



**HAL**  
open science

# Coordinative Chain Transfer Polymerization of Butadiene Using Nickel(II) Allyl Systems: A Straightforward Route to Branched Polybutadiene

Catarina Garcia Bravo, Nicolas Merle, Mathieu Sauthier, Marc Bria, Julien de Winter, Philippe Zinck

## ► To cite this version:

Catarina Garcia Bravo, Nicolas Merle, Mathieu Sauthier, Marc Bria, Julien de Winter, et al. Coordinative Chain Transfer Polymerization of Butadiene Using Nickel(II) Allyl Systems: A Straightforward Route to Branched Polybutadiene. *Macromolecules*, 2023, *Macromolecules*, 56 (20), pp.8106-8115. <10.1021/acs.macromol.3c01385>. <hal-04274125>

**HAL Id: hal-04274125**

**<https://lilloa.hal.science/hal-04274125v1>**

Submitted on 3 Apr 2026

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Copyright - All rights reserved

# **CCTP of butadiene using nickel(II) allyl systems : a straightforward route to branched polybutadiene**

Catarina Bravo<sup>1</sup>, Nicolas Merle<sup>1</sup>, Mathieu Sauthier<sup>1</sup>, Marc Bria<sup>2</sup>, Julien De Winter<sup>3</sup>, Philippe Zinck<sup>1\*</sup>

<sup>1</sup>Univ. Lille, CNRS, Centrale Lille, Univ. Artois, UMR 8181 – UCCS – Unité de Catalyse et Chimie du Solide, F-59000 Lille, France

<sup>2</sup>Univ. Lille, CNRS, INRA, Centrale Lille, ENSCL, Univ. Artois, FR 2638—IMEC—Institut Michel-Eugène Chevreul, Pôle RMN, F-59000 Lille, France

<sup>3</sup>Organic Synthesis and Mass Spectrometry Laboratory (S2MOs), University of Mons-UMONS, 23 Place du Parc, 7000 Mons, Belgium

[Philippe.zinck@univ-lille.fr](mailto:Philippe.zinck@univ-lille.fr)

## Abstract

Nickel allyl complexes are catalysts for the 1,4 regioselective polymerization of butadiene (BD). Coordinative chain transfer polymerization (CCTP) was not yet assessed using these systems. We report in this work the polymerization of butadiene in the presence of  $\pi$ -allyl nickel(II) trifluoroacetate (TFA) and  $\text{Mg}^n\text{BuEt}$  or  $\text{AlEt}_3$  as chain transfer agent (CTA) case studies. The reaction follows a first order kinetic *vs.* the monomer. Chain transfer is evidenced in the presence of the CTA, together with the formation of polybutadiene bearing a conjugated diene moiety. This allows a one pot access to branched polybutadiene by reinsertion of the chains. The branching is quantitatively analyzed by  $^{13}\text{C}$  NMR after hydrogenation of the polybutadiene, and its impact is assessed on the thermal properties of the hydrogenated samples, in particular for low degrees of branching that cannot be quantitatively determined. A full description of the catalytic cycle is tentatively provided. If similar tandem processes were described in the literature in the course of the polymerization of ethylene, it is as far as we know the only system reported so far for a conjugated diene, leading to branched polybutadiene, and extending the range of application of CCTP processes.

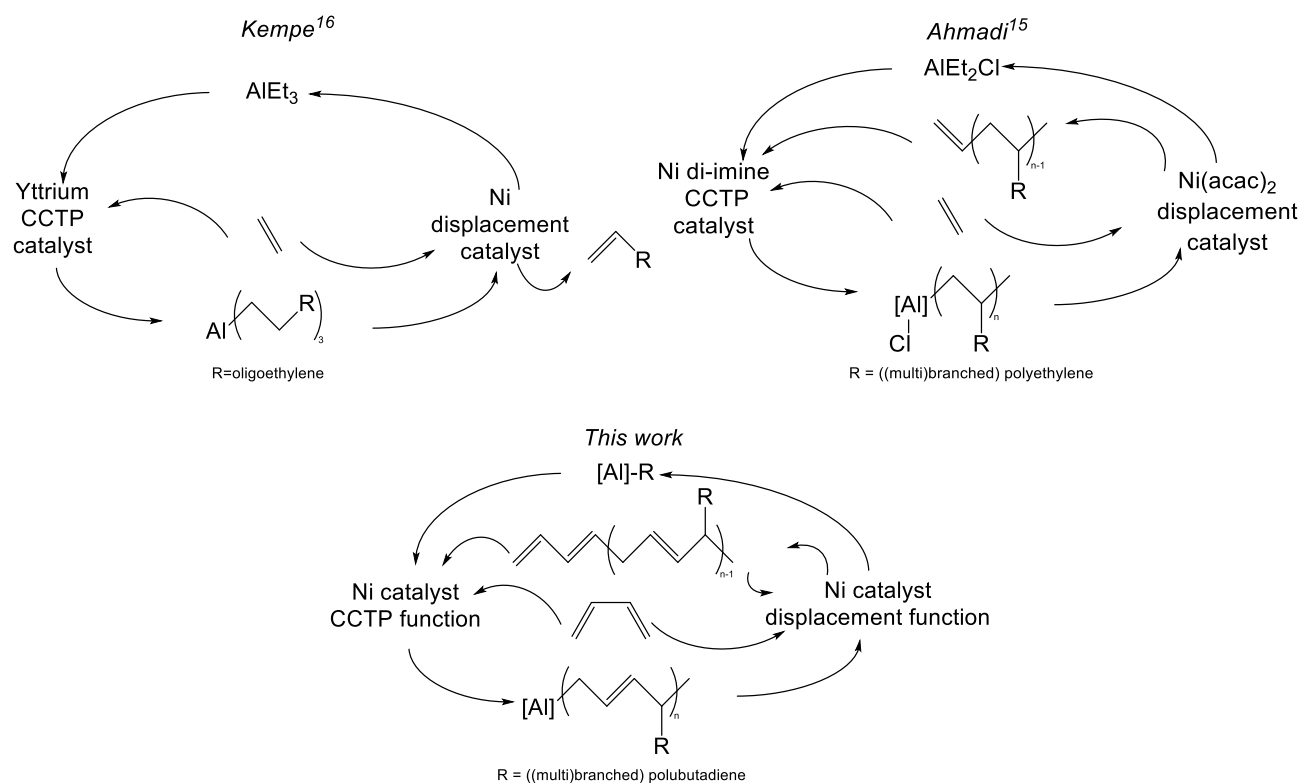
**Keywords:** CCTP; Nickel-allyl catalysts; polybutadiene; branched polymers

## INTRODUCTION.

Polydienes, which can be obtained by coordination polymerization, highly contribute as applied rubbers in tire industries in addition to natural rubbers. The properties of these materials mostly depends on the regio- and stereo-regularity of the polydiene, hence, on the selectivity of the employed catalysts for a 1,4-*cis* 1,4-*trans*, 1,2- or 3,4- polydiene.<sup>1,2</sup> Incorporating into one macromolecular chain different stereoregularities in a controlled manner is anticipated to provide high-performance materials. For instance, 1,4-*cis*/1,4-*trans* stereoblock polybutadiene combines the advantages of both poly(1,4-*cis*-butadiene) and poly(1,4-*trans*-butadiene) that exhibit disparate melting points and low glass transition temperatures ( $T_g$ ).<sup>3</sup> Recent strategies to access these new material relies on coordinative chain transfer polymerization (CCTP).<sup>4-8</sup> This degenerative chain transfer polymerization process allows for precise control of the molecular weight of the synthesized polymer, as well as the introduction of chemical functionality at the end of polymer chains. CCTP can also reduce the consumption of expensive transition metal-based catalysts, thereby promoting catalyst economy, and enables the possibility of copolymer engineering. Typically, the CCTP approach involves the use of a single transition metal-based catalyst and a chain transfer agent (CTA), usually in the form of a main group metal alkyl. During the process, the growing polymer chain can transfer from the catalyst metal to the chain transfer agent metal via transalkylation (Scheme 1). Hence, when chain transfer occurs, it enables the formation of several polymer chains per catalyst molecule, in contrast to conventional living systems.



of 1-alkene by  $\beta$ -hydride elimination (Scheme 3). An extension of such CCTP reactions is a Ni based displacement / polymerization tandem process where the reinsertion of the so formed olefin into the polyethylene backbone allows the formation of branched polyethylene (see Ahmadi *et al.*, Scheme 3).<sup>15;17-18</sup>



### Scheme 3. Combination of Ni displacement catalysis and CCTP

Branched polymers are of high interest as they offer a range of advantages over their linear counterpart. In particular, the branched structure provides lower crystallinity, thus improving elasticity and toughness, and a lower viscosity which enhances processability. In this study, we have investigated the polymerization of butadiene in the presence of  $\pi$ -allyl nickel(II) (TFA) and aluminum and magnesium alkyls as CTAs. The initiation of the chain transfer mechanism is studied. The formation of conjugated diene terminated polybutadiene is advanced, and a tandem process where the reinsertion

of the so formed macromonomer in the growing chain leads to branched polybutadiene in a one pot one step process (Scheme 3).

