

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

Catarina Bravo, Nicolas Merle, Mathieu Sauthier, Marc Bria, Julien De Winter, and Philippe Zinck*



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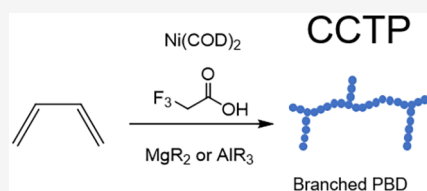


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ABSTRACT: Nickel allyl complexes are catalysts for the 1,4-regioselective polymerization of butadiene (BD). Coordinative chain transfer polymerization (CCTP) was not yet assessed by using these systems. We report in this work the polymerization of butadiene in the presence of π -allyl Nickel(II) trifluoroacetate (TFA) and $Mg^{n}BuEt$ or $AlEt_3$ as chain transfer agent (CTA) case studies. The reaction follows a first-order kinetic versus the monomer. Chain transfer is evidenced in the presence of CTAs, together with the formation of polybutadiene bearing a conjugated diene moiety. This allows one-pot access to branched polybutadiene by reinsertion of the chains. The branching is quantitatively analyzed by ^{13}C NMR after hydrogenation of the polybutadiene, and its impact on the thermal properties of the hydrogenated samples is assessed, 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 thus extending the range of application of CCTP processes.

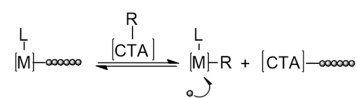


INTRODUCTION

Polydienes, which can be obtained by coordination polymerization, highly contribute as applied rubbers in the tire industries in addition to natural rubbers. The properties of these materials mostly depend on the regio- and stereoregularity of the polydiene and, hence, on the selectivity of the employed catalysts for a 1,4-*cis*, 1,4-*trans*, 1,2-, or 3,4-polydiene.^{1,2} Incorporating different stereoregularities into one macromolecular chain 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), which exhibit disparate melting points and low glass transition temperatures (T_g).³ Recent strategies to access this new material relies on coordinative chain transfer polymerization (CCTP).^{4–8} 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 enabling 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 CTA metal via transalkylation (Scheme 1). Hence, when chain transfer occurs, it enables the formation

of several polymer chains per catalyst molecule, in contrast with conventional living systems.

Scheme 1. CCTP Principle^a



^aM is the transition metal, L the ligand(s), CTA the chain transfer agent, R an alkyl group, and M the monomer

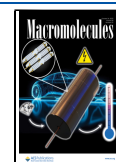
π -Allyl Nickel(II) complexes catalyze the 1,4-regioselective polymerization of butadiene, with a possible control of the *cis/trans* contents of the polymer, particularly when using trifluoroacetate (TFA) or halides as counteranions to arrange a bimetallic complex.^{9,10} Conveniently, these complexes can be quantitatively generated in situ by an oxidative addition involving $Ni(COD)_2$ (COD = cyclooctadiene) and trifluoroacetic acid followed by butadiene insertion (Scheme 2).¹¹

CCTP of conjugated dienes mainly relies on early transition metals or rare earth metals.⁸ If CCTP studies using nickel

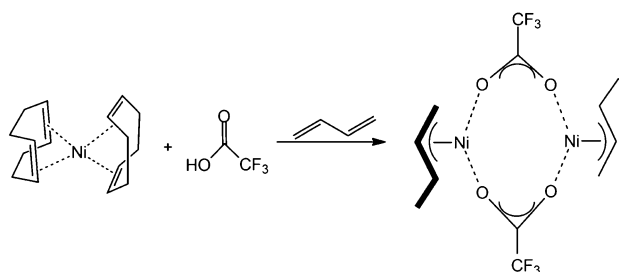
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Scheme 2. Synthesis of π -Allyl Nickel(II) (TFA) Complex Starting with Ni(COD)₂ as the Precursor



catalysts were reported for ethylene over the past decade,^{12–15} to the best of our knowledge, the ability of Ni(II) allyl catalysts for CCTP of conjugated dienes has not been explored so far. Nickel complexes such as Ni(COD)₂ or Ni(acac)₂ (acac = acetylacetonate) were in turn used as displacement catalysts in the course of ethylene CCTP, notably by Kempe et al.,¹⁶ allowing the selective formation of 1-alkene by β -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).^{15,17,18}

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 investigated the polymerization of butadiene in the presence of π -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 so is 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 SECTION

Materials. All operations were performed under an inert argon atmosphere by using a glovebox and Schlenk line techniques. Toluene was dried using an MBraun SPS 800 solvent purification system and degassed by three freeze–pump–thaw cycles. Butadiene (BD) was condensed in a Schlenk tube, cooled at $-20\text{ }^\circ\text{C}$ 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 ¹H NMR signals prior to use. *n*-Butylethylmagnesium (20 wt % in heptane from Texas Alkyl), triethylaluminum (1.3 M in heptane, ACROS), diethyl zinc (≥ 52 wt % Zn basis, Aldrich), Ni(COD)₂ ($>98\%$, Strem, COD = 1,5-cyclooctadiene), trifluoroacetic acid ($>99\%$, Fluka), allyl TFA ($>95\%$, TCI), 2,6-di-*tert*-butyl-4-methylphenol (BHT, $>99\%$, Aldrich), tris-(triphenylphosphine)rhodium(I) chloride {[Rh(PPh₃)₃Cl]} (99%, Strem), and triphenylphosphine (99%, Sigma-Aldrich) were used as received. With the exceptions of 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)₂ (for a BD/Ni ratio of 100 and 250 or 500, respectively) was weighed into a Schlenk tube and dissolved in 0.3–0.7 mL of toluene. An exact amount of *n*-butylethylmagnesium (MgⁿBuEt) or triethylaluminum (Et₃Al) was collected into a separate Schlenk tube using a microsyringe. Under an argon flow using a Schlenk line, trifluoroacetic acid was added to the Ni(COD)₂ 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 the CTA. The magnetically stirred reaction mixture was then heated at $60\text{ }^\circ\text{C}$. 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 into cold methanol with a small amount of BHT, which was then isolated and dried under vacuum in a desiccator.

