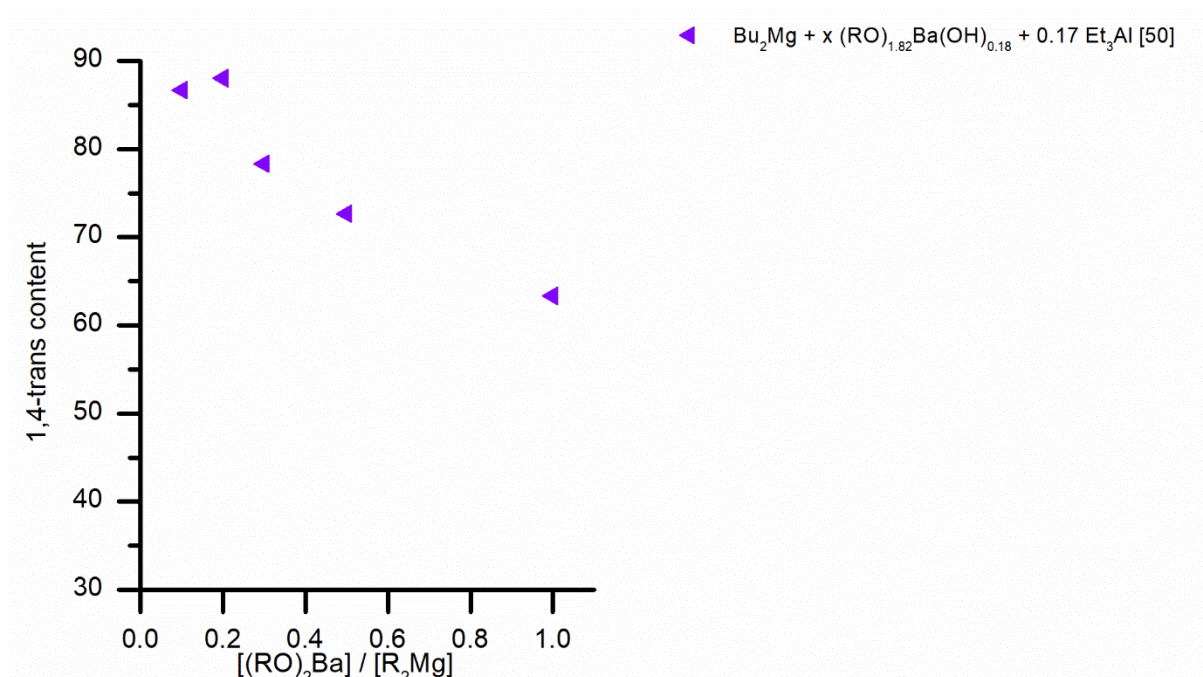
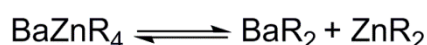


Figure 20. Influence of the ratio [Ba] / [Mg] on polybutadiene 1,4-trans content obtained with trimetallic system based on magnesium, barium and aluminum in cyclohexane at 50°C [50]

An initiation system based on $\text{Ba}(\text{OR})_2 + 3 \text{R}'_2\text{Mg}$ was patented by Halasa and coworkers [51]. The reported microstructure for polybutadiene synthesized under the influence of this system is 75% 1,4-trans, 19% 1,4-cis and 6% 1,2. In terms of microstructure, similar results (not shown on Figure 19 for a better reading of the figure) were obtained with barium salt of tetrahydrofurfuryl alcohol in association with 3 eq. *n,s*-dibutylmagnesium alone or in association with 1eq. potassium *tert*-pentoxide, or 1 eq. sodium mentholate / 1 eq. TMEDA, or 3 eq. *n*-butyllithium / 5eq. TMEDA, or 3 eq. *n*-butyllithium. [51].

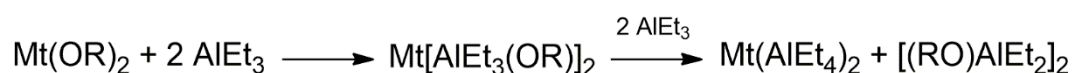
Fujio reported the ability of alkaline earth metalzinc-tetraalkyl (MtZnR_4) to polymerize and copolymerize butadiene with styrene in a hydrocarbon solvent. The 1,4-trans content increases from barium (64% for BaZnBu_4 in toluene and 67% for BaZnBu_4 in hexane) to strontium (70% for SrZnEt_4 in both solvent) and to calcium (75% for CaZnEt_4 in toluene and 73% for CaZnEt_4 in hexane) (Figure 21 for Ca and Sr, Figure 22 for Ba). The 1,2 content ranges from 7.5% for barium compounds to 9% for calcium ones in each solvent. Polybutadiene microstructure does not seem to be dependent on the conversion nor polymerization temperature. The styrene content in copolymer increases in the following order $\text{Ca} < \text{Sr} < \text{Ba}$ in either solvent from 10wt.% for calcium compound in toluene (15 wt.% in hexane) to 21.3 wt.% for barium compound in toluene (21.3 wt. % in hexane) [27].

Similar systems based on the product of the reaction between metallic Ba, 1,1-diphenylethylene and diethyl zinc, *i.e.* bis(1,1-diphenylbutyl)bariumzinc diethylate was studied by Baidakova *et al.* on butadiene polymerization in benzene [52]. Polybutadiene microstructure varies from 75% to 82% 1,4-trans, while 1,4-cis content is within the range 14% to 17% and the vinyl content is equal to 5% when varying polymerization temperature from 0°C to 60°C (Figure 22). When lowering the initiator concentration in benzene the 1,4-cis / 1,4-trans ratio is reported to increase from 0.23 to 1.73. It was pointed out that the addition of small amount of zinc diethylate suppresses the microstructure dependence on the initiator concentration. Knowing that 1,4-cis addition is typical of free alkylbarium moieties and according to these observations, it was suggested the existence of an equilibrium between free alkylbarium moieties and complexed one with alkylzinc (Scheme 18). Reducing the initiator concentration might shift the equilibrium toward free alkylbarium and leads to the formation of 1,4-cis polybutadiene, whereas the addition of alkylzinc shift the equilibrium toward complexed moieties leading to 1,4-trans polybutadiene [52].



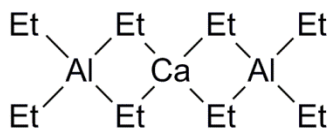
Scheme 18. Equilibrium between complexed bariumzinc tetraalkyl and free di-alkylbarium [52]

Aluminum / alkaline earth based initiators ($\text{Mt}(\text{AlR}_4)_2$) were also reported by Baidakova [52]. $\text{Mt}(\text{AlR}_4)_2$ can be prepared from a corresponding alkaline earth metal alkoxide and 4 eq. of triethylaluminium (Scheme 19) (Figure 17) [53], [54]. ROAlEt_2 can be removed by distillation under vacuum in the case of $\text{Mt} = \text{Ca}, \text{Sr}$ whereas in the case of $\text{Mt} = \text{Ba}$ purification is achieved through recrystallization [54].



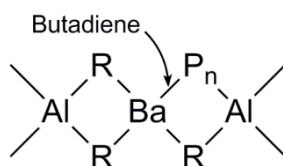
Scheme 19. Preparative route of $\text{Mt}(\text{AlR}_4)_2$ with $\text{Mt} = \text{Ca}, \text{Sr}, \text{Ba}$ [53], [54]

For calcium compound, the reported structure is presented in Scheme 20 [37].



Scheme 20. Reported structure of $\text{Ca}[\text{Al}(\text{Et})_4]_2$ [37]

A similar structure can be considered for other alkaline earth metals. With respect to this structure, Yakubovich suggested the insertion of the monomer in the polymer – barium bound as presented on Scheme 21 [37].



Scheme 21. Suggested site of monomer insertion for $\text{Ba}[\text{Al}(\text{Et})_4]_2$ [37]

Reported microstructure for such system is 85 – 91% 1,4-trans, 8 – 12% 1,4-cis and 1 – 3% 1,2 when $\text{Mt} = \text{Ba}$. For calcium compound the reported microstructure is 80% 1,4-trans, 15% 1,4-cis and 5% 1,2. The catalytic activity is low, and the polymerization is slow at room temperature. High concentrations of initiator were used but reported molar masses are higher than expected [52].

A summary of polybutadiene microstructure obtained with alkaline earth metal complexed with aluminum or zinc is given in Figure 21 for calcium and strontium, while barium-based systems are summarized in Figure 22.

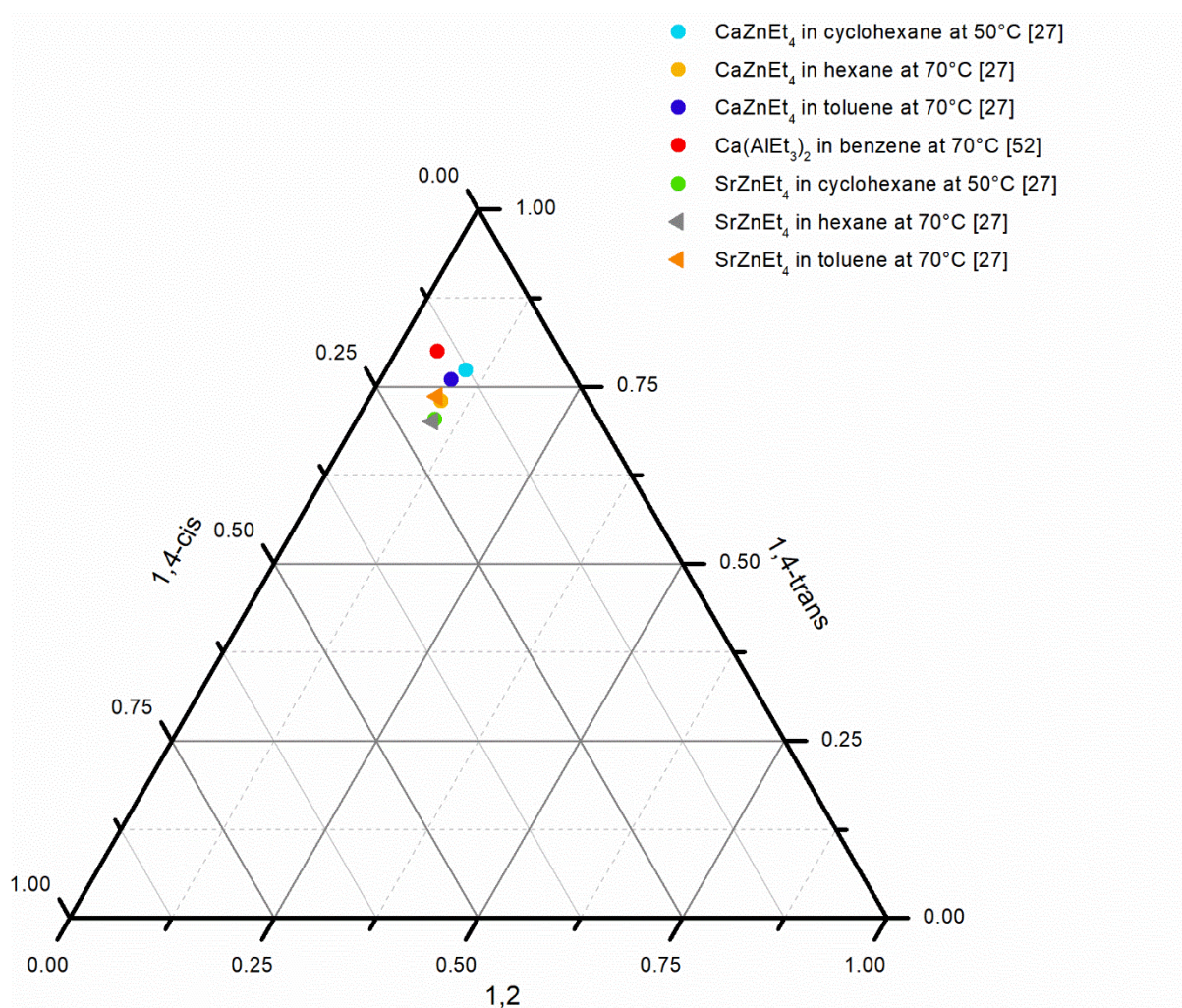


Figure 21. Microstructure of polybutadiene obtained from MtZnR₄ or Mt(AlR₄)₂ (Mt = Ca, Sr) [27], [52]

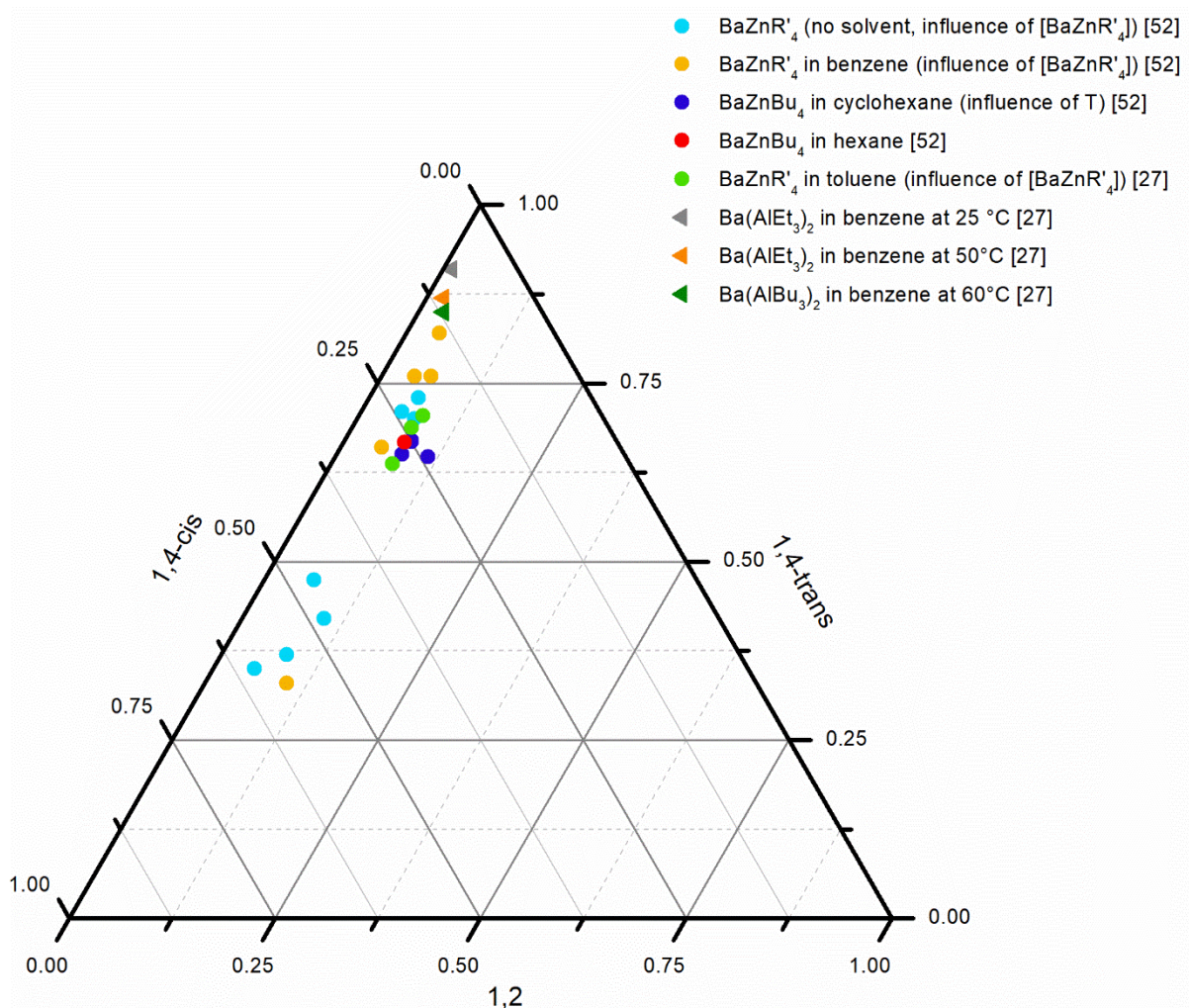


Figure 22. Microstructure of polybutadiene obtained from BaZnR_4 or $\text{Ba}(\text{AlR}_3)_2$ [27], [52]. (BaZnR'_4 = Bis-(1,1-diphenylbutyl) barium-zinc diethylate)

Systems based on $\text{Mt}[\text{Al}(\text{C}_2\text{H}_5)_4]_2$ with $\text{Mt} = \text{Ca}, \text{Sr}, \text{Ba}$ in association with alkyl lithium were patented for their ability to copolymerize styrene (25 wt. %) and butadiene (75 wt. %) mixture in heptane at 80°C and to produce copolymers with a high 1,4-trans content. For these systems, 80% conversion is reached in less than 2 hours and the styrene content increases from calcium based catalyst (10 wt. %) to barium one (15 wt. %). Meanwhile, the 1,4-trans content increases from 77% for calcium compound to 85% for barium one [55].

A bimetallic system based on calcium anthracene and trialkylaluminum was reported to be able to produce polybutadiene [56]. The 1,4-trans content can be increased from 82% to 87% when $[Al] / [Ca]$ is increased from 0 to 2.8. Reported 1,4-cis content and vinyl content are always below 12% [56]. A bimetallic system based on alkyllithium, calcium alkoxide and lithium alkoxide was said to produce polybutadiene with 50 – 80% 1,4-trans content, 10% – 45% 1,4-cis content and a 1,2 content between 5% to 20% [57].

A tri-metallic system composed of a di-alkyllithium derivatives in association with barium alkoxide and trialkylaluminum (with $[Ba] / [Li] = 0.25$ and various $[Al] / [Li]$ in cyclohexane at 70°C) was reported by Zhang and coworkers [58], [59]. Increasing amount of alkyl aluminum was shown to increase the 1,4-trans content from 55.5% ($[Al] / [Li] = 0$) to 90.1% ($[Al] / [Li] = 1.8$) and to reduce the 1,2 content from 7.8% to 3.1% (Figure 23, Figure 24). Meanwhile, the yield after 3h at 70°C increases from 82% ($[Al] / [Li] = 0$) to 92% ($[Al] / [Li] = 1$) then drops down to 14% for $[Al] / [Li] = 1.8$. This phenomenon was explained by the retarding effect of trialkylaluminum on anionic polymerization. It is reported that polymerization does not occur above 2 eq. of trialkylaluminum with respect to the lithium compound. It might be a consequence of the formation of $LiAlR_4$ which was observed to be inactive with respect to anionic polymerization. Such system was reported to be able to produce stereotriblock, polyisoprene-*block*-high-trans-1,4-polybutadiene-*block*-polyisoprene and polystyrene-*block*-high-trans-1,4-polybutadiene-*block*-polystyrene [58], [59]. A similar system was used by Benvenuta-Tapia *et al.* to copolymerize butadiene and styrene. Microstructures reported are 78% 1,4-trans, 16% 1,4-cis and 6% vinyl content at 70°C in cyclohexane [60]. The addition of styrene with such systems was shown to be random [60].

Addition of alkali metal alkoxide to these trimetallic systems was said to increase the 1,4-trans content, and to decrease the polymerization time. For example [61], the addition of $ROLi$ (0.6 eq.) to a system 1 RLi : 0.3 $Ba(OR)_2$: 1.33 R_3Al was reported to increase the 1,4-trans content from 78% to 90%, and to decrease the 1,2 content from 5% to 2%, while the polymerization time to reach 70% conversion was 6 times lower. The addition of $RONa$ however seems to be less effective to increase the 1,4-trans content (85%) [61]. A summary of polybutadiene microstructure with such systems is presented on Figure 23.

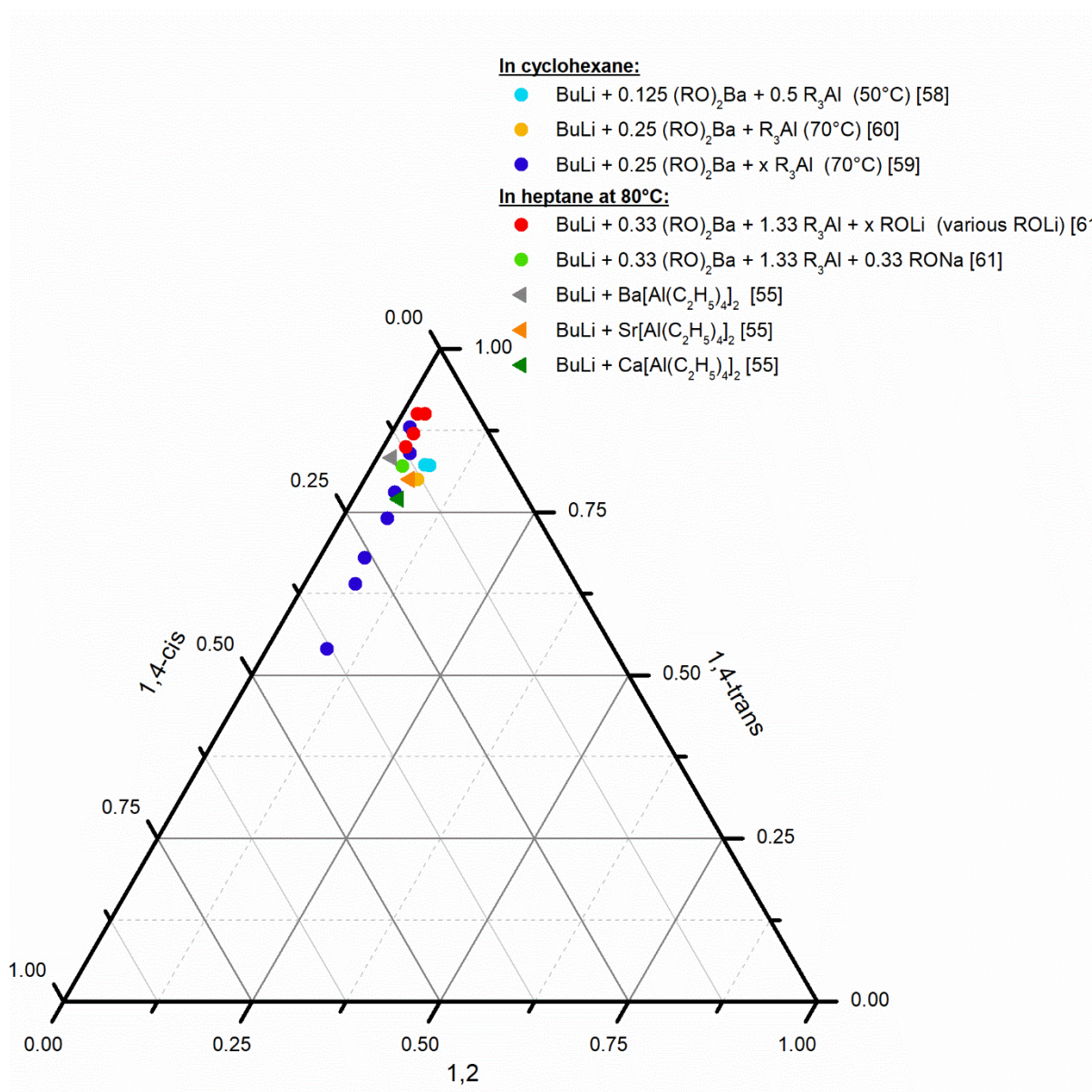


Figure 23. Microstructure of polybutadiene obtained with Li / Ba / Al based systems [55], [58]–[61] where (R'O)₂Ba = barium bis(nonylphenolate)

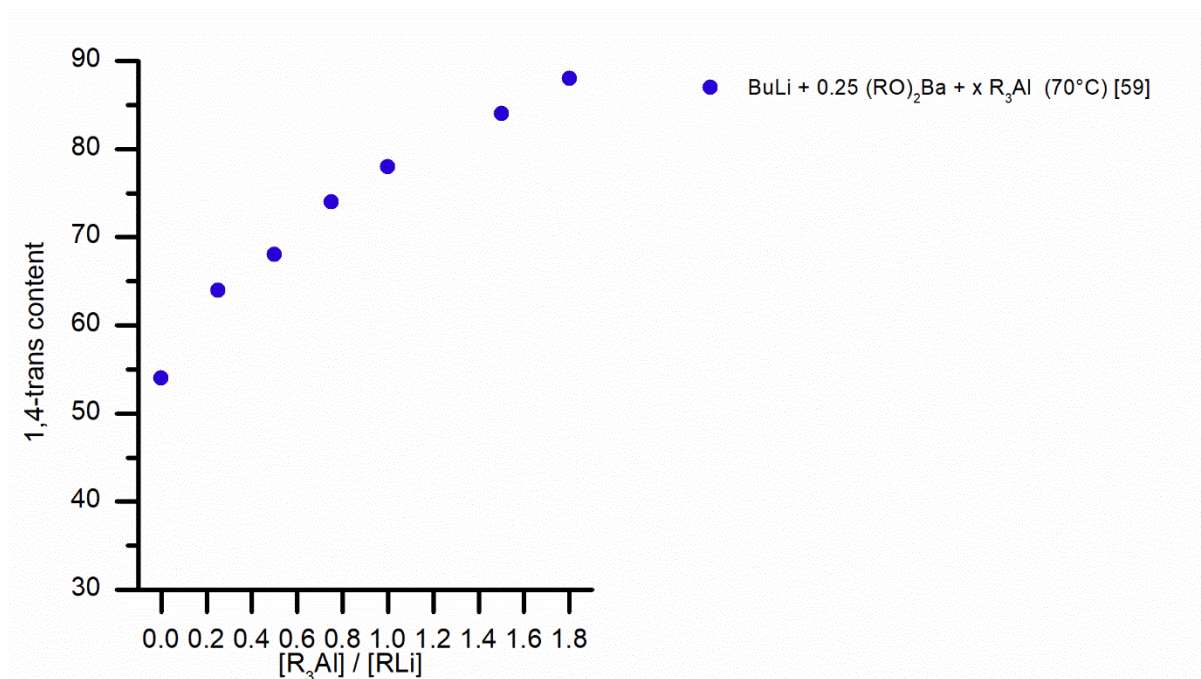


Figure 24. Influence of the aluminum content on trimetallic systems based on barium alkoxide, alkyl aluminum and alkyllithium in cyclohexane at 70°C [59]

7. Conclusion

The aim of this work was to review the composition of the active species enabling to reach various polybutadiene microstructures by anionic polymerization. Anionic polymerization allows copolymerization and chain-end functionalization along with a real possibility to tune polybutadiene microstructure.

Unlike the coordination methodology, the anionic approach does not yield to highly stereoregular polymerization but allows much more versatility in terms of obtained polybutadiene microstructure. Two main axes relative to the anionic method may be drawn as presented on Figure 25.

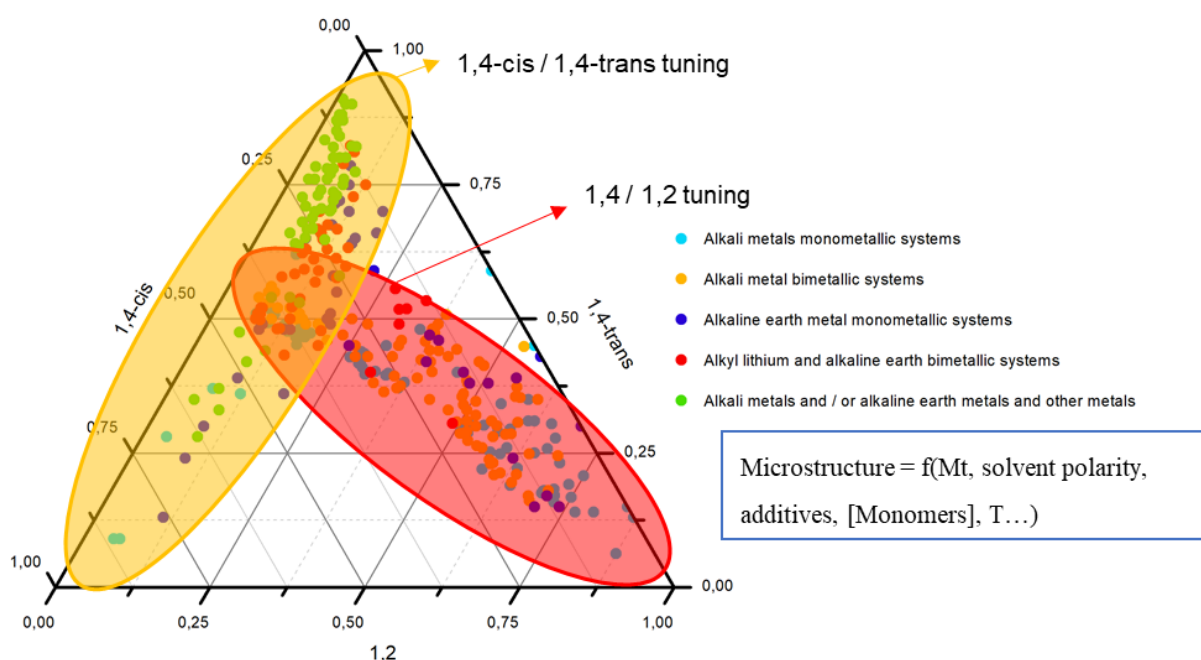


Figure 25. Accessible microstructures of polybutadiene by anionic polymerization

A first one represents polybutadienes with a 1,2 content below 10% and a 1,4-cis within the range 7%-86%, while the 1,4-trans content ranges from 9% to 90%. Polybutadiene with 86% 1,4-cis content, 9% 1,4-trans content and 5% vinyl content is reported when alkyllithium is used as an initiator (neat polymerization, $[RLi] \approx 10^{-6} \text{ mol.L}^{-1}$), whereas 7% 1,4-cis, 90% 1,4-trans and 3% vinyl content is reported when a multimetallic system is used as initiator (alkyllithium / trialkylaluminum / barium alkoxide, in heptane at 80°C). Moving along this axis can be generally achieved with lithium initiator in bulk by changing the initiator concentration or by

using barium-based initiator (alkylbarium or by associating barium alkoxide with alkyllithium and trialkylaluminum).

