

Polymerization

International Edition: DOI: 10.1002/anie.201909843
German Edition: DOI: 10.1002/ange.201909843

Coordinative Chain Transfer Polymerization of Butadiene with Functionalized Aluminum Reagents

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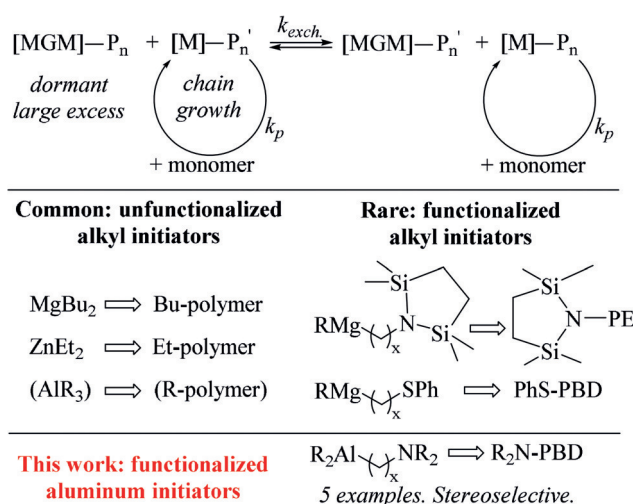
In memory of Hans-Herbert Brintzinger

Abstract: Functionalized aluminum alkyls enable effective coordinative chain transfer polymerization with selective chain initiation by the functionalized alkyl. (ω -Aminoalkyl)diisobutylaluminum reagents (12 examples studied) obtained by hydroalumination of α -amino- ω -enes with diisobutylaluminum hydride promote the stereoselective catalytic chain growth of butadiene on aluminum in the presence of Nd(versatate)₃, Cp*₂Nd(allyl), or Cp*₂Gd(allyl) precatalysts and [PhNMe₂H⁺]/[B(C₆F₅)₄⁻]. Carbazolyl- and indolylaluminum reagents result in efficient molecular weight control and chain initiation by the aminoalkyl rather than the isobutyl substituent bound to aluminum. As confirmed for (3-(9H-carbazol-9-yl)propyl)-initiated polybutadiene (PBD), for example, by deuterium quenching studies, polymer chain transfer by β -hydride transfer is negligible in comparison to back-transfer to aluminum.

Introduction

Coordinative chain transfer polymerization (CCTP) using main group metals has become an important strategy in insertion polymerization. This reversible chain transfer of polymeryl chains between chain-growth-active metal centers and chain-growth-inactive metal centers (Scheme 1) reduces the amount of polymerization catalyst required, controls the molecular weight and molecular weight distribution of polymers, and enables chain-end functionalization by appropriate quenching of the main group metal polymeryl species.^[1–10]

An obvious major potential of CCTP is chain-end functionalization by the main group metal initiator. This approach to functionalize the initiating chain end, however, has been hardly developed (Scheme 1). Most commonly, unfunctionalized commercial aluminum and zinc alkyl species have been used, with zinc alkyls performing much better in



Scheme 1. Concept and current status of coordinative chain transfer polymerization. MGM = main group metal, M = transition metal, PE = polyethylene, PBD = polybutadiene.

terms of transfer efficiency and thus molecular weight control. With respect to functionalized metal alkyls, which easily provide access to functional-group-initiated polymers, recently homoleptic di(ω -aminoalkyl) magnesiums have been used as chain transfer reagents (CTAs) to yield end functionalized amino polyethylenyl magnesiums.^[4b,8] Functionalized magnesium species were also used to initiate polybutadiene chain growth to end-functionalized high-*trans* polybutadiene,^[9] or with increased chain transfer numbers, to functionalized polybutadienes of less uniform stereochemistry.^[10]

For practical uses in catalytic polymerizations, the cost of zinc and magnesium alkyls and their synthesis by oxidative addition of alkyl halides are problematic if not prohibitive. Thus, industrial applications of main group metal alkyls in catalytic polymerization are restricted to aluminum alkyls exclusively.^[11]

However, functionalized aluminum reagents have scarcely been used both in organic synthesis and in polymer chemistry, as synthetically useful reactants for the transfer of functional-group-substituted carbon nucleophiles. Likely this is due to drawbacks in the synthesis of homoleptic aluminum alkyls or the expectedly low chemoselectivity of mixed aluminum alkyls.^[12,13] Herein, we report that functionalized and easily accessible mixed (ω -aminoalkyl)diisobutylaluminum reagents (**1b,c** and **1g-l**) promote coordinative chain transfer polymerizations of butadiene in the presence of neodymium and gadolinium complexes (**2–4**) and [PhNMe₂H⁺]/[B(C₆F₅)₄⁻] (**5**) with exemplary high transfer

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Supporting information and the ORCID identification number(s) for the author(s) of this article can be found under:
<https://doi.org/10.1002/anie.201909843>.

