Supplementary Information (SI) for Polymer Chemistry.

# Supporting Information

## Association of Zn- and Mg-based Chain Transfer Agents in Coordinative Chain Transfer Polymerizations of Olefins for Enhanced Control and Activity

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## General experimental information

All operations or sensitive chemicals were performed or used under a dry argon atmosphere, in a glovebox or using Schlenk techniques. Toluene used as solvents for the polymerization was purified on a SPS800 MBraun system. BOMAG (20% in heptane, Chemtura), *n*-BuMgCl (2 M in $Et_2O$, Sigma-Aldrich), MesMgBr (1M in $Et_2O$, Sigma-Aldrich), $ZnEt_2$ (1 M in hexanes, Sigma-Aldrich), 4- *p*-toluoyl chloride (Sigma-Aldrich), 4-dimethylaminobenzoyl chloride (Sigma-Aldrich) were purchased and used as received. Deuterated solvents were purchased from Eurisotop. The bis(fluorenyl) neodymium complex **1** and $(C_5Me_5)_2NdCl_2Li(OEt)_2$ were synthesized according to the literature. 1,3-Butadiene (B) and ethylene (E) were supplied by Michelin and Air Liquide, respectively.

### $^1$H NMR investigation of a mixture of BOMAG and $ZnEt_2$

*The preparation were performed inside a glovebox.*

*$^1$H NMR of $ZnEt_2$*. A solution of $ZnEt_2$ (15wt% in toluene, Sigma Aldrich) was added in 0.6 mL of dry toluene-d8

*$^1$H NMR of BOMAG*. 1.5 mL of a solution of BOMAG in heptane was dried under vacuum during 4 hour. The product was solubilized in 3 mL of toluene-d8. 0.1 mL of this solution was diluted in 0.5 mL of dried toluene-d8.

*$^1$H NMR of a mixture of BOMAG and $ZnEt_2$*. In the NMR tube containing the BOMAG solution, 0.05 mL of the $ZnEt_2$ solution in toluene ((15wt% in toluene, Sigma Aldrich) was added (Zn/Mg = 1.25).

### ***Typical polymerization procedure***

*Ethylene polymerization*. Polymerizations were performed in a 250 mL glass reactor, equipped with a stainless-steel blade. The reactor is first inerted via three vacuum/argon cycles at 80°C. The complex **1** was mixed with the magnesium compound in 5 mL of toluene. The solution was then transferred in a flask containing $ZnEt_2$ in toluene (total volume 200 mL). The mixture was transferred into the reactor under a stream of argon. Argon was then pumped out, and the reactor was fed with ethylene. The pressure was then gradually increased to 4 bar at the same time as the desired temperature was reached. The pressure was maintained constant during the polymerization. Ethylene consumption was measured by pressure drop in the reservoir. When the targeted consumption of ethylene was achieved, the reactor was degassed and a few mL of methanol was added to quench the polymerization medium. In the case of the functionalization of polymer chains with acyl chloride, after degassing the reactor, an aliquot of approximately 10 mL was withdrawn by cannula into a vessel containing 2 mL of methanol. The acyl chloride compound was then introduced into the reactor under argon. The reaction medium was stirred during 45 min at 80°C before the addition of methanol. The polymer was precipitated in 600 mL of HCl/methanol solution (1 L of methanol for 10 mL of a solution of HCl in water). The polymer was filtrated, washed with methanol and dried under vacuum at 80°C for 4h.

*Copolymerization of ethylene and butadiene*. Polymerizations were performed in a 250 mL glass reactor, equipped with a stainless-steel blade. The reactor is first inerted via three vacuum/argon cycles at 80°C. The complex **1** was mixed with the magnesium compound in 5 mL of toluene. The solution was then transferred in a flask containing $ZnEt_2$ in toluene (total volume 200 mL). The mixture was transferred into the reactor under a stream of argon. Argon was then pumped out, and the reactor was fed with ethylene/butadiene mixture (80/20). The pressure was then gradually increased to 4 bar at the same time as the desired temperature was reached. The pressure was maintained constant during the polymerization. Monomer consumption was measured by pressure drop in the reservoir. When the targeted consumption of monomers was achieved, the reactor was degassed and a few mL of methanol was added to quench the polymerization medium. In the case of the functionalization of polymer chains with acyl chloride, after degassing the reactor, an aliquot of approximately 10 mL was withdrawn by cannula into a vessel containing 2 mL of methanol. The acyl chloride compound was then introduced into the reactor under argon. The reaction medium was stirred during 1 hour at 80°C before the addition of methanol. The polymer was precipitated in 600 mL of HCl/methanol solution (1 L of methanol for 10 mL of a solution of HCl in water). The solvent was eliminated and the polymer was washed with methanol. The polymer was then recovered and dried under vacuum at 70°C for 6h.