The second axis represents polybutadiene with an increasing vinyl content. Starting from alkyllithium-initiated polymerization in cyclohexane (42% 1,4-cis, 51% 1,4-trans, 7 % 1,2) to alkyllithium initiated polymerization in THF (6% 1,4-cis, 6% 1,4-trans, 88% 1,2). Moving along this axis using alkyllithium and apolar media can be achieved through the addition of heavy alkali metal alkoxides or polar modifier.

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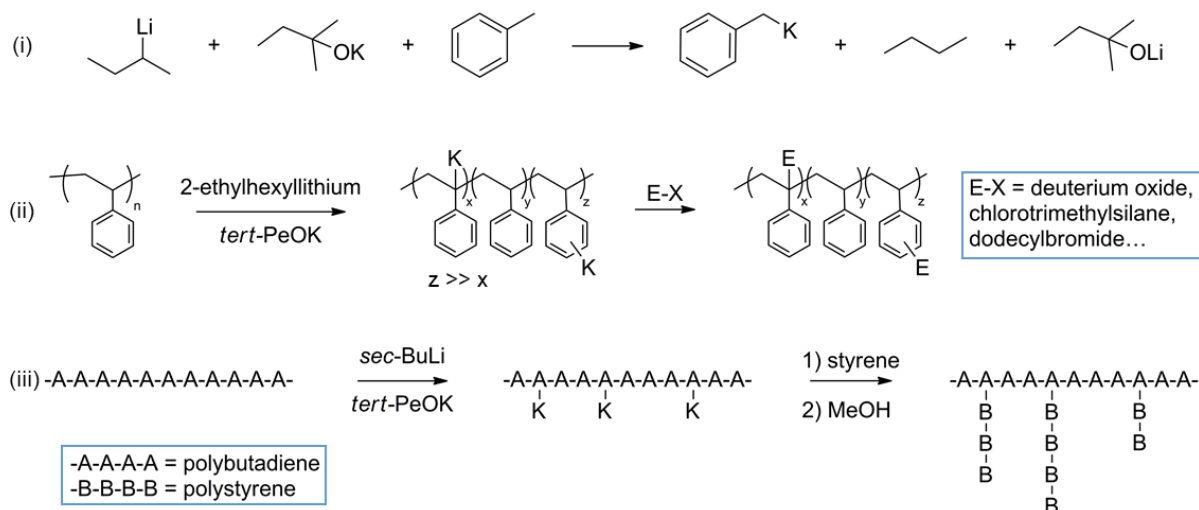
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Chapter II.

**Anionic polymerization of butadiene using lithium derivatives /
potassium alkoxides bimetallic systems: Influence on
polymerization control and polybutadiene microstructure**

1. Introduction

The reaction product between alkyl lithium and alkali metal alkoxides referred as “super-base” or Lochmann-Schlosser base are used to metalate a wide range of organic substrate (*e.g.* benzene, toluene, ethylbenzene... [1]–[4]). For instance, addition of toluene to a superbase composed of *sec*-butyllithium + 1eq. of potassium *tert*-pentoxide leads to the formation of benzylpotassium (Scheme 1(i)). Similarly, metalation of non-polar polymers backbone leads to functionalized polymers after addition of an electrophile (Scheme 1(ii)) [5], or to grafted polymers after addition of monomers (Scheme 1(iii)) [6].



Scheme 1. (i) Metalation of toluene with *sec*-butyllithium + 1 eq. of potassium *tert*-pentoxide [4]. (ii) Metalation and functionalization of polystyrene with 2-ethylhexyllithium + potassium *tert*-pentoxide [5]. (iii) Metalation of polybutadiene with *sec*-butyllithium + 1eq. of potassium *tert*-pentoxide for random grafting of polystyrene on polybutadiene backbone [6]

The ability of systems based on potassium alkoxides and alkyl lithium moieties was proven to be able to polymerize styrene and butadiene [7]–[10]. The one-pot / one-step copolymerization of a styrene / butadiene mixture with an alkyl lithium initiator in hydrocarbon media tends to produce a tapered copolymer, with a first block of polybutadiene with a low styrene content, followed by an almost pure block of polystyrene. This phenomenon is explained by the crossover reaction from styrene to butadiene being rather fast, unlike the crossover reaction from butadiene to styrene being slow. Meanwhile, the one-pot / one-step copolymerization of styrene and butadiene initiated by *n*-BuLi + ROMt (Mt = Na, K, Rb, Cs), tends to produce random copolymers without block segregation, and the resulting polymer structure tends to a

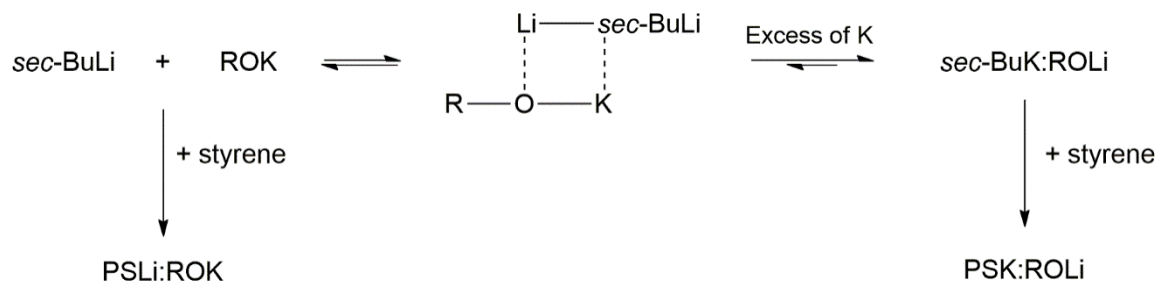
random one. This phenomenon was attributed to a greater acceleration of styrene polymerization with respect to butadiene thanks to the participation of the heavier alkali metal in the active species [11].

In terms of polybutadiene microstructure regulation, the use of alkyllithium in association with lithium *tert*-butoxide in cyclohexane have a minor influence on the vinyl content. For instance, when [lithium *tert*-butoxide] / [*n*-butyllithium] varies from 0 to 6 in cyclohexane at 30°C, obtained 1,2 content increases from 6% to 11% [12]. But for low molar masses ($\overline{DP} = 10$), reported vinyl content with such a system goes up to 60% in toluene [13]. The general trend for heavier alkali metal alkoxide in association with *n*-butyllithium is an increase of the vinyl content with the ratio [R'OMt] / [RLi]. When this ratio is equal to 1, polybutadiene microstructure tends to be the same one as for polybutadiene made with the corresponding alkyl metal initiator (68% vinyl for Na, 50% for K, 55% for Rb and 51% for Cs) [7].

Questions arise for polybutadiene microstructure when the ratio [ROMt] / [RLi] is above one. For instance, in the case of [potassium *tert*-pentoxide] / [*n*-butyllithium] > 1 in hexane, Halasa and coworkers reported the formation of polybutadiene with a soluble fraction and an insoluble one, the soluble fraction is identified as polybutadiene with 50% vinyl units while the insoluble one is supposed to be 100% 1,4-*trans* polybutadiene [10]. Meanwhile, in 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 [9]. When [K] / [Li] > 1 in hexane, Halasa reported molar masses close to the targeted ones for the soluble polybutadiene fraction with broad dispersity ($\overline{D} > 1.3$) [10]. For similar ratios in toluene, Yakubovich and coworkers reported increasing dispersities from 1.5 to 52 when [K] / [Li] is increased from 0.1 to 6 which is the consequence of chain transfer to toluene [9].

In terms of polymerization control, available data dealing with styrene polymerization show that increasing potassium *tert*-pentoxide to *sec*-butyllithium ratio allows a better control of the polymerization in cyclohexane at 20°C. For example, when the targeted molar mass is 10,000 g.mol⁻¹ (with respect to *sec*-butyllithium), experimentally obtained molar masses ranges from 73,000 g.mol⁻¹ ([K] / [Li] = 1, yield = 92%, $\overline{D}$ =2.0) to 11,000 g.mol⁻¹ ([K] / [Li] = 10, yield = 93%, $\overline{D}$ =1.5). Meanwhile, polystyrene tacticity is reported to not be affected by this ratio [8]. This increased initiation efficiency was said to be the consequence of a better solubilization of

the initiating species along with the displacement of an equilibrium toward alkylpotassium moieties (with a considerably higher propagation rate) as presented in Scheme 2.

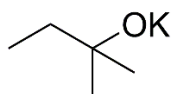


Scheme 2. Proposed mechanism to explain the influence of [K] / [Li] on the initiation efficiency for polystyrene synthesis with a bimetallic system based on *sec*-butyllithium + x eq. of potassium *tert*-pentoxide [8]

The present work aims to study initiating systems based on potassium alkoxides in association with different alkyllithium for butadiene polymerization and particularly to identify parameters, such as the nature of the alkoxide, the alkyllithium structure and the initiator preparation, affecting polymerization control and microstructure. For a better understanding of the initiation mechanisms, styrene was used when needed as a model monomer.

2. Influence of potassium *tert*-pentoxide / *sec*-butyllithium preparation on styrene polymerization

Since the formation of the active species requires the reaction between two organometallic species, the influence of the preformation time (time between active species synthesis and monomer addition) was first investigated with $[K] / [Li] = 0.5$ and 5. For these sets of experiments styrene was used as a model monomer, cyclohexane as the solvent, mixture of *sec*-butyllithium and potassium *tert*-pentoxide (*tert*-PeOK, Scheme 3) were 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 10,000 g.mol⁻¹ with the hypothesis of one polymer chain per alkyl lithium molecule.



Scheme 3. Structure of potassium *tert*-pentoxide (*tert*-PeOK) also known as potassium *tert*-amyloxide

2.1. Styrene polymerization with [potassium *tert*-pentoxide] / [*sec*-butyllithium] = 0.5

The influence of the initiator preformation time with $[K] / [Li] = 0.5$ was first investigated. As shown in Figure 1, molar masses are in good agreement with the targeted ones when the initiator preformation time is below 1h showing that the initial amount of *sec*-butyllithium controls the polymer chain length. However, for longer preformation time, an increase of molar mass is observed, and polymerization control is not achieved anymore. This phenomenon may be the consequence of active centers loss. In addition, obtained polymers exhibit a molar mass distribution ranging from $\bar{D} = 1.1$ to 1.6 and a tail on the low molar mass side. These observations may be associated to a slow initiation rate with respect to the propagation one. Potassium or potassium / lithium complexes are believed to be responsible of the propagation step since the UV maxima absorption changed from 326 nm, characteristic of polystyryllithium [8] to 333 nm upon addition of 0.5 eq. of potassium *tert*-pentoxide to PSLi seeds (Figure 2).

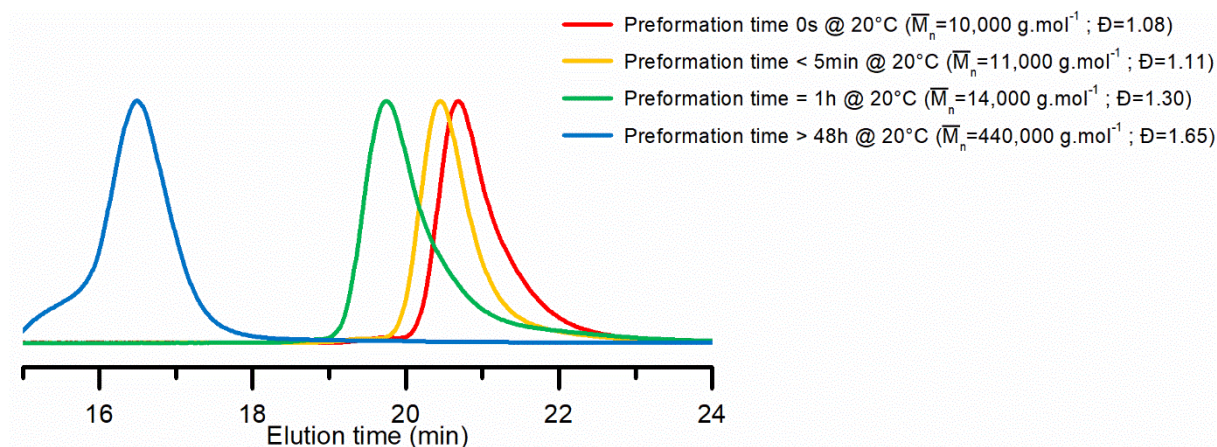


Figure 1. SEC chromatograms of polystyrene synthesized using *sec*-butyllithium + 0.5 eq. of potassium *tert*-pentoxide with various initiator preformation time in cyclohexane at 20°C. ([styrene] = 1 mol.L⁻¹, [sec-BuLi] = 10⁻² mol.L⁻¹, $\overline{M}_{nth}$ = 10,000 g.mol⁻¹, 16 h, yield = 100%)

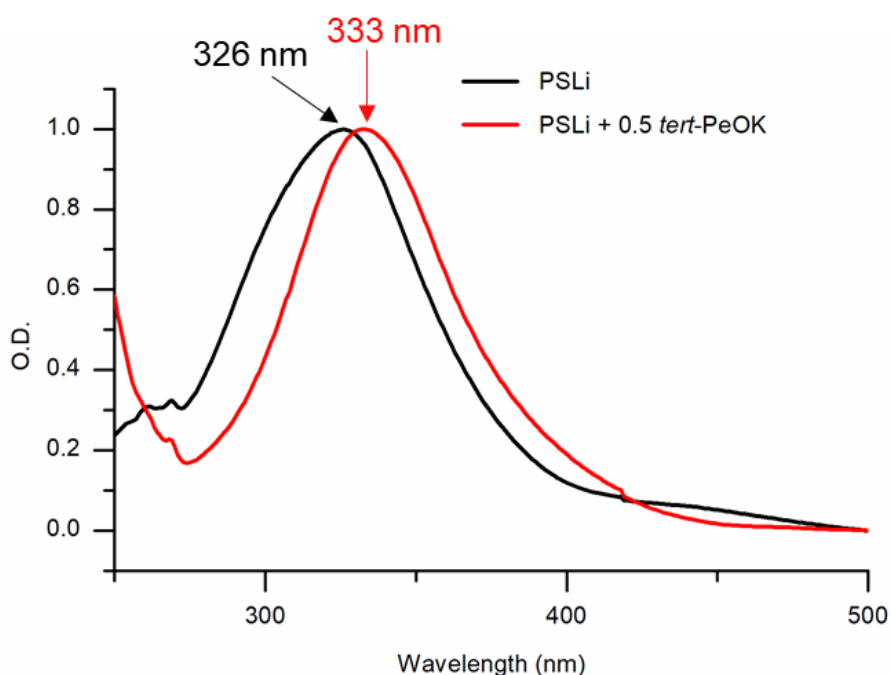


Figure 2. Evolution of the PSLi UV-visible spectrum 5 minutes after addition of 0.5 eq. of potassium *tert*-pentoxide in cyclohexane at 20°C, $\overline{M}_n=1,000$ g.mol⁻¹, [PSLi seed] = 8 x 10⁻³ mol.L⁻¹

The reaction between potassium *tert*-butoxide and *n*-butyllithium ($[t\text{-BuOK}] / [n\text{-BuLi}] < 1$), is reported in the scientific literature to produce a precipitate composed of *n*-butyllithium – *n*-butylpotassium adducts, free of alkoxide moieties (which remain in solution), with the ratio potassium to lithium dependent on the initial $[t\text{-BuOK}] / [\text{BuLi}]$ ratio [14].

Accordingly, in our polymerization experiments, the initiation by *sec*-butyllithium moieties is probably responsible for the slow initiation step with respect to the initiation by *sec*-butylpotassium moieties. Only one polystyrene population is observed, suggesting a fast counterion exchange between polystyrylpotassium and polystyryllithium chain ends.

2.2. Styrene polymerization with [potassium *tert*-butoxide] / [*sec*-butyllithium] = 5

For this set of experiments, and to validate the effect of the initiator preformation time on polymerization control, the use of potassium *tert*-butoxide / *sec*-butyllithium as an initiator with $[\text{K}] / [\text{Li}] = 5$ was studied. Since this organometallic system is not soluble in cyclohexane at a concentration as low as $4 \times 10^{-2} \text{ mol.L}^{-1}$, the initiating species was synthesized *in-situ* for each experiments and styrene was added within a range of 48 hours.

When initiator preformation was allowed, obtained polystyrene were partly precipitated before termination suggesting a high aggregation state of propagating centers. When no preformation time is allowed, polymerization control is achieved and, like in the case of $[\text{K}] / [\text{Li}] = 0.5$, the initial amount of *sec*-butyllithium controls the polymer chain length (Table 1, Figure 3).

Table 1. Polymerization of styrene using *sec*-butyllithium + 5 eq. of potassium *tert*-pentoxide ($\bar{M}_{n\ th} = 10,000$ g.mol⁻¹, [styrene] = 1 mol.L⁻¹, [sec-BuLi] = 10⁻² mol.L⁻¹, cyclohexane, 20°C, 16 h, yield = 100%)

Preformation time	$\bar{M}_n\ exp^a$ (g.mol ⁻¹)	$\bar{D}^a$	$\bar{M}_n\ exp$ shoulder (g.mol ⁻¹)	% second population
No preformation	11,000	1.07	25,000	5
< 5min	11,000	1.12	34,000	45
1h	13,000	1.13	40,000	34
> 48h	30,000	1.11	110,000	-
> 48h @ 60°C	69,000	1.31	260,000	16

^a Obtained for the main population

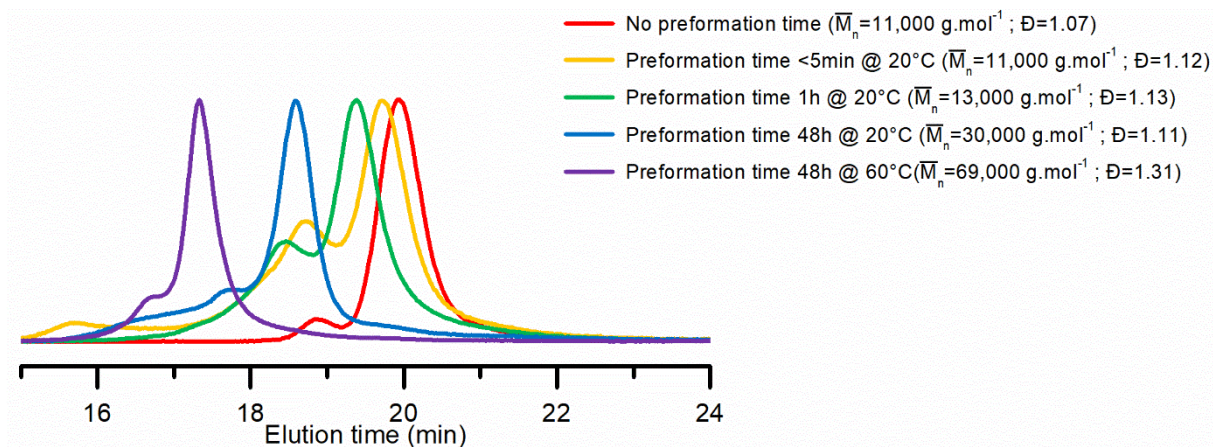
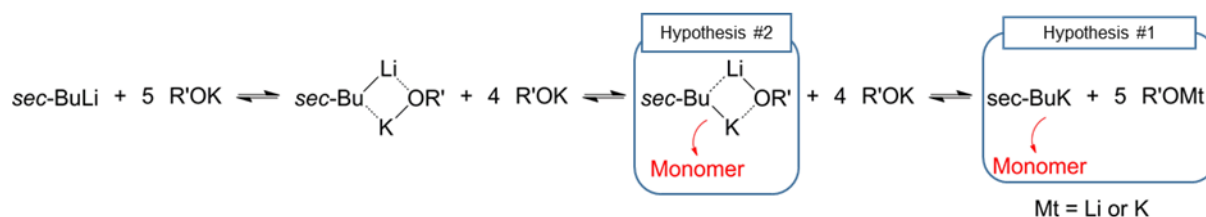


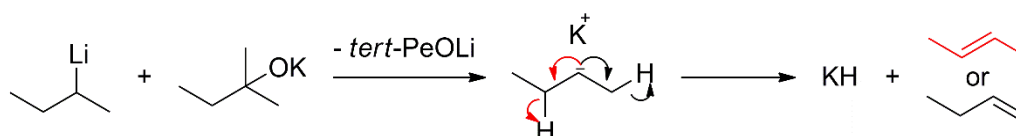
Figure 3. SEC chromatograms of polystyrene performed using [tert-PeOK] / [sec-BuLi] = 5, with various preformation time in cyclohexane at 20°C ($\bar{M}_{n\ th} = 10,000$ g.mol⁻¹, [styrene] = 1 mol.L⁻¹, [sec-BuLi] = 10⁻² mol.L⁻¹, 16 h, yield = 100%)

The nature of the active center remains unclear, since two hypotheses can be drawn. The first hypothesis is linked to reported results by Lochmann and coworkers. The association of *n*-butyllithium with potassium *tert*-pentoxide ($1 < [\textit{tert}\text{-PeOK}] / [\textit{n}\text{-BuLi}] < 3$) leads to the formation of a precipitate which was found, after isolation, to be composed of *n*-butylpotassium in aggregated form [1], [3]. Accordingly, with $[\textit{tert}\text{-PeOK}] / [\textit{sec}\text{-BuLi}] = 5$, a first hypothesis can assume here that the active center is a free styrylpotassium moieties (Scheme 4, hypothesis #1). However, in the frame of polymerization experiments without isolation of the precipitated initiator, the presence of potassium *tert*-pentoxide and lithium *tert*-pentoxide may lead to complexation of the chain end and have an influence on polymerization control (Scheme 4, hypothesis #2). Additional complexation of the propagation center with the remaining alkali metal alkoxide could also be envisaged to be part of a complex with a higher stoichiometry (Not represented on Scheme 2).



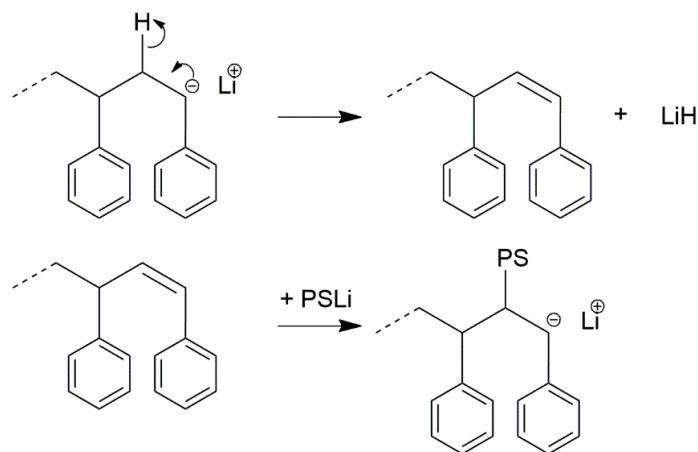
Scheme 4. Proposed mechanism for the formation of the initiator ($[\textit{tert}\text{-PeOK}] / [\textit{sec}\text{-BuLi}] = 5$)

When potassium *tert*-pentoxide and *sec*-butyllithium are let to react together before addition of styrene, molar mass control is not achieved anymore (Figure 3). This phenomenon is believed to be linked to a progressive deactivation of the active species resulting into a molar mass increase. This phenomenon may be related to 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 5) [15].



Scheme 5. Hypothetic mechanism for the formation of potassium hydride upon degradation of *sec*-butytpotassium

In all cases, polystyrenes obtained are multipopulated (Table 1, Figure 3) on SEC chromatograms with a double molar mass with respect to the main population. In the case of preformation time < 5 min and 48h, a third population can also be observed with high molar masses with respect to the main population. Oxygen coupling during the termination step could be a reasonable hypothesis but is quite unsatisfactory considering the magnitude of this second population and it does not provide explanation on the nature of the third population. Another hypothesis can be drawn from this observation. Viola and coworkers reported the progressive deactivation of polystyryllithium at high temperature ($70 - 115^{\circ}\text{C}$), this phenomenon leading to lithium hydride elimination and subsequent reaction of two polymer chain ends and finally to a second population with doubled molar masses [16] (Scheme 6). A similar mechanism could be envisaged with polystyrylpotassium at 20°C because of the higher reactivity of potassium moieties, but it does not provide any explanation with respect to the occurrence of a third population. Another hypothesis could be depicted as follow: since the initiator mixture undergoes deactivation upon standing, the coexistence of several active species could be envisaged with various aggregation states and propagation rates leading to multipopulated polymers. In our experiments, precipitation of the polymer growing chains upon addition of styrene due to aggregation and obtention of quantitative yield in less than 30 minutes at 20°C do not allow further investigation. Counterion exchange on polystyryllithium ($\bar{M}_n = 10,000 \text{ g.mol}^{-1}$) by the addition of 5 eq. of potassium alkoxide was attempted to mimic the polymer chain end deactivation, bimodal distributions were not observed on SEC chromatograms even after a week and polymer precipitation was not observed suggesting that the propagation center is different (Chapter II.4).



Scheme 6. Proposed mechanism for polystyryllithium deactivation in apolar media at high temperature [16]

3. Butadiene polymerization with *sec*-BuLi + x eq. of potassium *tert*-pentoxide: influence of [K] / [Li] ratios on polybutadiene microstructure and polymerization control

Butadiene polymerization with bimetallic initiating systems based on *sec*-butyllithium + x eq. of potassium *tert*-pentoxide (x=0.1, 0.35, 0.7, 1 and 5) were performed in cyclohexane, with no initiator preformation time. In all cases, butadiene polymerization experiments were carried out with a targeted molar masses of 10,000 g.mol⁻¹ with the hypothesis of one polymer chain per alkyllithium molecule.

In all cases for [K] / [Li] ≤ 1, 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 2). When 0.35 ≤ [K] / [Li] ≤ 1, the vinyl content ranges from 40% to 50% which is typical of potassium-based systems in apolar media [17]. Even if the nature of the chain end is not clear, polybutadiene microstructure is typical of potassium-based systems, and a potassium – carbon bond seems to be responsible of the propagation step.

Systems based on *n*-butyllithium + x eq. potassium *tert*-pentoxide (x > 1) were reported to metalate polybutadiene backbone and then to initiate anionic polymerization from it (Scheme 1) [6]. Accordingly, when [K] / [Li] = 5, polymer large distribution (Đ =2.21) might be the consequence of chain transfer to the polymer backbone.

Table 2. Polymerization of butadiene using *sec*-butyllithium + x eq. of potassium *tert*-pentoxide ($0 \leq x \leq 5$, no initiator preformation, $\bar{M}_{nth} = 10,000 \text{ g.mol}^{-1}$, [butadiene] = 2 mol.L^{-1} , [sec-BuLi] = $10^{-2} \text{ mol.L}^{-1}$, cyclohexane, 20°C , 16 h, yield = 100%)

[K] / [Li]	$\bar{M}_n \text{ exp}$ (g.mol^{-1})	$\bar{D}$	1,2 (%)	1,4-cis (%)	1,4-trans (%)
0	11,000	1.02	7	41	52
0.1	11,000	1.02	14	37	49
0.35	12,000	1.02	44	19	35
0.7	12,000	1.03	41	21	38
1	12,000	1.03	42	18	40
5	6,500	2.21	49	14	37

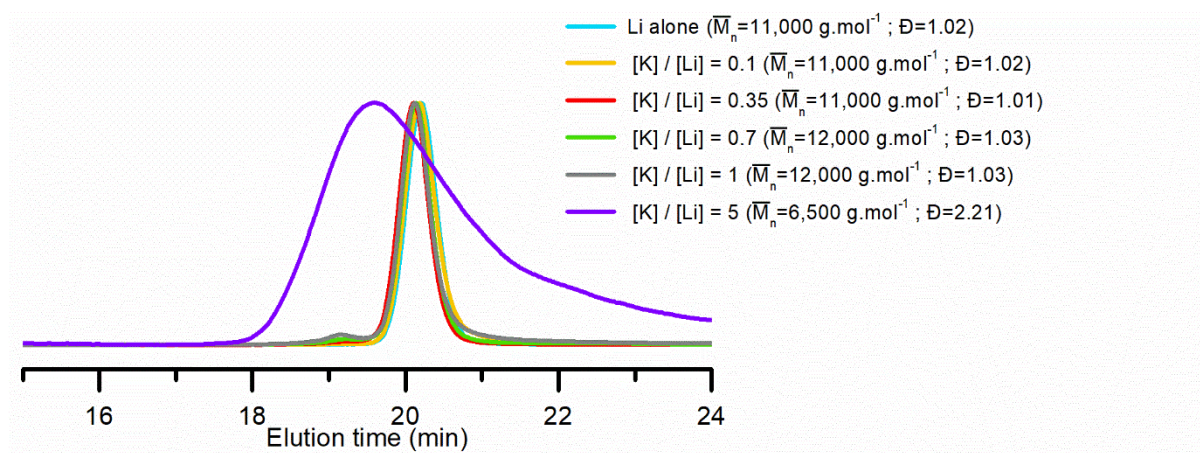


Figure 4. SEC chromatograms of polybutadiene samples synthesised using [tert-PeOK] / [sec-BuLi] ranging from 0 to 5 in cyclohexane at 20°C with no preformation time of the bimetallic initiator ($\bar{M}_{nth} = 10,000 \text{ g.mol}^{-1}$).

4. Influence of the alkyllithium structure in ROK + RLi systems on styrene and butadiene polymerization

To assess the influence of each component of the initiator, and to validate hypotheses previously described about the nature of the propagating center (complexes with alkyl and alkoxide derivatives of potassium and lithium, or alkylpotassium alone) and about the progressive deactivation of the initiator, two sets of experiments were performed with different lithium derivatives in association with 5 eq. of potassium *tert*-pentoxide as initiator. Changing the alkyllithium nature was expected to improve the solubility of the initiating species and / or to prevent its deactivation upon standing.

In the case of styrene polymerization with *n*-butyllithium + 5 eq. of potassium *tert*-pentoxide, polymerization control is affected by the preformation time (Table 3, Figure 5). Increasing the initiator preformation time leads to a decrease of the initiation efficiency, this behavior is quite similar to the one observed for *sec*-butyllithium + 5eq. of potassium *tert*-pentoxide. A second population is once again observed.