## **EXPERIMENTAL PART.**

### **Materials**

All operations were performed under inert argon atmosphere by using a glove box and Schlenk line techniques. Toluene was dried using a MBraun SPS 800 solvent purification system and degassed by three freeze-pump-thaw cycles. Butadiene (BD) was condensed in a Schlenk tube cooled at -20 °C with a precooled acetone bath and diluted with dry toluene. The amount of butadiene stored in toluene was quantified by relative toluene and butadiene peaks integration of the corresponding <sup>1</sup>H NMR signals prior to use. *n*-butylethylmagnesium (20 wt.-% in heptane from Texas Alkyl), triethylaluminium (1.3 M in heptane, ACROS), diethyl zinc (≥52 wt. % Zn basis, Aldrich), Ni(COD)<sub>2</sub> (>98%, Strem, COD = 1,5-cyclooctadiene), trifluoroacetic acid (> 99%, Fluka), allyl trifluoroacetate (>95%, TCI), 2,6-di-*tert*-butyl-4-methylphenol (BHT, >99%, Aldrich), tris(triphenylphosphine)rhodium(I) chloride ([Rh(PPh<sub>3</sub>)<sub>3</sub>Cl]) (99%, Strem) and triphenylphosphine (99%, Sigma Aldrich) were used as received. With exception to trifluoroacetic acid and butadiene all compounds were manipulated inside the glovebox filled with argon.

### **Polymerization**

In a glovebox, in a typical experiment, 13.7 mg or 27.5 mg of Ni(COD)<sub>2</sub> (for a BD/Ni ratio of 100 and 250 or 500, respectively) was weighed into a Schlenk tube and was dissolved in 0.3 to 0.7 mL of toluene. Exact amount of *n*-butylethylmagnesium (Mg<sup>n</sup>BuEt) or triethylaluminium (Et<sub>3</sub>Al) was collected into a separate Schlenk tube using a micro syringe. Under an argon flow using a Schlenk line, trifluoroacetic acid was added to the Ni(COD)<sub>2</sub> solution, followed by the addition of the solution

of butadiene in toluene, which was placed in a cold acetone bath prior to use. The cold mixture was transferred using a cannula into the Schlenk tube containing CTA. The magnetically stirred reaction mixture was then heated at 60 °C. To quench the reaction, a small portion of acidic methanol (with hydrochloric acid, 2% v/v) was added dropwise to the reaction medium, resulting in an immediate color change from red/orange to white. The product was then precipitated by pouring the crude reaction mixture in cold methanol with a small amount of 2,6-di-*tert*-butyl-4-methylphenol (BHT), isolated and dried under vacuum in a desiccator.

### **Hydrogenation of Polybutadiene**

The hydrogenation of the polybutadiene samples was performed according to literature procedure,<sup>19</sup> using the Wilkinson catalyst [Rh(PPh<sub>3</sub>)<sub>3</sub>Cl] with an excess of triphenyl phosphine, in solution in dry toluene in an autoclave with an hydrogen pressure of 50 bar for 24 h at 100 °C. To quench the reaction, the autoclave was cooled, the dihydrogen pressure released, and the reaction mixture was precipitated in cold methanol, filtrated and washed three times with methanol. The white polyethylene powder was dried and weighed. The conversion measured by <sup>1</sup>H NMR was found to be quantitative in all cases.

### **Polymer characterizations**

NMR spectra of the polybutadiene samples were recorded on a Bruker Avance III HD 300 MHz instrument at room temperature in CDCl<sub>3</sub>. 3 to 45 mg of compound was dissolved in 0.6 mL of solvent directly into the NMR tube. The chemical shifts were calibrated using the residual resonances of the solvent. Quantitative <sup>13</sup>C NMR spectra were acquired using the zgig sequence (Bruker library). The relaxation time d1 was set to 5s to allow the full relaxation of all carbon nuclei. The 1,2/1,4 polybutadiene ratio was calculated by integration of the corresponding resonances in <sup>1</sup>H NMR spectra (4.9-5.5 ppm), whilst the percentage of 1,4-*cis/trans* enchainments were determined by integration of the methylene peaks (27.6 and 32.8 ppm, respectively) in quantitative <sup>13</sup>C NMR spectra.

The NMR spectroscopy method to analyze hydrogenated polybutadiene was adapted from the literature:<sup>20</sup> 70 mg of the PE sample were dissolved in a mixture of *ortho*-dichlorobenzene (*o*-DCB)/C<sub>6</sub>D<sub>6</sub> (4/1, v/v) with a total volume of 0.70 mL, at 80 °C, in a 5 mm diameter NMR tube. The samples were analyzed at 130 °C on an NMR spectrometer (Bruker Avance Neo 400). <sup>1</sup>H and quantitative <sup>13</sup>C NMR spectra were obtained at 400.33 and 100.66 MHz, respectively. The pulse program used was zgpg30-avance-version (12/01/11), 1D sequence with inverse gated decoupling.

Size Exclusion Chromatography (SEC) was performed with THF as eluent at 40 °C using a Waters SIS HPLC-pump, a Waters 410 refractometer, and Waters styragel column calibrated with polystyrene standards. A correction factor of 0.5 was applied for the determination of the true number-average molecular weight of polybutadiene.<sup>21-22</sup>

Positive-ion Matrix Assisted LASER Desorption/Ionization-Mass Spectrometry (MALDI-MS) experiments were performed using a Waters QToF Premier mass spectrometer equipped with a Nd:YAG laser operating at 355 nm (third harmonic) with a maximum output of 65 μJ delivered to the sample in 2.2 ns pulses at 50 Hz repeating rate. Time-of-flight mass analysis was performed in the reflectron mode at a resolution of about 10k (*m/z* 569). All samples were analyzed using *trans*-2-[3-(4-*tert*-butylphenyl)-2-methylprop-2-enylidene]malononitrile (DCTB) as a matrix. Polymer samples were dissolved in THF to obtain 1 mg.mL<sup>-1</sup> solution. Additionally, one drop (~1μL) of 1 mg.mL<sup>-1</sup> AgNO<sub>3</sub> solution in acetonitrile was added to the stainless-steel plate target bearing the matrix and analyte crystals.

Thermal properties were evaluated using Differential Scanning Calorimetry (DSC) on a TA Discovery DSC 25 instrument. The instrument was calibrated with a high purity indium sample following standard procedures. Samples weighing 4 mg were placed in sealed pans and subjected to analysis in a temperature range of -89 to 180 °C, with a heating rate of 10 °C/min, under a nitrogen atmosphere.

## RESULTS AND DISCUSSION.

### Polymerization of butadiene mediated by $\pi$ -Allyl nickel(II) (TFA) / $Mg^nBuEt$ or $AlEt_3$ systems

The polymerization of butadiene was conducted using  $Ni(COD)_2$  and 1 equiv. trifluoroacetic acid with butadiene/Ni ratio of 100, 250 or 500, via *in situ* formation of the catalyst  $\pi$ -allyl nickel(II) (TFA). Results for the reactions obtained with and without the presence of chain transfer agents such as  $Mg^nBuEt$  and  $AlEt_3$  are shown in **Table 1**. Without CTA, an almost full butadiene conversion in 21 h at 60 °C is obtained for BD/Ni ratio ranging from 100 to 500 (entry 1, 5 and 8). A regioregular poly(1,4-butadiene) with high 1,4-*cis* content is obtained in agreement with the literature.<sup>9</sup> The obtained 1,4-*cis* contents are respectively 89% and 86% with respectively 250 equiv. (entry 5) and 500 equiv. of butadiene (entry 8). A lower quantity of butadiene resulted in a noticeable decrease in poly(1,4-*cis*-butadiene) (entry 1, 59% with 100 equiv. butadiene). This was attributed in the literature to a slower propagation accompanied by an isomerization of the anti- $\pi$ -allyl form to the syn-form.<sup>23</sup> At a higher butadiene content in the reaction medium (5 and 8) the theoretical and calculated number-average molecular weights ( $M_n$ ) are not of the same order, which might indicate  $\beta$ -hydride elimination reactions, represented in Scheme 4, that were previously reported with nickel(II) allyl complexes.<sup>24-26</sup> However, with a BD/Ni ratio of 100, the calculated  $M_n$  is closer to the measured one. The higher the amount of butadiene, the higher the discrepancy between calculated and measured  $M_n$ . This suggests a beta hydride mechanism governed by transfer to the butadiene monomer rather than by elimination. The dispersity is as a consequence lower for lower amount of butadiene.