## Characterization Techniques

### *Nuclear magnetic resonance (NMR)*

NMR spectra of metallic complexes were obtained at 295K with a Bruker AV 300 spectrometer equipped with BBFO-BBF probe. Chemical shift $\delta$ values are given in parts per million (ppm) using the signal at 2.08 ppm of residual proton of toluene-d8.

High-resolution NMR spectroscopy of polymers was performed on a Bruker 400 Avance III spectrometer equipped with a 5 mm BBFO probe for $^1$H NMR. The NMR analysis of PE were carried out at 363 K in in a mixture of tetrachloroethylene (TCE) and deuterated benzene (2/1 v/v) and at 298 K in $CDCl_3$ for copolymers with a concentration of 17 mg mL$^{-1}$. Chemical shift $\delta$ values are given in parts per million (ppm) using the signal at 7.16 ppm for benzene and at 7.26 ppm for chloroform as internal standard for $^1$H NMR and that of $CH_2$ of ethylene units at 30 ppm for $^{13}$C NMR.

Determination of functionalization yield by $^1$H NMR:

In the case of PE-C(O)$C_6H_4$Me, the integral of characteristic signals provides the number of vinyl, methyl and functional chain-ends. The total number of chain-ends are normalized to 2.

In the case of functionalization obtained using $(C_5Me_5)_2NdCl_2Li(OEt)_2$/BOMAG catalyst, the number of $\omega$ chain-ends are determined using the characteristics signals of vinyl, methyl, secondary alcohol and tertiary alcohol extremities (figure S3).

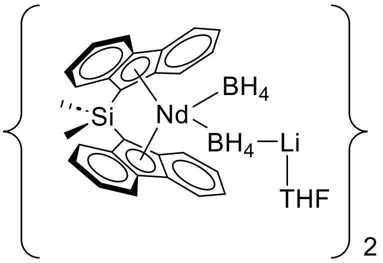
In the case of EBR-C(O)$C_6H_4(NMe_2)$, $M_n^{NMR}$ is determined considering the number of monomer units for a quantitative functionalization, which corresponds to an integral of $NMe_2$ group of 6 (Figure S4).