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efficiencies and chemoselective chain initiation by the amino-alkyl group.

Results and Discussion

(ω -Aminoalkyl)diisobutylaluminum reagents were obtained by hydroalumination of α -amino- ω -enes with diisobutylaluminum hydride (DIBAL-H) in the absence of any solvent, in C_6D_6 , toluene, or heptane solution at 298–343 K to give **1a–k** in high purity (ca 90–95% by 1H NMR analysis). Addition of $NdVs_3$ (**2**; Vs = versatate),^[14] $Cp^*_2Nd(allyl)$ ^[15] (**3**), or $Cp^*_2Gd(allyl)$ ^[16] (**4**; ORTEP plots shown in Figure 2) to the reaction mixture is beneficial in that the hydroalumination reaction is enhanced, and the resulting product mixtures may directly be used for butadiene polymerization upon activation with $[Ph_2NMe_2H^+][B(C_6F_5)_4^-]$ (**5**; Figure 1, Scheme 2, and Table 1). Hydroalumination of *N*-allyl-pyrrolidine to afford **1l** only proceeds under Nd or Gd catalysis of **2–4** (see the Supporting Information).

Initial butadiene (BD) polymerization experiments were conducted with the system $Cp^*_2Gd(allyl)$ (**4**; Figure 2)/**1c**/ $[Ph_2NMe_2H^+][B(C_6F_5)_4^-]$ (ANBCF, **5**)/BD as the $Cp^*_2Gd^+$ fragment may enable very high selectivity for 1,4-*cis* enchainment.^[17] In addition, the reported activation sequence of the

$Cp^*_2Gd^+$ fragment by triisobutylaluminum (TIBA) suggests that polymer chains may be initiated by aluminum-bound isobutyl groups. Finally, the carbazole substituent in **1c** is UV/Vis-active and fluorescent, and will result in UV/Vis-active polymers, if incorporated.

Upon addition of 5–30 equiv of **1c** to mixtures of **4**/**5**/BD (1:1.3:1000), increasing amounts of carbazolypropyl end groups were detected in the isolated polymers after polymerization at 323 K while M_n (from GPC) dropped from $148 \times 10^3 \text{ g mol}^{-1}$ (5 equiv **1c**) to $27 \times 10^3 \text{ g mol}^{-1}$ (30 equiv **1c**).

UV/Vis- and RI-detected GPC, DOSY, and most convincingly 1D TOCSY NMR experiments confirmed the connection of the carbazolypropyl group to the polymer backbone. However, the initiation and transfer efficiency of **1c** stays low, and only about 5% of all carbazolypropyl groups present in the reaction mixture were found in the isolated polymers. In contrast to this low transfer efficiency, the selectivity for chain initiation by the carbazolypropyl vs. *i*Bu group is remarkably high on the basis of a normalized 93:7 ratio of the respective NCH_2 and $CH_2CH(CH_3)_2$ signals in the 1H NMR spectra of the isolated polymers. In addition, *cis*- and *trans*- $CH_3-CH=CH$ groups were also identified to initiate polymer chains, while *cis*- and *trans*- $CH_3-CH=CH$ as well as unusual $R_2CH-CH(CH=CH_2)CH_3$ groups (formed by 1,2-insertion of BD into the 3-position of the last 1,4-inserted BD unit and protolysis) were identified as terminating groups of polymer chains (Scheme 2A–E; see also Supporting Information).^[18]