Polymerization reactions conducted in the presence of 5 equiv. magnesium dialkyl or aluminum triethyl (entries 2, 3, 6, 7, and 9) lead to a lower number-average molecular weight, highlighting the occurrence of chain transfer reaction in the presence of the CTA. In entries 2, 6, and 9, the use of magnesium dialkyl as a CTA results in a quantitative yield, independently of the BD/Ni ratio. Conversely, the same behaviour is not observed in entries 7, and 10, where  $AlEt_3$  is used as CTA.

Notably, the reaction achieves full conversion with a low butadiene/nickel ratio in entry 3, while the yield drastically decreases from 64% to 3% as the ratio increases, from 250 to 500 (entries 7 and 10).

**Table 1. Polymerization of butadiene mediated by  $\pi$ -Allyl nickel(II) (TFA) /  $Mg^nBuEt$  or  $AlEt_3$  systems**

Entry <sup>a</sup>	BD/Ni	CTA	CTA/Ni	Yield		Mn calc ( $gmol^{-1}$ ) <sup>b</sup>	Mn SEC ( $gmol^{-1}$ ) <sup>c</sup>	$D_M^d$	Polybutadiene microstructure (%) <sup>e</sup>		
				(g)	(%)				1,4- cis	1,4- trans	1,2-
1	100	-	-	0.54	>99	5500	5200	3.4	59	40	1
2	100	$Mg^nBuEt$	5	0.53	99	5400	1000	2.7	37	55	8
3	100	$AlEt_3$	5	0.53	98	5300	1600	6.2	59	37	8
4	100	$Et_2Zn$	5	-	-	-	-	-	-	-	-
5	250	-	-	0.67	98	13300	9000	3.7	89	8	3
6	250	$Mg^nBuEt$	5	0.67	98	11700	1850	2.6	52	41	7
7	250	$AlEt_3$	5	0.39	64	9000	1400	2.2	45	46	8
8	500	-	-	1.22	91	24600	10800	3.6	86	11	3
9	500	$Mg^nBuEt$	5	1.34	>99	27000	1300	3.1	48	47	6
10	500	$AlEt_3$	5	0.05	3	nd	nd	nd	nd	nd	nd

<sup>a</sup> Reactions conducted at 60 °C for 21 h using the precatalyst  $Ni(COD)_2$  with a given added ratio of TFA in the presence of butadiene stored in toluene;

The volume of the reaction was 4 mL for 100:1 BD/Ni, 5 mL for 250:1 BD/Ni and 8 mL for 500:1 BD/Ni; the concentration has no significant influence on the data, see SI section

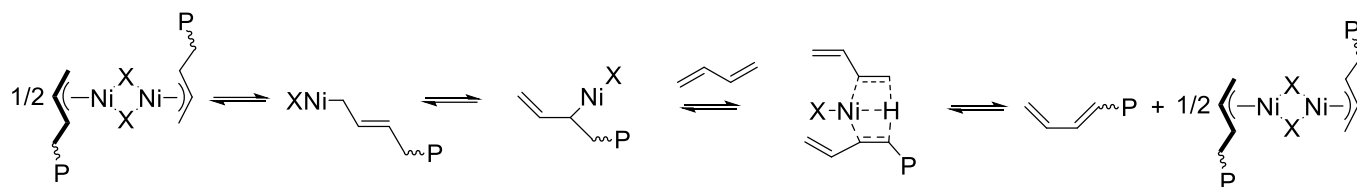
<sup>b</sup> Expected molecular weight taking the yield into account and considering 1 growing chain per nickel;

<sup>c</sup> Number-average molecular weight measured by size exclusion chromatography and corrected (see experimental part)

<sup>d</sup> Dispersity measured by size exclusion chromatography.

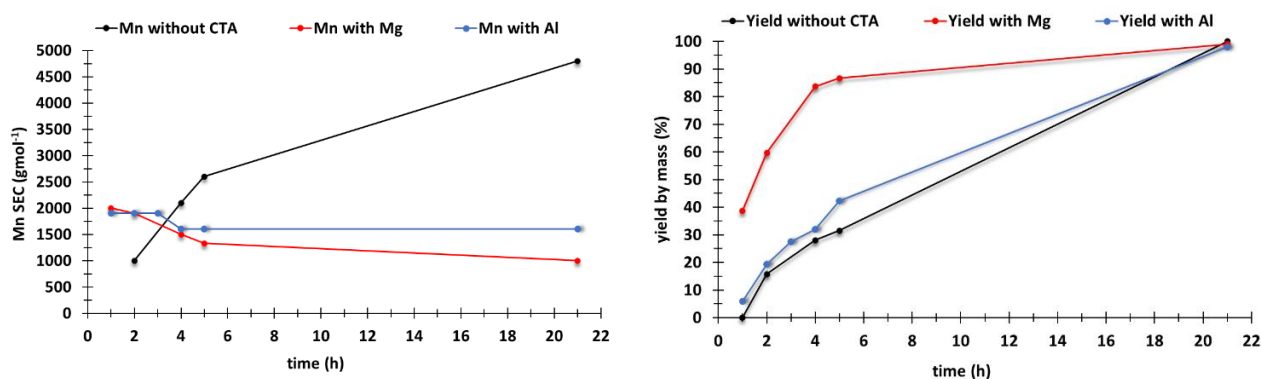
<sup>e</sup> Calculated using  $^1H$  and quantitative  $^{13}C$  NMR data.

**Scheme 4. Proposed mechanism of  $\beta$ -H transfer to monomer in the butadiene polymerization process of using  $\text{BDNi(II)X}$ , where  $\text{X}=\text{TFA}$**



Experiments conducted in presence of  $\text{ZnEt}_2$  as CTA under similar conditions (entry 4) did not lead to any polymerization. The observed formation of black particles suggests a rapid reduction of the nickel catalyst. The influence of a CTA on the output of the reaction is also notable on the polymerization stereoselectivity with an increase of 1,4-*trans* enchainments, leading to a similar quantity of the two configurations (1,4-*cis*/1,4-*trans*). An increase of 1,4-*trans* stereoselectivity was already observed in the literature using the nickel allyl TFA system upon addition of small molecules,<sup>3</sup> and attributed to a increase of  $\eta_1$  coordination mode vs. induced  $\eta_3$  by steric hindrance. A slight increase of poly(1,2-butadiene) is also observed in the presence of the  $\text{Mg}^n\text{BuEt}$  and  $\text{AlEt}_3$  chain transfer agents.