### *High-temperature size exclusion chromatography (HT-SEC)*

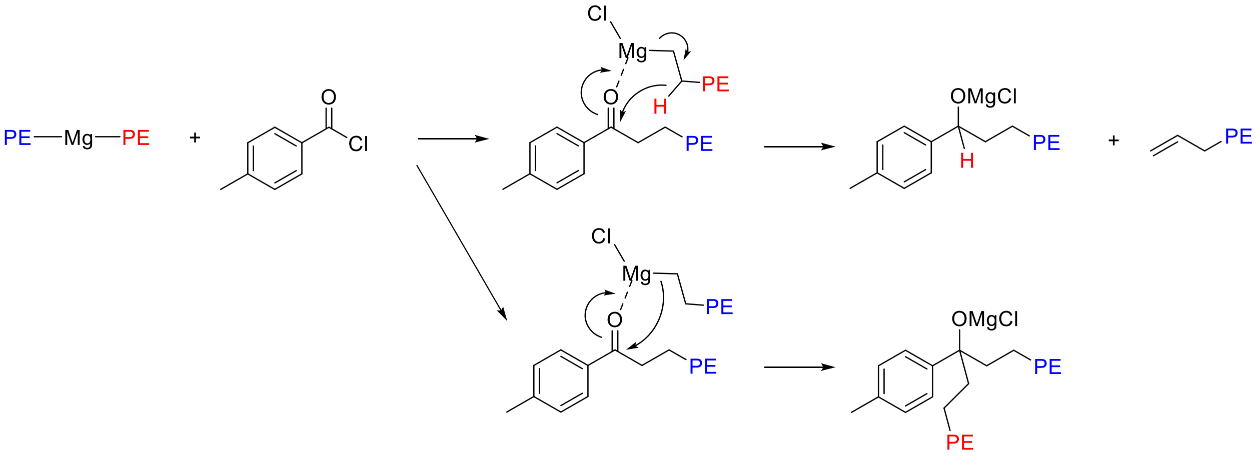
Molar mass measurements were performed using a Viscotek High-Temperature Triple Detection SEC (HT-SC) system (Malvern Instruments) that incorporates a differential refractive index, a viscometer, and a light scattering detector. 1,2,4-Trichlorobenzene (TCB) was used as the mobile phase at a flow rate of 1 mL min$^{-1}$. TCB was stabilized with 2,6-di(*tert*-butyl)-4-methylphenol (400 mg mL$^{-1}$). The separation was carried out on three mixed bed columns (PLgel Olexis 300 × 7.8 mm I.D. from Agilent Technologies) and a guard column (75 × 7.5 mm). Columns and detectors were maintained at 150°C. Sample volumes of 200 µL with concentrations of 5 mg mL$^{-1}$. The Omnisec software (version 5.12) was used for data acquisition and data analysis. A conventional calibration curve constructed with narrow polyethylene standards (Mp: 338 to 78 400 g mol$^{-1}$) from Polymer Standards Service (Mainz, Germany) was used to calculate average molar masses of polyethylenes.

### *Size exclusion chromatography using THF as eluent (SEC-THF)*

Measurements were performed with a Viscotek TDAmax system from Malvern Instruments that consists of a sample delivery module (GPCmax) including a four-capillary differential viscometer and a differential refractive index detector (RI). The separation was carried out on a guard column and three columns (SDVB, Mixed C, 5 µm, 300 × 7.5 mm I.D. from Agilent Technologies) THF was used as the mobile phase at a flowrate of 1 mL min$^{-1}$. Samples were dissolved in THF with a concentration of 3 mg mL$^{-1}$ and filtered on a PTFE membrane (0.45 µm). 100 µL of sample solutions were injected and eluted at a flow rate of 1 mL $\text{min}^{-1}$. Columns and detectors were maintained at 35 °C. The OmniSEC 5.12 software was used for data acquisition and data processing. A universal calibration curve constructed with narrow polystyrene standards (Mp: 1 306 to 2 520 000 g $\text{mol}^{-1}$) from Polymer Standards Service (Mainz, Germany) was used to calculate average molar masses.