Hydrogenation of Polybutadiene. The hydrogenation of the polybutadiene samples was performed according to literature procedure,¹⁹ using the Wilkinson catalyst [Rh(PPh₃)₃Cl] with an excess of triphenyl phosphine in solution in dry toluene in an autoclave with a hydrogen pressure of 50 bar for 24 h at $100\text{ }^\circ\text{C}$. To

Scheme 3. Combination of Ni Displacement Catalysis and CCTP

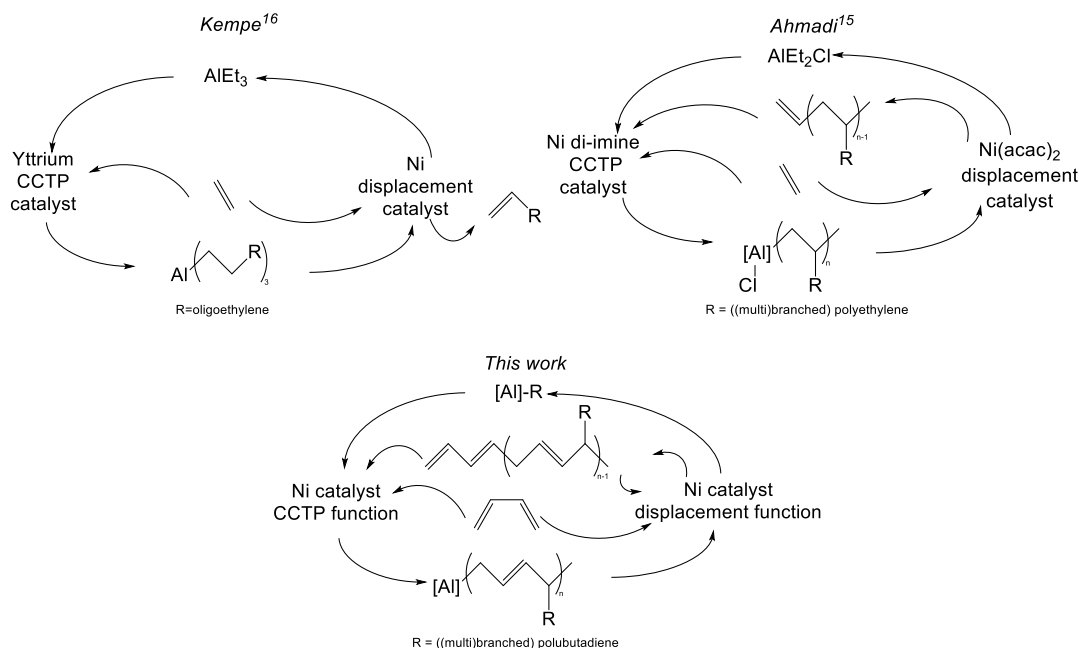
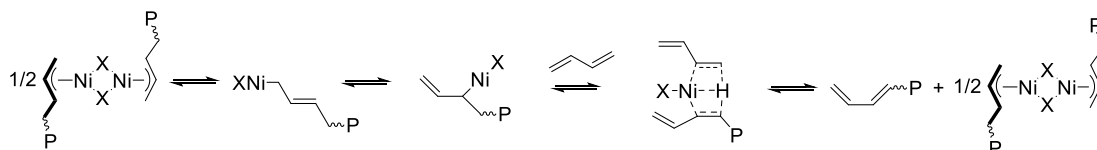


Table 1. Polymerization of Butadiene Mediated by π -Allyl Nickel(II) (TFA)/MgⁿBuEt or AlEt₃ Systems

entry ^a	BD/Ni	CTA	CTA/Ni	yield		M_n calc (g mol ⁻¹) ^b		M_n SEC (g mol ⁻¹) ^c	D_M ^d	polybutadiene microstructure (%) ^e		
				(g)	(%)					1,4-cis	1,4-trans	1,2-
1	100			0.54	>99	5500		5200	3.4	59	40	1
2	100	Mg ⁿ BuEt	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 ₂ Zn	5									
5	250			0.67	98	13,300		9000	3.7	89	8	3
6	250	Mg ⁿ BuEt	5	0.67	98	11,700		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	24,600		10,800	3.6	86	11	3
9	500	Mg ⁿ BuEt	5	1.34	>99	27,000		1300	3.1	48	47	6
10	500	AlEt ₃	5	0.05	3	nd		nd	nd	nd	nd	nd

^aReactions 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 the Supporting Information section. ^bExpected molecular weight taking the yield into account and considering 1 growing chain per Nickel. ^cNumber-average molecular weight measured by SEC and corrected (see Experimental Part). ^dDispersity measured by SEC. ^eCalculated using ¹H and quantitative ¹³C NMR data.