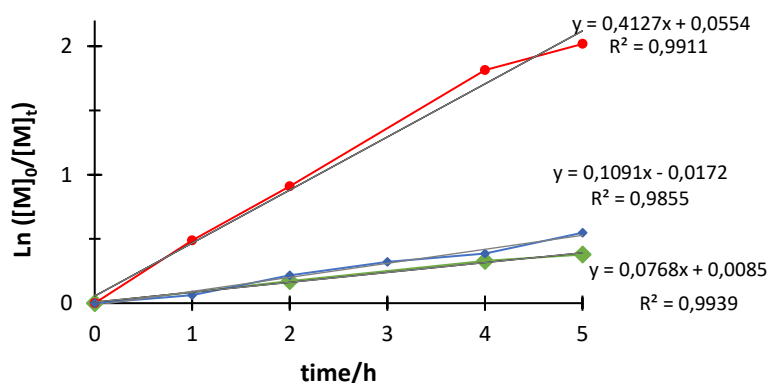
**Figure 1. Kinetic study for a BD/Ni ratio of 100 with 5 equiv. CTA. Number-average molecular weight on the left and yield on the right side**



A kinetic study was further conducted for a BD/Ni ratio of 5. The results represented in Figure 1 show a significant increase of the activity in the presence of  $\text{Mg}^n\text{BuEt}$ , with a yield by weight of *ca.* 40% in 1h reaction time, when no polymer could be isolated without CTA. With either no CTA or with  $\text{AlEt}_3$ , both reactions proceed at a slower rate, producing less than 40% yield after five hours reaction time when the Mg system is already at more than 80%.  $\text{Mg}^n\text{BuEt}$  and  $\text{AlEt}_3$  may interact with the trifluoroacetate counter ion of the nickel catalyst in a different manner due to a different Lewis acidity. The Mg based CTA most probably leads to a stronger interaction, leading to a decrease of the electron density around the nickel atom, resulting in a faster coordination step. Such increase in the reactivity upon addition of a Lewis acid to a carboxylate nickel allyl dimer has previously been reported.<sup>27</sup>

On the right side of Figure 1, the number-average molecular weight values increase over time in the absence of a CTA, whereas they were generally stable or even decreased at the early stages of the reaction in the presence of a CTA, which suggests the occurrence of fast and irreversible chain transfer reactions. In order to determine whether the reactions conform to a first-order kinetic model, the  $\ln([M_0]/[M_t])$  over time graph was plotted (Figure 2) where  $[M_0]$  represents the initial concentration of the monomer and  $[M_t]$  represents the monomer concentration at a specific time. All 3 reactions exhibit a linear relationship over a period of five hours reaction, highlighting a first order kinetic. The concentration of active species is thus constant throughout the reaction, *i.e.* deactivation is not occurring in this chain transfer polymerizations mediated by  $\pi$ -allyl nickel(II) (TFA) /  $\text{Mg}^n\text{BuEt}$  or  $\text{AlEt}_3$  systems.

**Figure 2. 1<sup>st</sup> order kinetic study for the 3 systems. Polymerization with Mg/Ni in red, with Al/Ni in blue and in green without CTA.**



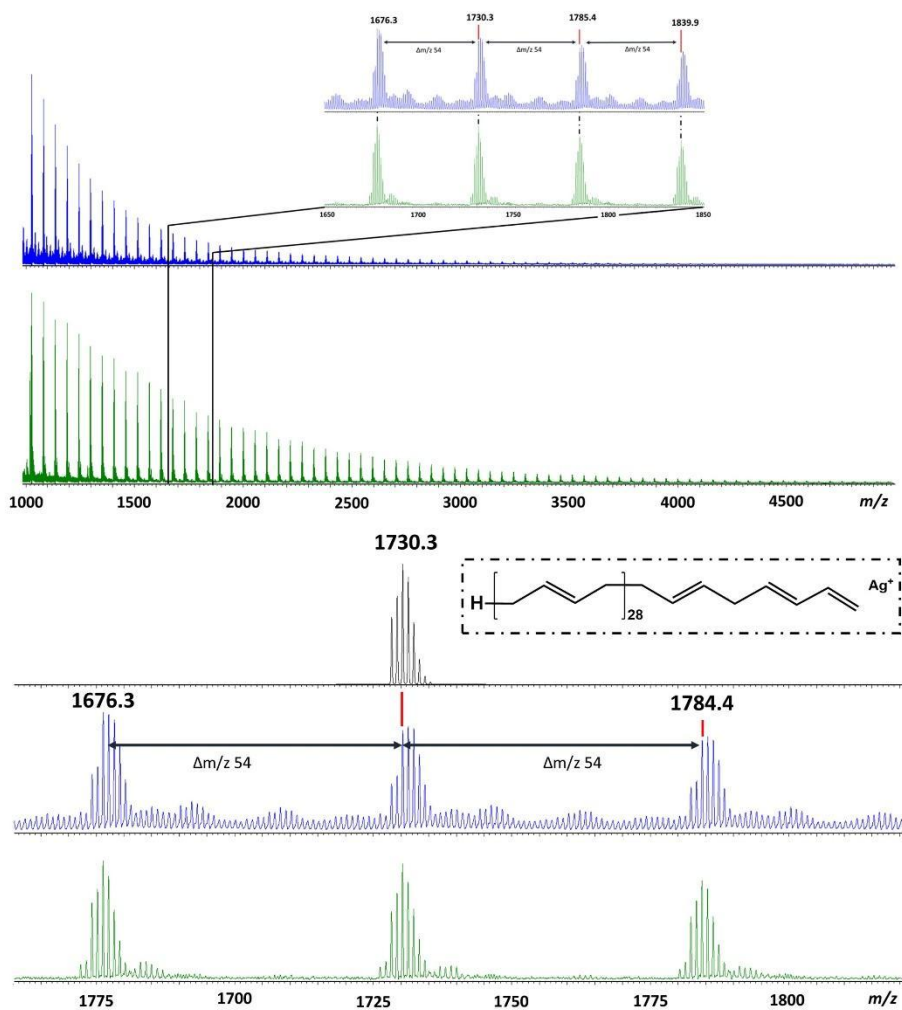
### Polybutadiene chain end analysis

MALDI-ToF-MS analysis was performed to determine the nature of the chain ends of the so formed polybutadienes. Representative results are shown in Figure 3. The trace shows a population with a  $m/z$  of  $n \cdot M_{\text{butadiene}} - 2$  Da. In a conventional CCTP mechanism, insertion of the monomer takes place in the transition metal alkyl bond formed following the transalkylation (see Scheme 1). This would result here in ethyl and butyl chain ends, which are not observed on the MALDI-ToF-MS analysis.

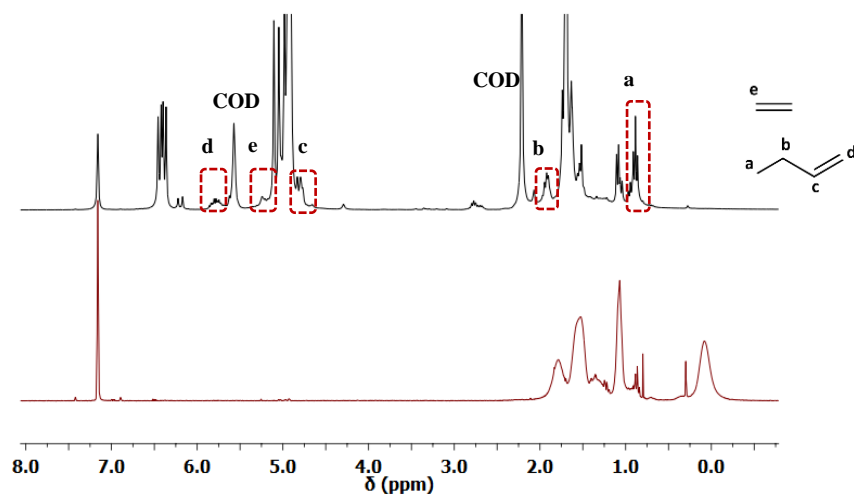
In order to get more insight into the mechanism, the reaction between 1 equiv.  $\text{Ni}(\text{COD})_2$ , 1 equiv. of allyltrifluoroacetate, 1 equiv. of  $\text{Mg}^n\text{BuEt}$  and 10 equiv. of isoprene as a case study was monitored by  $^1\text{H}$  NMR in benzene- $d_6$  (Figure 4). The presence of signals representative of ethene and 1-butene, together with the disappearance of signals representative of  $\text{Mg}^n\text{BuEt}$  suggest that the transalkylation of the ethyl and butyl groups to the nickel occurs, and is followed by a  $\beta$ -H elimination / transfer process, leading to the olefin. A plausible mechanism is depicted in Scheme 5. A similar mechanism was observed for styrene CCTP using rare earth chlorides and borohydrides combined to an excess of dialkyl magnesium, which promote both the initial alkylation of the precatalysts and the

transmetallation reaction during the course of the polymerization.<sup>28</sup> Note that the reaction of allyltrifluoroacetate and nickel (COD)<sub>2</sub> is a well-established reaction that quantitatively leads to [η<sup>3</sup>-(C<sub>3</sub>H<sub>5</sub>)NiTFA]<sub>2</sub>.<sup>29-30</sup> This procedure was used to avoid possible side reaction between the acid and the Grignard reagent due to a difference of reaction kinetics between butadiene and isoprene.