**Scheme S1**. Structure of the bis(fluorenyl) neodymium metallocene complex (**1**).



**Scheme S2**. Reaction mechanism of the reaction between $MgPE_2$ and p-toluoyl chloride.

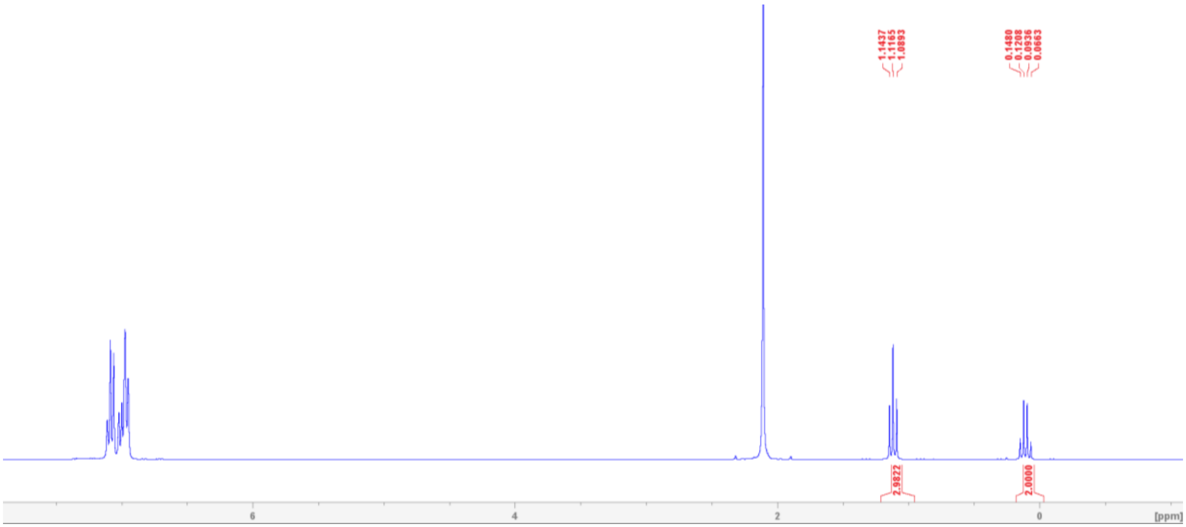


**Figure S1.** $^1$H NMR spectrum of $ZnEt_2$ in toluene-d8 at 295K.

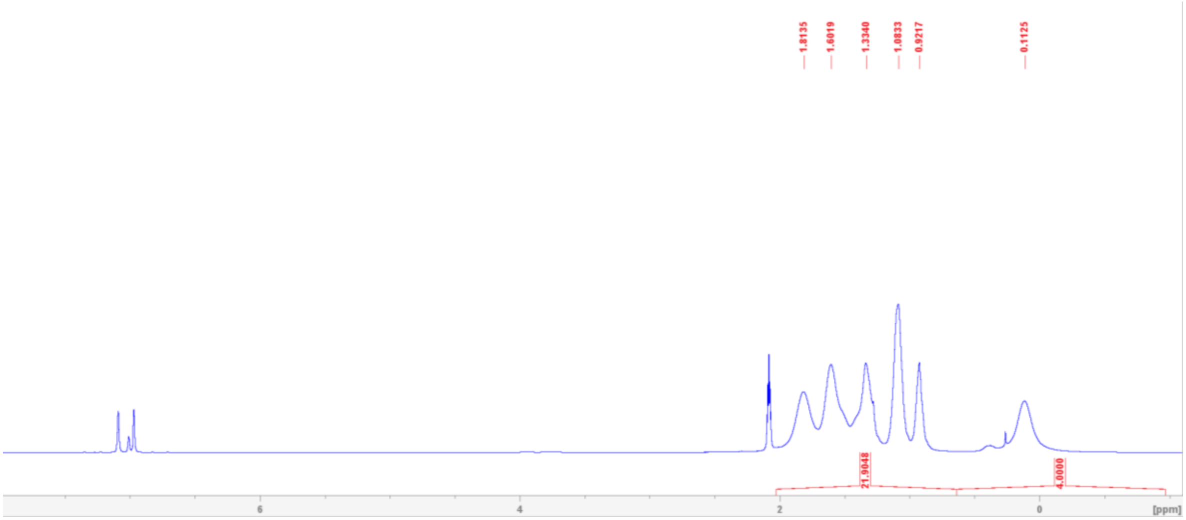


**Figure S2.** $^1$H NMR spectrum of BOMAG in toluene-d8 at 295K.

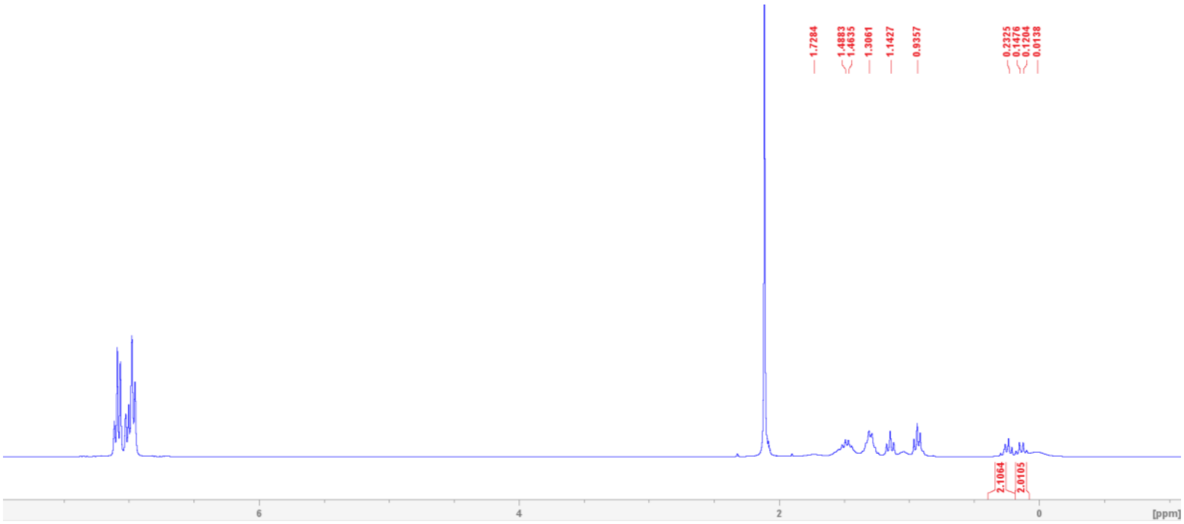