Scheme 4. Proposed Mechanism of β -H Transfer to the Monomer in the Butadiene Polymerization Process Using π Ni(II)X, Where X = TFA



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 ¹H 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 CDCl₃. 3–45 mg of the compound was dissolved in 0.6 mL of solvent directly into the NMR tube. The chemical shifts were calibrated by using the residual resonances of the solvent. Quantitative ¹³C NMR spectra were acquired using the ztig sequence (Bruker library). The relaxation time d1 was set to 5 s 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 ¹H NMR spectra (4.9–5.5 ppm), while 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 ¹³C NMR spectra.

The NMR spectroscopy method to analyze hydrogenated polybutadiene was adapted from the literature:²⁰ 70 mg of the PE sample was dissolved in a mixture of *ortho*-dichlorobenzene (*o*-DCB)/C₆D₆ (4/1, v/v) with a total volume of 0.70 mL at 80 °C in a NMR tube with a diameter of 5 mm. The samples were analyzed at 130 °C on an NMR spectrometer (Bruker AVANCE Neo 400). ¹H and quantitative ¹³C NMR spectra were obtained at 400.33 and 100.66 MHz, respectively. The pulse program used was ztig AVANCE-version (12/01/11), a 1D sequence with inverse gated decoupling.

Size exclusion chromatography (SEC) was performed with THF as an eluent at 40 °C using a Waters SIS HPLC-pump, a Waters 410 refractometer, and a 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.^{21,22}

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 μ J delivered to the sample in 2.2 ns pulses at a repeating rate of 50 Hz. 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 as a matrix. Polymer samples were dissolved in THF to obtain 1 mg mL⁻¹ solution. Additionally, one drop (\sim 1 μ L) of 1 mg mL⁻¹ AgNO₃ 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 -89–180 °C with a heating rate of 10 °C/min under a nitrogen atmosphere.

RESULTS AND DISCUSSION

Polymerization of Butadiene Mediated by π -Allyl Nickel(II) (TFA)/MgⁿBuEt or AlEt₃ Systems. The polymerization of butadiene was conducted using Ni(COD)₂ and 1 equiv of trifluoroacetic acid with a butadiene/Ni ratio of 100, 250, or 500, via in situ formation of the catalyst π -allyl nickel(II) (TFA). Results for the reactions obtained with and without the presence of CTAs such as MgⁿBuEt and AlEt₃ are shown in Table 1. Without a CTA, an almost full butadiene conversion in 21 h at 60 °C is obtained for BD/Ni ratios ranging from 100 to 500 (entries 1, 5, and 8). A regioregular poly(1,4-butadiene) with high 1,4-*cis* content is obtained in agreement with the literature.⁹ The obtained 1,4-*cis* contents are, respectively, 89 and 86% with, respectively, 250 equiv (entry 5) and 500 equiv (entry 8) of butadiene. A lower quantity of butadiene resulted in a noticeable decrease in poly(1,4-*cis*-butadiene) (entry 1, 59% with 100 equiv of butadiene). This was attributed in the literature to a slower propagation accompanied by an isomerization of the anti- π -allyl form to the syn-form.²³ At a higher butadiene content in

Table 2. Hydrogenation of Polybutadiene Samples: Microstructure of PE Using ^{13}C NMR and DSC

entry ^a	t/h	BD/Ni	CTA	CTA/Ni	M_n PBD ^b (g mol ⁻¹)	D_M PBD ^c	yield PBD (%)	entry after hydrogenation	microstructure ^d		DSC data	
									EB/1000C	LCB/1000C	T_m °C peak 1	T_m °C peak 2
1	21	100			5200	3.4	>99	1H	3.5		120	
11	5	100	Mg ⁿ BuEt	5	1300	2.8	87	11H	13.1	3.3	99	107
12	5	100	AlEt ₃	5	1500	3.7	37	12H	14.4	9.0	92	109
13	5	100	Mg ⁿ BuEt	2.5	1800	2.3	79	13H	6.3	n.d ^e	102	115
14	5	100	AlEt ₃	2.5	1400	2.9	41	14H	13.3	4.7	96	107
6	21	250	Mg ⁿ BuEt	5	1850	2.6	98	6H	13.5	n.d ^e	107	110
7	21	250	AlEt ₃	5	1400	2.2	64	7H	9.2	2.5	103	114
15	5	500	Mg ⁿ BuEt	5	2200	3.4	36	15H	8.5	n.d ^e	98	115

^aReactions conducted at 60 °C for 21 h using the precatalyst Ni(COD)₂ with a equimolar ratio of trifluoroacetic acid in the presence of butadiene stored in toluene. ^bNumber-average molecular weight measured of PBD by SEC and corrected (see Experimental Part). ^cDispersity of PBD measured by SEC. ^dCalculated using high-temperature quantitative ^{13}C NMR data. ^eSignal-to-noise ratio on the ^{13}C NMR spectrum too high for accurate quantification.