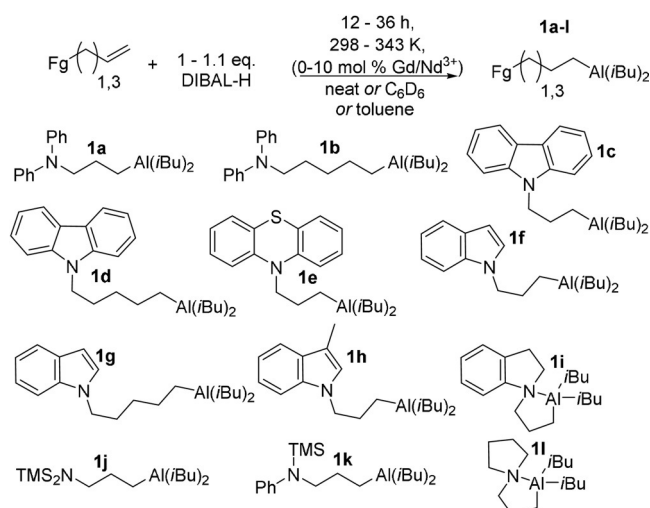


Figure 1. Functionalized aluminum alkyls **1a–l** obtained by hydroalumination of terminal olefins with DIBAL-H (see the Supporting Information for synthetic procedures).

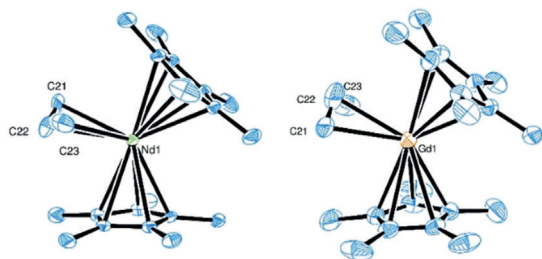
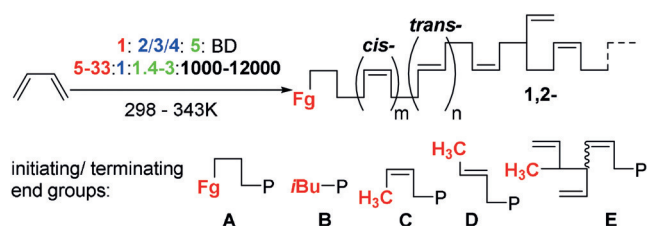


Figure 2. X-ray diffraction analysis of complexes **3** and **4** with 50% probability ellipsoids.^[19]



Scheme 2. Polymerization of butadiene initiated by **1a–m**, $NdVs_3$ (**2**), $Cp^*_2Nd(allyl)$ (**3**), or $Cp^*_2Gd(allyl)$ (**4**), and $[Ph_2NMe_2H^+][B(C_6F_5)_4^-]$ (**5**) yielding functional group (Fg)-initiated polybutadiene.

The latter $R_2CH-CH(CH=CH_2)CH_3$ groups were also found in control experiments conducted with DIBAL-H or TIBA in combination with protonating **5**. Based on this end-group analysis, NMR molecular weights indicate that the number of polymer chains stays in the range of 0.25 (5 equiv **1c**) to 2 (30 equiv **1c**) per gadolinium, which is not in accordance with an effective CCTP. Similar results were obtained by use of the neodymium complex **3**, but with markedly decreased selectivities for 1,4-*cis* enchainment of butadiene (see the Supporting Information).

Much more efficient chain transfer behavior and effective CCTP was observed when neodymium versatate (**2**) was combined with **1c**, **5**, and BD. Thus, carbazolypropyl-initiated PBD with DP_n values closely resembling the Al/BD (10–30:1000) rather than the Nd/BD (1:1000) ratios were obtained after 2 h reaction time at 343 K (Table 1, entries 3–6, Table 2, entries 10 and 11, and Figure 3), while the incorpo-

Table 1: Polymerization of butadiene (BD) by NdVs₃ (**2**)/FgAl(*i*Bu)₂ (**1a–h**)/ANBCF (**5**).^[a]