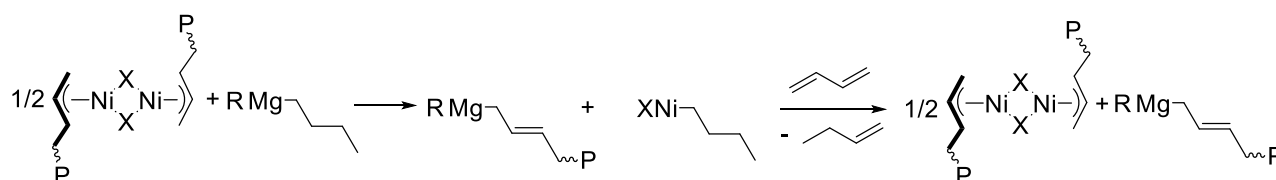
**Figure 3. MALDI-ToF-MS of entry 1 in blue and 9 in green, amplification of the mass spectrum (blue) matches the predicted (black) corresponding to a polybutadiene with a diene chain end.**



**Figure 4.**  $^1\text{H}$  NMR spectra of  $\text{Mg}^n\text{BuEt}$  (bottom) and of a 1/10/5 Ni/isoprene/ $\text{Mg}^n\text{BuEt}$  ratio in deuterated benzene after 48 hours at room temperature (top).



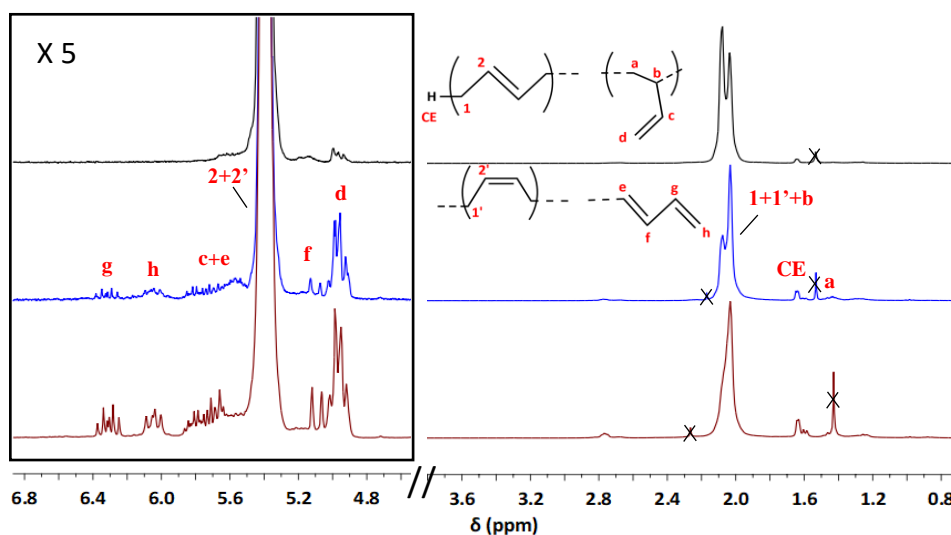
**Scheme 5.** Proposed mechanism of  $\beta$ -H elimination of the alkyl chain, where  $\text{X}=\text{TFA}$



The MALDI ToF analysis (Figure 3) suggests that all polybutadiene chains have an additional unsaturation ( $m/z$  of  $n^*M_{\text{butadiene}} - 2$  Da). The unsaturation is confirmed on the  $^1\text{H}$  NMR spectra of low molecular weight samples obtained at short reaction time that allow the observation of chain ends. In particular in the case of Ni(II)/CTA systems, the  $^1\text{H}$  NMR spectrum shows a set of signal between 5.64 and 6.37 ppm that are attributed to a conjugated dienic structures (**Erreur ! Référence non valide pour un signet.**). The NMR pattern, from the comparison of the spectra of 1,3 pentadiene with 2,4 hexadiene, as well as simulation on a Chemdraw software, suggests a terminal conjugated diene rather

than an internal. Regarding the other chain end, the typical methyl group (CE) can be observed at 1,64 ppm on the  $^1\text{H}$  NMR spectrum. The later signal has been attributed to the polymer chain end with 1,4-*trans* selectivity,<sup>31</sup> which is favored for this Ni(II) catalytic system.

**Figure 5.**  $^1\text{H}$  NMR spectra in  $\text{CDCl}_3$  of polybutadiene obtained from:  $[(\eta^3\text{-C}_4\text{H}_7)\text{Ni}(\text{TFA})]_2$  (entry 1) in black,  $[(\eta^3\text{-C}_4\text{H}_7)\text{Ni}(\text{TFA})]_2 + \text{Mg}^n\text{BuEt}$  (entry 17) in blue,  $[(\eta^3\text{-C}_4\text{H}_7)\text{Ni}(\text{TFA})]_2 + \text{Et}_3\text{Al}$  (quenched and isolated after 1 h of reaction) in dark red.



### Analysis of the branched microstructure

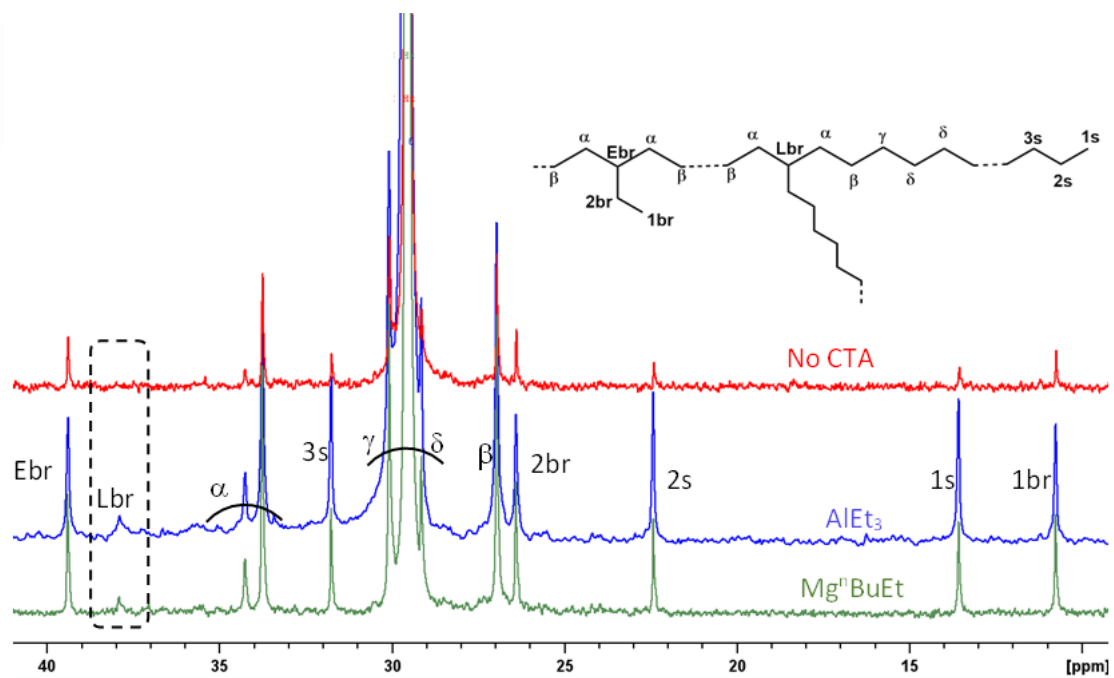
The presence of a conjugated diene chain end offers the possibility of a reinsertion into the growing polymer chain, leading to the formation of a branched polymer, in a similar way to the tandem processes reported for ethylene in the presence of CCTP and Ni displacement catalysts (see introduction section). The potential formation of branched polybutadiene warrants therefore further investigation.  $^{13}\text{C}$  NMR studies were performed in order to ascertain the presence of branching. For

polybutadiene, the possibility of either a tertiary carbon (methine) or a quaternary carbon typical of branching should be observed. However, owing to the complex nature of polybutadiene NMR analysis, the detection of such evidence is challenging, making hydrogenation of polybutadiene into polyethylene a more viable alternative for  $^{13}\text{C}$  NMR analysis.<sup>20</sup> A high temperature quantitative dept  $^{13}\text{C}$  NMR sequence enabled the detection and quantification of long chain branching (LCB) in polyethylene chains, by observing the methine carbon signals of LCB (Figure 6).<sup>20</sup> The LCB density per sample was determined using Equation 1, by the peak areas of ethyl branch (EB, corresponding to a 1,2 regioselective insertion of butadiene, the only type of SCB, short chain branching that can be seen here) or LCB per sample obtained from the high temperature quantitative  $^{13}\text{C}$  NMR, where  $a$  is the peak area of the methine carbons in branch (EB + LCB),  $b$  the peak areas of the methylene carbons ( $\alpha$ ,  $\beta$ ,  $\gamma$ , and  $\delta$ ) present on the PE main chain and  $c$  the peak area of the methine carbon of LCB. With this equation, we obtain the quantity of LCB per 1000 carbons in a sample, as well as the quantity of EB/1000C, by replacing  $c$  by methine carbon of EB.