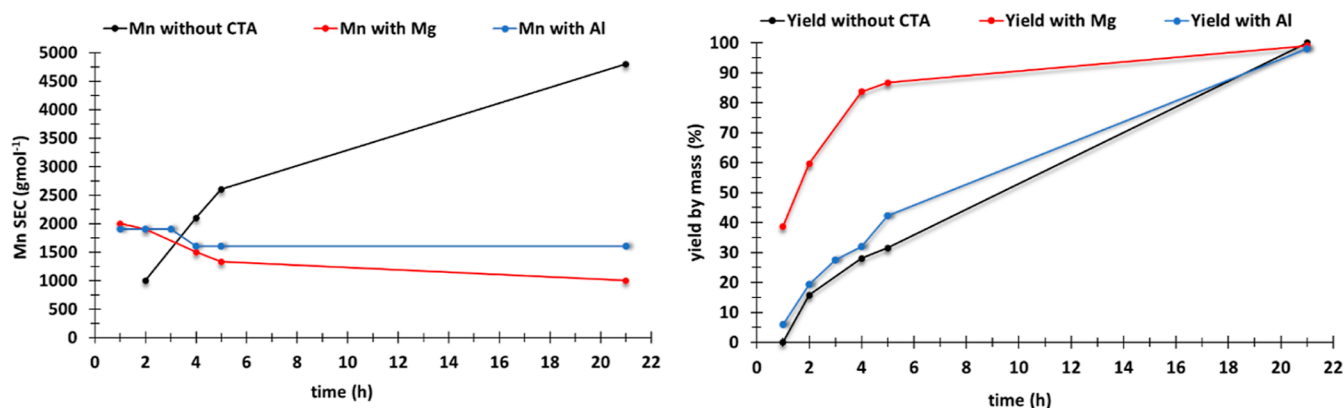


Figure 1. Kinetic study for a BD/Ni ratio of 100 with 5 equiv of CTA. Number-average molecular weight on the left and yield on the right sides.

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 β -hydride elimination reactions, as represented in Scheme 4, which were previously reported with Nickel(II) allyl complexes.^{24–26} 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 the calculated and the 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 a lower amount of butadiene (Table 2).

Polymerization reactions conducted in the presence of 5 equiv of 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 behavior is not observed in entries 7 and 10, where AlEt₃ is used as the 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).

Experiments conducted in the presence of ZnEt₂ as the 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 in 1,4-*trans*

enchainments, leading to a similar quantity of the two configurations (1,4-*cis*/1,4-*trans*). An increase in 1,4-*trans* stereoselectivity was already observed in the literature using the Nickel allyl TFA system upon addition of small molecules,³ and attributed to an increase in the η_1 coordination mode vs. was η_3 induced by steric hindrance. A slight increase in poly(1,2-butadiene) is also observed in the presence of the MgⁿBuEt and AlEt₃ CTAs.

A kinetic study was further conducted for a BD/Ni ratio of 100. The results represented in Figure 1 show a significant increase in the activity in the presence of MgⁿBuEt, with a yield by weight of ca. 40% in 1 h of reaction time, when no polymer could be isolated without a CTA. With either no CTA or with AlEt₃, both reactions proceed at a slower rate, producing less than 40% yield after 5 h of reaction time when the Mg system is already at more than 80%. MgⁿBuEt and AlEt₃ may interact with the TFA counterion 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 in the electron density around the nickel atom, resulting in a faster coordination step. Such an increase in the reactivity upon the addition of a Lewis acid to a carboxylate nickel allyl dimer has previously been reported.²⁷

On the left 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, although the branched microstructure may also lead

to a lower Mn. 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

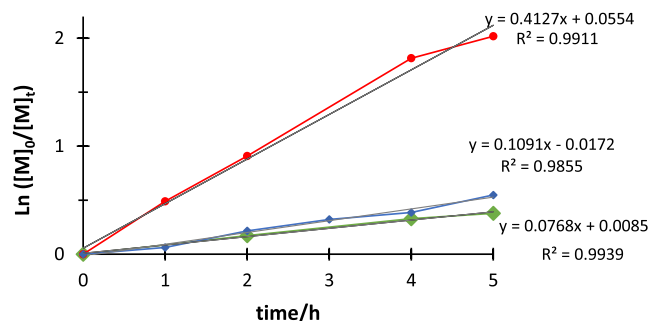


Figure 2. First-order kinetic study for the 3 systems. Polymerization with Mg/Ni in red, with Al/Ni in blue, and without a CTA in green.

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 5 h of 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 polymerization mediated by π -allyl Nickel(II) (TFA)/MgⁿBuEt or AlEt₃ systems.