Entry	FgAl(<i>i</i> Bu) ₂ ^[b]	Nd/ANBCF/Al/BD ^[c]	Conditions	M _n (GPC) ^[d] [× 10 ⁻³ g mol ⁻¹]	Đ ^[d]	M _n (NMR) ^[e] [× 10 ⁻³ g mol ⁻¹]	DP _n ^[e] (NMR)	incorp. Fg ^[f] [%]/ (Fg Nd ⁻¹)	cis/trans/1,2 [%] ^[g]
1	1a	1:1.5:20:1000	16 h, 328 K	37	2.5	20.7	383	1.5/(0.3)	88.5:10.5:1
2	1b	1:1.4:20:1000	2 h, 343 K	21.5	1.8	15.4	282	15.6/(3.1)	70.5:28.5:1
3	1c	1:1.4:10:1000	2 h, 343 K	15	1.7	7.3	131	71/(7.1)	74:24:2
4	1c	1:1.4:20:1000	2 h, 343 K	7	1.7	3.5	61	76/(15.3)	70:28:2
5 ^[h]	1c	1:2.5:20:1000	12 h, 328 K	7.4	1.6	3.8	67	73/(14.5)	79:20:2
6	1c	1:1.4:30:1000	2 h, 343 K	3.9	1.8	2.5	42	74/(22.3)	70.5:28.5:1
7	1d	1:1.4:20:1000	16 h, 328 K	23	1.8	9.1	164	28/(5.6)	75.5:23:1.5
8	1e	1:2.5:20:1000	2 h, 343 K	53	1.9	29	533	2.2/(0.4)	81:15.5:3.5
9	1f	1:2.5:10:1000	2 h, 343 K	26	2.5	13.2	242	36/(3.6)	77:22:1
10	1f	1:2.5:20:1000	2 h, 343 K	15.5	2.1	8.5	154	27/(5.3)	69:29.5:1.5
11	1f	1:2.5:30:1000	2 h, 343 K	9.8	1.9	5.1	106	24/(7.3)	53:45.5:1.5
12	1g	1:2.5:20:1000	2 h, 343 K	n.d.	n.d.	13.7	250	16/(3.2)	74:25:1
13	1h	1:2.5:20:1000	2 h, 343 K	31	2.5	12.3	224	20/(4)	79:20:1
14	TIBA	1:1.5:33:1000	2 h, 343 K	127	3.6	89	1640	n.a.	79:20:1
15	TIBA	1:1.5:23:1000	2 h, 343 K	153	3.8	38.5	715	n.a.	79.5:19:1.5
16	DIBAL-H	1:1.5:21:4000	40 h, 298 K	29	2.5	20.3	377	n.a.	93.4:6.5:0.6

[a] All reactions conducted with 2.2 M BD solution in benzene-*d*₆ or toluene in 12 mL screw-cap vials until full BD consumption. Polymers were isolated in quantitative yield by precipitation, redissolution, and reprecipitation. [b] (Functional) aluminum reagent. [c] Ratio of NdVs₃/[Ph₂NMe₂H⁺][B(C₆F₅)₄]/FgAl(*i*Bu)₂/BD. [d] Refractive index detected GPC in THF solution at 298 K vs. linear polystyrene standards. [e] Based on initiating amino-functionalized, isobutyl, and CH₃CH=CH groups. [f] Percentage of amino functionalities found in the polymer from starting amino functionalities in the aluminum reagent/number of amino-functionalized polymer chains per neodymium (= number of functionalized chain transfers). [g] Determined by inverse-gated ¹³C NMR experiments. [h] Polymerization quenched by addition of 1 mmol CD₃OD before isolation.

Table 2: Polymerization of BD by **2/1c/5** yielding high 1,4-*cis* enchainment or high functionalized chain transfer.^[a]

Entry	Nd/ANBCF/Al/BD ^[b]	Conditions	M _n (GPC) ^[c] [× 10 ⁻³ g mol ⁻¹]	Đ ^[d]	M _n (NMR) ^[e] [× 10 ⁻³ g mol ⁻¹]	DP _n ^[e] (NMR)	Incorp. Fg ^[f] [%]/ (Fg Nd ⁻¹)	cis/trans/1,2 ^[g] [%]
1	1:1.5:20:2000	13 h 318 K	13.7	1.5	6.3	113	85/(17.1)	89:10:1
2	1:1.5:20:2000	1 h 298 K, 12 h 318 K	11.4	1.8	5.8	103	93.7/(18.7)	88:11:1
3	1:1.5:20:3000	40 h, 298 K	18.6	1.5	8.8	160	91.6/(18.3)	94.5:4.5:1
4	1:1.5:20:4000	13 h, 318 K	21	1.9	11.9	216	88.8/(17.8)	92:7:1
5	1:1.4:30:6000	60 h, 298 K	32	1.9	12.5	227	84.7/(25.4)	95:4:1
6	1:1.5:10:2000	40 h, 298 K	42	3.3	12.6	230	84.6/(16.7)	93/6/1
7	1:1.5:20:4000	40 h, 298 K	28	1.7	12.2	223	89.6/(17.9)	95.5:3.5:1
8	1:1.5:20:5000	60 h, 298 K	32	1.7	14.3	261	96/(19)	95.5:3.5:1
9	1:1.4:30:20000 ^[h]	60 h, 318 K	86.8	3.1	37.6	692	89/(26.5)	91.5:7:1.5
10	1:1.5:80:6000	40 h, 328 K	2.6	1.7	3.5	61	94/(75)	84.5:13.5:2
11	1:1.5:120:3000	40 h, 343 K	2.5	1.6	1.8	29	77.5/(93)	65.5:33:1.5