**Equation 1. LCB density per PE sample, adapted from**<sup>20</sup>

$$\frac{\text{LCB}}{1000\text{C}} = \frac{1000}{(a + b)} \times c$$

**Figure 6. High temperature  $^{13}\text{C}$  NMR of hydrogenated polybutadiene samples. Entry 1H in red (without CTA), entry 12H in blue ( $\text{AlEt}_3$  as CTA) and entry 11H in green ( $\text{Mg}^n\text{BuEt}$  as CTA)**



**Table 2. Hydrogenation of polybutadiene samples: microstructure of PE using  $^{13}\text{C}$  NMR and DSC**

<i>Entry</i> <sup>a</sup>	<i>t/h</i>	<i>BD/Ni</i>	<i>CTA</i>	<i>CTA/Ni</i>	<i>M<sub>n</sub> PBD</i> <sup>b</sup> ( $\text{g mol}^{-1}$ )	<i>D<sub>M</sub>PBD</i> <sup>c</sup>	<i>Yield PBD</i> (%)	<i>Entry after hydrogenation</i>	<i>Microstructure</i> <sup>d</sup>		<i>DSC data</i>	
									<i>EB/1000C</i>	<i>LCB/1000C</i>	<i>T<sub>m</sub> °C Peak 1</i>	<i>T<sub>m</sub> °C Peak 2</i>
<i>1</i>	21	100	-	-	5200	3.4	>99	1H	3.5	-	120	-
<i>11</i>	5	100	$\text{Mg}^n\text{BuEt}$	5	1300	2.8	87	11H	13.1	3.3	99	107
<i>12</i>	5	100	$\text{AlEt}_3$	5	1500	3.7	37	12H	14.4	9.0	92	109
<i>13</i>	5	100	$\text{Mg}^n\text{BuEt}$	2.5	1800	2.3	79	13H	6.3	n.d. <sup>e</sup>	102	115
<i>14</i>	5	100	$\text{AlEt}_3$	2.5	1400	2.9	41	14H	13.3	4.7	96	107
<i>6</i>	21	250	$\text{Mg}^n\text{BuEt}$	5	1850	2.6	98	6H	13.5	n.d. <sup>e</sup>	107	110
<i>7</i>	21	250	$\text{AlEt}_3$	5	1400	2.2	64	7H	9.2	2.5	103	114
<i>15</i>	5	500	$\text{Mg}^n\text{BuEt}$	5	2200	3.4	36	15H	8.5	n.d. <sup>e</sup>	98	115

Reactions conducted at 60 °C for 21 h using the precatalyst  $\text{Ni}(\text{COD})_2$  with a equimolar ratio of trifluoroacetic acid in the presence of butadiene stored in toluene;

<sup>b</sup> Number-average molecular weight measured of PBD by size exclusion chromatography and corrected (see experimental part)

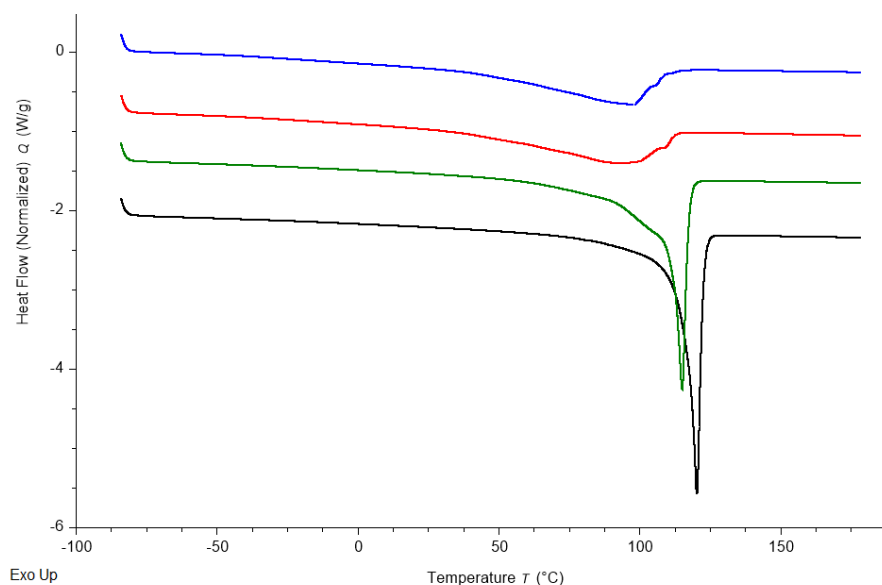
<sup>c</sup> Dipsersity of PBD measured by size exclusion chromatography;

<sup>d</sup> Calculated using high temperature quantitative  $^{13}\text{C}$  NMR data;

<sup>e</sup>Signal-to-noise ratio on  $^{13}\text{C}$  NMR spectrum too high for accurate quantification.

A differential scanning calorimetry (DSC) analysis was further conducted on the hydrogenated polybutadiene samples and representative results can be seen in Figure 7. The hydrogenated polybutadiene obtained from the  $\pi$ -allyl nickel(II) (TFA) /  $Mg^nBuEt$  or  $AlEt_3$  system displays an alteration on the melting temperatures depending on the degree of branching present in the sample, which is consistent with prior findings in the literature on branched polyethylene.<sup>32</sup> A sharp melting point (120 °C) was observed in the case of the linear polyethylene resulting from the hydrogenation of the polybutadiene obtained without CTA. In samples obtained with the CTA, a shift of the melting temperature towards lower values was observed, along with the appearance of new melting temperatures. For samples where the density of LCB was as low as it could not be determined by NMR such as *e.g.* entry 15H, signs of branching can still be observed by DSC, with however a less accentuated shift of the melting point.

**Figure 7. DSC results of the hydrogenated polybutadiene samples: entry 1 in black, entry 15H in green, entry 12H in red and entry 11H in blue**



From these results, it can be seen that Al based catalytic systems lead to more LCB than Mg based systems, *e.g* by a factor 3 (entries 17H-18H). This might be attributed to a higher displacement / elimination rate of the chain from an Al-polybutadienyl compared to a Mg-polybutadienyl moiety. Then, both CTA based catalytic systems are able to reinsert the unsaturated polybutadiene into the growing chain, which is not the case for the system without CTA.