**Figure S3.** $^1H$ NMR spectrum of a mixture of BOMAG and $ZnEt_2$ in toluene-d8 at 295K.

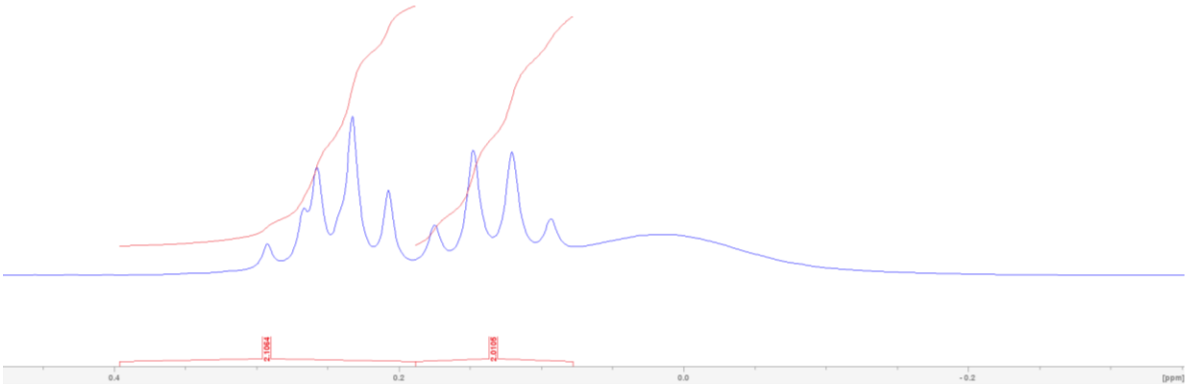


**Figure S4.** Enlargement between -0.3 and 0.4 ppm of the spectrum of a mixture of BOMAG and $ZnEt_2$ in toluene-d8 at 295K.

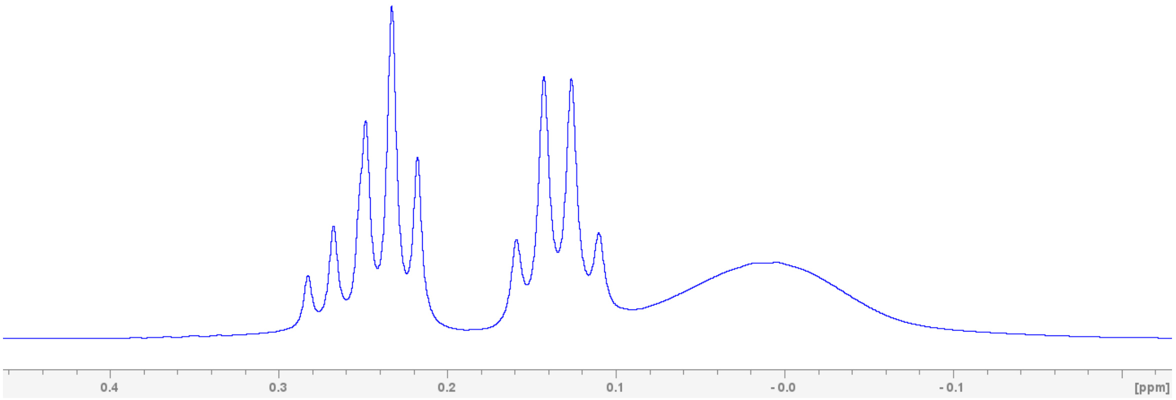


**Figure S5.** Enlargement between -0.2 and 0.4 ppm of the spectrum of a mixture of BOMAG and $ZnEt_2$ in toluene-d8 at 298K (Bruker AV 500 spectrometer).