Table 3. Polymerization of styrene using *n*-butyllithium + 5 eq. of potassium *tert*-pentoxide ([styrene] = 1 mol.L⁻¹, [n-BuLi] = 10⁻² mol.L⁻¹, $\bar{M}_{nth}$ = 10,000 g.mol⁻¹, cyclohexane, 20°C, 16 h, yield = 100%)

Preformation time	$\bar{M}_n \text{ exp}^a$ (g.mol ⁻¹)	$\bar{D}^a$	% second population
No preformation	11,600	1.04	19
1h	12,600	1.03	18
16h	14,000	1.04	20

^a Obtained for the main population

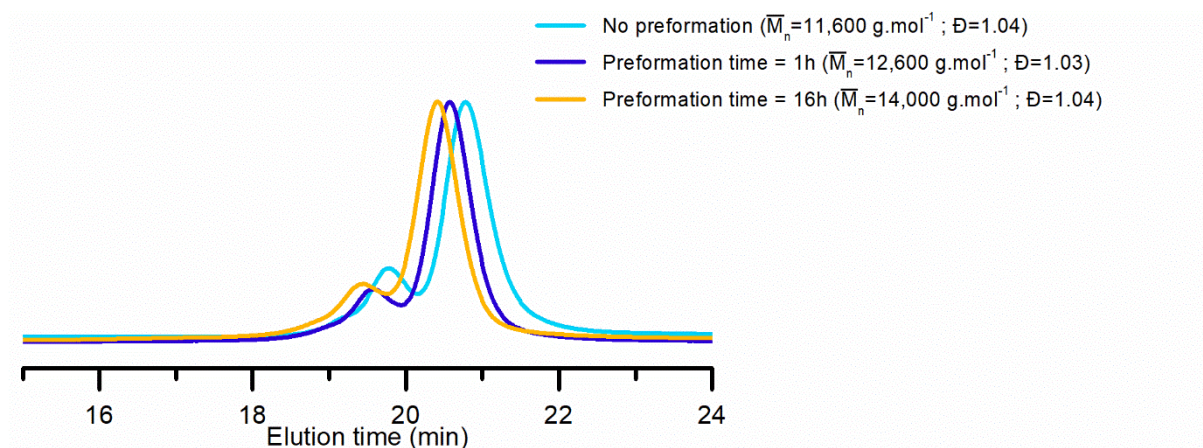


Figure 5. SEC chromatograms of polystyrene synthesized using *n*-butyllithium + 5 eq. of potassium *tert*-pentoxide with various preformation time in cyclohexane at 20°C ($\overline{M}_{nth} = 10,000 \text{ g.mol}^{-1}$, yield =100%)

For initiating systems based on polystyryllithium seeds + 5 eq. of potassium *tert*-pentoxide, the bimetallic initiator remains soluble even if the bimetallic initiator is kept 16 hours at 20°C. Polystyrene remains soluble all along the polymerization process unlike in the case of alkyllithium / potassium *tert*-pentoxide, suggesting that the structure of the lithium compound in the initiating system has an influence on the initiating / propagating center structure and on its aggregation state. In the case of polystyryllithium seeds + 5 eq. of potassium *tert*-pentoxide, polymerization control is not subjected to the initiator preformation time (Figure 6), and deactivation of the initiator does not occur unlike in the case of alkyllithium / potassium *tert*-pentoxide based systems (Scheme 5). In the case of PSLi + 5 eq. potassium *tert*-pentoxide, retention of actives species can be the consequence of the stabilization through mesomeric effect on the last unit of the initiator and / or by the solubility of the initiating species. Second population is negligible in all cases with respect to what was observed with alkyllithium / potassium *tert*-pentoxide. These observations tend to show that the nature of the living chain end is somehow different from what was previously observed with simple alkyllithium + 5 eq. of potassium *tert*-pentoxide. This assumption is supported by the fact that after the first few additions of styrene for a system based on butyllithium + 5 eq. of potassium *tert*-pentoxide should be soluble and stabilization through resonance should occur, which is not the case since polymer precipitation is observed in the case of simple alkyllithium.

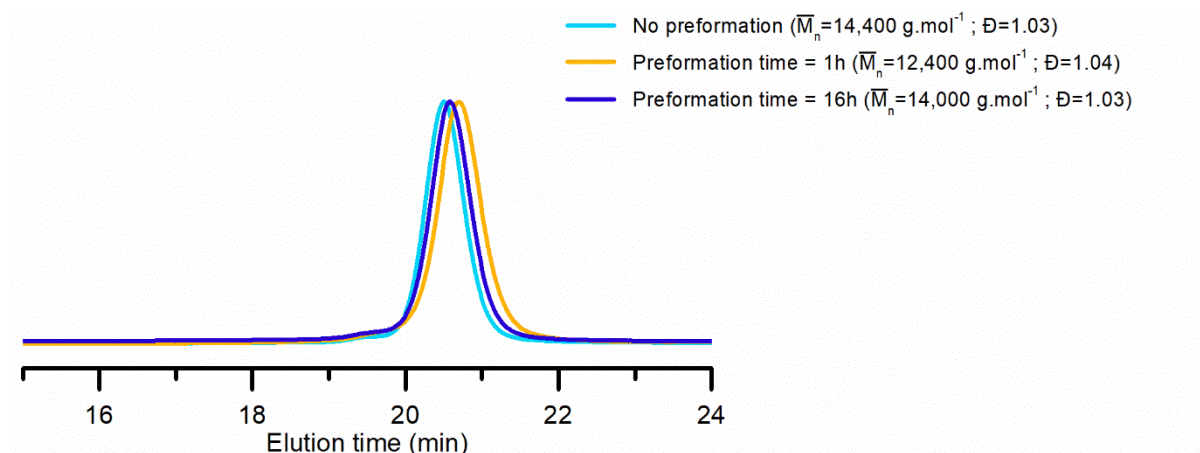


Figure 6. SEC chromatograms of polystyrene synthesized using PSLi seeds + 5 eq. potassium *tert*-pentoxide with various preformation time in cyclohexane at 20°C ([styrene] = 1 mol.L⁻¹, [PSLi] = 10⁻² mol.L⁻¹, 16 h, yield = 100%)

Experiments conducted on butadiene polymerization with polystyryllithium seeds in association with 5 eq. of potassium *tert*-pentoxide showed a monomodal and broad distribution with $\overline{D} > 2$ (Table 4, Figure 7). 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 on polybutadiene produced with *sec*-butyllithium + 5 eq. of potassium *tert*-pentoxide. Obtained microstructures are typical of potassium-based initiation systems and suggests that the carbon-potassium species is responsible of the polymerization (Table 4). Like in the case of *sec*-butyllithium + 5 eq. 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.

Table 4. Polymerization of butadiene using PSLi seeds + 5 eq. of potassium *tert*-pentoxide ([butadiene] = 2 mol.L⁻¹, [PSLi] = 10⁻² mol.L⁻¹, $\bar{M}_{nth}$ = 10,000 g.mol⁻¹, 20°C, 16 h, yield =100%)

Initiator	Preformation time	$\bar{M}_n \text{ exp}$ (g.mol ⁻¹)	$\bar{D}$	1,2 (%)	1,4-cis (%)	1,4-trans (%)
<i>tert</i> -PeOK / <i>sec</i> -BuLi	No preformation	6,500	2.21	53	11	36
<i>tert</i> -PeOK / PSLi	No preformation	5,300	1.97	53	13	33
<i>tert</i> -PeOK / PSLi	1h	5,500	2.18	54	11	35
<i>tert</i> -PeOK / PSLi	16h	5,000	2.08	53	11	36

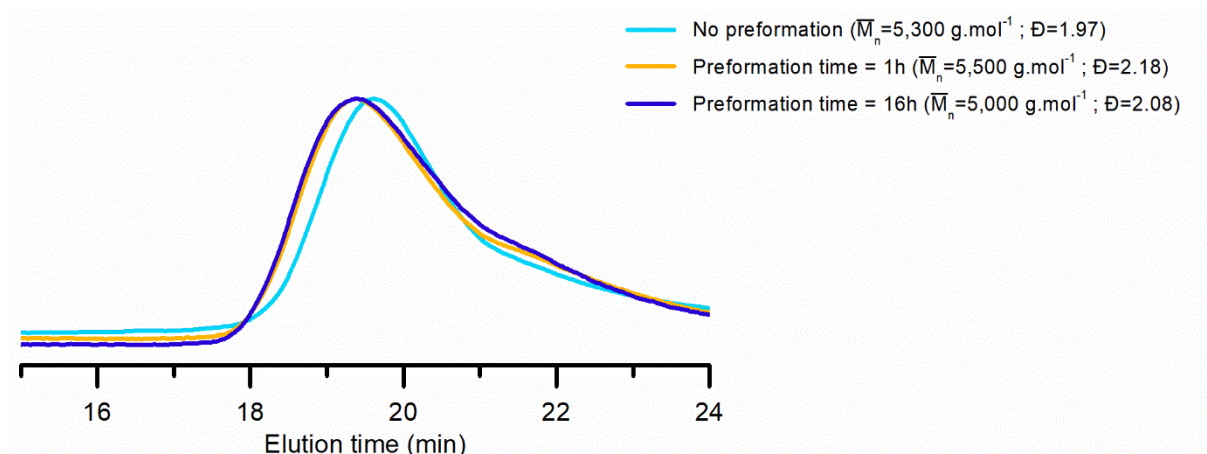
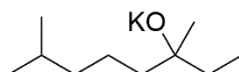


Figure 7. SEC chromatograms of polybutadiene obtained using polystyryllithium seeds + 5 eq. of potassium *tert*-pentoxide in cyclohexane with various preformation time ([butadiene] = 2 mol.L⁻¹, [PSLi] = 10⁻² mol.L⁻¹, $\bar{M}_{nth}$ = 10,000 g.mol⁻¹, 20°C, 16 h, yield = 100%)

5. Influence of potassium alkoxide structure in R'OK / *sec*-butyllithium systems on styrene and butadiene polymerization

Previous experiments have shown that using polystyryllithium seeds rather than simple alkyllithium allows to prevent the deactivation of the bimetallic initiating species upon standing and to enhance its solubility. Accordingly, another parameter to play with is the nature of potassium alkoxide and, in this set of experiments, potassium *tert*-pentoxide was replaced by potassium 3,7-dimethyl-3-octanoxide (Scheme 7). The longer carbon chain of this alkoxide was expected to improve the solubility of the initiating species and favor formation of bimetallic complexes, allowing to reduce the reactivity of the propagating center by changing its electronic environment.



Scheme 7. Structure of potassium 3,7-dimethyl-3-octanoxide

A preliminary experiment was performed using styrene initiated by *sec*-butyllithium and 5 eq. of 3,7-dimethyl-3-octanoxide without preformation time. The obtained molar mass was in the expected range (10,000 g.mol⁻¹) and the SEC chromatogram (Figure 8) is similar to the one obtained for with *sec*-butyllithium and 5 eq. of potassium *tert*-pentoxide initiator (Figure 3).

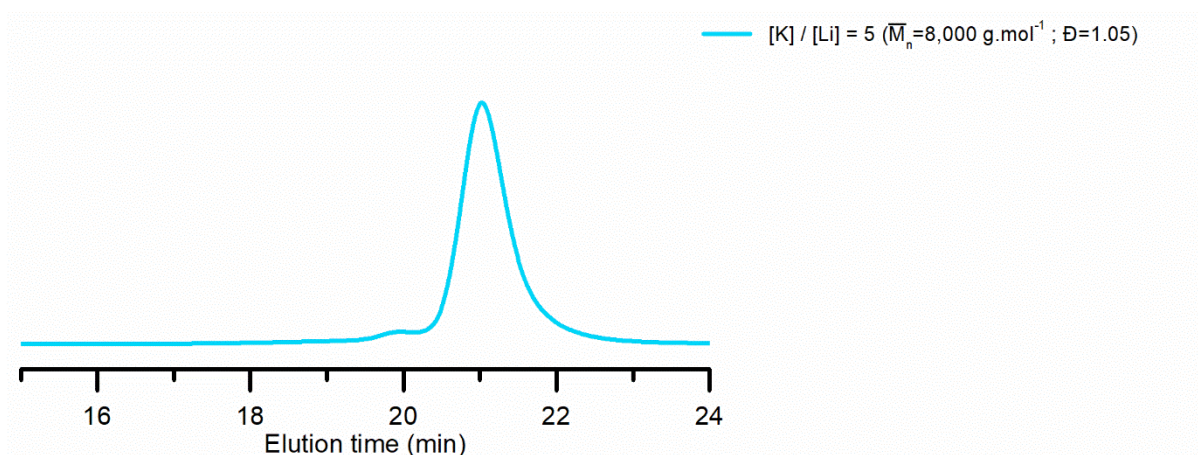


Figure 8. SEC chromatogram of polystyrene synthesized using [potassium 3,7-dimethyl-3-octanoxide] / [*sec*-BuLi] = 5 ([styrene] = 1 mol.L⁻¹, [*sec*-BuLi] = 10⁻² mol.L⁻¹, $\bar{M}_{nth}$ = 10,000 g.mol⁻¹, cyclohexane, 20°C, 16 h)

Potassium 3,7-dimethyl-3-octanoxide / *sec*-butyllithium system was then attempted for butadiene polymerization. For $[K] / [Li] = 0.5$ and 1, molar masses were obtained in the expected range ($\bar{M}_{nth} = 10,000 \text{ g.mol}^{-1}$), and polybutadiene microstructure was shown in line with the one reported for potassium based systems (Table 5, Figure 9). When $[K] / [Li]$ is equal to 5, dispersity increases similarly to previously described for systems with potassium *tert*-pentoxide ($[K] / [Li] = 5$ see Figure 4). Obtained polybutadiene have a vinyl content around 50% which is typical of potassium-based systems (Table 5). The broad dispersity obtained when $[K] / [Li] = 5$ might be the consequence of chain transfer to the polymer backbone, leading to branched polymer chain as mentioned before for *sec*-butyllithium + 5 eq. of potassium *tert*-pentoxide initiating species.

Table 5. Polymerization of butadiene using *sec*-butyllithium + x eq. of potassium 3,7-dimethyl-3-octanoxide ($0.5 \leq x \leq 5$, no initiator preformation, $[butadiene] = 2 \text{ mol.L}^{-1}$, $[sec-BuLi] = 10^{-2} \text{ mol.L}^{-1}$, $\bar{M}_{nth} = 10,000 \text{ g.mol}^{-1}$, cyclohexane, 20°C, 16 h, yield = 100%)

$[K] / [Li]$	$\bar{M}_n \text{ exp}$ (g.mol^{-1})	$\bar{D}$	1,2 (%)	1,4-cis (%)	1,4-trans (%)
0.5	8,500	1.02	53	9	38
1	8,000	1.02	51	15	34
5	7,500	1.91	46	19	35

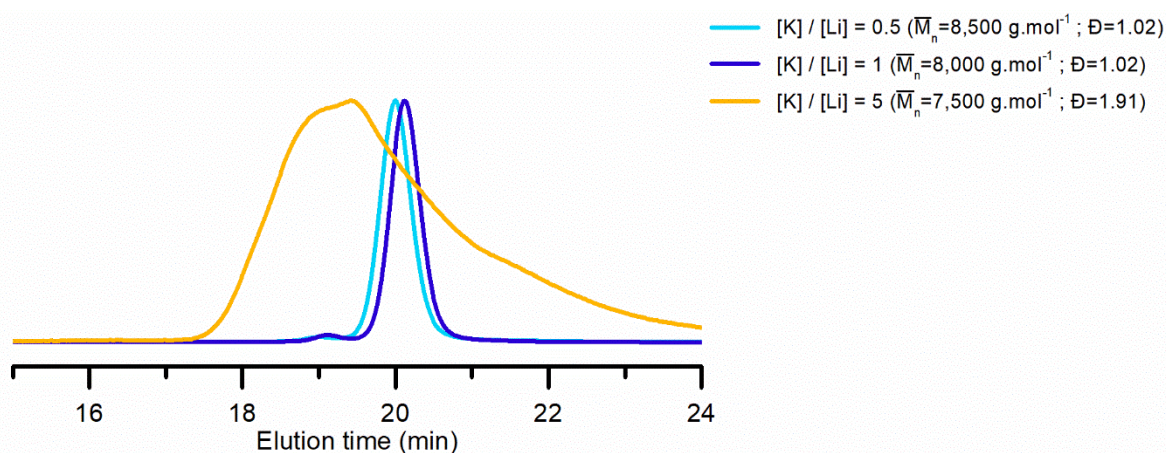


Figure 9. SEC chromatograms of polybutadiene synthesized using *sec*-butyllithium + x eq. of potassium 3,7-dimethyl-3-octanoxide ($0.5 \leq x \leq 5$, no initiator preformation, $[butadiene] = 2 \text{ mol.L}^{-1}$, $[sec-BuLi] = 10^{-2} \text{ mol.L}^{-1}$, $\bar{M}_{nth} = 10,000 \text{ g.mol}^{-1}$, cyclohexane, 20°C, 16 h, yield = 100%)

Polymerization control and obtained microstructures with an initiating system composed of *sec*-butyllithium + x eq. of potassium 3,7-dimethyl-3-octanoxide are similar to the one observed with *sec*-butyllithium + x eq. of potassium *tert*-pentoxide. These sets of experiments tend to indicate that the nature of the potassium alkoxide has no influence on butadiene polymerization initiated by RLi / R'OK bimetallic systems

6. Polystyryllithium seeds + 5 eq. of potassium 3,7-dimethyl-3-octanoxide for butadiene polymerization

With the objective to increase the solubility of the initiating species to favor a bimetallic complex formation in order to reduce the reactivity of the propagating chain end, a set of experiments was performed using polystyryllithium seeds in association with 5 eq. of potassium 3,7-dimethyl-3-octanoxide as the initiator. A soluble system is obtained whatever the preformation time is, but no significant improvement was observed in terms of polymerization control with respect to *sec*-butyllithium + 5 eq. of potassium *tert*-pentoxide. Broad dispersities are observed and attributed to metalation of polymer chains leading to branched polymers. Polybutadiene microstructure remains typical of potassium-based systems with about 50% vinyl content (Table 6, Figure 10).

Table 6. Polymerization of butadiene using PSLi seeds + 5 eq. of potassium 3,7-dimethyl-3-octanoxide with various preformation time of the initiator ([butadiene] = 2 mol.L⁻¹, [PSLi] = 10⁻² mol.L⁻¹, $\bar{M}_{nth}$ = 10,000 g.mol⁻¹, cyclohexane, 20°C, 16 h, yield = 100%)

Preformation time	$\bar{M}_n \text{ exp}$ (g.mol ⁻¹)	$\bar{D}$	1,2 (%)	1,4-cis (%)	1,4-trans (%)
No preformation	6,000	1.97	54	14	32
1 h	6,500	2.08	53	14	33
16 h	7,000	1.96	55	13	32

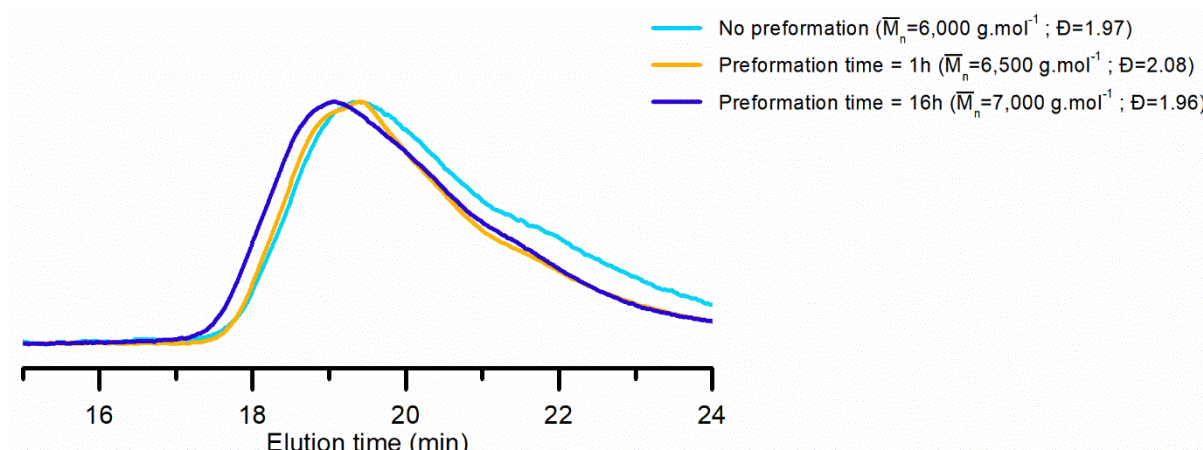
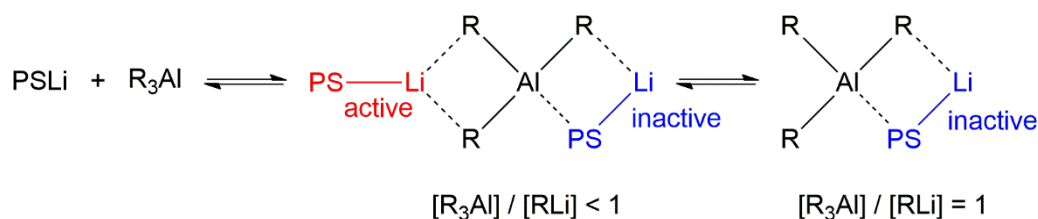


Figure 10. SEC chromatograms of polybutadiene synthesized using polystyryllithium seeds / potassium 3,7-dimethyl-3-octanoxide as a bimetallic initiator ($[K] / [Li] = 5$, $[butadiene] = 2 \text{ mol.L}^{-1}$, $[PSLi] = 10^{-2} \text{ mol.L}^{-1}$, $\overline{M}_{nth} = 10,000 \text{ g.mol}^{-1}$, cyclohexane, 20°C, 16 h, yield = 100%)

7. Addition of trialkylaluminum to potassium-based initiation systems: Influence of trimetallic initiator composition on butadiene polymerization control

In the scientific literature, the use of trialkylaluminum + butyllithium based systems were shown to be relevant for the polymerization of butadiene and styrene at high temperature in bulk [18], [19]. For $0.7 < [Al] / [Li] < 1$ in apolar media, a strong decrease of the polymerization rate was reported, whereas polymerization did not occur when $[Al] / [Li] \geq 1$ due to the formation of a 1:1 inactive complex. When $[R_3Al] / [RLi]$ is below one, two complexation sites are coexisting (Scheme 8), one being inactive toward anionic polymerization and the second one being active, polymerization control is achieved through a fast exchange between these positions. When $[R_3Al] / [RLi] > 1$, only inactive site remains.



Scheme 8. Evolution of the relative proportion of $R_3Al:PSLi$ active complex (1:2) and $R_3Al:PSLi$ inactive complex (1:1) depending on $[Al]/[Li]$ ratios

Accordingly, the addition of triisobutylaluminum to *sec*-butyllithium / potassium *tert*-pentoxide initiating systems was attempted for butadiene polymerization. The objective being the formation of aluminate complexes to modify the electronic environment of the propagating center and to reduce its reactivity in order to improve polymerization control and to assess the influence of such a system on polybutadiene microstructure.

7.1. Butadiene polymerization with *sec*-butyllithium / potassium *tert*-pentoxide / triisobutylaluminum based systems: $[K] / [Li] = 0.5$ and $[Al] / [Li] = 0.5$

With such a trimetallic systems, the propagating center is believed to be an aluminate complex with a reduced basicity with respect to the bimetallic system. Since the formation of complex between alkyllithium and trialkylaluminum was reported to be slow [20] (several hours at 50°C in cyclohexane $[Al] / [Li] = 0.9$), a first experiment was conducted on polystyryllithium seeds with $[K] / [Li] = 0.5$ and $[K] / [Al] = 0.5$ (Figure 11).

Upon addition of potassium *tert*-pentoxide and triisobutylaluminum, the absorption band of polystyryllithium is shifted from 327 nm to 339 nm. This new absorption maximum does not match the one observed for the bimetallic system ($PSLi + 0.5 \text{ } tert\text{-}PeOK$, 333 nm, see Figure 2). In addition, upon ageing at 20°C the intensity of this absorption band decreases while another band appears around 285 nm. These changes in the UV absorption spectra are consistent with the formation of an aluminate complex as described in the literature, with the rapid formation of “kinetic” complexes which rearrange into more stable ones upon ageing [20].

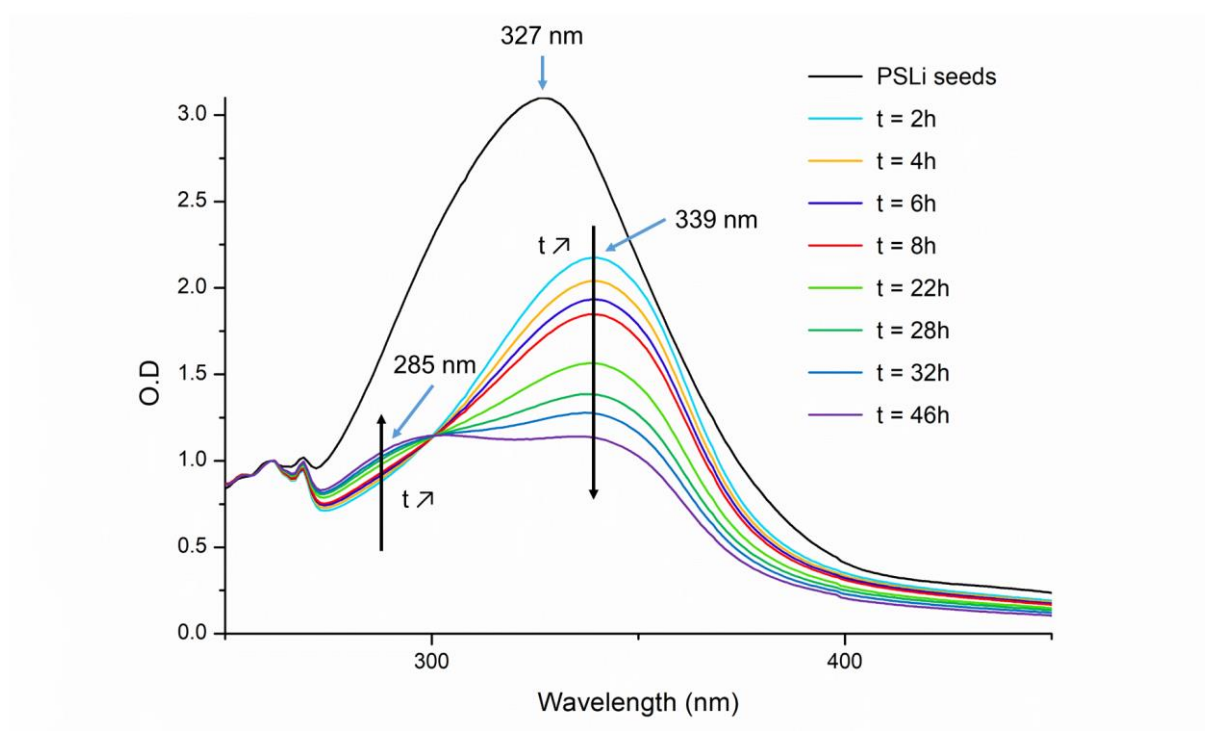


Figure 11. Evolution of UV spectra of PSLi seeds upon addition of *i*-Bu₃Al and *tert*-PeOK at 20°C in cyclohexane ([K] / [Li] = 0.5 and [Al] / [Li] = 0.5)

Butadiene polymerization was attempted with the same initiator composition with 24 hours of initiator preformation. In this condition, and according to Figure 11, the rearrangement of the aluminate complexes is not quantitative. Nevertheless, a preliminary result (Figure 12) was found to produce polybutadiene with molar mass in the expected range (10,000 g.mol⁻¹) indicating that the initial amount of alkyllithium control polybutadiene chain length.

The microstructure of the resulting polybutadiene is shifted from 50% vinyl content for bimetallic system [K] / [Li] > 0.35 to mainly 1,4 content (25% 1,4-cis, 43% 1,4-trans and 33% vinyl) for the trimetallic one. It is supposed that potassium and lithium living chain ends coexist within an aluminate complex with a fast counter-ion exchange providing an intermediate microstructure.

Obtained microstructure with this initiating system is also reachable with a bimetallic system (0.1 < [K] / [Li] < 0.35, Table 2). However, such system is nonetheless an improvement with respect to the bimetallic one, since the complex can be preformed as it will keeps its reactivity upon storage.

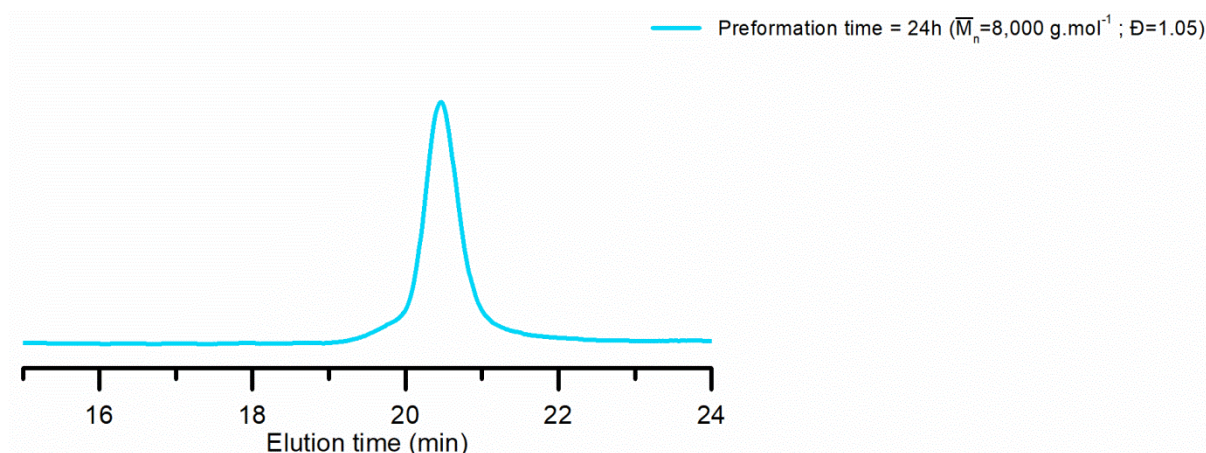


Figure 12. SEC chromatogram of polybutadiene synthesized using $[tert\text{-}PeOK] / [sec\text{-}BuLi] = 0.5$ and $[i\text{-}Bu_3Al] / [sec\text{-}BuLi] = 0.5$ (preformation time = 24 h, cyclohexane, 20°C, $[butadiene] = 2 \text{ mol.L}^{-1}$, $[sec\text{-}BuLi] = 10^{-2} \text{ mol.L}^{-1}$, $\bar{M}_{nth} = 10,000 \text{ g.mol}^{-1}$)

7.2. Butadiene polymerization with lithium / potassium / aluminum based systems: $[K] / [Li] = 5$ and $[Al] / [Li] > 0.5$

For the second set of experiments on trimetallic systems in cyclohexane at 20°C, potassium *tert*-pentoxide was added first, followed by triisobutylaluminum then *sec*-butyllithium with $[K] / [Li] = 5$ and $[Al] / [Li] = 0.5$. These systems were left to react during various times at 20°C before the addition of butadiene, in order to assess the influence of the preformation time on trimetallic systems when $[K] / [Li] = 5$.