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 $n^*M_{\text{butadiene}} - 2$ Da. In a conventional CCTP mechanism, insertion of the monomer takes place in the transition-metal alkyl bond formed following the transalkylation (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 of Ni(COD)₂, 1 equiv of allyltrifluoroacetate, 1 equiv of MgⁿBuEt, and 10 equiv of isoprene as a case study was monitored by ¹H 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 MgⁿBuEt, suggests that the transalkylation of the ethyl and butyl groups to the nickel occurs

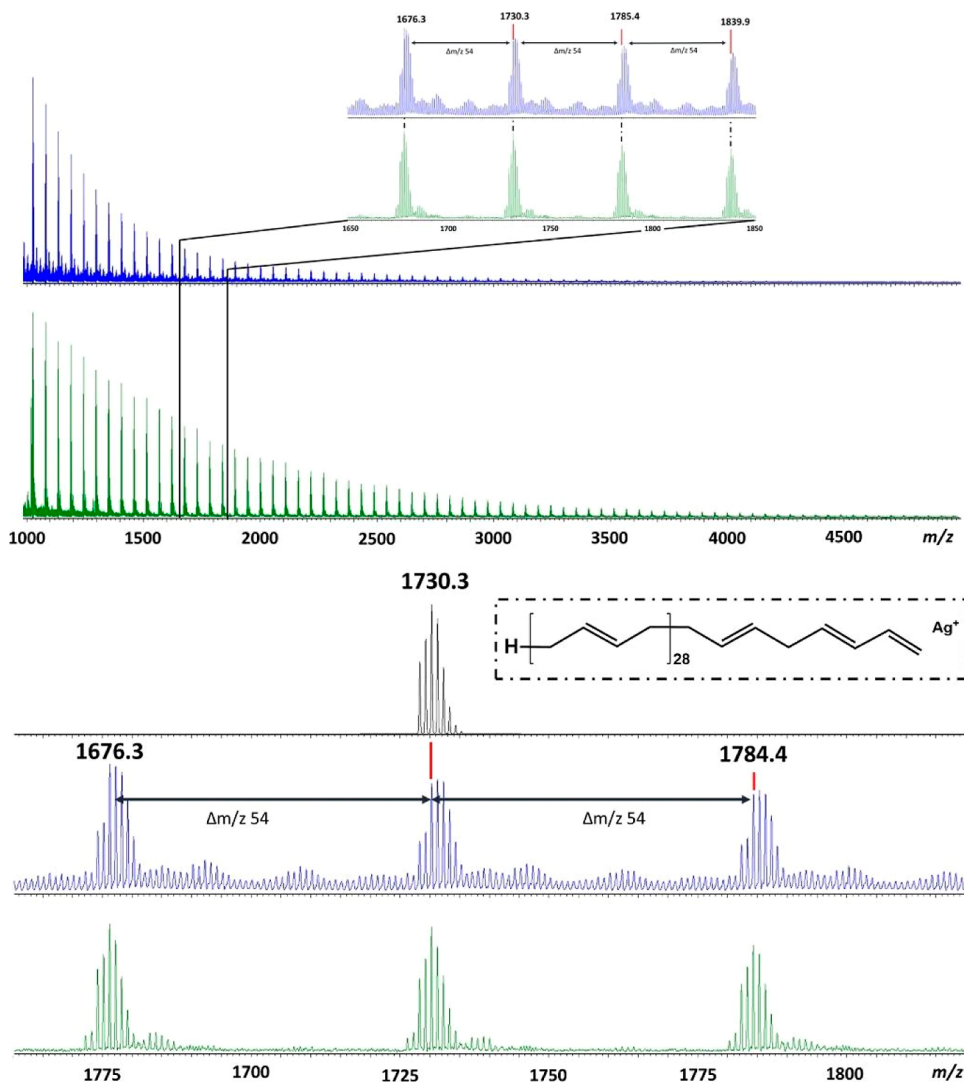


Figure 3. MALDI-ToF-MS of entries 1 in blue and 9 in green; amplification of the mass spectrum (blue) matches the prediction (black), corresponding to a polybutadiene with a diene chain end.

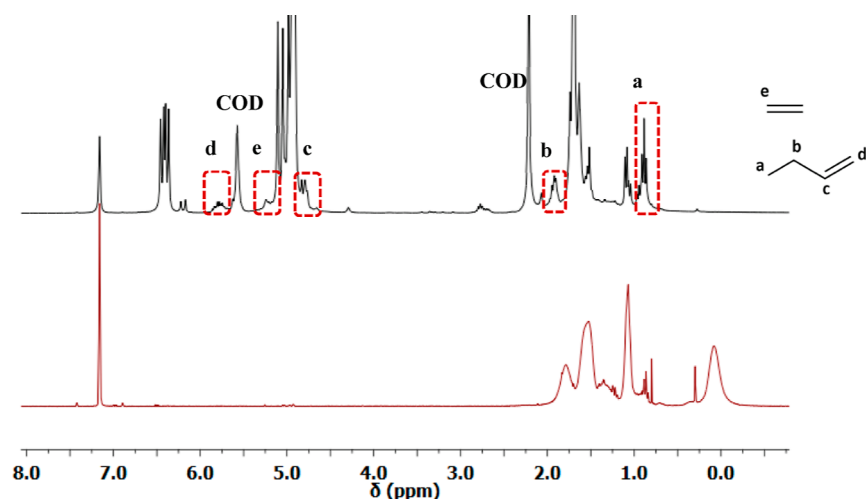


Figure 4. ^1H NMR spectra of Mg^nBuEt (bottom) and of a 1/10/1 Ni/isoprene/ Mg^nBuEt ratio in deuterated benzene after 48 h at room temperature (top).