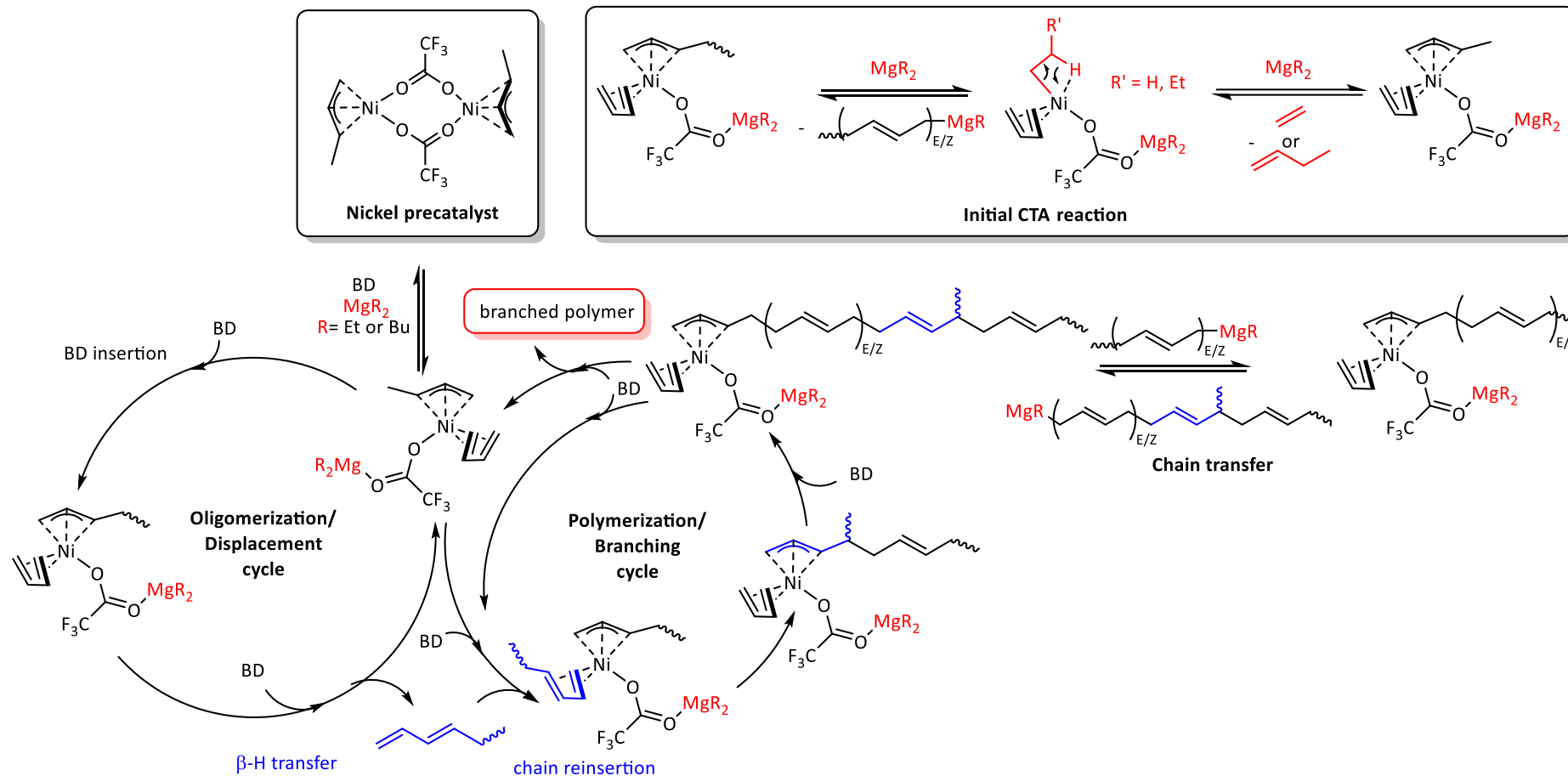
## **Mechanism**

It is noteworthy that the CCTP approach can be extended to the production of branched polybutadiene. We propose a full analysis of the mechanism leading to the branching using  $\pi$ -allyl nickel(II) (TFA) catalyst along with a chain transfer agent, which functions simultaneously as a CCTP and as a displacement catalyst. This is represented in Scheme 6.

By adding a chain transfer agent to the  $\pi$ -allyl nickel(II) (TFA) / BD solution, we suppose a formation of an intermediate species, that not only allows the exchange of an alkyl group for a polybutadiene growing chain, but also, a change on the stereoselectivity, and an increase of the reaction rate in the case of magnesium dialkyl. For this process, we propose a coordination of 1 equiv. of the  $MgR_2$  CTA with an oxygen present on the coordinated TFA moiety, present on the nickel catalyst.

The transfer of the CTA alkyl group to the Ni center leads via  $\beta$ H transfer to the monomer to the growth of additional chains. The polybutadienyl chains are terminated by a  $\beta$ H process leading to a conjugated diene. The resulting macromonomer can be reinserted into a polybutadienyl growing chain, leading to branched PBD.

**Scheme 6. Proposed catalytic polymerization cycle using the catalyst resulting from Ni(COD)<sub>2</sub> and trifluoro acetic acid in the presence of Mg<sup>n</sup>BuEt as chain transfer agents**



## **Conclusion.**

We have assessed the polymerization of butadiene using  $\pi$ -allyl nickel(II) (TFAin combination with a Mg and a Al based CTA). Lower molecular weights are obtained, highlighting the occurrence of chain transfer reaction. The initiation of the chain transfer occurs via  $\beta$ -hydride elimination of the Ni-alkyl moieties / transfer to the monomer. The resulting polybutadiene bears an additional unsaturation, and can be reinserted into the growing chain as long as a CTA has been introduced in the reactive medium. In other words, this is a kind of CCTP based tandem reaction, where the Ni catalyst plays the role of both the polymerization and displacement catalyst. If such reactions were already reported for ethylene, it is as far as we know the first example of a conjugated diene CCTP tandem process leading in one pot to branched polybutadiene. The latter has been unambiguously analyzed by  $^{13}\text{C}$  NMR after hydrogenation, which allows a quantitative determination of the LCB (for  $\text{LCB} > 2/1000$ ), and a qualitative analysis of the branching effect via the thermal signature of the samples.

**Supporting Information:** Influence of catalyst and monomer concentrations

## **Acknowledgments**

The University of Lille is acknowledged for funding CB's PhD. Chevreul Institute (FR 2638), Ministère de l'Enseignement Supérieur, de la Recherche et de l'Innovation (MESRI) and Région Hauts de France are acknowledged for supporting and funding partially this work. Aurélie Malfait and Maxence Epina are acknowledged for SEC measurements.

## Bibliography.

- (1) Srivastava, V. K.; Maiti, M.; Basak, G. C.; Jasra, R. V. Role of Catalysis in Sustainable Production of Synthetic Elastomers. *J. Chem. Sci.* **2014**, *126* (2), 415–427. <https://doi.org/10.1007/s12039-014-0580-5>.
- (2) Ricci, G.; Pampaloni, G.; Sommazzi, A.; Masi, F. Dienes Polymerization: Where We Are and What Lies Ahead. *Macromolecules* **2021**, *54* (13), 5879–5914. <https://doi.org/10.1021/acs.macromol.1c00004>.
- (3) *Preparation and Properties of Stereoregular Polymers*; Lenz, R. W., Ciardelli, F., Eds.; Springer Netherlands: Dordrecht, 1979.
- (4) Phuphuak, Y.; Bonnet, F.; Stoclet, G.; Bria, M.; Zinck, P. Isoprene Chain Shuttling Polymerisation between Cis and Trans Regulating Catalysts: Straightforward Access to a New Material. *Chem Commun* **2017**, *53* (38), 5330–5333. <https://doi.org/10.1039/C7CC01016H>.
- (5) Dai, Q.; Zhang, X.; Hu, Y.; He, J.; Shi, C.; Li, Y.; Bai, C. Regulation of the *Cis* -1,4- and *Trans* -1,4-Polybutadiene Multiblock Copolymers via Chain Shuttling Polymerization Using a Ternary Neodymium Organic Sulfonate Catalyst. *Macromolecules* **2017**, *50* (20), 7887–7894. <https://doi.org/10.1021/acs.macromol.7b01049>.
- (6) Zheng, W.; Yang, Q.; Dong, J.; Wang, F.; Luo, F.; Liu, H.; Zhang, X. Neodymium-Based One-Precatalyst/Dual-Cocatalyst System for Chain Shuttling Polymerization to Access *Cis*-1,4/*Trans*-1,4 Multiblock Polybutadienes. *Mater. Today Commun.* **2021**, *27*, 102453. <https://doi.org/10.1016/j.mtcomm.2021.102453>.
- (7) Kempe, R. How to Polymerize Ethylene in a Highly Controlled Fashion? *Chem. - Eur. J.* **2007**, *13* (10), 2764–2773. <https://doi.org/10.1002/chem.200601842>.
- (8) Valente, A.; Mortreux, A.; Visseaux, M.; Zinck, P. Coordinative Chain Transfer Polymerization. *Chem. Rev.* **2013**, *113* (5), 3836–3857. <https://doi.org/10.1021/cr300289z>.
- (9) Durand, J. P.; Dawans, F.; Teyssie, Ph. Polymerization by Transition Metal Derivatives. IX. Factors Controlling the *Cis/Trans* Orientation in the 1,4-Polymerization of Butadiene. *J. Polym. Sci. [B]* **1967**, *5* (9), 785–788. <https://doi.org/10.1002/pol.1967.110050909>.
- (10) Durand, J. P.; Teyssié, Ph. Equimolecular Binary Polydienes. III. Nickel Catalyst for the Preparation of Equibinary Poly(*Cis* 1,4-*Trans* 1,4)Butadiene. *J. Polym. Sci. [B]* **1968**, *6* (4), 299–301. <https://doi.org/10.1002/pol.1968.110060406>.
- (11) Dawans, F.; Marechal, J. C.; Teyssie, Ph. Bis( $\pi$ -Allylnickel Haloacetates). *J. Organomet. Chem.* **1970**, *21* (1), 259–261. [https://doi.org/10.1016/S0022-328X\(00\)90619-3](https://doi.org/10.1016/S0022-328X(00)90619-3).
- (12) Xiao, A.; Wang, L.; Liu, Q.; Yu, H.; Wang, J.; Huo, J.; Tan, Q.; Ding, J.; Ding, W.; Amin, A. M. A Novel Linear–Hyperbranched Multiblock Polyethylene Produced from Ethylene Monomer Alone via Chain Walking and Chain Shuttling Polymerization. *Macromolecules* **2009**, *42* (6), 1834–1837. <https://doi.org/10.1021/ma802352t>.
- (13) Zhao, Y.; Wang, L.; Yu, H.; Zhang, L.; Li, C.; Ding, W.; Jing, G. Controllable Preparation of Branched Polyethylene with Different Microstructures via Chain Transfer Ethylene Polymerization Catalyzed by  $\alpha$ -Diimine Ni Complex/Methylaluminumoxane/Diethylzinc. *J. Polym. Res.* **2013**, *20* (7), 184. <https://doi.org/10.1007/s10965-013-0184-7>.
- (14) Maddah, Y.; Ahmadjo, S.; Mortazavi, S. M. M.; Sharif, F.; Hassanian-Moghaddam, D.; Ahmadi, M. Control over Branching Topology by Introducing a Dual Catalytic System in Coordinative Chain Transfer Polymerization of Olefins. *Macromolecules* **2020**, *53* (11), 4312–4322. <https://doi.org/10.1021/acs.macromol.0c00358>.