Unlike for bimetallic systems, where no preformation time are mandatory to achieve polymerization control, this set of experiments with a trimetallic system shows that a long preformation is required to achieve polymerization control (Figure 13). A shoulder can be observed in the high molar mass region, and as mentioned before, side reactions linked to potassium moieties are believed to occur. A second set of butadiene polymerization was performed with $[tert\text{-}PeOK] / [sec\text{-}BuLi] = 5$ and $[i\text{-}Bu_3Al] / [sec\text{-}BuLi] = 0.5, 1$ and 3.5 in cyclohexane with 24h preformation time to confirm this hypothesis. One can note that $[Al] / ([K] + [Li])$ is always below 1, and accordingly, the formation of 1:1 inactive aluminate complex is not expected.

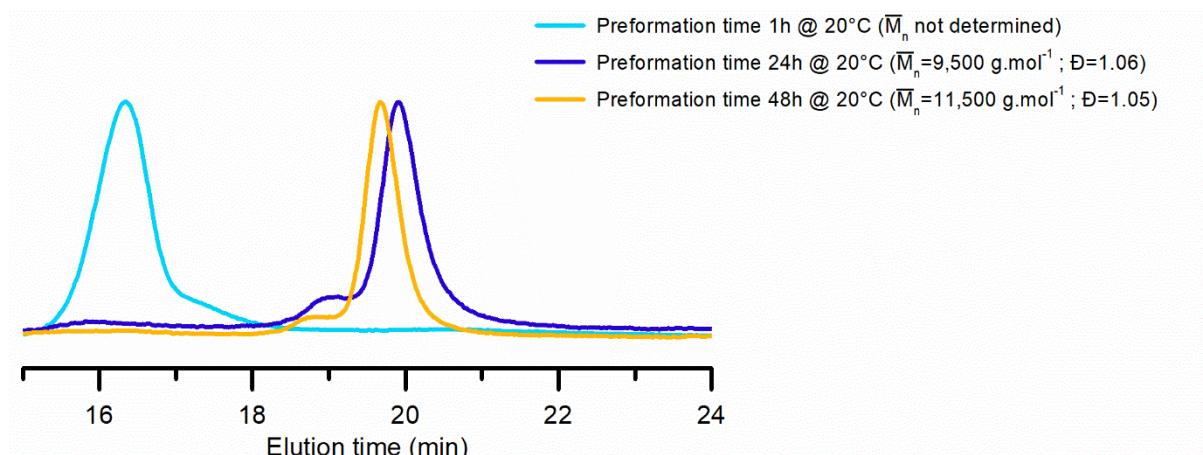


Figure 13. Influence of the initiator preformation time on SEC chromatograms of polybutadiene synthesized using $[tert\text{-}PeOK] / [sec\text{-}BuLi] = 5$ and $[i\text{-}Bu_3Al] / [sec\text{-}BuLi] = 0.5$. ($[butadiene] = 2 \text{ mol.L}^{-1}$, $[sec\text{-}BuLi] = 10^{-2} \text{ mol.L}^{-1}$, $\overline{M}_{nth} = 10,000 \text{ g.mol}^{-1}$, cyclohexane, 20°C, 16h, yield = 100%,).

As can be seen on Figure 14, 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 7). No shoulder was observed when $[Al] / [Li] = 1$ or 3.5. Microstructure remains typical of potassium-based initiators with high vinyl content, indicating that polymerization occurs inside a carbon – potassium bond. These phenomena can be explained through complete complexation of alkylpotassium moieties in a lower basicity complex thanks to the trialkylaluminum compound preventing chain transfer to the polymer backbone. A mechanism pathway for the formation of the initiating complex is proposed on Scheme 9. The excess of alkali metal alkoxide might be part of a higher stoichiometry aluminate complex. However, for a better reading of Scheme 9, the additional complexation of the aluminate complex by alkali metal alkoxide was not represented.

Table 7. Polymerization of butadiene using *sec*-butyllithium + 5 eq. of potassium *tert*-pentoxide + x eq. of triisobutylaluminum ($0 \leq x \leq 3.5$, preformation time = 24 h, [butadiene] = 2 mol.L⁻¹, [sec-BuLi] = 10⁻² mol.L⁻¹, $\bar{M}_{nth} = 10,000$ g.mol⁻¹, cyclohexane, 20°C, 16 h)

[K] / [Li]	[Al] / [Li]	$\bar{M}_n \text{ exp}$ (g.mol ⁻¹)	$\bar{D}$	1,2 (%)	1,4-cis (%)	1,4-trans (%)
5	0	5,000	2.5	54	14	32
5	0.5	8,500	1.21	53	14	33
5	1	9,500	1.09	56	13	32
5	3.5	10,200	1.11	67	9	24

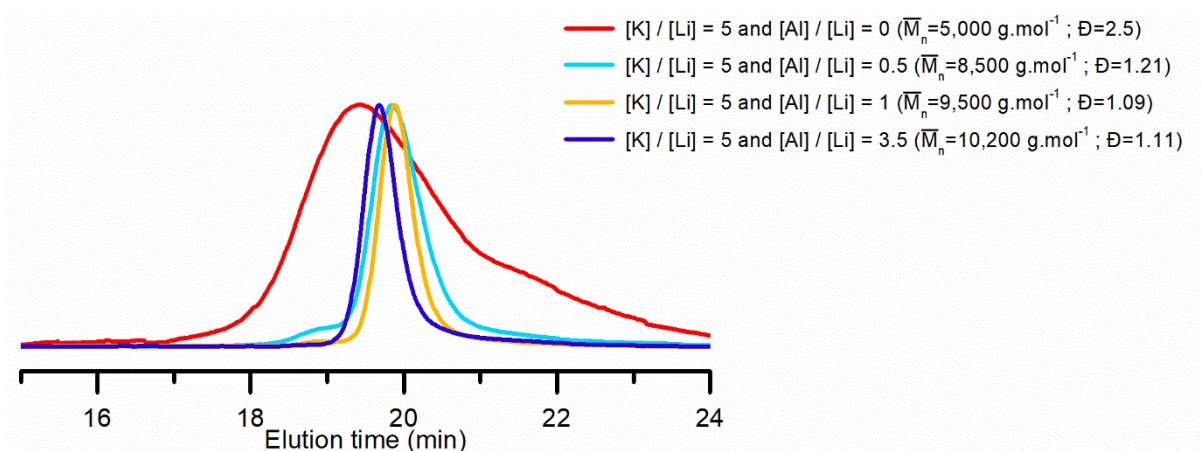
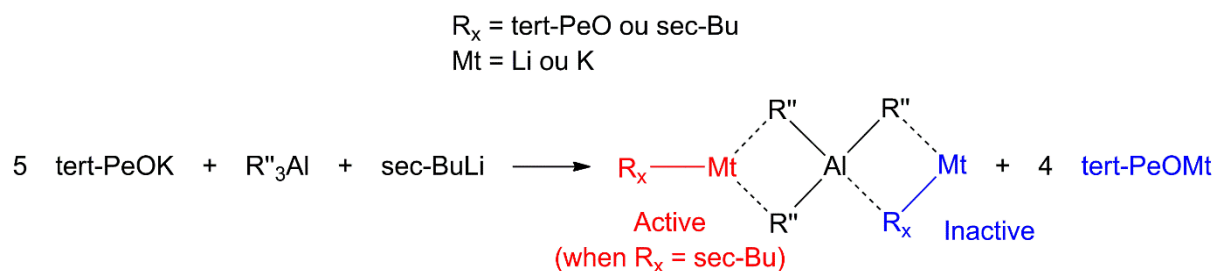


Figure 14. SEC chromatograms of polybutadiene synthesized using [tert-PeOK] / [sec-BuLi] = 5 and $0 < [i\text{-Bu}_3\text{Al}] / [\text{sec-BuLi}] < 3.5$ (preformation time = 24h, [butadiene] = 2 mol.L⁻¹, [sec-BuLi] = 10⁻² mol.L⁻¹, $\bar{M}_{nth} = 10,000$ g.mol⁻¹, cyclohexane, 20°C, 16h)

Chapter II. Anionic polymerization of butadiene using lithium derivatives / potassium alkoxides bimetallic systems: Influence on polymerization control and polybutadiene microstructure



Scheme 9. Proposed mechanism for the formation of the initiating complex with *sec*-butyllithium, potassium *tert*-pentoxide and triisobutylaluminum ([K] / [Li] = 5 and [Al] / [Li] = 1)

8. Conclusion

This chapter intends to assess the influence of potassium-based systems on polybutadiene microstructure and polymerization control.

Bimetallic systems composed of lithium derivatives / potassium alkoxides were studied and parameters such as $[K] / [Li]$ ratios, preformation time of the initiator, structure of alkyllithium derivatives and structure of potassium alkoxides were varied. Styrene was used as a model monomer and was first initiated by using *sec*-butyllithium / potassium *tert*-pentoxide ($[Li] / [K] = 0.5$ and 5). Polymerization control is only achieved if no initiator preformation time is allowed. On butadiene polymerization, with no preformation time, polymerization control is achieved when $[K] / [Li] \leq 1$ and a broad dispersity is obtained when $[K] / [Li] = 5$. Addition of potassium alkoxide to alkyllithium initiation system 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 of the nucleophilic attack on butadiene monomers.

Styrene polymerization using polystyryllithium seeds + 5 eq. potassium *tert*-pentoxide as an initiator showed that polymerization control is also achieved. The initiator preformation time had no influence on the polymerization control and the obtained polymers are monodisperse suggesting that the initiator solubility is a key parameter. This initiating system for butadiene polymerization leads to polymers with a broad dispersity, similar to what was observed for *sec*-butyllithium + 5 eq. of potassium *tert*-pentoxide. Obtained microstructure are typical of potassium-based systems with 50% vinyl content.

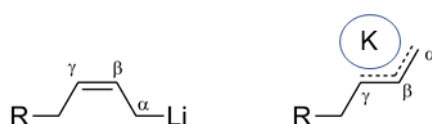
Using potassium 3,7-dimethyl-3-octanoxide in association with *sec*-butyllithium for butadiene polymerization was shown to produce polybutadiene with molar masses close to the targeted ones with 50% vinyl content when $[K] / [Li] = 0.5$ and 1 . For $[K] / [Li] = 5$, broad dispersity is obtained like in the case of *sec*-butyllithium + 5 eq. of potassium *tert*-pentoxide. Accordingly, the structure of potassium alkoxide seems to have no influence on polymerization control nor on polybutadiene microstructure.

Finally, a trimetallic system with potassium *tert*-pentoxide, *sec*-butyllithium and triisobutylaluminum was shown to produce polybutadiene in a controlled way, even with a large

excess of potassium alkoxide, and with a microstructure typical of potassium-based systems (50% vinyl content). Improvements in terms of polymerization control with respect to bimetallic systems were explained through the formation of a lower basicity complex lowering the reactivity of the active chain end and preventing side reactions.

Potassium based systems are known to produce polybutadiene with a 50% vinyl content and this might be explained as follow:

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 [17], the carbon-potassium bond is a more dissociated ion-pair due to the higher ionic radius of potassium (Scheme 10). 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 through a nucleophilic attack from the γ position. Obtained microstructures in this work using multi-metallic systems are in line with the one reported for potassium dispersion [17], indicating that the carbon – potassium bond remains a dissociated ion pair despite aggregation and / or complexation (with alkali metal alkoxide moieties or trialkylaluminum). It can be also envisaged that an incoming monomer can interact with the counter-ion which may also influence its position before the nucleophilic attack.



Scheme 10. Proposed structure for the chain for butadienyllithium and butadienylpotassium

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Chapter III.

Anionic polymerization of butadiene using lithium derivatives / alkaline earth derivatives bimetallic systems: polybutadiene microstructure and polymerization control

1. Introduction

The use of alkali metal alkoxides in association with alkyllithium for butadiene polymerization are reported in the literature as randomizer for butadiene – styrene polymerization, and microstructure regulator since increasing amount of heavy alkali metal alkoxides leads to a vinyl content increase for the resulting polybutadiene. The influence of alkaline earth derivatives in association with alkyllithium is less reported in the literature. The influence of these systems on polybutadiene microstructure is studied in this chapter.

In terms of alkaline earth metal alkoxides, barium-based systems are the most reported and patented because of their ability to produce polybutadiene with a 1,4-trans content up to 90% [1]–[14].

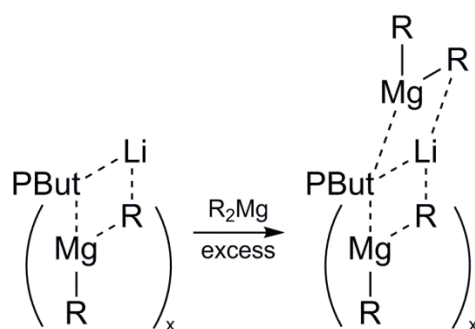
For bimetallic systems based on alkyllithium and barium *tert*-butoxide-hydroxide ($\text{Ba}(\text{OH})_{0.18}(\text{tert-BuO})_{1.82}$), an optimum initiator composition is reported at $[\text{Ba}] / [\text{Li}] = 0.5$ leading to a 1,4-trans content equal to 75% with a low vinyl content (7%) [7]. However, polymerization control is not achieved and broad dispersities are reported (molar masses ranging from 26,000 to 2,800,000 $\text{g}\cdot\text{mol}^{-1}$). Similar behavior was reported by Fujio and coworkers in terms of polybutadiene microstructure and polymerization control. Obtained polymer distributions were also said to be broad [2].

A system based on a barium salt of di(ethylene glycol) ethyl ether / triisobutylaluminum / dilithium derivative was used by Zhang and coworkers to produce triblock with high 1,4-trans polybutadiene segments [11], [12]. The addition of trialkylaluminum is reported to increase the 1,4-trans content from 54% to 88% when $[\text{R}_3\text{Al}] / [\text{RLi}]$ varies from 0 to 1.8 (cyclohexane, $[\text{Ba}] / [\text{Li}] = 0.25$, 70°C). The obtained dispersity is said between 1.2 and 1.3. Similar results with a trioctylaluminum / *n*-butyllithium / barium 2-ethylhexoxide system were reported by Benvenuta-Tapia and coworkers [13], with the one-step copolymerization of styrene and butadiene leading to random copolymers with 78% 1,4-trans, 16% 1,4-cis and 6% vinyl content at 70°C in cyclohexane ($[\text{Ba}] / [\text{Li}] = 0.25$, $[\text{Al}] / [\text{Li}] = 1$).

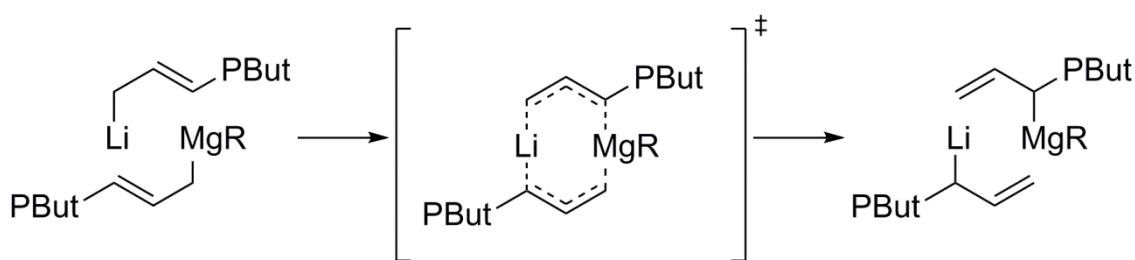
Other systems based on barium, aluminum and lithium were patented and said to produce polybutadiene with a 1,4-trans content up to 90% [8], [14]. For instance, addition of alkali metal alkoxide to a barium alkoxide / alkyllithium / alkylaluminium trimetallic system was said to increase the 1,4-trans content up to 90% [14]. The use of a $\text{Ba}[\text{Al}(\text{C}_2\text{H}_5)_4]_2$, rather than two

discrete components, in association with butyllithium was said to produce polybutadiene with up to 85% 1,4-trans [10].

Magnesium derivatives are known to be inactive in the anionic polymerization of butadiene alone in apolar media. Polymerization is known to occur for systems based on alkyllithium and dialkylmagnesium with the propagating center being inside a magnesiate complex [15], [16]. When $[R_2Mg] / [RLi] < 1$, the propagating center is reported to be a complex between lithium polymer chain end and dialkylmagnesium, these systems being reported to have no specific influence on polybutadiene microstructure keeping a low vinyl content (7%) and 1,4-cis / 1,4-trans ratio equal to 0.8 in cyclohexane at 50°C. When $[R_2Mg] / [RLi] > 1$, the propagating center is also a complex based on alkyllithium derivatives and dialkylmagnesium, leading to a reduced polymerization rate and to a vinyl content increase. For $[R_2Mg] / [RLi] = 1$ in cyclohexane at 40°C, reported polybutadiene microstructure is 13% vinyl, 34% 1,4-cis and 50% 1,4-trans. In the same experimental conditions with $[R_2Mg] / [RLi] = 10$, reported microstructure is 49% vinyl, 20.5% 1,4-cis and 30.5% 1,4-trans [15]. This phenomenon was explained by additional complexation of lithium species by free dialkylmagnesium moities (Scheme 1), and / or through a chain end isomerization reaction during exchange between polybutadienyl active chains and polybutadienyl dormant chains (Scheme 2) [15]. The vinyl content increase with such a system is not related to the counter-ion nature but only to a complexation effect.



Scheme 1. Suggested additional complexation of living chain-end under the influence of R_2Mg in excess [15]



Scheme 2. Suggested mechanism for chain-end isomerization inside magnesiate complex [15]

Since the magnesium – carbon bond is inactive toward anionic polymerization, the addition of magnesium alkoxide to lithium derivatives was not attempted.

Strontium based systems are by far the less reported in the literature. In bulk, initiators based on $\text{Ph}_3\text{CSrX}(\text{THF})_y$ ($\text{X} = \text{Cl}$ or Br) are reported to produce polybutadiene with a vinyl content around 20% and the 1,4-cis / 1,4-trans ratio equal to 0.6 when $\text{X} = \text{Cl}$ and 0.3 when $\text{X} = \text{Br}$ [4]. An initiation system based on butyllithium + 0.5 eq. of strontium *tert*-butoxide in apolar media at 70°C, is reported to produce styrene / butadiene copolymers with 15% vinyl content and a 1,4-cis / 1,4-trans ratio equal to 0.4 [2]. Reported yields after 20 hours at 70°C are in the range 60 – 70%.

Alkylcalcium derivatives are reported to produce polybutadiene. For instance, a mixture of di-*n*-butylcalcium and *n*-butylcalcium iodide is reported to polymerize butadiene with a living character as a linear increase of molar mass with conversion was observed [17]. Nevertheless, molar masses are said to be higher than the expected ones, indicating a non-quantitative initiation step. Obtained polybutadienes in apolar media (bulk, benzene and heptane) exhibit a 1,4-trans content ranging from 67.5% to 78.5%, and a vinyl content below 10% [17]. Meanwhile, organo-calcium compound with the formula $\text{Ph}_3\text{CCaX}(\text{THF})_y$ ($\text{X} = \text{Cl}$ or Br) are reported to produce polybutadiene with a 1,4-trans content up to 66% (81% of 1,4 units) and with a broad dispersity (1.6 – 2.7) [4]. Calciumzinc-tetraalkyl (CaZnR_4) are shown to copolymerize butadiene (55 wt%) and styrene (45 wt%) with about 70 – 75% of 1,4-trans content and a low vinyl content (< 10%) [1]. Copolymerization of butadiene and styrene with alkyllithium, under the influence of calcium di-alkoxide (or calcium stearate), was also shown to slightly influence the copolymers microstructure (36 – 42% 1,4-cis, 48 – 52% 1,4-trans and 8 – 12% 1,2 for $0.1 < [\text{Ca}] / [\text{Li}] < 1$ in apolar media) with respect to alkyl lithium initiated polymerization (37% 1,4-cis, 53% 1,4-trans, 10% vinyl) [2]. A bimetallic system based on alkyllithium, calcium alkoxide and lithium alkoxide was said to produce polybutadiene with 50

– 80% 1,4-trans content, 10% – 45% 1,4-cis content and a vinyl content between 5% to 20% [18].

The trend of calcium-based systems, in apolar media, is to yield predominantly 1,4 units and more specifically a high 1,4-trans content. A summary of these calcium-based systems is presented on Figure 1.

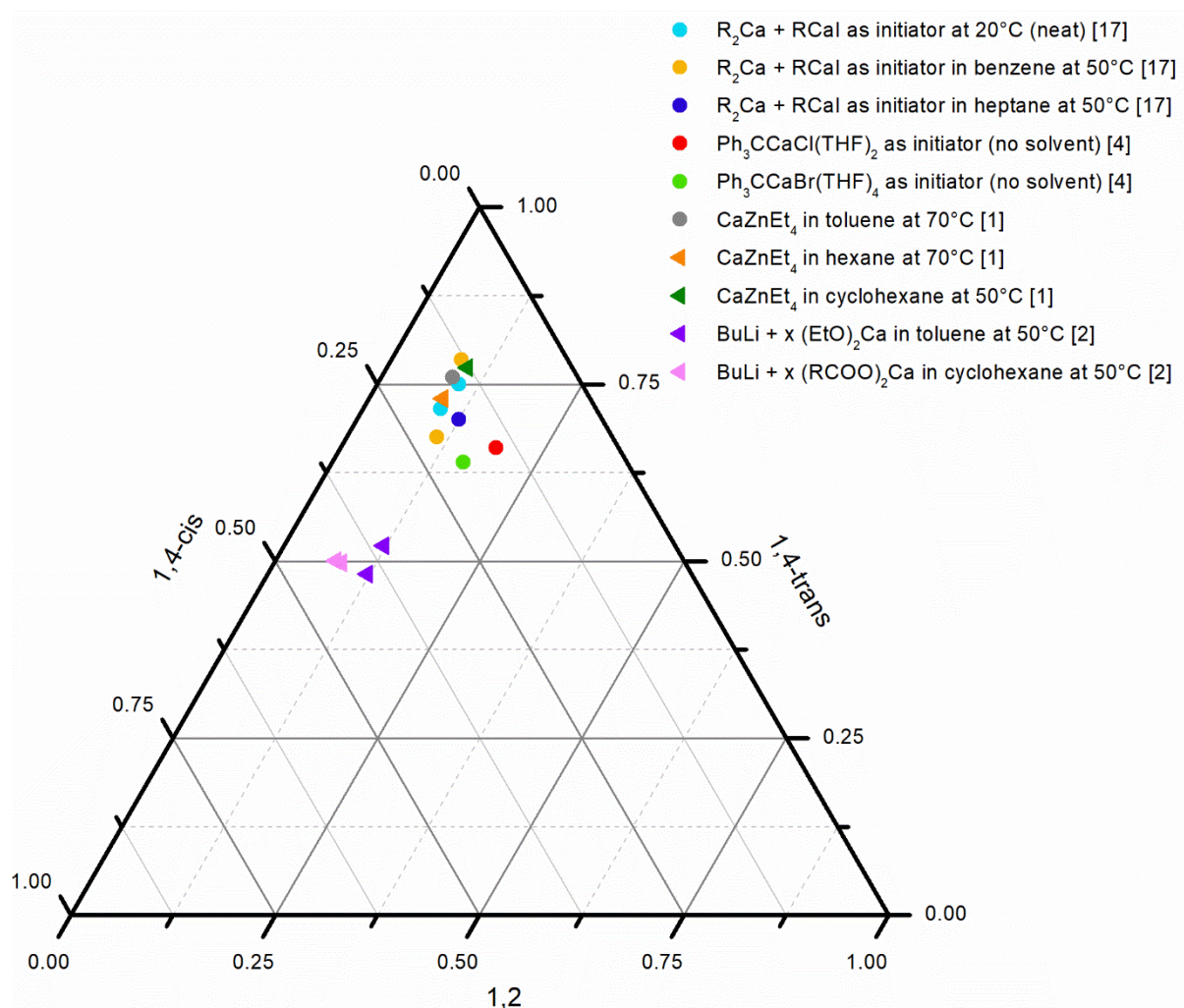


Figure 1. Reported microstructure for calcium-based systems [1], [2], [4], [17]

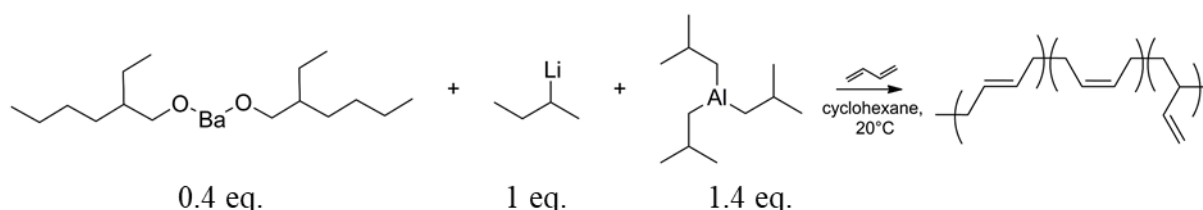
The reports on polybutadiene microstructure under the influence of alkylcalcium derivatives and calcium-zinc derivatives (up to 75% 1,4-trans) are quite antagonist with the one reported for alkyllithium / calcium derivatives (50% 1,4-trans, similar to the 1,4-trans content obtained with alkyllithium alone in apolar media). Several hypotheses to these differences in terms of microstructure can be drawn such as the solubility of calcium salt derivatives, preformation time of the initiating species, influence of the ratio $[Ca] / [Li]$, or finally the non-participation of calcium derivatives in the active center for reported polymerization experiments. In addition, the obtention of dialkylcalcium derivatives is generally achieved through calcium metal activation by formation of an amalgam, and subsequent reaction with alkyl halide [17], [19], [20]. The obtention of calcium derivatives using mercury, is not satisfactory from an industrial and environmental point of view, and alternatives should be found in the objective to propose an initiating system able to reach high 1,4-trans content.

The present work aims to study initiating systems based on calcium derivatives in association with alkyllithium to obtain polybutadiene with a high 1,4-trans content in a controlled way. Trimetallic systems based on barium alkoxide, alkyllithium and trialkylaluminum are well known to achieve such an objective, nonetheless the aim of this chapter was to develop an easier synthetic route using calcium-based bimetallic initiation system.

2. Barium-based trimetallic systems for the synthesis of polybutadiene

As mentioned in the introduction, trimetallic systems based on alkyllithium, trialkylaluminum and barium alkoxide are known to produce polybutadiene with a high 1,4-trans content and with a good polymerization control [11], [13].

A set of experiment was performed using $[Ba] / [Li] = 0.4$ and $[Al] / [Li] = 1.4$ (ref. Michelin) in cyclohexane at 20°C in order to confirm the obtention of high 1,4-trans content polybutadiene (Scheme 3). Butadiene polymerization experiments were carried out with a targeted molar mass of 10,000 g.mol⁻¹ with the hypothesis of one polymer chain per alkyllithium molecule. The initiating system was synthesized *in-situ* by addition of *sec*-butyllithium to barium 2-ethylhexoxide. This mixture was kept at room temperature for one hour before addition of triisobutylaluminum and butadiene. After 3 days at 20°C, degassed methanol was added to stop the reaction. Results are presented in Table 1 and Figure 2.



Scheme 3. Polymerization of butadiene in the presence of *sec*-butyllithium + 1.4 eq. of triisobutylaluminum + 0.4 eq. of barium 2-ethylhexoxide in cyclohexane at 20°C

Table 1. Butadiene polymerization initiated by *sec*-butyllithium, + 0.4 eq. of barium 2-ethylhexoxide + 1.4 eq. of triisobutylaluminum in cyclohexane ($[butadiene] = 2 \text{ mol.L}^{-1}$, $[sec-BuLi] = 10^{-2} \text{ mol.L}^{-1}$, $\bar{M}_{n\text{ th}} = 10,000 \text{ g.mol}^{-1}$, 20°C, 3 days, yield =100%).