Scheme 5. Proposed Mechanism of β -H Elimination of the Alkyl Chain, Where X = TFA

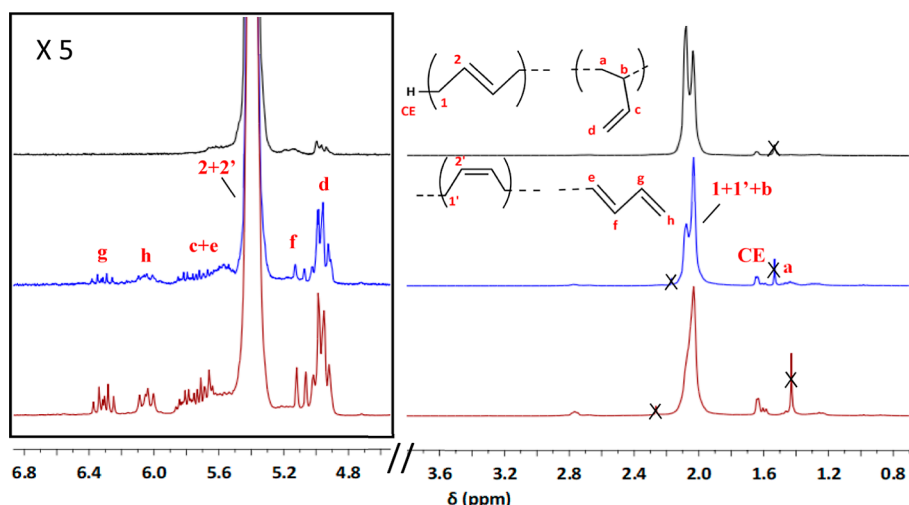
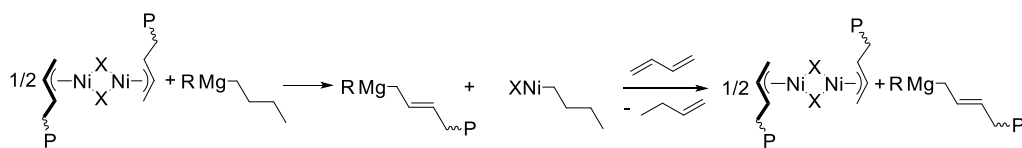


Figure 5. ^1H NMR spectra in CDCl_3 of polybutadiene obtained from $[(\eta^3\text{-C}_4\text{H}_7)\text{Ni}(\text{TFA})]_2$ (entry 1) in black, $[(\eta^3\text{-C}_4\text{H}_7)\text{Ni}(\text{TFA})]_2 + \text{Mg}^n\text{BuEt}$ (entry 17) in blue, and $[(\eta^3\text{-C}_4\text{H}_7)\text{Ni}(\text{TFA})]_2 + \text{Et}_3\text{Al}$ (quenched and isolated after 1 h of reaction) in dark red.

and is followed by a β -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 transmetalation reaction during the course of the polymerization.²⁸ Note that the reaction of allyltrifluoroacetate and nickel (COD)₂ is a well-established reaction that quantitatively leads to $[\eta^3\text{-}(\text{C}_3\text{H}_5)\text{Ni}(\text{TFA})]_2$.^{29,30} This procedure was used to avoid possible side reactions between the acid and the Grignard reagent due to a difference of reaction kinetics between butadiene and isoprene.

The MALDI ToF analysis (Figure 3) suggests that all polybutadiene chains have an additional unsaturation (m/z of

$n^*M_{\text{butadiene}} - 2 \text{ Da}$). The unsaturation is confirmed on the ^1H NMR spectra of low-molecular weight samples obtained at short reaction times that allow for the observation of chain ends. In particular, in the case of Ni(II)/CTA systems, the ^1H NMR spectrum shows a set of signals between 5.64 and 6.37 ppm that are attributed to a conjugated dienic structures (Figure 5). The NMR pattern, from the comparison of the spectra of 1,3 pentadiene with 2,4 hexadiene, as well as simulation on 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 ^1H NMR spectrum. The later signal has been attributed to the polymer chain end with 1,4-