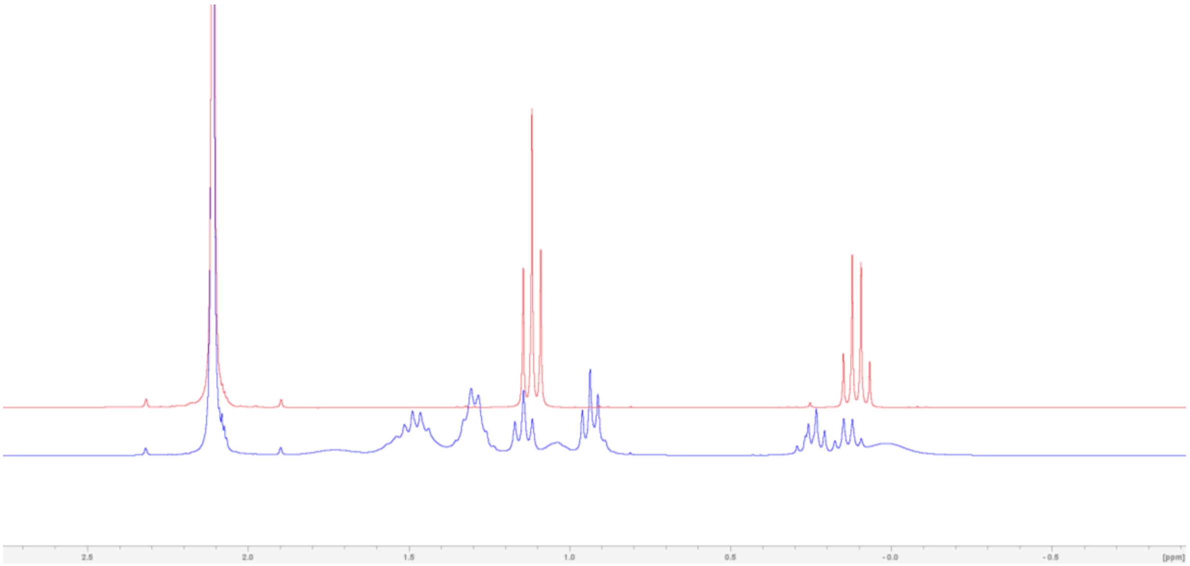


**Figure S6.** Superimposition of the spectra of $ZnEt_2$ (red) and of $ZnEt_2$ / BOMAG mixture (blue).

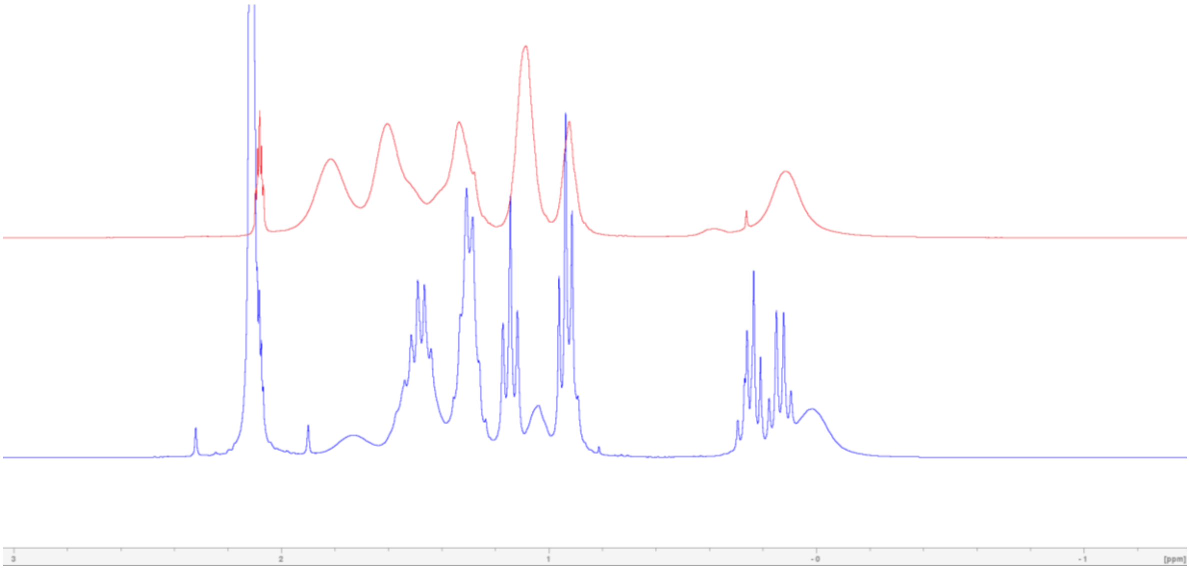


**Figure S7.