$[Ba] / [Li]$	$[Al] / [Li]$	$\bar{M}_{n\text{ exp}}$ (g.mol ⁻¹)	$\bar{D}$	1,2 (%)	1,4-cis (%)	1,4-trans (%)
0 ^a	0 ^a	11,000	1.03	7	41	52
0.4 ^b	1.4 ^b	13,500	1.10	4	22	74
0.4 ^b	1.4 ^b	12,000	1.16	4	16	80

^a *sec*-butyllithium was used as the initiator. ^b reproducibility experiments

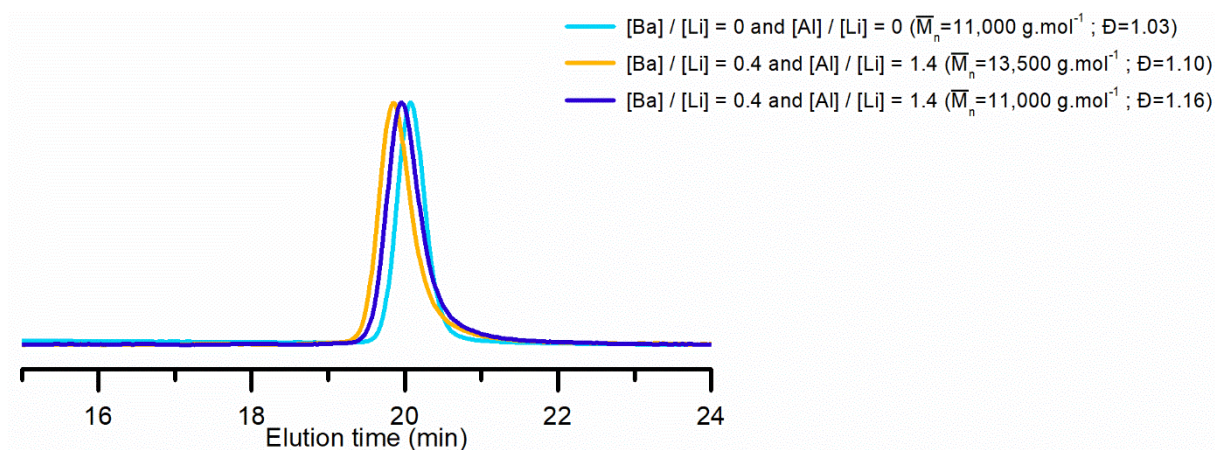


Figure 2. SEC chromatograms of polybutadienes obtained using a system made of *sec*-butyllithium / barium 2-ethylhexoxide / triisobutylaluminum in cyclohexane at 20°C after 3 days ([Ba] / [Li] = 0.4, [Al] / [Li] = 1.4, $\bar{M}_{n \text{ theo}} = 10,000 \text{ g.mol}^{-1}$)

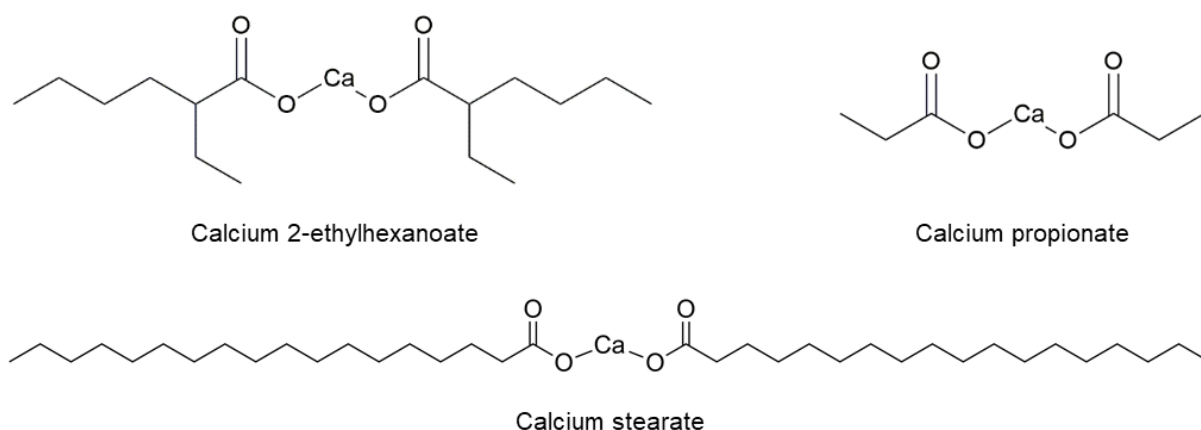
Experimental molar masses are in good agreement with the calculated one, indicating that the initial amount of *sec*-butyllithium control polymers chain length. Polybutadiene microstructure is shifted from 53% 1,4-*trans* content (typical of alkyllithium initiated polymerization) to 80%, keeping a low vinyl content. One can note that quantitative yields are obtained after several days at 20°C suggesting a slow polymerization rate.

This barium-based trimetallic system is used as a reference for our investigation on the influence of other alkaline earth metal derivatives on butadiene polymerization.

3. Calcium-based systems for the synthesis of polybutadiene

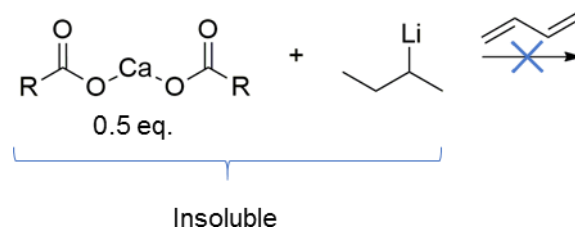
3.1. Commercially available materials and their use for butadiene polymerization

A couple of calcium carboxylate were used as component of a bimetallic initiation system in association with *sec*-butyllithium (Scheme 4).



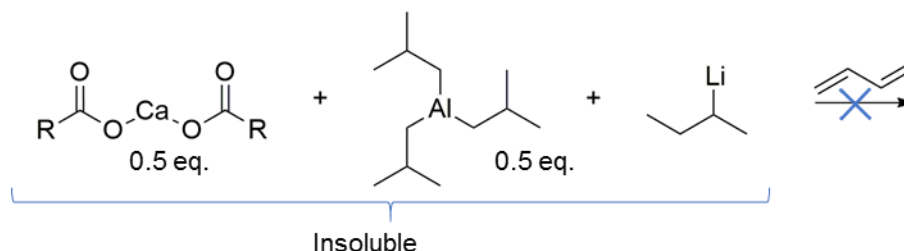
Scheme 4. Structures of calcium 2-ethylhexanoate, calcium propionate and calcium stearate

The first observation we made is that calcium 2-ethylhexanoate and calcium propionate are not soluble in hydrocarbon media, such as toluene and cyclohexane, addition of *sec*-butyllithium did not improve their solubility. Attempted polymerizations with these heterogenous solutions did not yield any polymer (Scheme 5). In the literature, the use of calcium stearate / butyllithium initiation systems, with similar ratios, are reported to produce polybutadiene [2]. This difference in terms of reactivity might be the consequence of the higher solubility of calcium stearate in apolar media due to its longer aliphatic chain.



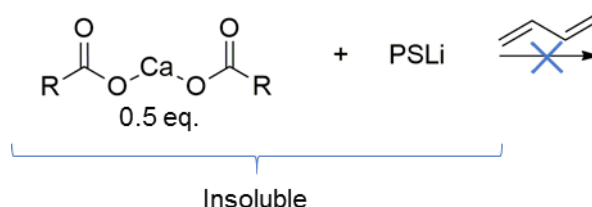
Scheme 5. Non-polymerization of butadiene in the presence of *sec*-butyllithium + 0.5 eq. of calcium dicarboxylate of in cyclohexane (RCOO = 2-ethylhexanoate or propionate)

Addition of triisobutylaluminum to a *sec*-butyllithium / calcium carboxylate dispersion does not improve the solubility of calcium carboxylate moieties either, and attempted butadiene polymerization with this heterogenous trimetallic systems did not yield polybutadiene (Scheme 6).



Scheme 6. Non-polymerization of butadiene in the presence of *sec*-butyllithium + 0.5 eq. of triisobutylaluminum + 0.5 eq. of calcium dicarboxylate in cyclohexane (RCOO = 2-ethylhexanoate or propionate)

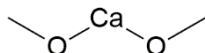
The association of polystyryllithium seeds with calcium carboxylate was then investigated in order to obtain a soluble initiator solution. This wasn't successful, and butadiene polymerization experiments with such a system did not produce polybutadiene (Scheme 7).



Scheme 7. Non-polymerization of butadiene in the presence of polystyryllithium seeds ($\overline{DP}_n = 5$) + 0.5 eq. calcium dicarboxylate in cyclohexane (RCOO = 2-ethylhexanoate or propionate)

The lack of solubility, a low nucleophilicity and a low reactivity of calcium derivatives, which can be decreased by the conjugation on the carboxylate, is believed to highly reduce the initiator activity or efficiency. In addition, initiation systems based on calcium stearate and alkyllithium were reported to produce polybutadiene with 50% 1,4-*trans* content [2], and accordingly the use of calcium carboxylate was not further investigated for the obtention of polybutadiene with a high 1,4-*trans* content.

A second set of experiments was conducted with calcium methoxide (Scheme 8).



Scheme 8. Structure of calcium methoxide

Once again, this compound was not soluble in hydrocarbon media, and upon addition of 4 eq. polystyryllithium seeds, a heterogenous system was obtained. But after addition of butadiene in this heterogenous solution polymerization occurred. Results are presented in Table 2 and Figure 3. Molar masses of the polymer are in good agreement with the targeted ones with a narrow dispersity. A white precipitate was observed, suggesting that calcium salts were not part of the initiating / propagating complex. This hypothesis is reinforced by the microstructure of the resulting polybutadiene which is the same one that the one obtained with *sec*-butyllithium in cyclohexane at 20°C. The hypothesis is that calcium alkoxide must be soluble to allow a complex formation or a ligand exchange with alkyllithium moieties, and to produce polybutadiene with a high 1,4-trans content. In addition, the observation of a precipitate even in the presence of a 12,000 g.mol⁻¹ living polybutadiene is an indicator that complexation with lithium species is not occurring. The lack of solubility of the initiation species is probably the explanation to the low influence of calcium compound on polybutadiene microstructure observed by Fujio and coworkers in the case of butyllithium / calcium ethoxide systems [2].

Table 2. Polybutadiene microstructure obtained with a heterogenous solution of PSLi + 0.25 eq. of (MeO)₂Ca in cyclohexane at 20°C ([butadiene] = 2 mol.L⁻¹, [PSLi] = 10⁻² mol.L⁻¹, $\bar{M}_{nth}$ = 10,000 g.mol⁻¹, cyclohexane, 20°C, 16h, yield = 100%)

[Ca] / [Li]	$\bar{M}_n \text{ exp}$ (g.mol ⁻¹)	$\bar{D}$	1,2 (%)	1,4-cis (%)	1,4-trans (%)
0 ^a	11,000	1.02	7	41	52
0.25	12,000	1.01	7	41	52

^a *sec*-butyllithium was used as the initiator

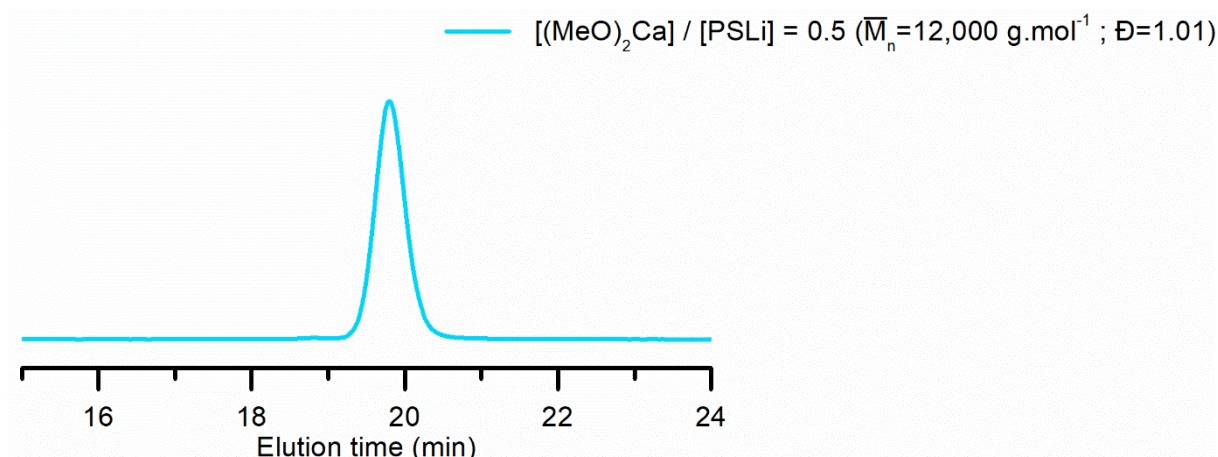
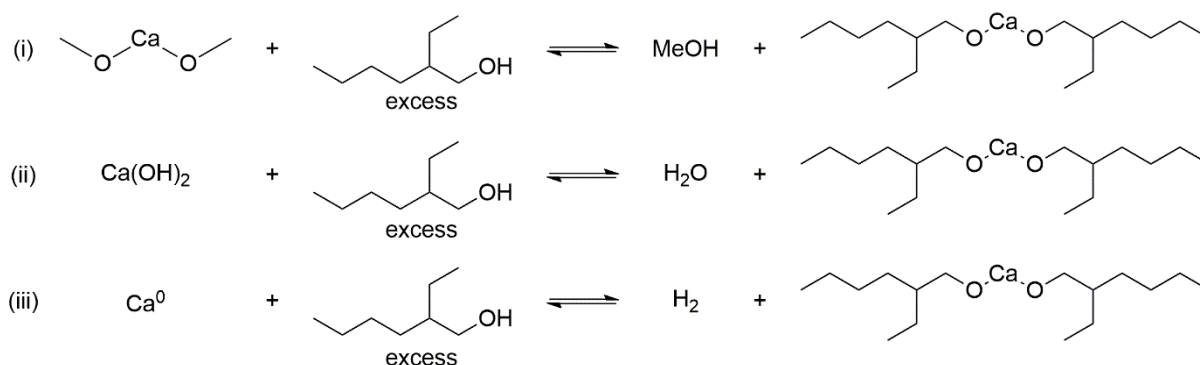


Figure 3. SEC chromatogram of polybutadiene synthesized with an heterogeneous initiator solution of PSLi seeds + 0.25 eq. of $(\text{MeO})_2\text{Ca}$ in cyclohexane at 20°C ($\bar{M}_{nth} = 10,000 \text{ g.mol}^{-1}$)

3.2. Calcium derivatives synthesis

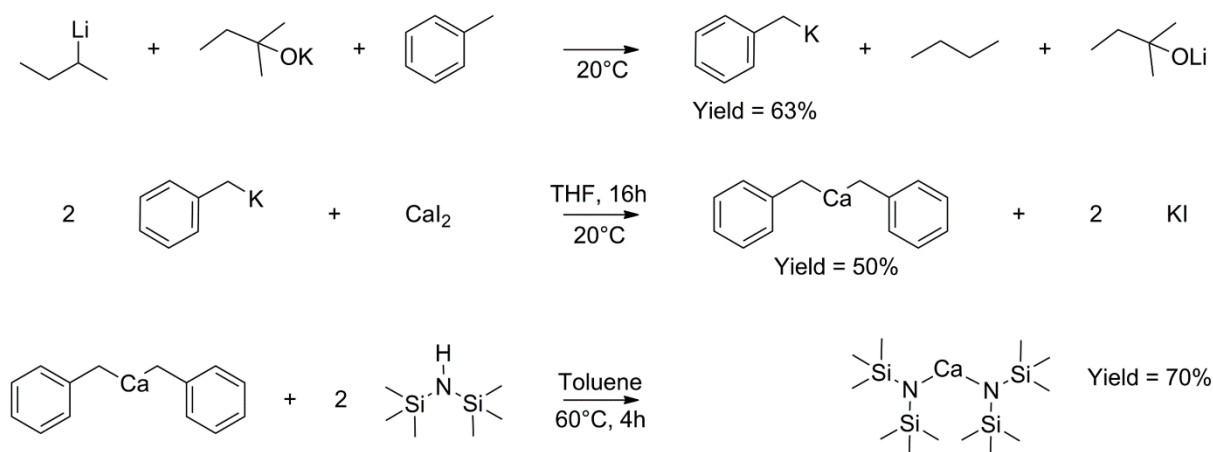
Knowing that the solubility is a key parameter, hydrocarbon soluble calcium derivatives was then studied. The synthesis of calcium 2-ethylhexoxide was envisaged to obtain a hydrocarbon soluble calcium compound. Several synthetic routes were attempted including ligand exchange from calcium methoxide in 2-ethylhexanol at high temperature (adapted from [21], Scheme 9 (i)), or from calcium hydroxide in 2-ethylhexanol with continuous water removal (Dean–Stark trap, adapted from [22], Scheme 9 (ii)) and finally with the direct reaction of metallic calcium with 2-ethylhexanol ([23], Scheme 9 (iii)) in bulk or in toluene at high temperature. These procedures were all attempted but these synthetic pathways suffer from a major drawback, at the laboratory scale, which is the removal of the excess 2-ethylhexanol (b.p. 185°C). Direct reaction with an excess of calcium with respect to the alcohol was also attempted but this reaction pathway suffers from the low reactivity of calcium metal and was not successful.



Scheme 9. Attempted synthesis for the obtention of calcium 2-ethylhexoxide

Calcium metal activation appears to be mandatory to obtain reaction with an alcohol. Several activation pathways are described in the literature such as formation of an amalgam of calcium ([4], [17]), calcium dissolution in liquid ammonia or ammonia-saturated solvents at low temperature (*e.g.* in toluene 48h @ -95°C) ([24]–[26]), or reaction of calcium iodide with potassium metal or potassium biphenylide to form highly reactive metals (Rieke method, [26]). Another method reported in the literature to obtain calcium derivatives is through the use of calcium iodide and potassium bis(trimethylsilyl)amide, but a substantial amount of potassium was said to remain in the product in the form as $\text{K}[\text{Ca}\{\text{N}(\text{SiMe}_3)_2\}_3]$ [27]. This compound might be a threat to our study since potassium is known to produce polybutadiene with a high vinyl content ($\approx 50\%$, [28]).

A reaction pathway involving the reaction of benzylpotassium with calcium iodide in THF, leading to the formation of dibenzylcalcium is reported in the literature [27]. This synthetic route was selected because benzylpotassium is obtained through toluene metalation with superbases (*sec*-butyllithium + potassium *tert*-pentoxide), and these systems were already used for butadiene polymerization experiments (see chapter I). A subsequent reaction of dibenzylcalcium with bis(trimethylsilyl)amine produces calcium bis(trimethylsilyl)amide ($\text{Ca}(\text{HMDS})_2$) which is soluble in toluene (Scheme 10) [27]. This reaction was attempted and the overall yield for this synthesis was 22%.



Scheme 10. Synthesis of calcium bis(trimethylsilyl)amide (also known as $\text{Ca}(\text{HMDS})_2$) [27]

Obtained ^1H NMR (Figure 4) and ^{13}C NMR (Figure 5) spectra in benzene- d_6 at 20°C were found conform to the published one [27], except that THF moieties are remaining in solution either free or complexed to calcium (estimated $[\text{THF}] / [\text{Ca}] = 0.22 - 0.24$)

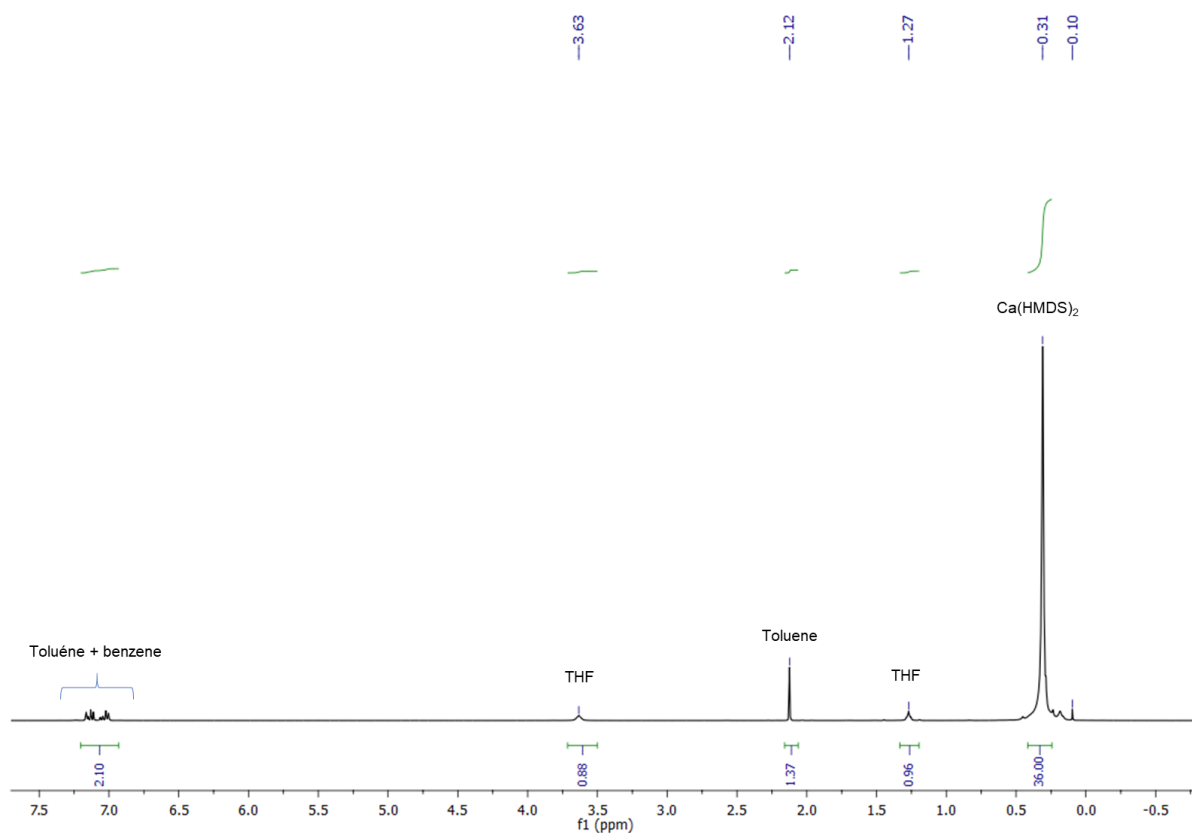


Figure 4. ^1H NMR spectrum of the obtained $\text{Ca}(\text{HMDS})_2$ in C_6D_6 at 20°C

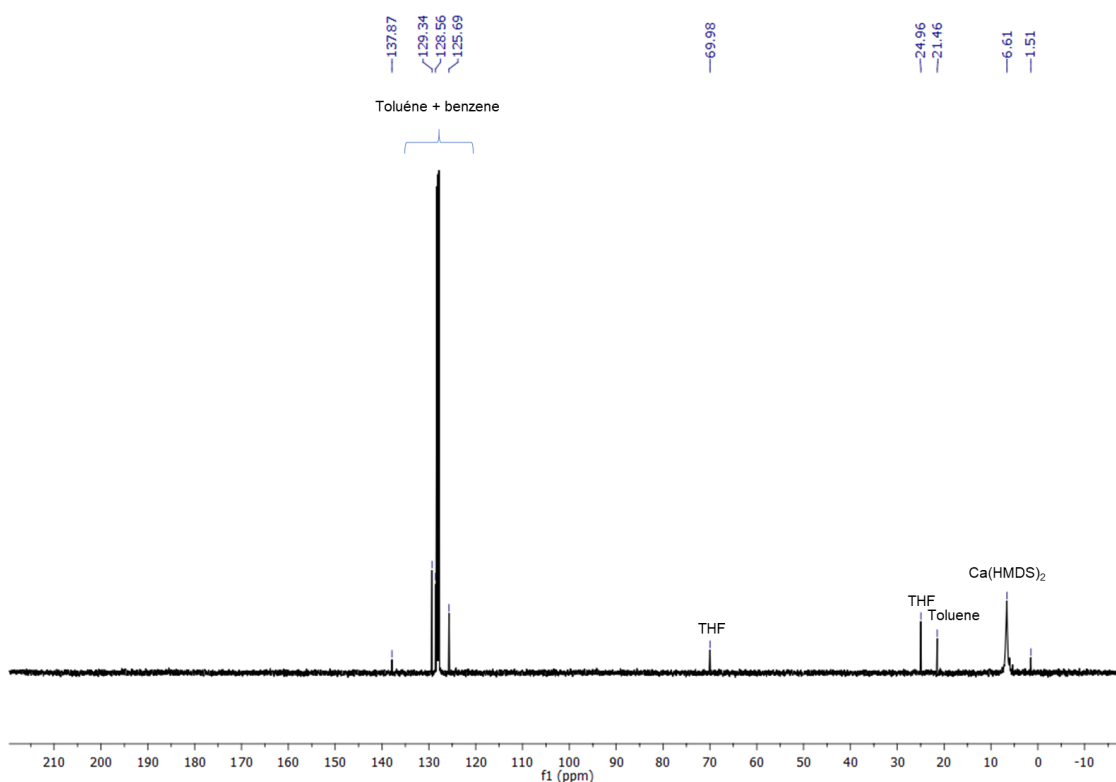


Figure 5. ^{13}C NMR spectrum of the obtained $\text{Ca}(\text{HMDS})_2$ in C_6D_6 at 20°C

The obtained calcium salt of amine was found to be soluble in toluene, and for this study we decided to use it in association with alkyllithium for the anionic polymerization of butadiene. Nonetheless, the reaction of calcium bis(trimethylsilyl)amide with an alcohol can lead to a variety of calcium alkoxides through a transamination reaction [26]. For future work the use of calcium derivatives with other ligand (such as alkoxide, phenoxide, and sulfoxide) has to be considered to assess the influence of calcium ligands on polybutadiene microstructure.

4. Anionic polymerization of butadiene using *sec*-butyllithium / calcium bis(trimethylsilyl)amide based system

Butadiene polymerization experiments were performed using a bimetallic system with *sec*-butyllithium + x eq. of calcium bis(trimethylsilyl)amide ($0 \leq x \leq 1$) and different parameters like the initiator preformation time and the $[Ca] / [Li]$ ratio were investigated to determine the influence of such parameters on polymerization control and polybutadiene microstructure.

4.1. Influence of the preformation time of the initiator

The influence of the initiator preformation time, generated *in-situ*, was first investigated. When no preformation time is allowed butadiene was introduced into the reaction vessel between the amine salt of calcium and *sec*-butyllithium. Obtained results are presented in Table 3 and Figure 6. Microstructures present a high 1,4-trans content up to 76%. Polymerization time is quite long since 100% yield is not reached even after 3 days at 20°C. However, molar masses are in good agreement with the targeted ones after taking the yield into consideration and low dispersity values are observed. Initiator preformation time seems to have a minor influence both on polybutadiene microstructure and polymerization control. Obtained yields for experiments with 1h and 16h preformation time, 72h after the addition of butadiene, are quite different, however these differences were ascribed to reproducibility issue rather than to a real influence of the preformation time. Obtained microstructures tend to suggest that a carbon – calcium bond is responsible of the propagation step. The nature of the propagating center remains unclear since it may be part of a complex with lithium (Scheme 11, hypothesis #1) or free alkylcalcium moieties (Scheme 11, hypothesis #2).