- (15) Dashti, A.; Ahmadi, M.; Haddadi-Asl, V.; Ahmadjo, S.; Mortazavi, S. M. M. Tandem Coordinative Chain Transfer Polymerization for Long Chain Branched Polyethylene: The Role of Chain Displacement. *Eur. Polym. J.* **2023**, *190*, 112008. <https://doi.org/10.1016/j.eurpolymj.2023.112008>.
- (16) Gollwitzer, A.; Dietel, T.; Kretschmer, W. P.; Kempe, R. A Broadly Tunable Synthesis of Linear  $\alpha$ -Olefins. *Nat. Commun.* **2017**, *8* (1). <https://doi.org/10.1038/s41467-017-01507-2>.
- (17) Hassanian-Moghaddam, D.; Maddah, Y.; Ahmadjo, S.; Mortazavi, S. M. M.; Sharif, F.; Ahmadi, M. Mechanistic Study on the Metallocene-Based Tandem Catalytic Coordinative Chain Transfer Polymerization for the Synthesis of Highly Branched Polyolefins. *Eur. Polym. J.* **2021**, *152*, 110454. <https://doi.org/10.1016/j.eurpolymj.2021.110454>.
- (18) Wolff, P.; Dickert, A.; Kretschmer, W. P.; Kempe, R. I PP/PE Multiblock Copolymers for Plastic Blend Recycling Synthesized by Coordinative Chain Transfer Polymerization. *Macromolecules* **2022**, *55* (15), 6435–6442. <https://doi.org/10.1021/acs.macromol.2c00709>.
- (19) Doi, Y.; Yano, A.; Soga, K.; Burfield, D. R. Hydrogenation of Polybutadienes. Microstructure and Thermal Properties of Hydrogenated Polybutadienes. *Macromolecules* **1986**, *19* (9), 2409–2412.
- (20) Ishii, Y.; Kida, M.; Gogota, T.; Maru, Y.; Miyauchi, K. Determination of Low Degrees of Long-Chain Branching in Polybutadiene by Double-Bond Hydrogenation Followed by <sup>13</sup>C NMR and DEPT Spectroscopies. *Polymer* **2019**, *185*, 121965. <https://doi.org/10.1016/j.polymer.2019.121965>.
- (21) Takahashi, M. F. K.; de Lima, M.; Polito, W. L. Molecular Weight Determination of HTPB Resins by Vapor Pressure Osmometry (VPO) and Gel Permeation Chromatography (GPC): The Effect of Calibration Standards. *Polym. Bull.* **1997**, *38* (4), 455–460.
- (22) Zinck, P.; Terrier, M.; Mortreux, A.; Visseaux, M. On the Number-Average Molecular Weight of Poly(1,4-Trans Isoprene) Determined by Conventional GPC. *Polym. Test.* **2009**, *28* (1), 106–108. <https://doi.org/10.1016/j.polymertesting.2008.09.010>.
- (23) Furukawa, J. Mechanism of Diene Polymerization. *Pure Appl. Chem.* **1975**, *42* (4), 495–508. <https://doi.org/10.1351/pac197542040495>.
- (24) Taube, R.; Wache, S.; Kehlen, H. Complex Catalysis. Part XLVII. The Mechanism of Mol Mass Regulation in the Allyl Nickel Complex Catalyzed 1,4-Cis Polymerization of Butadiene. *J. Mol. Catal. Chem.* **1995**, *97* (1), 21–27. [https://doi.org/10.1016/1381-1169\(94\)00071-9](https://doi.org/10.1016/1381-1169(94)00071-9).
- (25) Winter, H. The Polymerization of Butadiene by His(\$\text{-Allylnickeltrifluoro-Acetate}\$)/Tetrachloro-1,4-Benzoquinone Revisited. **1998**, 4.
- (26) Tobisch, S. Mechanism of the Chain Termination of the Allylnickel(II)-Catalyzed Polymerization of 1,3-Butadiene. A Density Functional Investigation for the Cationic  $[\text{Ni}^{\text{II}}(\text{RC}_3\text{H}_4)(\text{Cis-C}_4\text{H}_6)\text{L}]^+$  Active Catalyst. *Macromolecules* **2003**, *36* (16), 6235–6244. <https://doi.org/10.1021/ma034369v>.
- (27) Lee, B. Y.; Kim, Y. H.; Shin, H. J.; Lee, C. H. Synthesis, Molecular Structures, and Norbornene Polymerization of Methallyl Nickel(II) Complexes of 2-(Diphenylamino)Benzoate. *Organometallics* **2002**, *21* (16), 3481–3484. <https://doi.org/10.1021/om020134g>.
- (28) Zinck, P.; Valente, A.; Bonnet, F.; Violante, A.; Mortreux, A.; Visseaux, M.; Ilinca, S.; Duchateau, R.; Roussel, P. Reversible Coordinative Chain Transfer Polymerization of Styrene by Rare Earth Borohydrides, Chlorides/Dialkylmagnesium Systems. *J. Polym. Sci. Part Polym. Chem.* **2010**, *48* (4), 802–814. <https://doi.org/10.1002/pola.23828>.
- (29) Dawans, F.; Teyssié, Ph. Polymerization by Transition Metal Derivatives XI. Stereospecific Polymerization of Butadiene in the Presence of  $\pi$ -Allyl Nickel Halogenoacetates. *J. Polym. Sci. [B]* **1969**, *7* (2), 111–114. <https://doi.org/10.1002/pol.1969.110070205>.
- (30) Durand, J. P.; Dawans, F. Stereospecific Polymerization of Isoprene by Monometallic Nickel Catalysts. *Polymer Letters* **1970**, *8*, 743–747. <https://doi.org/10.1002/pol.1970.110081101>.

- (31) Ziaee, F.; Ronagh-Baghbani, M.; Jozaghkar, M. R. Microstructure Characterization of Low Molecular Weight Polybutadiene Using the Chain End Groups by Nuclear Magnetic Resonance Spectroscopy. *Polym. Bull.* **2020**, *77* (5), 2345–2365. <https://doi.org/10.1007/s00289-019-02863-3>.
- (32) Zou, H.; Zhu, F. M.; Wu, Q.; Ai, J. Y.; Lin, S. A. Synthesis of Long-Chain-Branched Polyethylene by Ethylene Homopolymerization with a Novel Nickel(II)  $\pi$ -Diimine Catalyst. *J. Polym. Sci. Part Polym. Chem.* **2005**, *43* (7), 1325–1330. <https://doi.org/10.1002/pola.20596>.