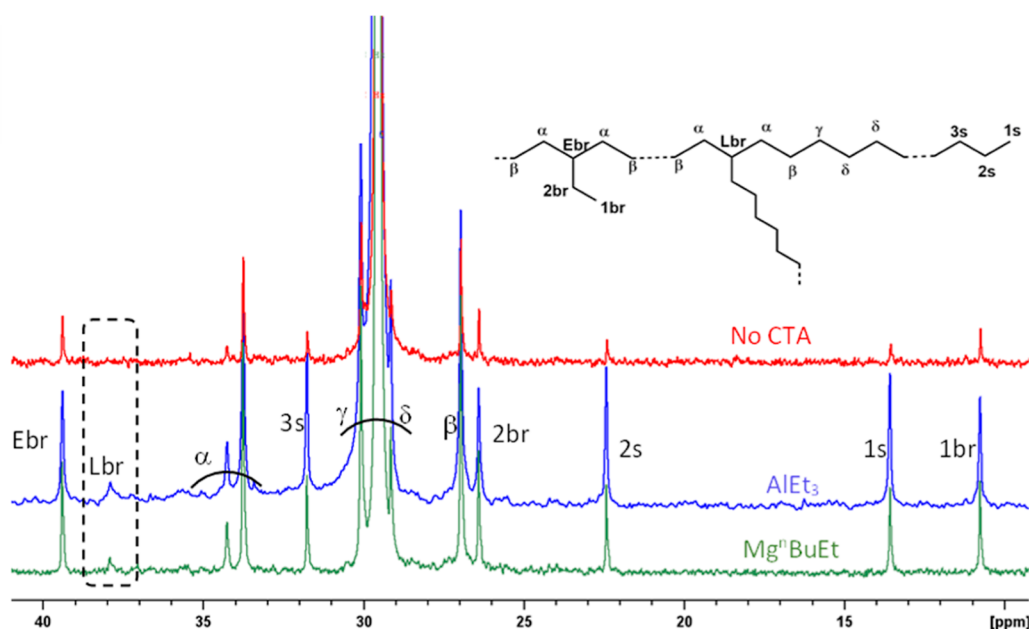


Figure 6. High-temperature ^{13}C NMR spectra of hydrogenated polybutadiene samples. Entry 1H in red (without a CTA), entry 12H in blue (AlEt_3 as the CTA), and entry 11H in green ($\text{Mg}^{\text{II}}\text{BuEt}$ as the CTA).

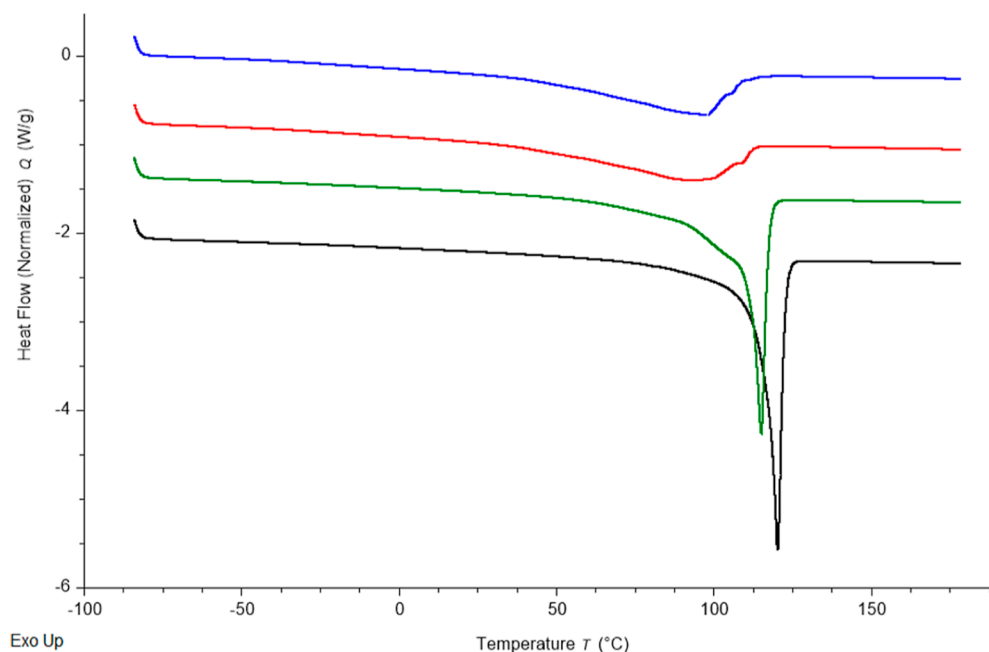


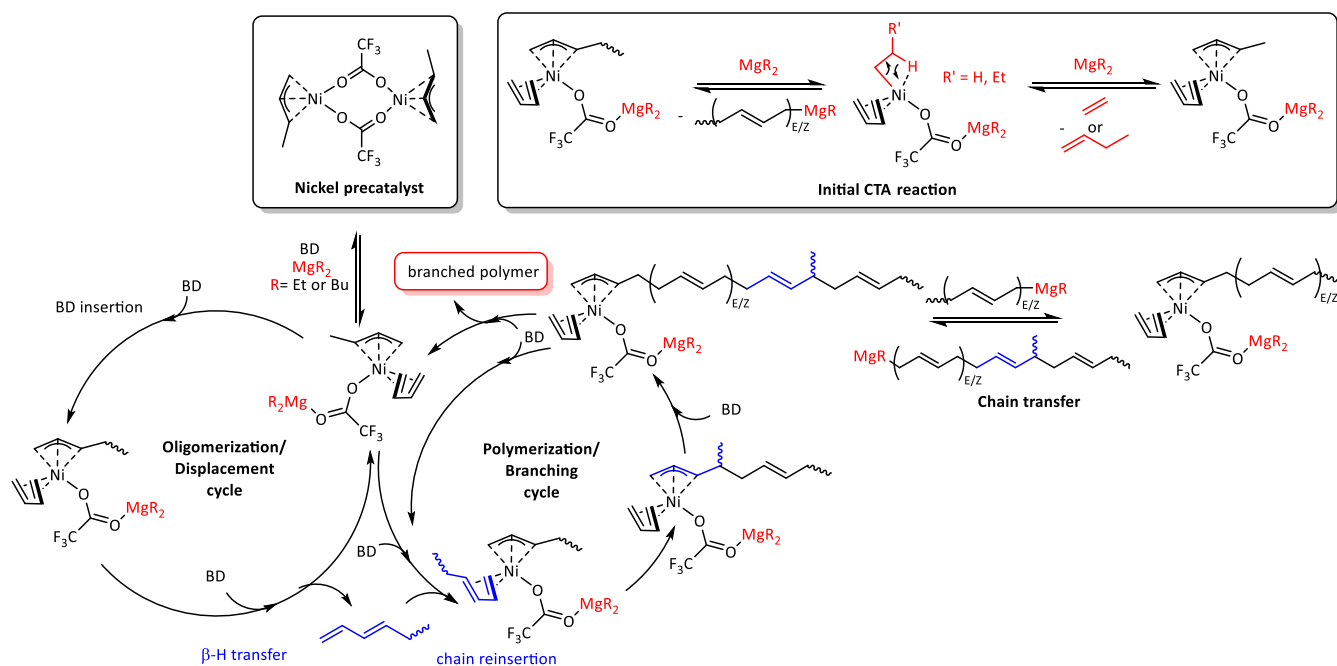
Figure 7. DSC results of the hydrogenated polybutadiene samples: entry 1H in black, entry 15H in green, entry 12H in red, and entry 11H in blue.