Table 3. Influence of the initiator preformation time on butadiene polymerization using *sec*-butyllithium + 1 eq. of calcium bis(trimethylsilyl)amide (cyclohexane, 20°C, $[butadiene] = 2 \text{ mol.L}^{-1}$, $[sec-BuLi] = 10^{-2} \text{ mol.L}^{-1}$, $\bar{M}_{n\text{ th}} = 10,000 \text{ g.mol}^{-1}$)

Preformation time	Time (h)	Yield (%)	$\bar{M}_n \text{ exp}$ (g.mol ⁻¹)	$\bar{D}$	1,2 (%)	1,4-cis (%)	1,4-trans (%)
No preformation	16	27	3,400	1.04	10	20	70
1h	72	80	8,000	1.04	8	17	76
16h	72	53	7,600	1.06	8	18	74

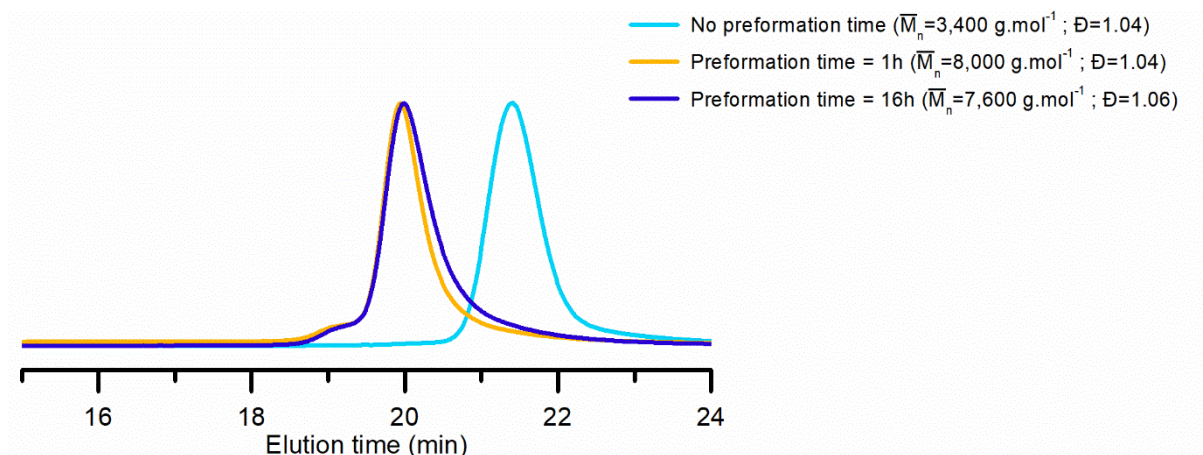
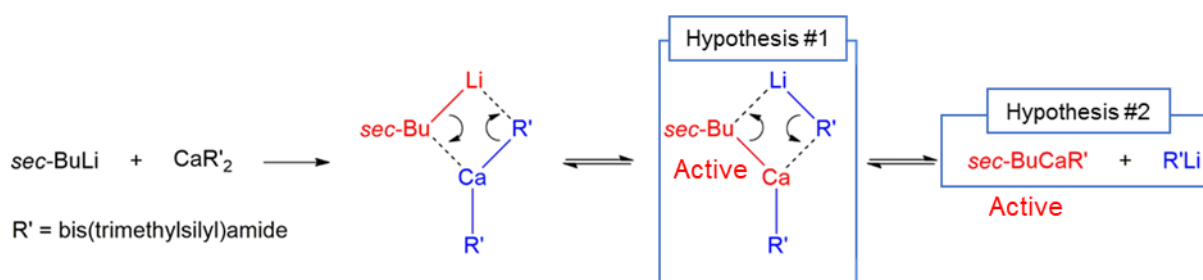


Figure 6. Influence of the initiator preformation time on SEC chromatograms of polybutadienes obtained with calcium bis(trimethylsilyl)amide + *sec*-butyllithium in cyclohexane at 20°C



Scheme 11. Suggested mechanism for the initiator formation from *sec*-butyllithium and 1 eq. of calcium bis(trimethylsilyl)amide

4.2. Influence of the ratio $[\text{Ca}] / [\text{Li}]$ on polybutadiene microstructure

The influence of the ratio $[\text{Ca}] / [\text{Li}]$ on polybutadiene microstructure was then studied, the targeted molar mass was $10,000 \text{ g.mol}^{-1}$ with the hypothesis of one polymer chain per *sec*-butyllithium molecule. Results are presented in Table 4 and Figure 7. All these experiments were performed at 20°C in cyclohexane, with one hour of initiator preformation since it was shown that the initiator preformation time has a minor influence on both polymerization control and polybutadiene microstructure. Polymerizations were allowed to proceed during a week, except in the case of $[\text{Ca}] / [\text{Li}] = 1$ in order to get an idea of polymerization kinetic with respect to the trimetallic system based on barium (see Section 2, and Table 1)

Table 4. Polymerization of butadiene using *sec*-butyllithium + x eq. of calcium bis(trimethylsilyl)amide ($0 \leq x \leq 1$, cyclohexane, 20°C, [butadiene] = 2 mol.L⁻¹, [sec-BuLi] = 10⁻² mol.L⁻¹, $\bar{M}_{nth} = 10,000$ g.mol⁻¹)

[Ca] / [Li]	Time (days)	Yield (%)	$\bar{M}_n \text{ exp}$ (g.mol ⁻¹)	$\bar{D}$	1,2 (%)	1,4-cis (%)	1,4-trans (%)
0	1	100	11,000	1.02	7	41	52
0.1	7	100	11,000	1.02	10	40	49
0.4	7	100	14,000	1.02	9	22	69
0.7	7	100	11,400	1.06	8	17	75
1	3	80	8,000	1.04	9	15	76

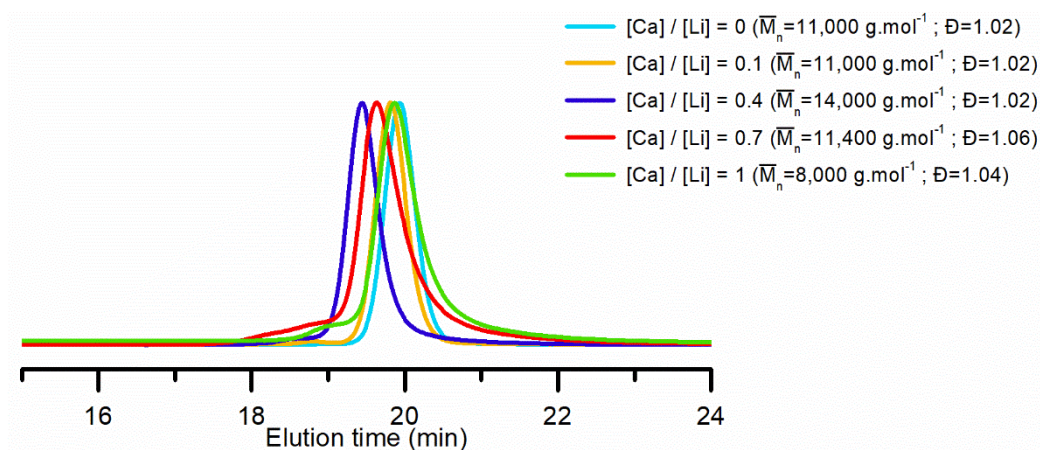


Figure 7. SEC chromatograms obtained for polybutadienes synthesized with a bimetallic system based on *sec*-butyllithium + x eq. of calcium bis(trimethylsilyl)amide in cyclohexane at 20°C ($0.1 \leq x \leq 1$, $\bar{M}_{nth} = 10,000$ g.mol⁻¹)

For $[Ca] / [Li] < 1$, reactions were allowed to proceed during a week to achieve full monomer conversion, and obtained yields are equal to 100%. For $[Ca] / [Li] = 1$, obtained yield after 72h was 80%. In all cases, molar masses are in the expected range and low dispersities are observed. While the ratio $[Ca] / [Li]$ is increased from 0 to 0.4, obtained 1,4-trans content are increasing from 50% (*sec*-BuLi alone) to 70%. Initiation systems with a ratio $[Ca] / [Li]$ equal to 0.4 are sufficient to reach high 1,4-trans content. Beyond that value, increasing the $[Ca] / [Li]$ ratio allows to obtain microstructure up to 76% when $[Ca] / [Li] = 1$. In other words, varying the initiator composition with such a bimetallic system allows a fine tuning of the 1,4-cis / 1,4-trans between 0.8 and 0.2 keeping a vinyl content below 10% (Figure 8).

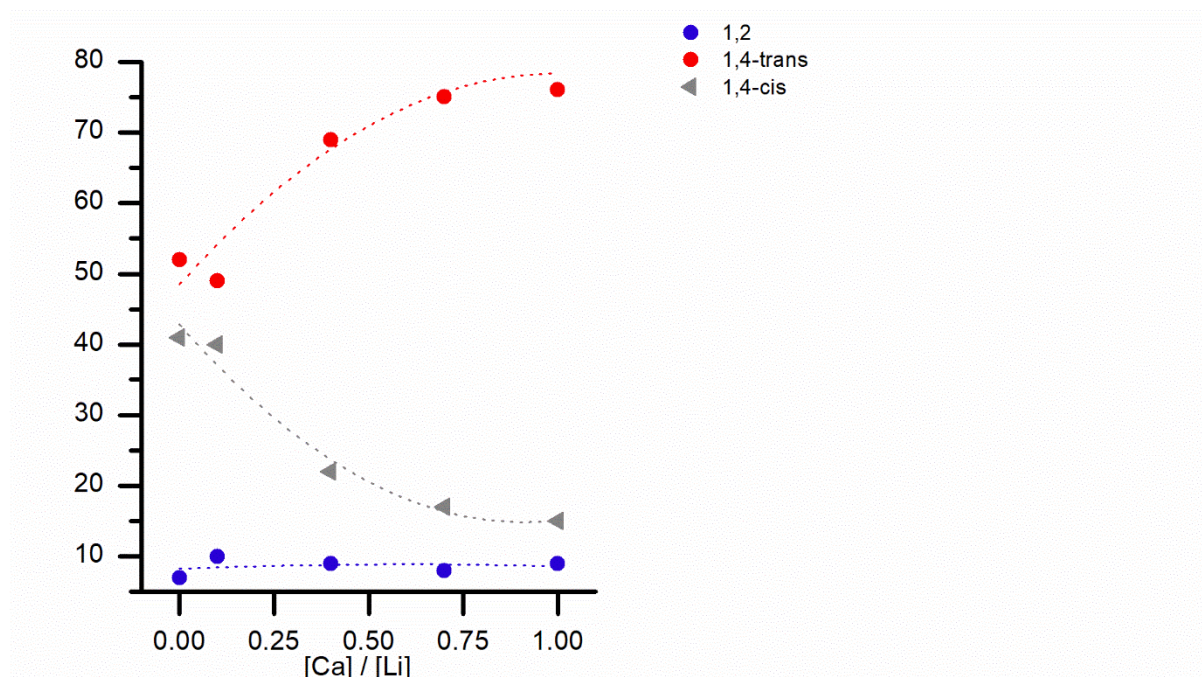


Figure 8. Evolution of the microstructure obtained for polybutadienes synthesized with $[Ca] / [Li]$ ratios ranging from 0 to 1 in cyclohexane at 20°C ($0.1 \leq x \leq 1$)

5. Influence of calcium bis(trimethylsilyl)amide on the polymerization propagation rate

Observing that the obtained yield after 3 days of polymerization ($[Ca] / [Li] = 1$ in cyclohexane at $20^{\circ}C$) is equal to 80%, a set of experiment was conducted in order to assess the polymerization rate of such a system. This set of experiments was performed in cyclohexane at $40^{\circ}C$ and the targeted molar mass was $10,000 \text{ g.mol}^{-1}$. Monomer conversion was determined by removing an aliquot from the reaction media under a flow of argon and the remaining amount of butadiene was determined by ^1H NMR in cyclohexane- d_{12} using toluene as an internal standard.

In these polymerization conditions a strong decrease of the reactivity of the active species is observed as compared to *sec*-butyllithium initiated polymerization while the living-like polymerization characteristics are preserved (Figure 9). Under such conditions the propagation rate for *sec*-butyllithium was estimated to be $2.19 \text{ mol.h}^{-1}.L^{-1}$ against $2.63 \times 10^{-1} \text{ mol.h}^{-1}.L^{-1}$ for the bimetallic system indicating a reduction of the propagation rate by almost an order of magnitude.

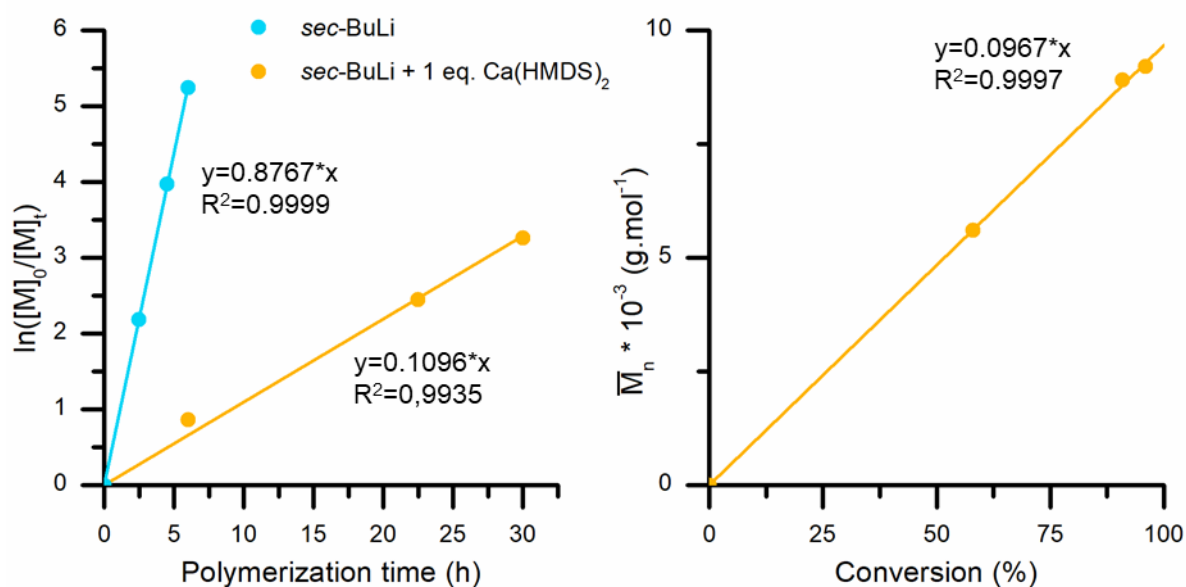


Figure 9. Influence of $Ca(HMDS)_2$ on *sec*-butyllithium-initiated butadiene polymerization kinetic in cyclohexane at $40^{\circ}C$. Toluene added as an internal standard. (●: $C_0, \text{butadiene} = 2.5 \text{ mol.L}^{-1}$, $C_0, \text{toluene} = 0.94 \text{ mol.L}^{-1}$, $\bar{M}_{nth} = 10,000 \text{ g.mol}^{-1}$. ●: $C_0, \text{butadiene} = 2.4 \text{ mol.L}^{-1}$, $C_0, \text{toluene} = 0.90 \text{ mol.L}^{-1}$, $\bar{M}_{nth} = 10,000 \text{ g.mol}^{-1}$, $[Ca] / [Li] = 1$)

In terms of microstructure, at 40°C in cyclohexane, the obtained 1,4-trans content with the calcium-based system remains high and found equal to 70% with respect to 52% in the case of *sec*-butyllithium keeping a vinyl content below 10% (Table 5).

Table 5. Microstructure of butadiene obtained using *sec*-butyllithium + *x* eq. of calcium bis(trimethylsilyl)amide in cyclohexane at 40°C (*x*= 0 or 1, [butadiene] = 2 mol.L⁻¹, [*sec*-BuLi] = 10⁻² mol.L⁻¹)

[Ca] / [Li]	1,2 (%)	1,4-cis (%)	1,4-trans (%)
0	8	41	52
1	8	22	70

6. Conclusion

This chapter intends to assess the influence of alkaline earth metal-based systems on polybutadiene microstructure and polymerization control. In particular, the idea is to find an alternative to barium-based trimetallic systems in order to obtain polybutadiene with a high 1,4-trans content in a controlled way.

Barium-based multi-metallic systems are the most reported and are known to produce high 1,4-trans content. Magnesium derivatives alone are not active with respect to butadiene anionic polymerization. Alkylmagnesium / alkyllithium systems ($1 < [\text{Mg}] / [\text{Li}] < 10$) are reported to increase polybutadiene vinyl content because of the isomerization of the chain end inside of a magnesiate complex. Calcium / lithium based initiating systems are less studied and scientific literature show antagonist results in terms of microstructure, and only a few information on polymerization control is reported.

The use of commercially available calcium derivatives *i.e* calcium 2-ethylhexanoate, calcium propionate and calcium methoxide in association with alkyllithium derivatives was envisaged but the lack of solubility in hydrocarbon media of these compounds prevent calcium participation to the polymerization process. Attempted solubilization through complexation

with polystyryllithium and triisobutylaluminum were not effective and soluble calcium derivatives had to be synthesized.

Several synthetic route to obtain a soluble calcium alkoxide from calcium hydroxide, calcium methoxide and calcium metal were attempted but were not successful. Obtention of calcium derivatives requires metal activation and is usually achieved by using calcium amalgam or calcium metal dissolution in hydrocarbon media using ammonia. In this work, the selected reaction pathway is a multi-step synthesis starting from superbases chemistry followed by metal exchange with calcium iodide, and subsequent reaction with bis(trimethylsilyl)amine lead to the synthesis of calcium bis(trimethylsilyl)amide which is soluble in toluene.

The use of bimetallic systems based on *sec*-butyllithium / calcium bis(trimethylsilyl)amide were found to produce polybutadiene. The initiator preformation time has a minor influence on the control of butadiene polymerization. Obtained polybutadienes present a 1,4-trans content increasing from 50% to 76% when $[Ca] / [Li]$ is increasing from 0 to 1. Observed molar masses are in the range of the targeted one with a low dispersity. The polymerization rate was shown to be decreased upon addition of calcium bis(trimethylsilyl)amide by almost one order of magnitude. With such a bimetallic system a carbon – calcium bound is believed to be involved in the propagation reaction and to be responsible of the obtention of polybutadiene with a high 1,4-trans content.

As a perspective for following work, a transamination reaction could be envisaged with calcium bis(trimethylsilyl)amide to obtain calcium derivatives with different structures (*e.g.* alkoxide, sulfoxide, phenoxide) to assess the influence of calcium ligand on polymerization control and polybutadiene microstructure.

Calcium monometallic systems are reported in the literature to produce non-controlled polybutadiene with a high 1,4-trans content keeping a vinyl content below 10% [17]. Similarly, calcium / lithium bimetallic systems were shown, in the present experimental work, to produce polybutadiene with a high 1,4-trans content. According to the present study, the polymerization rate of calcium / lithium bimetallic systems is quite low.

Mono-metallic initiation systems with barium alone as a counter-ion are reported to produce polybutadiene with a high 1,4-cis content [6]. However, as soon as involved in multi-metallic propagation center, barium tends to produce polymers with a high 1,4-trans content. Such

systems are usually involving barium alkoxide in association with dialkylzinc [1], dialkylmagnesium [7], alkyllithium [2] or alkyllithium + trialkylaluminum [11]–[13]. In all cases, the formation of a complex with other organometallics species is believed to reduce the rate of polymerization with respect to alkylbarium alone.

Accordingly, the ability of alkaline earth metals derivatives to generate 1,4 units and especially high 1,4-trans content can be explained as follow. A similar mechanism with respect to the one depicted in the literature for lithium-based systems [28] could be envisaged for alkaline earth derivatives. Such a mechanism involves a σ carbon – metal bond localized on the α position of the last unit which might explain the preferential formation of 1,4 units. Meaning that we consider the carbon – barium / carbon – calcium bond as poorly dissociated ions pairs. This last unit can also isomerize until the following nucleophilic attack on monomer. One can also assume that alkaline earth derivatives can interact with incoming monomers and are able to constrain their geometry until the following nucleophilic attack leading to 1,4-trans units when organo-barium or -calcium are used.

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Chapter IV.

**Toward polybutadiene microstructure modulation in a lithium
free approach**

1. Introduction

Lithium-based anionic polymerization is a well-established route for the obtention of polybutadiene in a controlled way. Polybutadiene mechanical and thermal properties can be tuned by adjusting molar masses, dispersity, chain end functionalization, chain architecture, styrene content (in the case of styrene-butadiene rubber) and by varying polybutadiene microstructure [1], [2].

Using alkyllithium as an initiator, polybutadiene microstructure can be tuned by adjusting the reaction media polarity (solvent choice, addition of polar modifier in apolar media) or in apolar media by the addition of alkali metal or alkaline earth metals derivatives. Alkali metal derivatives are known to vary the 1,4 / 1,2 content of the obtained polybutadiene, meanwhile addition of alkaline earth metals derivatives (Ca, Sr, and Ba) enables tuning of 1,4-cis / 1,4-trans ratio [3].

Even though lithium-based anionic polymerization is well established to achieve microstructure tuning, lithium-free initiating systems are also reported. For instance, the use of monometallic systems based on sodium, potassium, calcium, strontium and barium are already described. Alkylsodium initiator in hydrocarbon media tends to produce polybutadiene with 60 – 80% vinyl content, and in aliphatic solvent, obtained molar masses are close to the theoretical ones with dispersity ranging from 1.2 to 1.5 [4], [5]. Alkylpotassium systems are known to produce polybutadiene with about 50% vinyl content [6], but synthesis and storage of alkylpotassium derivatives is challenging since a rapid deactivation occurs [7], [8]. The use of alkylcalcium ([9]–[11]), alkylstrontium [11] and alkylbarium ([11]–[13]) derivatives in apolar media is 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. Such initiators are not readily available and metal activation is often required through the use of amalgam or electronic transfer in THF.

Several lithium-free multi-metallic systems are also described in the literature and are typically based on sodium, potassium, magnesium, or aluminum derivatives. These systems are commonly based on alkylsodium / trialkylaluminum ([14], [15], for butadiene polymerization), sodium hydride / trialkylaluminum ([16]–[18], for styrene polymerization), potassium hydride / alkali metal alkoxide / trialkylaluminum ([19], for isoprene and butadiene polymerization), alkylmagnesium / alkali or alkaline earth derivatives ([20]–[24], for butadiene polymerization), and metal-zinc tetraalkyl ([25], metal = Ca, Sr or Ba, for diene / styrene copolymerization). The

development of such systems is either motivated by economical reason and / or to obtain polybutadiene with a desired microstructure.

The aim of this chapter is to prospect and develop initiating systems allowing to tune polybutadiene microstructure with readily available materials without using lithium derivatives. In a first part the use of dialkylmagnesium in association with potassium alkoxide, as a lithium free approach, will be discussed to obtain polybutadiene with a high vinyl content. In a second part, initiation systems based on alkali metal hydride / trialkylaluminum in association with barium alkoxide will be investigated to achieve polybutadiene synthesis with a high 1,4-trans content.

2. Dialkylmagnesium-based lithium free systems

2.1. Dialkylmagnesium / potassium *tert*-pentoxide systems for the synthesis of polybutadiene

The objective of this part is to develop an initiator based on di-*n*-butylmagnesium and potassium *tert*-pentoxide for butadiene anionic polymerization. Dialkylmagnesium alone, as well as potassium alkoxide, are known to be inactive toward anionic polymerization of styrene or diene.

2.1.1. Bimetallic systems

A bimetallic system based on potassium *tert*-pentoxide in association with *n,s*-dibutylmagnesium ($[K] / [Mg] = 1$, hexane, 10°C, $t \geq 24$ h) was developed by Halasa and coworkers [21]. After polymerization two polybutadiene fractions were observed. A first fraction soluble in hexane (2 – 15%) is described to be polybutadiene with 50% of vinyl content. A second fraction (76 – 84 %), is said to be an insoluble 1,4-trans polybutadiene resin. Even if this last assertion is only supported by the insolubility of the resulting polymers, this system allows butadiene polymerization without lithium.

Systems based on *n,s*-dibutylmagnesium + 1 eq. of alkali metal *tert*-butoxide (Li, Na, K) are described for styrene polymerization [24]. In all cases at 20°C in cyclohexane, polymerization control is not achieved and reported initiation efficiency are between 33% and 50% depending on the counterion. Lowering temperature was reported to decrease the initiation efficiency and the reactivity of the initiating complex.

A lack of information for such systems drive us to re-discover this chemistry. In particular we were interested to investigate the influence of $[K] / [Mg]$ ratio and of the initiator preformation time. For the initiating systems based on potassium alkoxide in association with alkyllithium (Chapter II), these parameters were shown to have an influence on polymerization control and on the obtained microstructure.

In this work, butadiene polymerization experiments, initiated by a mixture of di-*n*-butylmagnesium and potassium *tert*-pentoxide were carried out in cyclohexane at 20°C for a targeted molar mass of 10,000 g.mol⁻¹ with the hypothesis of one polymer chain per di-*n*-butylmagnesium molecule.

The influence of the initiator preformation time (with $[K] / [Mg] = 1$) on polymerization control and polybutadiene microstructure was first investigated. Like in the case of alkyllithium / potassium *tert*-pentoxide, the initiating system was poorly soluble in cyclohexane and it was generated *in-situ* by mixing both components in cyclohexane. Experiments with no preformation time were achieved by introducing butadiene in the reaction media between potassium *tert*-pentoxide and di-*n*-butylmagnesium. Results are presented in Table 1 and Figure 1. Obtained yields for this system are quantitative within 24 hours, and polymerization control is not achieved regardless of the initiator preformation time. In all cases, initiation efficiency is comparable to the one reported in the literature for styrene polymerization (40% with potassium *tert*-butoxide in cyclohexane at 20°C, [24]) under similar conditions. Low initiation efficiency might be a consequence of the lack of solubility of the initiating system. Polybutadiene microstructure (Table 1) is typical of potassium-based systems and preformation time has no influence on it. A second population, representing between 15 and 20 % of each sample, can be observed on SEC chromatograms with double molar mass with respect to the main population. Oxygen coupling might be the cause of this second population, but previous work on lithium / potassium based bimetallic systems (Chapter II) tend to show that alkylpotassium moieties are responsible of it. One can also assume that propagating species with various structure and consequently various propagation rate are coexisting, leading to multi-populated polymers.

Table 1. Influence of the initiator preformation time on butadiene polymerization using di-*n*-butylmagnesium + 1 eq. of potassium *tert*-pentoxide ($\bar{M}_{n\ th} = 10,000\ \text{g.mol}^{-1}$ *, [butadiene] = 2 mol.L⁻¹, [(*n*-Bu)₂Mg] = 10⁻² mol.L⁻¹, cyclohexane, 20°C, 24h, yield = 100%)

Preformation time	$\bar{M}_n\ exp^a$ (g.mol ⁻¹)	$\bar{D}^a$	f (%) ^b	1,2 (%)	1,4-cis (%)	1,4-trans (%)
None	23,000	1.21	43	50	18	32
24h	24,000	1.15	41	51	17	32
48h	28,000	1.14	35	50	18	33

* Calculated with the hypothesis of one polymer chain per di-*n*-butylmagnesium molecule. ^a Obtained for the main population. ^b f = Initiator efficiency = $\left(\frac{Yield * \bar{M}_n\ exp}{\bar{M}_{n\ th}}\right)$

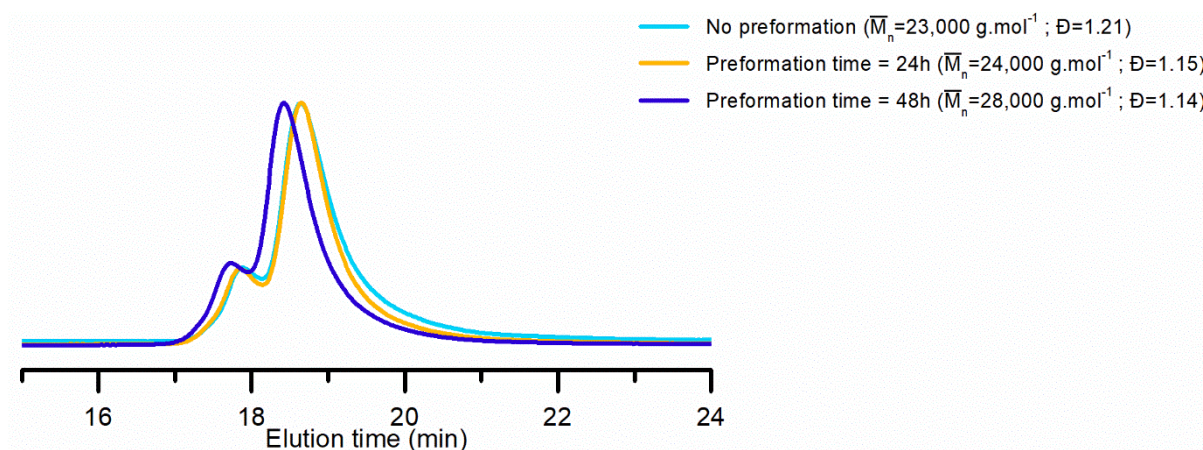
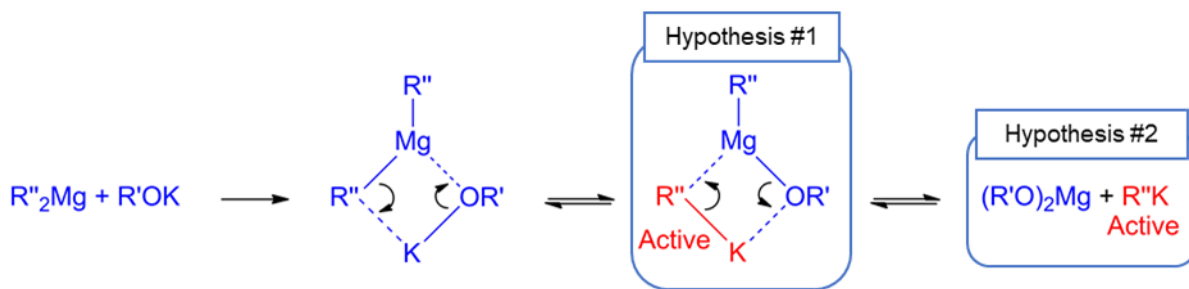


Figure 1. SEC chromatograms of polybutadiene obtained using [*tert*-PeOK] / [(*n*-Bu)₂Mg] = 1, with various preformation time in cyclohexane at 20°C ($\bar{M}_{n\ th} = 10,000\ \text{g.mol}^{-1}$, [butadiene] = 2 mol.L⁻¹, [(*n*-Bu)₂Mg] = 10⁻² mol.L⁻¹, 20°C, 24h, yield = 100%)

Proposed mechanism for the initiator formation is presented on Scheme 1, like in the case of lithium-based system, the propagation center may be a complex of di-*n*-butylmagnesium and potassium *tert*-pentoxide (hypothesis #1) or free alkylpotassium moieties (hypothesis #2).



Scheme 1. Suggested mechanism for initiator formation from di-*n*-butylmagnesium and potassium *tert*-pentoxide. ($R' = \text{tert-pentoxide}$, $R'' = n\text{-butyl}$, $[K] / [Mg] = 1$)

Since the initiator preformation time has no real influence on polymerization nor polybutadiene microstructure, following experiments to assess the influence of $[K] / [Mg]$ were performed with no preformation time. The ratio $[K] / [Mg]$ was varied from 0.75 to 5. Obtained results are presented in Table 2 and Figure 2.

Increasing $[K] / [Mg]$ ratios tend to bring closer the experimental molar mass and the targeted one, but polymerization control is not improved since dispersity is increased (Figure 2). The ratio $[K] / [Mg]$ have a minor influence on polybutadiene microstructure, which is not surprising since carbon – magnesium bonds are not active toward butadiene anionic polymerization, indicating that polymerization occurs inside of a carbon – potassium bond.

Table 2. Polymerization of butadiene with di-*n*-butylmagnesium + x eq. of potassium *tert*-pentoxide as initiator ($0.75 < x < 5$, no preformation time, $[\text{butadiene}] = 2 \text{ mol.L}^{-1}$, $[(n\text{-Bu})_2\text{Mg}] = 10^{-2} \text{ mol.L}^{-1}$, $\bar{M}_{n\text{th}} = 10,000 \text{ g.mol}^{-1}$ *, cyclohexane, 20°C , 16h, yield = 100%)

$[K] / [Mg]$	$\bar{M}_n \text{ exp}^b$ (g.mol^{-1})	$\bar{D}^b$	1,2 (%)	1,4-cis (%)	1,4-trans (%)
0.75	26,000	1.25	48	18	32
1	23,000	1.21	50	18	32
5	11,000	1.42	54	15	31

* Calculated with the hypothesis of one polymer chain per di-*n*-butylmagnesium molecule. ^a Obtained for the main population.

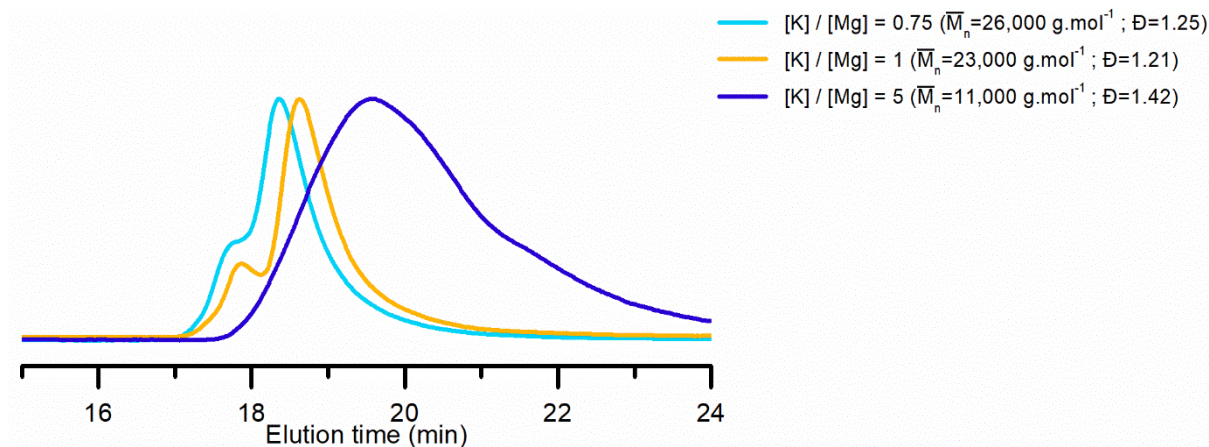


Figure 2. SEC chromatograms of polybutadienes obtained using various [*tert*-PeOK] / [(*n*-Bu)₂Mg], (No preformation time, cyclohexane, 20°C, $\bar{M}_{nth} = 10,000 \text{ g.mol}^{-1}$)

2.1.2. Addition of trialkylaluminum to magnesium / potassium initiating systems

Looking at the results obtained for [K] / [Li] = 5 (Chapter II), addition of triisobutylaluminum was shown to allow polymerization control by lowering the basicity of the propagating center. Observing that the SEC chromatogram obtained for [K] / [Mg] = 5 is quite similar, a trimetallic system, based on di-*n*-butylmagnesium / potassium *tert*-pentoxide / triisobutylaluminum was then studied. Initiator was generated *in situ* by addition of potassium *tert*-pentoxide to cyclohexane followed by triisobutylaluminum then di-*n*-butylmagnesium.