[a] All reactions conducted with 2.2 M BD solution in benzene-*d*₆ or toluene in 12 mL screw-cap vials. Polymers were isolated in quantitative yield by precipitation after quenching with CD₃OD, redissolution, and reprecipitation. [b] Ratio of NdVs₃/5/**1c**/BD. [c,d] Refractive index GPC in THF solution at 298 K vs. linear polystyrene standards. [e] Based on initiating propylcarbazole-functionalized and *i*Bu groups. [f] Percentage of propylcarbazole groups found in the polymer vs. starting propylcarbazole in **1c**/number of propylcarbazole-initiated polymer chains per Nd (= number of functionalized chain transfers). [g] Determined by inverse-gated ¹³C NMR experiments. [h] The reaction was started with an Al/BD ratio of 30:3000; the remaining BD was added after 20 h.

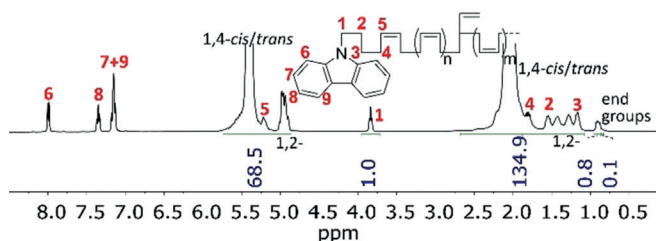


Figure 3. ¹H NMR spectrum of 3-(9H-carbazol-9-yl)propyl-initiated polybutadiene terminated by CD₃OD. **1c**/BD/Nd/5 = 20:1000:1:2.5, DP_n = 67 (based on incorporated carbazole + *i*Bu groups), 15 carbazole-initiated chains per Nd, 73% carbazole incorporated into the polymer; see Table 1, entry 5.

ration of carbazolypropyl groups into the polymer reaches 70–76%, and only ca 5–8% of all chains are initiated by *i*Bu groups (see the Supporting Information). These high incorporations and the observed M_n values translate into up to 22 carbazole-initiated PBD chains per neodymium (Table 1, entry 6). Notably, under otherwise identical conditions, TIBA hardly acts as a chain transfer agent (CTA) as the DP_n values resemble the Nd/BD rather than the Al/BD ratio (Table 1, entries 14 and 15). In contrast, DIBAL-H acts as a CTA similar to **1c** (Table 1, entry 16; see also Supporting Information).

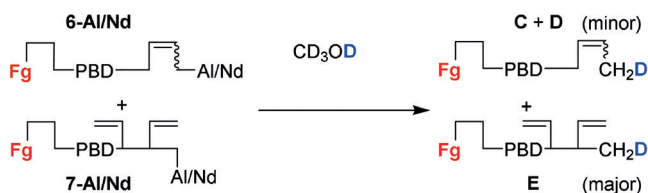
Encouraged by these results, a range of (ω-aminoalkyl)-diisobutylaluminum reagents (**1a–l**) were probed as CTAs in the BD polymerization by **2/5**. While **1a** and **1e** poorly

promote CCTP (Table 1, entries 1 and 8), **1b** and **1d–h** result in reasonably high functional group incorporation and functionalized chain transfer numbers per neodymium (Table 1, entries 2, 7, and 9–13). However, **1i–l** neither transferred their aminoalkyl groups to the formed PBD nor did they control the molecular weight of the obtained polybutadienes (see the Supporting Information).