trans selectivity,³¹ which is favored for this Ni(II) catalytic system.

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 the Introduction section). The potential formation of branched polybutadiene therefore warrants further investigation. ^{13}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}C NMR analysis.²⁰ A high-temperature quantitative dept ^{13}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).²⁰ The LCB density per sample was determined using eq 1 by the peak areas of ethyl branch [EB, corresponding to a 1,2 regioselective insertion of butadiene, the only type of short chain branching (SCB) that can be seen here] or LCB per sample obtained from the high-temperature quantitative ^{13}C NMR, where a is

Scheme 6. Proposed Catalytic Polymerization Cycle Using the Catalyst Resulting from Ni(COD)₂ and Trifluoroacetic Acid in the Presence of MgⁿBuEt as Chain Transfer Agents



the peak area of the methine carbons in branch (EB + LCB), *b* the peak areas of the methylene carbons (α , β , γ , and δ) 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* with the methine carbon of EB.

LCB density per PE sample, adapted from ref 20

$$\frac{\text{LCB}}{1000\text{C}} = \frac{1000}{(a + b)} \times c \quad (1)$$

A 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 π -allyl Nickel(II) (TFA)/MgⁿBuEt or AlEt₃ 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.³² A sharp melting point (120 °C) was observed in the case of the linear polyethylene resulting from the hydrogenation of the polybutadiene obtained without a CTA. In samples obtained with the CTA, a shift of the melting temperature toward lower values was observed, along with the appearance of new melting temperatures. For samples where the density of LCB was so low that it could not be determined by NMR, such as entry 15H, signs of branching can still be observed by DSC, with, however, a less accentuated shift of the melting point.

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 of 3 (entries 11H–12H). 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 a 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 an π -allyl Nickel(II) (TFA) catalyst along with a CTA, which functions simultaneously as a CCTP and as a displacement catalyst. This is represented in Scheme 6.

By adding a CTA to the π -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 allows a change on the stereoselectivity and an increase in the reaction rate in the case of magnesium dialkyl. For this process, we propose a coordination of 1 equiv of the MgR₂ 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 β H transfer to the monomer, to the growth of additional chains. The polybutadienyl chains are terminated by a β H process leading to a conjugated diene. The resulting macro-monomer can be reinserted into a polybutadienyl growing chain, leading to a branched PBD.

CONCLUSIONS

We have assessed the polymerization of butadiene using π -allyl Nickel(II) (TFA) in combination with a Mg- and an Al-based CTA. Lower molecular weights are obtained, highlighting the occurrence of a chain transfer reaction. The initiation of the chain transfer occurs via β -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 the displacement catalysts. 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}C NMR after hydrogenation, which allows a quantitative determination of the LCB (for LCB >2/1000) and a qualitative analysis of the branching effect via the thermal signature of the samples.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.macromol.3c01385>.

Influence of catalyst and monomer concentrations (PDF)

AUTHOR INFORMATION

Corresponding Author

Philippe Zinck – University of Lille, CNRS, Centrale Lille, University of Artois, UMR 8181—UCCS—Unité de Catalyse et Chimie du Solide, Lille F-59000, France; orcid.org/0000-0003-2329-9116; Email: Philippe.zinck@univ-lille.fr

Authors

Catarina Bravo – University of Lille, CNRS, Centrale Lille, University of Artois, UMR 8181—UCCS—Unité de Catalyse et Chimie du Solide, Lille F-59000, France

Nicolas Merle – University of Lille, CNRS, Centrale Lille, University of Artois, UMR 8181—UCCS—Unité de Catalyse et Chimie du Solide, Lille F-59000, France; orcid.org/0000-0002-1448-8858

Mathieu Sauthier – University of Lille, CNRS, Centrale Lille, University of Artois, UMR 8181—UCCS—Unité de Catalyse et Chimie du Solide, Lille F-59000, France; orcid.org/0000-0001-7047-0532

Marc Bria – University of Lille, CNRS, INRA, Centrale Lille, ENSCL, University of Artois, FR 2638 IMEC—Institute Michel-Eugène Chevreul, Pôle RMN, Lille F-59000, France

Julien De Winter – Organic Synthesis and Mass Spectrometry Laboratory (S2MOs), University of Mons-UMONS, Mons 7000, Belgium; orcid.org/0000-0003-3429-5911

Complete contact information is available at: <https://pubs.acs.org/doi/10.1021/acs.macromol.3c01385>

Notes

The authors declare no competing financial interest.

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