Along with observations made on Li / K / Al based systems indicating that the initiator preformation has an impact on polymerization since long preformation time is required to achieve polymerization control (Chapter II), the first set of experiments deals with the influence of the initiator preformation time on butadiene polymerization initiated by a trimetallic systems composed of di-*n*-butylmagnesium + 1 eq. of potassium *tert*-pentoxide + 0.25 eq of triisobutylaluminum (Table 3, Figure 3). When no initiator preformation time is allowed, obtained molar mass and dispersity are similar to the one obtained without trialkylaluminum, indicating that aluminum was not involved in the polymerization process. For a day long initiator preformation at 20°C, the initiator remains poorly soluble, and polymerization control is not improved but the magnitude of the second population is slightly reduced from 15 – 20% to 5 – 10%. This phenomenon might be the consequence of the formation of an aluminate

complex reducing the chain-end reactivity and preventing side reactions. Longer preformation time of the initiating system does not lead to any improvement, suggesting that initiator formation was complete after 24 hours at 20°C. The initiation efficiency remains low (40%) and is not improved with the addition of triisobutylaluminum which might be explain by the lack of solubility of the initiating species.

Table 3. Influence of the initiator preformation time on butadiene polymerization using di-*n*-butylmagnesium + 1 eq. of potassium *tert*-pentoxide + 0.25 eq. of triisobutylaluminum ([butadiene] = 2 mol.L⁻¹, [(*n*-Bu)₂Mg] = 10⁻² mol.L⁻¹, $\bar{M}_{n\ th}$ = 10,000 g.mol⁻¹*, cyclohexane, 20°C, 16h, yield = 100%)

Preformation time	[K] / [Mg]	[Al] / [Mg]	$\bar{M}_n\ exp^a$ (g.mol ⁻¹)	$\bar{D}^a$
None	1	0	23,000	1.21
None	1	0.25	26,000	1.24
24h	1	0.25	27,000	1.28
72h	1	0.25	27,000	1.27

* Calculated with the hypothesis of one polymer chain per di-*n*-butylmagnesium molecule. ^a Obtained for the main population.

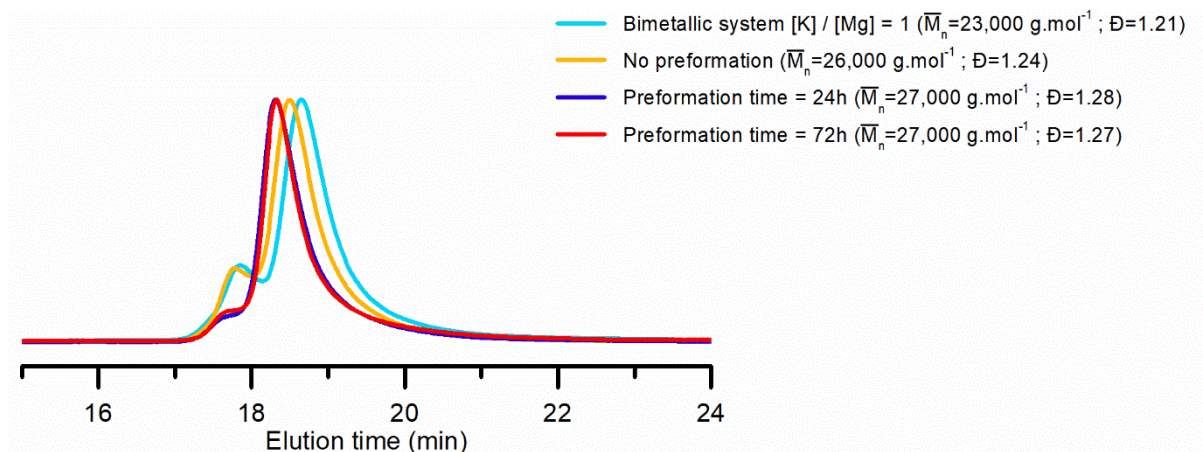


Figure 3. SEC chromatograms of polybutadiene obtained with trimetallic systems based on di-*n*-butylmagnesium + 1 eq. of potassium *tert*-pentoxide + 0.25 eq. of triisobutylaluminum after various preformation time (cyclohexane, 20°C, $\bar{M}_{n\ th}$ = 10,000 g.mol⁻¹, 16h, yield = 100%)

The influence of the $[Al] / [Mg]$ was then investigated with a constant $[Mg] / [K]$ ratio and a 24 hours preformation time at 20°C. For this set of experiments $[Mg] / [K]$ was equal to 1 and $[Al] / [Mg]$ was varied from 0 to 0.4. Polymerization experiments with higher aluminum content were conducted but did not yield any polymer. Results are presented in Table 4 and Figure 4.

In all cases, polymerization control is not achieved. When $[Al] / [Mg] = 0.15$, the magnitude of the second population remains similar to what was observed without aluminum. For higher trialkylaluminum content, the magnitude of the second population is slightly reduced. Obtained polybutadienes have a microstructure which remain typical of potassium-based systems with a vinyl content around 50%.

Table 4. Polymerization of butadiene using di-*n*-butylmagnesium + 1 eq. of potassium *tert*-pentoxide + x eq. of triisobutylaluminum ($0 < x < 0.4$, initiator preformation time = 24h, cyclohexane, 20°C, $[butadiene] = 2 \text{ mol.L}^{-1}$, $[(n-Bu)_2Mg] = 10^{-2} \text{ mol.L}^{-1}$, $\bar{M}_{n\text{ th}} = 10,000 \text{ g.mol}^{-1}$ *, 16h)

$[K] / [Mg]$	$[Al] / [Mg]$	Yield (%)	$\bar{M}_n \text{ exp}^a$ (g.mol ⁻¹)	$\bar{D}^a$	1,2 (%)	1,4-cis (%)	1,4-trans (%)
1	0	100	23,000	1.21	50	18	32
1	0.15	96	26,000	1.37	54	17	29
1	0.25	97	27,000	1.28	54	17	29
1	0.4	89	25,000	1.42	56	17	27

* Calculated with the hypothesis of one polymer chain per di-*n*-butylmagnesium molecule ^a Obtained for the main population

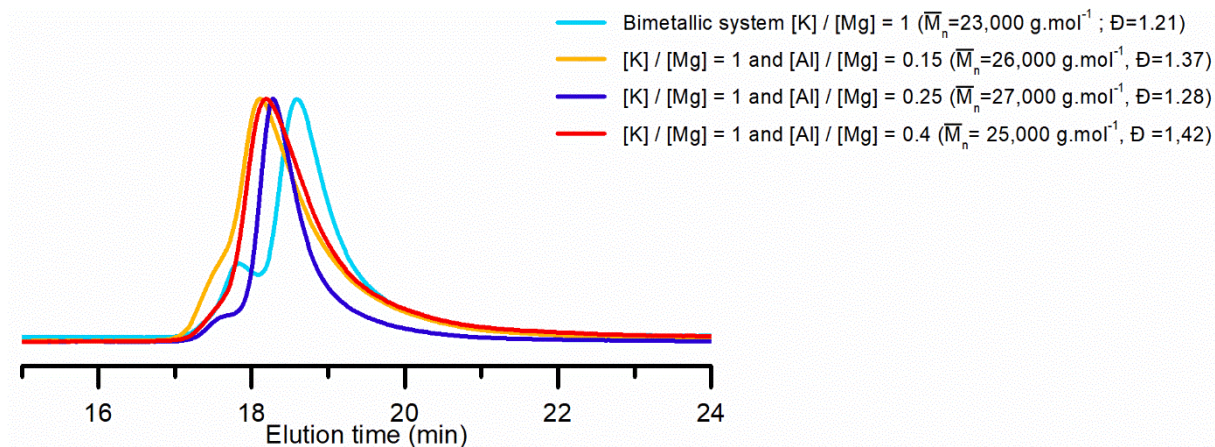


Figure 4. SEC chromatograms of polybutadiene obtained with trimetallic systems based on di-*n*-butylmagnesium, + 1 eq. of potassium *tert*-pentoxide + *x* eq. of triisobutylaluminum ($0 < x < 0.4$, preformation time = 24h, cyclohexane, 20°C, $\bar{M}_{n\ th} = 10,000 \text{ g.mol}^{-1}$)

According to the previous set of experiment, the addition of trialkylaluminum does not improve initiation efficiency and polymerization control (Table 3, Table 4), even if the magnitude of the second population is reduced. To conclude on the relevance of such a system, a last set of experiments was conducted in the worst-case scenario when $[K] / [Mg] = 5$ (Table 5, Figure 5). When $[Al] / [Mg] = 2.5$, polymer yield is below 30% after 48 hours and a low molar mass polybutadiene is obtained with a broad dispersity. For intermediate aluminum content ($[Al] / [Mg] = 0.5$ and 1), addition of triisobutylaluminum leads to a clear improvement in terms of dispersity with respect to the corresponding bimetallic system ($[K] / [Mg] = 5$, see Figure 2). Polymerization control is improved since obtained molar masses are in the expected range but chains distribution is still broad. Like in the case of Li / K / Al, this improvement in terms of polymerization control is supposed to be the consequence of the formation of a lower basicity complex thanks to the addition of trialkylaluminum (Scheme 2). The excess of potassium alkoxide might also be involved in the propagation center in a higher stoichiometry aluminate complex, but such complex was not represented for a better reading of Scheme 2. It is worth mentioning that this trimetallic system ($[K] / [Mg] = 5$ and $0 < [Al] / [Mg] < 2.5$) are the first ones to get close to some polymerization control in this series of experiments on dialkylmagnesium / potassium alkoxide based systems despite the presence of a second population in the high molar mass side.

Table 5. Polymerization of butadiene using di-*n*-butylmagnesium + 5 eq. of potassium *tert*-pentoxide + *x* eq. of triisobutylaluminum (0 < *x* < 2.5, preformation time = 24h, cyclohexane, 20°C, [butadiene] = 2 mol.L⁻¹, [(*n*-Bu)₂Mg] = 10⁻² mol.L⁻¹, $\bar{M}_{nth} = 10,000$ g.mol⁻¹*, 16h)

[K] / [Mg]	[Al] / [Mg]	Yield (%)	$\bar{M}_n exp^a$ (g.mol ⁻¹)	$\bar{D}^a$
5	0	100	11,000	1.42
5	0.5	100	13,000	1.23
5	1	100	12,000	1.28
5	2.5	25	3,800	2.06

* Calculated with the hypothesis of one polymer chain per di-*n*-butylmagnesium molecule ^aObtained for the main population

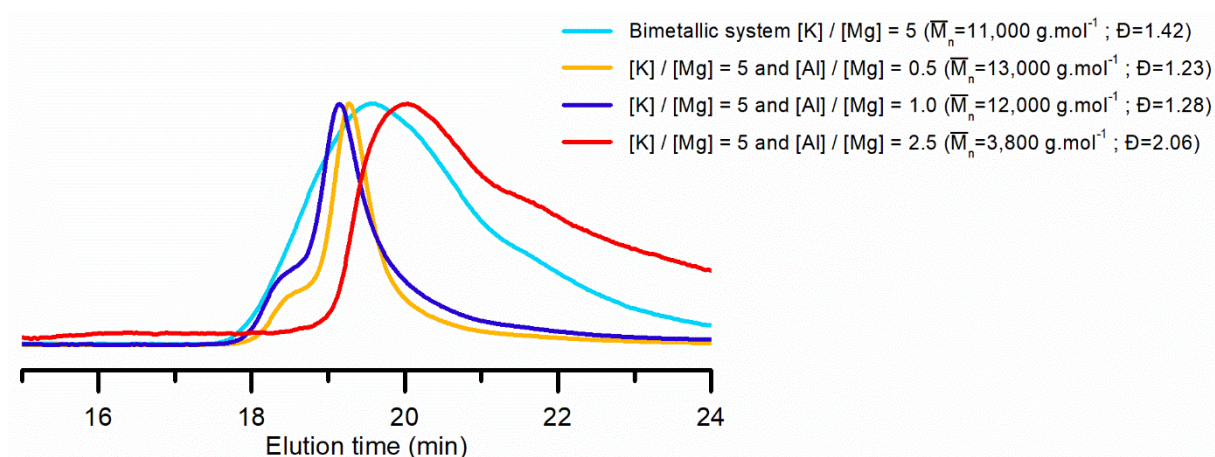
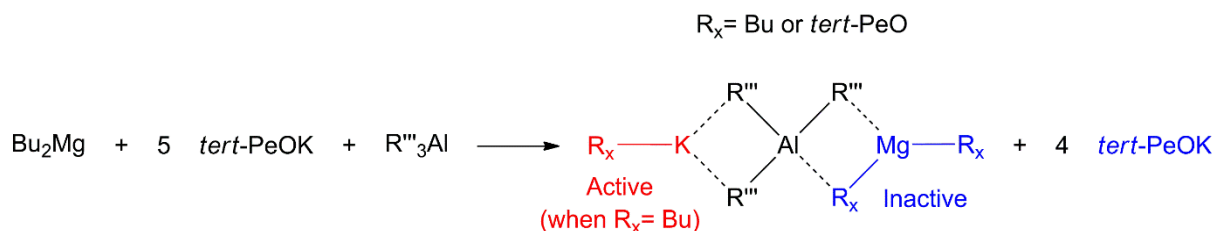


Figure 5. SEC chromatograms of polybutadiene obtained with trimetallic systems based on di-*n*-butylmagnesium, + 5 eq. of potassium *tert*-pentoxide + *x* eq. of triisobutylaluminum (0 < *x* < 2.5, preformation time = 24h, cyclohexane, 20°C, 16h, $\bar{M}_{nth} = 10,000$ g.mol⁻¹)



Scheme 2. Expected mechanism for the formation of the initiating complex with di-*n*-butylmagnesium, potassium *tert*-pentoxide and triisobutylaluminum.

The association of di-*n*-butylmagnesium and potassium *tert*-pentoxide ($0 < [\text{K}] / [\text{Mg}] \leq 1$) allows the synthesis of polybutadiene with 50% vinyl content. Polymerization control is not achieved and the initiation efficiency is about 40%. All the samples analyzed present a second population certainly linked to a coupling reaction as discussed in previous chapter. For $[\text{K}] / [\text{Mg}] = 5$, relatively high dispersities were obtained and polymerization control was still not achieved. The nature of the propagating species is believed to be a carbon – potassium bond either free or inside a magnesiate complex.

The behavior of such lithium-free system, when $[\text{K}] / [\text{Mg}] = 5$, was found to be similar in terms of polymerization control to the one observed for *sec*-butyllithium + 5 eq. of potassium *tert*-pentoxide. In this latter case, addition of triisobutylaluminum was shown to be relevant to achieve polymerization control and preventing side reaction. The same approach was applied to di-*n*-butylmagnesium / potassium *tert*-pentoxide based systems. Addition of triisobutylaluminum was shown to reduce the magnitude of the second population ($[\text{K}] / [\text{Mg}] = 1$ and $0.25 \leq [\text{Al}] / [\text{Mg}] \leq 0.4$) but did not have any influence on polymerization control and polybutadiene microstructure. At higher potassium content ($[\text{K}] / [\text{Mg}] = 5$ and $0.5 \leq [\text{Al}] / [\text{Mg}] \leq 1$), polymerization control is greatly improved and obtained molar masses are in the range of the expected ones with the hypothesis of one chain per dialkylmagnesium molecule, but a second population is still observed and molar masses distributions remain broader than the one observed for lithium / potassium based systems ($[\text{K}] / [\text{Li}] \leq 1$).

2.2. Dialkylmagnesium / barium 2-ethylhexoxide systems for the synthesis of polybutadiene

A lithium-free system is described in the scientific literature as a tri-component system based on barium alkoxide derivatives ($\text{Ba}(\text{OH})_{0.18}(\text{OR})_{1.82}$), dialkylmagnesium and trialkylaluminum and was said to produce polybutadiene with 90% 1,4-trans content when $[\text{Al}] / [\text{Mg}] = 0.17$ and $[\text{Ba}] / [\text{Mg}] = 0.2$ in cyclohexane at 50°C [21]. The aim of this set of experiment was to explore lithium-free bimetallic systems to obtain polybutadiene with a high 1,4-trans content.

These systems were composed of di-*n*-butylmagnesium and barium 2-ethylhexoxide in cyclohexane at 20°C. The influence of the initiator preformation time was not studied but experiments were performed without initiator preformation time by default. The ratio $[\text{Ba}] / [\text{Mg}]$ was varied between 0.5 and 2.5, results are presented in Table 6 and Figure 6.

Polybutadienes were obtained for systems in the sub-stoichiometry region ($[\text{Ba}] / [\text{Mg}] \leq 1$). Molar masses are not controlled, and molar masses distributions are broad. The 1,2 content for these systems is higher than the trimetallic system based on *sec*-butyllithium, triisobutylaluminum and barium 2-ethylhexoxide, but the 1,4-trans content remains high (up to 65%).

Table 6. Polymerization of butadiene using di-*n*-butylmagnesium + x eq. of barium 2-ethylhexoxide ($0.5 < x < 2.5$, no initiator preformation, cyclohexane, 20°C, 16h, $[\text{butadiene}] = 2 \text{ mol.L}^{-1}$, $[(\text{n-Bu})_2\text{Mg}] = 10^{-2} \text{ mol.L}^{-1}$, $\bar{M}_{n \text{ th}} = 10,000 \text{ g.mol}^{-1*}$)

$[\text{Ba}] / [\text{Mg}]$	Yield (%)	$\bar{M}_n \text{ exp}$ (g.mol ⁻¹)	$\bar{D}$	1,2 (%)	1,4-cis (%)	1,4-trans (%)
Ref. ^a	100	12,000	1.16	4	16	80
0.5	100	34,000	1.25	6	29	65
1	90	11,000	3.27	15	19	66
2.5	0	<i>No polymer recovered</i>				

* Calculated with the hypothesis of one polymer chain per di-*n*-butylmagnesium molecule ^a Polybutadiene synthesized using *sec*-butyllithium, barium 2-ethylhexoxide (0.4 eq) and triisobutylaluminum (1.4 eq.) as initiating system (ref. Michelin).

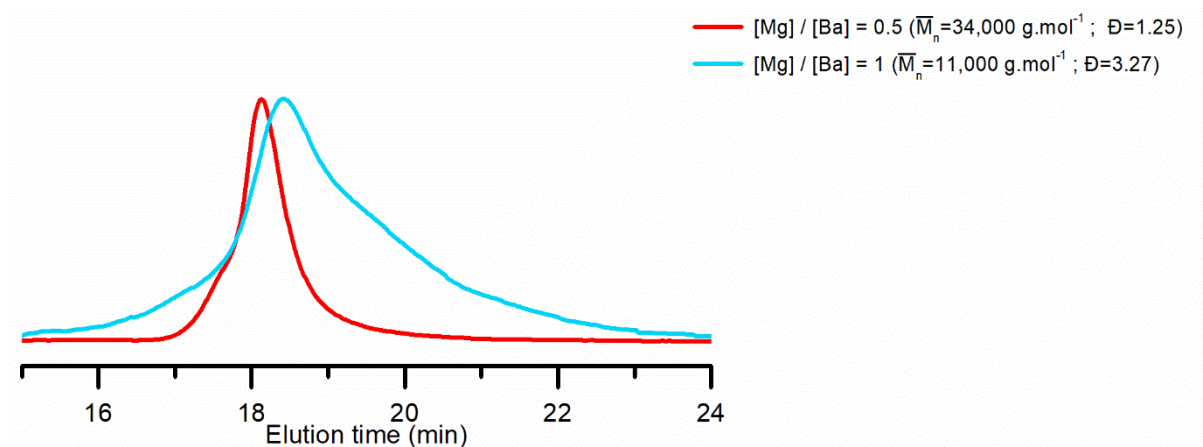
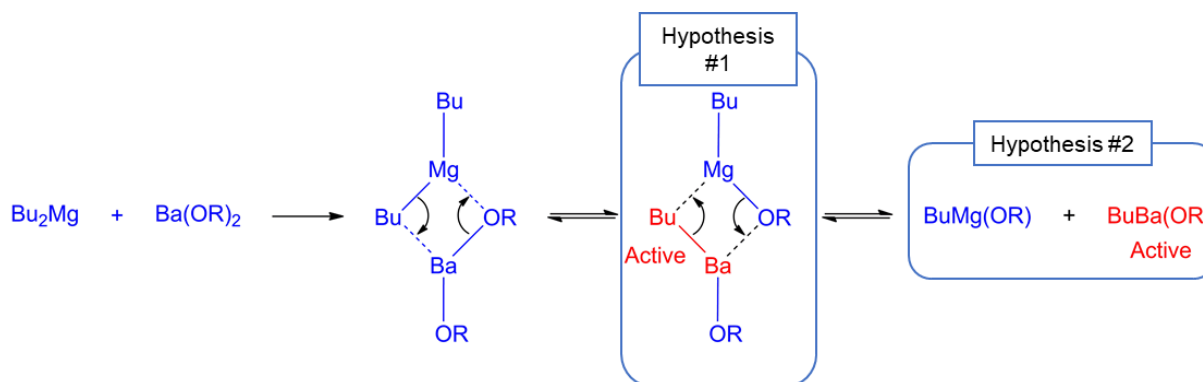


Figure 6. SEC chromatograms of polybutadiene obtained with an initiation system based on di-*n*-butylmagnesium and barium 2-ethylhexoxide in cyclohexane at 20°C ($\bar{M}_{nth} = 10,000 \text{ g.mol}^{-1}$)

Proposed mechanism for the initiator formation is presented on Scheme 3. The propagation center may be a complex of di-*n*-butylmagnesium and barium 2-ethylhexoxide (hypothesis #1) or free alkylbarium moieties (hypothesis #2). The carbon – barium bond is assumed to be active toward butadiene anionic polymerization.



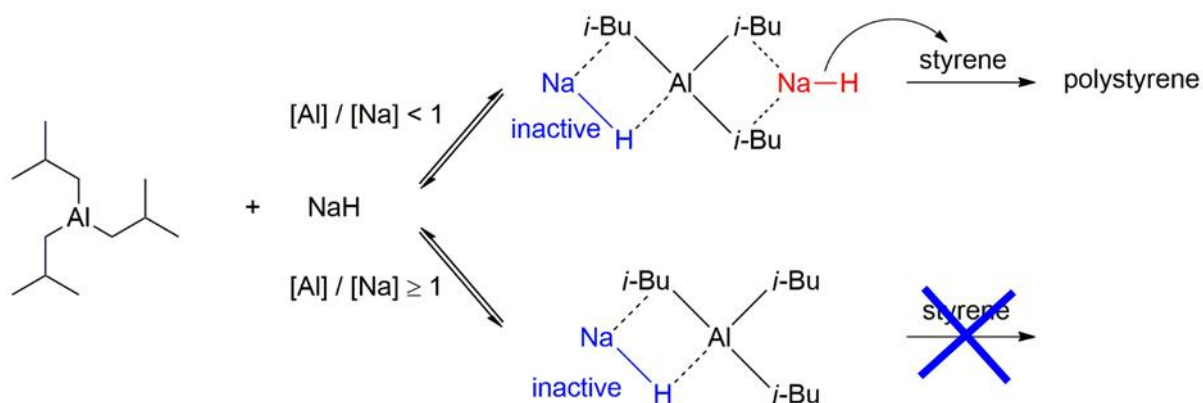
Scheme 3. Suggested mechanism for initiator formation from di-*n*-butylmagnesium and barium 2-ethylhexoxide. ([Ba] / [Mg] = 1, R= 2-ethylhexoxide)

The addition of trialkylaluminum to improve polymerization was not attempted since similar systems are already reported in the scientific literature and are said to produce polybutadiene with a high 1,4-trans content.

3. Trimetallic system based on barium alkoxide, sodium hydride, and triisobutylaluminum

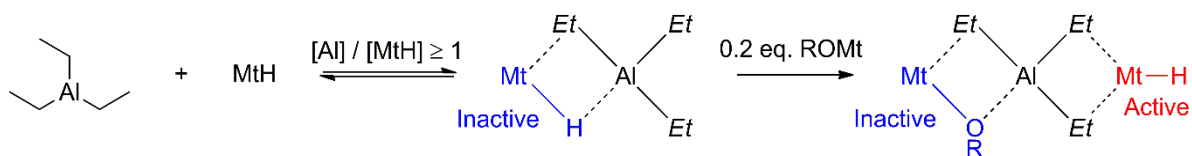
Trimetallic system based on barium alkoxide, trialkylaluminum and alkyl lithium are well known to produce polybutadiene with a 1,4-trans content up to 80% in hydrocarbon media and in a controlled way (see chapter III). The aim of this part is to prospect their lithium-free counterpart based on sodium hydride.

Sodium hydride is not soluble in hydrocarbon media and reported to be inactive toward anionic polymerization. Therefore, upon addition of trialkylaluminum ($[Al] / [Na] < 1$) their solubility is increased, and styrene polymerization occurs in bulk and in toluene at 100°C or lower temperature with 100% conversion [16]. When $[Al] / [Na] \geq 1$, complete solubilization of NaH is achieved through the formation of 1:1 aluminate complex which is inactive toward anionic polymerization in apolar media (Scheme 4).



Scheme 4. Proposed mechanism for the retarded styrene anionic polymerization initiated by sodium hydride / triisobutylaluminum [17]

Another approach consists to solubilize metal hydride moieties by synthesizing an inactive 1:1 aluminate complex ($[\text{R}_3\text{Al}] / [\text{MtH}] = 1$), and to activate the complex thanks to the addition of a third component such as an alkali metal alkoxide (Scheme 5) [19]. For instance, an initiation with a $\text{KH}/\text{Et}_3\text{Al}$ (1:1) + 0.2 eq. of *tert*-PeOK system was described to produce polybutadiene with a good polymerization control in terms of molar masses with polymer dispersities ranging from 1.4 to 1.8 at 80°C in cyclohexane. Obtained 1,4 / 1,2 ratio are similar to the one reported for potassium-based systems (30 – 40% vinyl, 60 – 70% 1,4) [19].



Scheme 5. Suggested reaction pathway for the initiator formation

The aim of this part is to develop barium-based trimetallic systems without the use of lithium. The strategy employed is similar to the one described by Labbé and coworkers [19], but the 1:1 inactive aluminate complex will be activated by using barium alkoxide rather than alkali metal alkoxide.

Upon addition of triisobutylaluminum, solubilization of sodium hydride was achieved in toluene after a 3 – 4 days at 50°C. After addition of 0.2 eq. of barium 2-ethylhexanoxide and butadiene to this inactive aluminate complex no polymerization occurred at 20°C after 3 days. However, at 50°C a polymer was obtained in a quantitative yield after 16 hours. SEC chromatograms and obtained microstructures are presented respectively in Table 7 and Figure 7. Obtained molar masses are close to the targeted ones with a slight increase of the dispersity with respect to lithium- / barium-based systems ($1.1 \leq \mathcal{D} \leq 1.2$). A sodium – carbon bond is not believed to be involved in the polymerization process since sodium as a counter-ion is reported to produce polybutadiene with up to 65% vinyl units. In the present system, obtained microstructure are typical of barium-based initiating systems with a high 1,4-trans content (57 – 78% 1,4-trans units indicating that propagation occurs in a carbon – barium bond. One can note some variations in the obtained results, for instance in terms of microstructure or dispersity. That is why, deeper investigation might be valuable to find key parameters (such as initiator preformation time, or initiator composition) to achieve better control of these features and that is also why this set of experiments should be considered as a proof of concept.

Table 7. Polymerization of butadiene using alkali metal derivatives in association with barium 2-ethylhexoxide, and triisobutylaluminum (cyclohexane, [butadiene] = 2 mol.L⁻¹, [alkali metal] = 10⁻² mol.L⁻¹, $\bar{M}_{nth}$ = 10,000 g.mol⁻¹*, yield = 100%)

Mt	[Ba] / [Mt]	[Al] / [Mt]	T (°C)	Time (h)	$\bar{M}_n exp$ (g.mol ⁻¹)	$\bar{D}$	1,2 (%)	1,4-cis (%)	1,4- trans (%)
Ref ^a	0	0	20	16h	11,000	1.03	7	41	52
Li ^b	0.4 ^b	1.4 ^b	20	72h	13,500	1.10	4	22	74
Na	0.2	1.0	50	16h	10,000	1.10	4	18	78
Na	0.2	1.0	50	16h	10,200	1.18	20	23	57
Na	0.4	1.0	50	16h	16,000	1.17	6	19	75

* Calculated with the hypothesis of one polymer chain per alkali metal. ^a sec-butyllithium alone. ^b Polybutadiene synthesized using sec-butyllithium, barium 2-ethylhexoxide (0.4 eq) and triisobutylaluminum (1.4 eq.) as initiating system (ref. Michelin).