With respect to the stereo- and regiochemistry of butadiene enchainment (Table 1, last column) the highest 1,4-*cis* selectivity was observed for the poorest CTAs **1a** and **1e**. While 1,2-enchainment is consistently low in the range of 1–2%, the 1,4-*cis* selectivity drops down to 53% for **1f** at its highest investigated concentration (Table 1, entry 11). However, as exemplified for **1c**, significant improvement with a selectivity for 1,4-*cis* enchainment of BD of 90–95% is feasible by lowering the reaction temperature (Table 2, entries 3–9).

The high efficiency of the CCTP of BD, particularly with **1c/2/5**, implies that a substantial share of all polymer chains is bound to aluminum during the polymerization reaction. Consequently, quenching of these polymerizations with CD₃OD led to the identification of isobutane-*d*₁, traces of *N*-propylcarbazole-*d*₀, as well as traces of *N*-propylcarbazole-*d*₁. The occurrence of *N*-propylcarbazole-*d*₀ is based on the protonation of **1c** by **5** during the initial catalyst activation. In contrast, *N*-propylcarbazole-*d*₁ is formed by deuterolysis of the carbazolypropyl aluminum moieties still present in the reaction mixture (maximum of 5% vs. initial **1c**).

In addition to isobutane-*d*₁ and *N*-propylcarbazole-*d*₁, deuterium incorporation was found with very high selectivity in the terminating R₂CH-CH(CH=CH₂)CH₂D group (**E-d**₁) of the formed polybutadiene as evidenced by comparative ¹H/²H NMR analysis as well as by phase-sensitive gHSQC experiments of isolated polymers (Scheme 3).



Scheme 3. Quenching of aluminum (and neodymium) polymeryls by deuterolysis with CD₃OD.

Based on the ¹H and gHSQC experiments, the deuteration can reach very high levels (exclusive detection of the CH₂D vs. CH₃ group in **E**). In addition, ²H NMR analysis indicates that **6-Al** is also present prior to deuterolysis, but the ratio of **E-d**₁/(**C-d**₁ + **D-d**₁) is >10:1. These results indicate that a R₂CH-CH(-CH=CH₂)CH₂-AlR₂ species (**7-Al**) is the prominent dormant species in the CCTP of BD with **1c/2/5**.^[18] A detailed NMR-spectroscopic characterization of **7-Al** prior to deuterolysis includes the detection of diastereotopic methylene protons of R₂CH-CH(-CH=CH₂)CH₂-AlR₂ by gHSQC and the proximity of this CH₂-Al group to methine and olefinic groups as confirmed by gHSQC-TOCSY experiments (see the Supporting Information).

Conclusion

In summary, easily accessible (ω -aminoalkyl)diisobutyl-aluminum reagents transfer their ω -aminoalkyl moiety with high chemoselectivity to neodymium and gadolinium complexes to initiate butadiene polymerizations in the presence of [PhNMe₂H⁺]/[B(C₆F₅)₄⁻]. As shown for UV/Vis-active and fluorescent propylcarbazole-initiated polybutadiene, up to 90% of all aluminum-bound carbazole groups initiate polymer chains in an effective CCTP while retaining a high (90–95%) 1,4-*cis* enchainment of butadiene. At very high Al/Nd ratios (>80:1), molecular weight control and the level of functional chain initiation is still very high, while the high levels of 1,4-*cis* enchainment of butadiene drop at the expense of 1,4-*trans* enchainment. As shown by deuterium quenching experiments and characterization of aluminum polymeryl species, the prominent dormant species R₂CH-CH(-CH=CH₂)CH₂-AlR₂ (**7-Al**) is formed after an unusual chain growth event. To our knowledge, this is the first example of a CCTP providing amino-initiated polymers based on aluminum reagents. Our findings underline the potential in polymerization and organic synthesis of functionalized aluminum alkyl reagents, which are attractive compared to other main group alkyl species because of their low cost and synthetic accessibility.

Acknowledgements

We gratefully acknowledge funding by the Goodyear Tire & Rubber Company. We thank Maggie Flook Vielhaber, Karen Burke, and Stefan Rodewald for stimulating discussions.

Conflict of interest

The authors declare no conflict of interest.

Keywords: aluminum · chain transfer polymerization · chain transfer reagents · neodymium · polybutadiene

How to cite: *Angew. Chem. Int. Ed.* **2019**, *58*, 17777–17781
Angew. Chem. **2019**, *131*, 17941–17945

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Manuscript received: August 3, 2019

Revised manuscript received: September 17, 2019

Accepted manuscript online: September 30, 2019

Version of record online: October 24, 2019