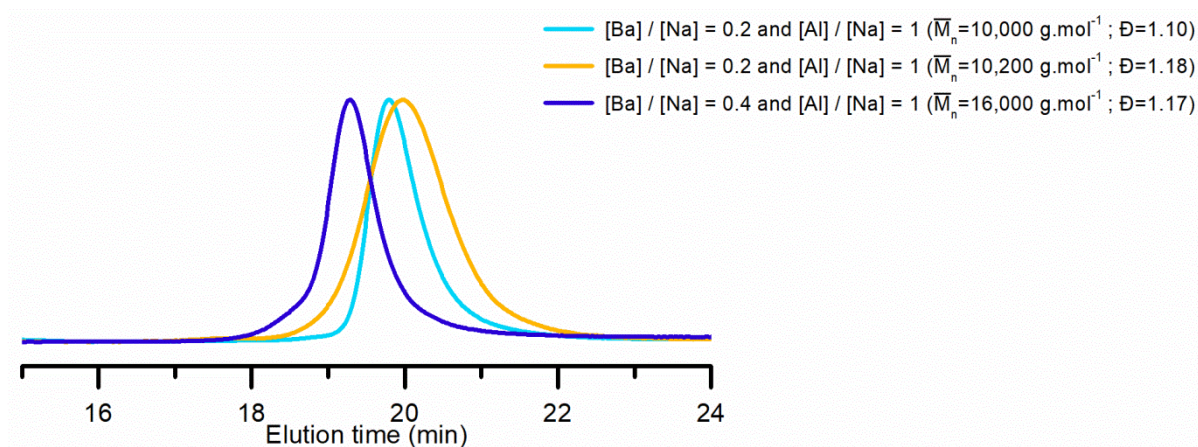


Figure 7. SEC chromatograms of polybutadiene obtained with an initiation system based on sodium hydride + 1 eq. of triisobutylaluminum + x eq. of barium 2-ethylhexoxide in cyclohexane at 20°C (x= 0.2 or 0.4, $\bar{M}_{nth}$ = 10,000 g.mol⁻¹)

4. Conclusion

This chapter intended to find alternatives to lithium allowing to perform butadiene anionic polymerization and to access to a variety of polybutadiene microstructures. Two systems were prospected. The first one is based on dialkylmagnesium associated to potassium or barium alkoxide, the second one is a trimetallic system based on alkali metal hydride, alkyl aluminum and a barium alkoxide.

Di-*n*-butylmagnesium + potassium *tert*-pentoxide initiation system was found to be able to produce polybutadiene with 50% vinyl content with a low initiation efficiency (30 – 40%). Addition of triisobutylaluminum was shown to be relevant to improve polymerization control keeping a polybutadiene microstructure typical of potassium-based systems (50% vinyl content), but bimodal population were observed due to a coupling secondary reaction (15 – 20%).

Di-*n*-butylmagnesium + barium alkoxide initiation systems were shown to be able to produce polybutadiene with up to 65% 1,4-trans content with a low initiation efficiency and with broad dispersity. This system was not further studied, since addition of trialkylaluminum was reported in the scientific literature to improve polymerization control, and to increase the 1,4-trans content up to 90%.

The third lithium-free system studied is based on sodium hydride + trialkylaluminum + barium alkoxide, and it was shown to be relevant to produce polybutadiene in a controlled way with up to 78% 1,4-trans content. It is believed that a carbon – barium bond is formed (complexed or not) and is responsible for the butadiene polymerization. However, a deeper evaluation of this systems and a closer investigation of experimental parameters such as the initiator composition or the initiator preformation time should be conducted to improve the reproducibility.

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Conclusion

Polybutadiene microstructure is identified in the literature as a key lever to modulate rubber properties. For instance, in the tire industry framework, a fine microstructure tuning may lead to improved compromise between rolling resistance (related to vehicle fuel efficiency) and grip (related to tire safety performance).

Lithium is usually recognized as unique among the alkali metals because of its ability to produce polybutadiene in a controlled way with a low vinyl content in apolar media. The 1,4-cis / 1,4-trans ratio can be tuned by varying the initiator and / or the monomer concentration. Heavier alkali metal alkyls, which are not readily available materials, tend to produce polybutadiene with a vinyl content above 50%.

Addition of alkali metal alkoxides to alkyllithium-initiated butadiene polymerization is reported to increase the vinyl content of the resulting polymer. In this research work, the influence of potassium alkoxide was examined over a wide range of ratio ($0 < [\text{K}] / [\text{Li}] < 5$) and experimental parameters such as the initiator preformation time, and the alkyllithium structure were found to have an impact on polymerization control. The initiator preformation time was showed to be a critical parameter since initiation efficiency drops down if alkyllithium and potassium alkoxide are let to react during a prolonged time. Accordingly, with no initiator preformation time, polymerization control was achieved in all cases, and when $[\text{K}] / [\text{Li}] \geq 0.35$ obtained polybutadiene had a vinyl content around 50% (typical of potassium-based systems). When $[\text{K}] / [\text{Li}] = 5$, polymerization control is not achieved anymore and broad dispersities were observed. Chain transfer to the polymer backbone is a possible explanation for this phenomenon. Varying potassium alkoxide structure and / or alkyllithium nature had no influence on polymerization control and did not prevent molar masses distribution broadening at $[\text{K}] / [\text{Li}] = 5$. Obtained polybutadiene microstructures are typical of potassium-based systems, and it tend to show that butadienylpotassium moieties are responsible of the propagation reaction either free or complexed with alkali metal derivatives. Addition of triisobutylaluminum to the initiating species was found to change the propagating center nature and the formation of an aluminate complex was suggested. With such a trimetallic initiation system, butadiene polymerization control is achieved even when $[\text{K}] / [\text{Li}] = 5$ with 50% vinyl content. With this trimetallic system, butadienylpotassium moieties are also believed to be responsible of the propagation reaction inside an aluminate complex.

Conclusion

The use of organoalkaline earth metals derivatives for butadiene polymerization exhibits a quite different behavior in apolar media with respect to their alkali metal counterparts. Barium monometallic initiating species tend to produce polybutadiene with a high 1,4-cis content (up to 70%), while multi-metallic initiation systems tend to produce polybutadiene with up to 90% 1,4-trans units (for trimetallic systems based on Li / Ba / Al). The focus of this present research work was to investigate the influence of calcium derivatives on the anionic polymerization of butadiene with the objective of developing bimetallic systems allowing the synthesis of polybutadiene with a high 1,4-trans content and in a controlled way. The association of calcium bis(trimethylsilyl)amide with *sec*-butyllithium was found to polymerize butadiene. Varying the ratio $[Ca] / [Li]$ allows to tune polybutadiene microstructure from 50% to 76% 1,4-trans, keeping a vinyl content below 10% in cyclohexane at 20°C. In all cases, obtained molar masses were in the expected range and observed dispersities were below 1.1. With such a system, the propagation reaction is believed to be a consequence of a nucleophilic attack on butadiene from a carbon – calcium bond. As a perspective for following work, a transamination reaction could be envisaged with calcium bis(trimethylsilyl)amide to obtain calcium derivatives with different structures (*e.g.* alkoxide, sulfoxide, phenoxide) and to assess the influence of calcium ligand on polymerization control and polybutadiene microstructure.

The use of multimetallic lithium-free systems was prospected for the obtention of polybutadiene with the microstructure of potassium-based systems. Such microstructure was achieved by using dialkylmagnesium in association with potassium alkoxide. Polymerization control is not achieved whatever the ratio $[K] / [Mg]$ due to the non-solubility of the initiating species. However, it was found that polymers synthesized with $[K] / [Mg] = 5$ exhibit a similar SEC profile with respect to their lithium-based counterpart. Accordingly, the development of a trimetallic system with dialkylmagnesium, potassium alkoxide and trialkylaluminum was attempted and obtained molar masses were found to be close to the targeted ones with some side coupling reactions. In all cases obtained polybutadienes had a microstructure with 50% vinyl content. Obtained microstructures suggest that butadienylpotassium moieties are responsible of the polymerization reaction. The active center could either be free or part of a magnesiate complex.

Conclusion

The use of systems based on potassium hydride / trialkylaluminum / potassium alkoxide was already reported in the scientific literature to produce polybutadiene with a 40% vinyl content. A similar system based on sodium hydride, trialkylaluminum, and barium alkoxide as an initiator for butadiene polymerization was attempted and shown to produce polybutadienes with a high 1,4-trans content. Obtained vinyl contents are below 20% and obtained 1,4-trans content are above 50% suggesting the formation of a barium – carbon bond within an aluminate complex, which is believed to be responsible of the propagation reaction. Further investigation on the influence of the metal alkoxide moieties (*e.g.* Na, K, Ca, Sr, Ba) using NaH:R₃Al in such trimetallic systems may allow to tune polybutadiene microstructure similarly to what can be achieved with lithium.

Experimental part

1. Materials

Sec-butyllithium (1.4M in cyclohexane), *n*-butyllithium (1.6M in cyclohexane) triisobutylaluminum (25 wt. % in toluene), *n,s*-dibutylmagnesium (0.7M in hexane), di-*n*-butylmagnesium (1M in heptane) were obtained from Aldrich and used as received. 2-methyl-2-butanol (99%, Aldrich) and 3,7-Dimethyl-3-octanol (98%, Aldrich) were 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, mineral oil was removed through cyclohexane washing prior to use. Barium 2-ethylhexoxide (Abcr, ca. 1M in hexane/toluene) was diluted with dry cyclohexane and stored in an argon filled glovebox. Calcium iodide (Abcr, > 99%) was stored in an argon filled glovebox and used as received. Hexamethyldisilazane was obtained from Fluka and dried over CaH₂ prior to use. NaH (Aldrich, 60 wt. % dispersion in mineral oil) was washed with dry cyclohexane, dried under reduced pressure and stored in an argon filled glovebox.

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 an hour, distilled off and stored in high pressure glass burette.

Cyclohexane, toluene, heptane (VWR) were dried over freshly crushed calcium hydride (Acros, 93%) and stored over polystyryllithium seeds. Tetrahydrofuran (VWR) is purified using sodium benzophenone. Deuterated solvents were dried in the same way as their non-deuterated counterparts.

2. Potassium alkoxide synthesis

Potassium *tert*-pentoxide was obtained through the reaction of dry 2-methyl-2-butanol (1 mL) and an excess of potassium metal ([ROH] / [K] = 0.7) 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 (1mL) 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).

Potassium 3,7-dimethyl-3-octanoxide was obtained through the reaction of dry 3,7-dimethyl-3-octanol (1.7 mL) and an excess potassium metal ($[ROH] / [K] = 0.7$) in cyclohexane (50 mL) at 80°C for 3 – 5 days, leading to a 0.18 M of potassium 3,7-dimethyl-3-octanoxide.

3. Synthesis of Calcium Bis(trimethylsilyl)amides

Synthesis of amine salt of calcium was performed according to published procedures [1]–[3].

3.1. Benzylpotassium

Potassium *tert*-pentoxide solution (0.18 M in cyclohexane, 100 mL) was brought to dryness and 80 mL of toluene were added. Upon addition at 0°C of *sec*-butyllithium (1.4 M in cyclohexane, 13mL), formation of an orange precipitate is observed. The mixture was then let to react for another hour at 20°C. The dispersion was then filtrated under inert atmosphere and the resulting solid was washed with dry toluene (2 x 20mL), dry heptane (2 x 20 mL) to obtain 1.5 g of benzylpotassium (Yield = 63%).

3.2. Dibenzylcalcium

Calcium iodide (2.2 g) was vigorously stirred in dry THF (22 mL) overnight to obtain a dispersion of calcium iodide. To this dispersion was added dropwise a solution of benzylpotassium (1.5 g) in dry THF (20 mL), producing a pale-yellow dispersion. This mixture was let to react overnight at 20°C before filtration over Celite (flame dried under vacuum) to remove KI and unreacted CaI_2 . Obtained solution was dried under reduced pressure leading to a red oily substance. Subsequent trituration in toluene (50 mL) and addition of pentane (50 mL) produced a fine orange dispersion. After filtration and washing with heptane (2 x 20 mL), 1.41g of dibenzylcalcium were obtained (Yield = 50%).

3.3. Calcium Bis(trimethylsilyl)amides

To a dispersion of dibenzylcalcium (1.30 g) in toluene (15 mL) was added 2.5 mL of dry hexamethyldisilazane. After 4 hours at 60°C, filtration over Celite (flame dried under vacuum) under inert atmosphere yields a clear solution, which was dried under reduced pressure overnight leading to 1.43 g of calcium bis(trimethylsilyl)amides. Upon addition of dry toluene (30mL), the amine salt was found to not be soluble anymore. Another filtration over Celite under inert condition yield a clear solution, and obtention calcium bis(trimethylsilyl)amides

was confirmed by ^1H NMR in benzene- d_6 and concentration was 0.135M (assessed by titration with HCl / phenolphthalein) (Yield = 70%).

4. Synthesis of NaH / *i*-Bu₃Al [4]

NaH:*i*-Bu₃Al solution were prepared by reaction of sodium hydride with triisobutylaluminum in toluene. Typically, cyclohexane-washed NaH (0.053 g, 4.67×10^{-3} mol) was placed in a flame dried Schenk flask, degassed under vacuum before addition of 26 mL of dry toluene. Then, a known amount of *i*-Bu₃Al (2.2 mL, 25 wt. % in toluene) was added with a syringe under argon flow to reach a ratio $[\text{Al}]/[\text{Na}] = 1$. This mixture was maintained under stirring in a thermostated bath at 50°C until obtention of clear solution (generally after 3 – 5 days).

5. Polymerizations

A typical anionic polymerization was carried as follow: A glass reactor equipped with a magnetic stirrer and fitted with PTFE stopcocks was flame dried under vacuum, 10 mL of cyclohexane were added through connected glass tubes, *sec*-BuLi (71 μL , 1.4 M in cyclohexane) was added via syringe under argon flow. Then a known amount of styrene (1,10 mL, 1g) was added under vacuum using a graduated burette. The polymerization was allowed to proceed overnight and was terminated through addition of degassed methanol. Solvent was evaporated under vacuum and the polymer was then dried to constant weight. Butadiene polymerization was performed in a similar way but using high-pressure glass reactor, in addition butadiene was vacuum distilled (rather than poured) into the solution of *sec*-BuLi.

Polymerization involving potassium alkoxide were performed in a similar way. A glass reactor equipped with a magnetic stirrer and fitted with PTFE stopcocks was flamed under vacuum, 10 mL of cyclohexane were added under vacuum through connected glass tubes, followed by the desired amount of potassium alkoxide and alkyllithium via syringes under argon flow. After preformation of the initiator, butadiene (resp. styrene) was vacuum distilled (resp. poured) into the reaction apparatus. If no preformation time was required monomer was introduced between potassium alkoxide and alkyllithium. Similarly, for trimetallic systems based on K / Al / Li, the aluminum compound was always added into the reaction media, via a syringe, between potassium alkoxide and alkyllithium.

Polymerization involving calcium derivatives / *sec*-butyllithium, di-*n*-butylmagnesium / potassium *tert*-pentoxide, di-*n*-butylmagnesium / barium 2-ethylhexanoate, NaH:*i*-Bu₃Al / barium 2-ethylhexanoate were performed using the same technic.

Kinetic studies were performed in the same way with respect to initiator and butadiene addition. Removing of aliquots were performed via syringe under argon flow, obtained aliquot was then diluted with cyclohexane-d₁₂ in an NMR tube fitted with a PTFE Young valve. Conversion was calculated using toluene as an internal standard. The amount of butadiene remaining in the polymerization media was calculated as follow:

$$n_{butadiene}(t) = \frac{5 \times I_{6.0-6.4} \times n_{0,toluene}}{2 \times I_{6.8-7.2}}$$

In the example provided on Figure 1, the initial amount of butadiene was $n_{0, butadiene} = 2.5 \times 10^{-2}$ mol and the initial amount of toluene was $n_{0, toluene} = 9.41 \times 10^{-3}$ mol. Accordingly, the calculated amount of butadiene in the polymerization media was $n_{butadiene}(2.5h) = 2.82 \times 10^{-3}$ mol and the conversion calculated equal to 88%.

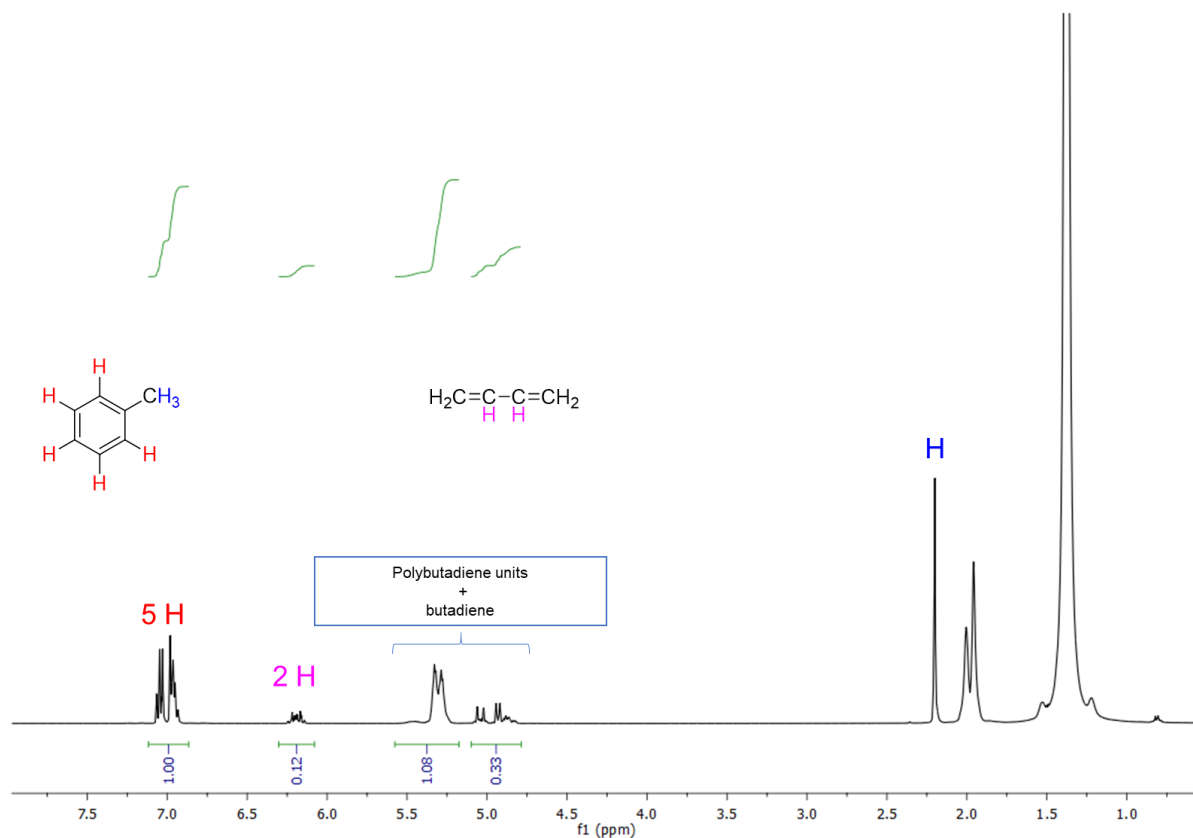


Figure 1. ^1H NMR spectrum of an aliquot removed from polymerization media under a flow of argon. (butadiene polymerization, *sec*-butyllithium, cyclohexane, 40°C , $t = 2.5\text{h}$, n_0 , butadiene = $2.5 \times 10^{-2} \text{ mol}$, n_0 , toluene = $9.41 \times 10^{-3} \text{ mol}$)

6. Analytical techniques

6.1. Liquid NMR

Liquid-state ^1H NMR and ^{13}C NMR spectra were recorded at 298 K on a Bruker Avance 400 spectrometer operating at 400.2 MHz and 100.6 MHz respectively in CDCl_3 . A set of spectrum is presented on Figure 2 and Figure 3.

The 1,2 / 1,4 ratio for polybutadiene was determined using ^1H NMR analysis by integration from 5.2 to 5.7 (I_1), and from 4.7 to 5.1 (I_2). The relative amount of vinyl units and 1,4 units was calculated as follow:

$$1,2 \text{ content} = C_{1,2} = \frac{0.5 * I_2}{\frac{I_1 - 0.5 * I_2}{2} + \frac{I_2}{2}}$$

$$1,4 \text{ content} = C_{1,4} = 1 - C_{1,2}$$

In the example presented on Figure 2, the vinyl content was determined equal to 8% and the 1,4 content to 92%.

The 1,2 / 1,4 ratio for polybutadiene was determined using ^{13}C NMR analysis (Inversed gated decoupling, 100.6 MHz, D1 = 10 sec, 4096 scans, Inverse gated decoupling ^{13}C NMR is suitable for quantitative analysis due to the suppression of NOE) by integration from the peak at 32.8 (I_3), and 27.5 (I_4). The relative number of 1,4-cis units to 1,4-trans units was calculated as follow:

$$C_{1,4-trans} = \frac{C_{1,4}}{1 + \frac{I_4}{I_3}}$$

$$C_{1,4-cis} = C_{1,4} - C_{1,4-trans}$$

In the example presented on Figure 3, the 1,4-trans content was determined equal to 74% and the 1,4-cis content to 18%.

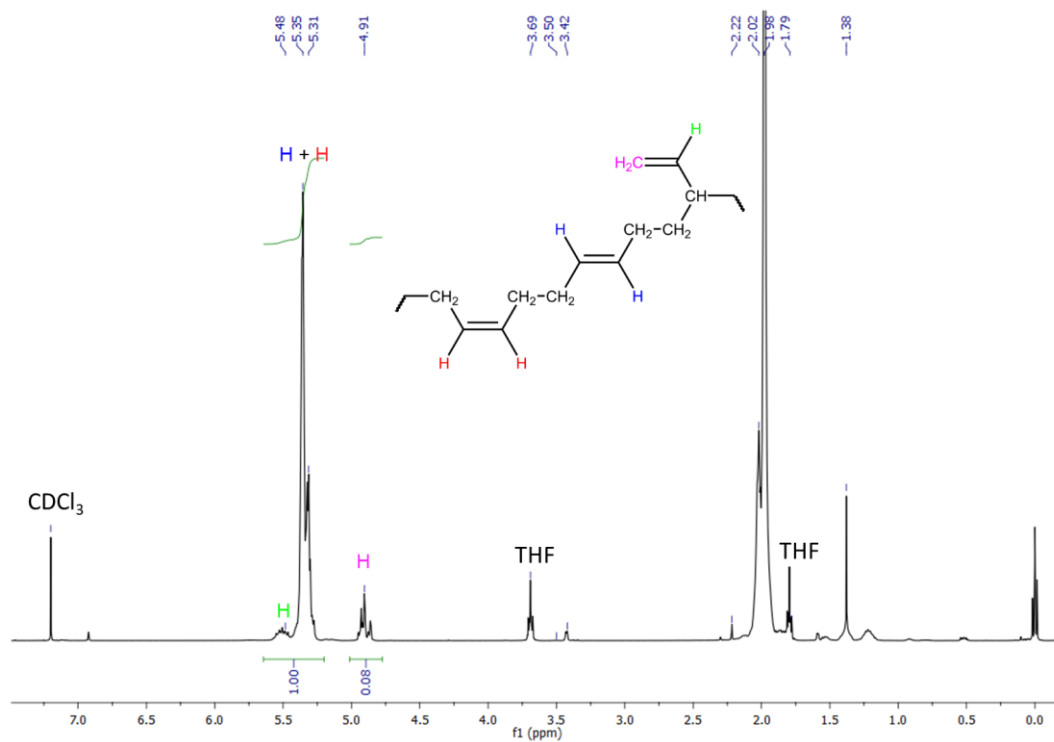


Figure 2. ^1H NMR spectrum of polybutadiene obtained using a calcium / lithium bimetallic initiation system

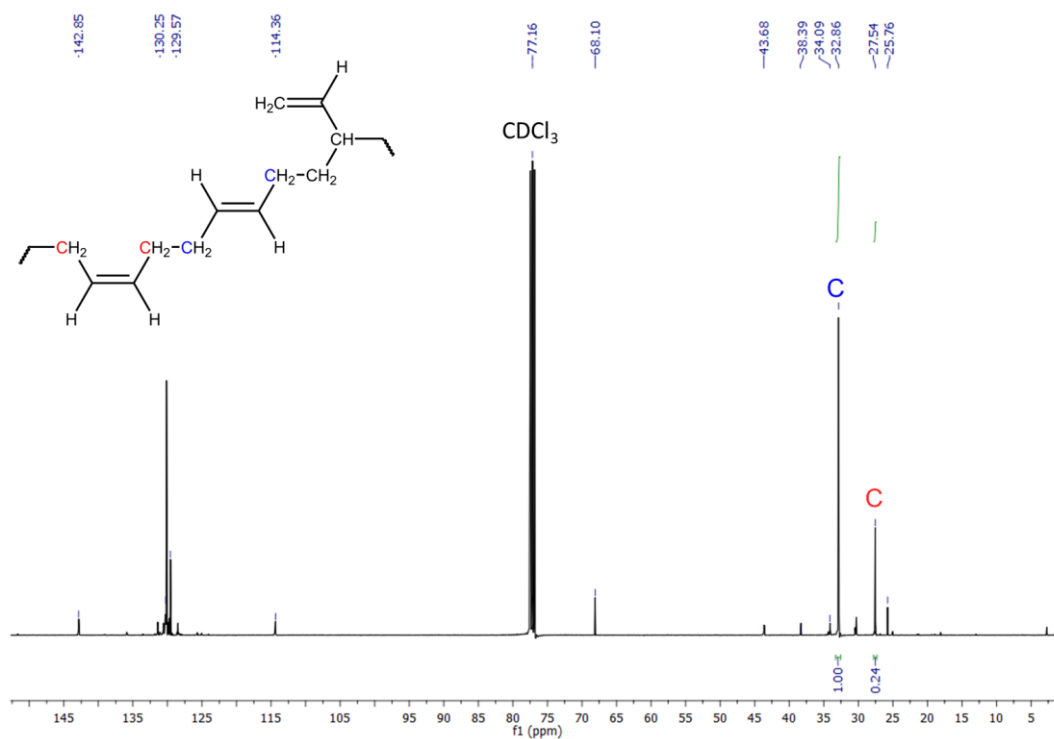
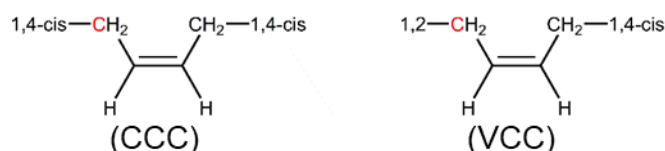


Figure 3. ^{13}C NMR spectra of polybutadiene obtained using a calcium / lithium bimetallic initiation system

Remark: For polybutadiene with a high vinyl content, the same method was used to determine polybutadiene microstructure. Nonetheless, the sequence distribution determination should be considered for future work, since it affects the microstructure determination. For instance, the chemical shift for CH_2 in the sequence CCC (see Scheme 1) is equal to 27.5 ppm while it is reported equal to 25.13 ppm in the case of a VCC sequence [5]. (V = vinyl, C = 1,4-cis)



Scheme 1. Example of sequence distribution

6.2. SEC analysis

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 flowrate of 1 mL/min. Columns temperature was held at 40°C. Polystyrene was used as the standard.

Polybutadiene molar masses were either determined using polystyrene standard and application of a corrective factor equal to 0.52, or by triple detection SEC with light scattering using a dn/dc value equal to 0.124.

6.3. UV-Visible spectroscopy

The absorption spectra of the polystyryllithium seeds derivatives solutions were recorded on a Cary 4000 UV-Vis spectrometer using a quartz cell (0.01 cm path-length) attached to a glass reactor equipped with a magnetic stirrer and fitted with PTFE stopcocks.

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Utilisation de systèmes d'amorçage multi-métalliques pour la polymérisation anionique du butadiène et le contrôle de sa microstructure

L'objet de ces travaux de thèse est d'étudier la synthèse de polybutadiène au moyen de systèmes d'amorçage multi-métalliques. Dans un premier temps, l'utilisation d'alcoolates de potassium en association avec des dérivés d'alkyllithium a été étudiée afin d'obtenir du polybutadiène de façon contrôlée avec 50% d'unités vinyliques en milieu apolaire. Dans un second temps, l'utilisation de composés alcalino-terreux en association avec du sec-butyllithium a été étudiée pour la synthèse de polybutadiène à fort taux d'unités 1,4-trans. Un dérivé du calcium a été synthétisé et a permis de préparer du polybutadiène de façon contrôlée avec 76 % d'unités 1,4-trans. La troisième partie de ces travaux démontre que des systèmes d'amorçage sans lithium permettent la synthèse de polybutadiène par voie anionique. Lorsque le dialkylmagnesium est associé à un alcoolate de potassium, il permet l'obtention de polybutadiène avec 50% d'unités vinyliques, alors que le système dialkylmagnesium / alcoolate de baryum permet la synthèse de polybutadiène à fort taux de 1,4-trans (65%).

Mots clés : Polymérisation anionique, Polybutadiène, Microstructure, Contrôle de la polymérisation, Systèmes d'amorçage multi-métalliques

Tuning polybutadiene microstructure using multi-metallic initiation systems by anionic polymerization

The goal of this research work is to find original ways to obtain polybutadiene with defined microstructure by developing multimetallic initiation systems. The aim of the first experimental chapter was to obtain polybutadiene with a 50% vinyl content in a controlled way in apolar media. This objective was achieved by using a bimetallic system based on potassium alkoxide and alkyllithium. The second experimental chapter focuses on the controlled synthesis of polybutadiene with a high 1,4-trans content by using alkaline earth derivatives. An amine salt of calcium was synthesized, and when associated to sec-butyllithium, was found to produce polybutadiene with up to 76% 1,4-trans content in a controlled way. The goal of the third experimental chapter was to prospect multimetallic initiation systems allowing obtention of polybutadiene without using lithium derivatives. The use of dialkylmagnesium in association with potassium alkoxide was found relevant to produce polybutadiene with a 50% vinyl content, while the association of dialkylmagnesium and barium alkoxide allows the synthesis of polybutadiene with a high 1,4-trans content (up to 65%).

Key words: Anionic polymerization, Polybutadiene, microstructure, polymerization control, multimetallic initiation systems

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