** Superimposition of the spectra of BOMAG (red) and of $ZnEt_2$ / BOMAG mixture (blue).

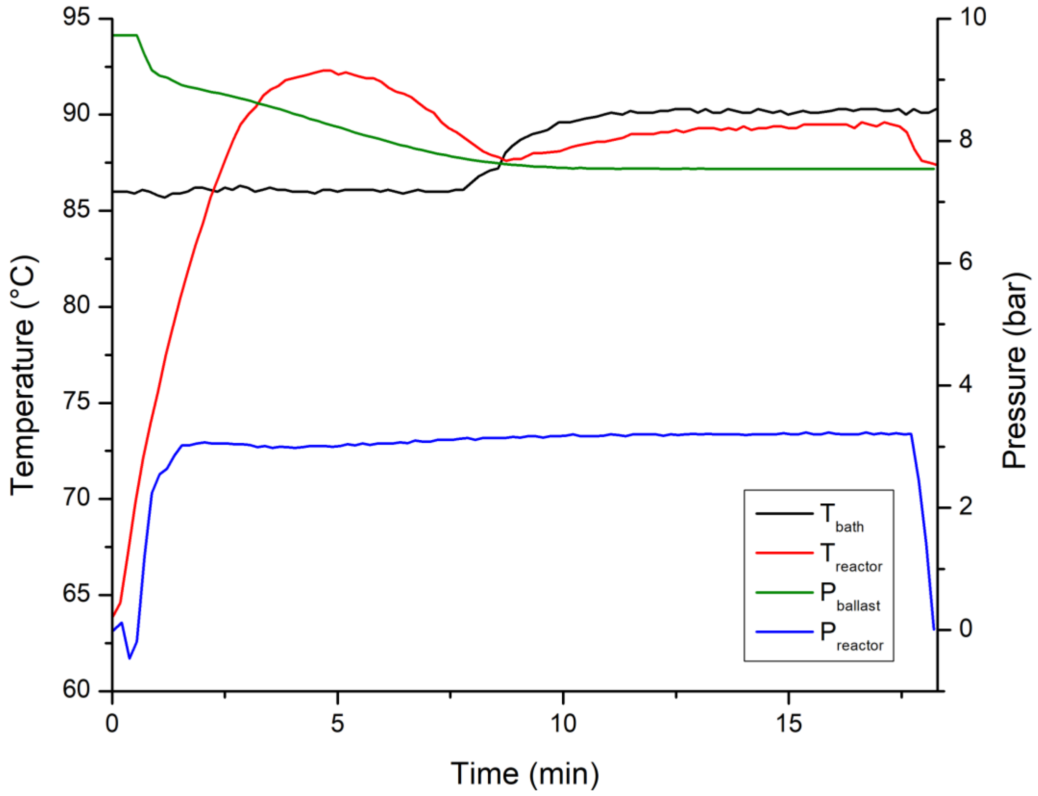


**Figure S8**. Changes in temperature and pressure in the monomer reservoir and the reactor during polymerization (run 9).

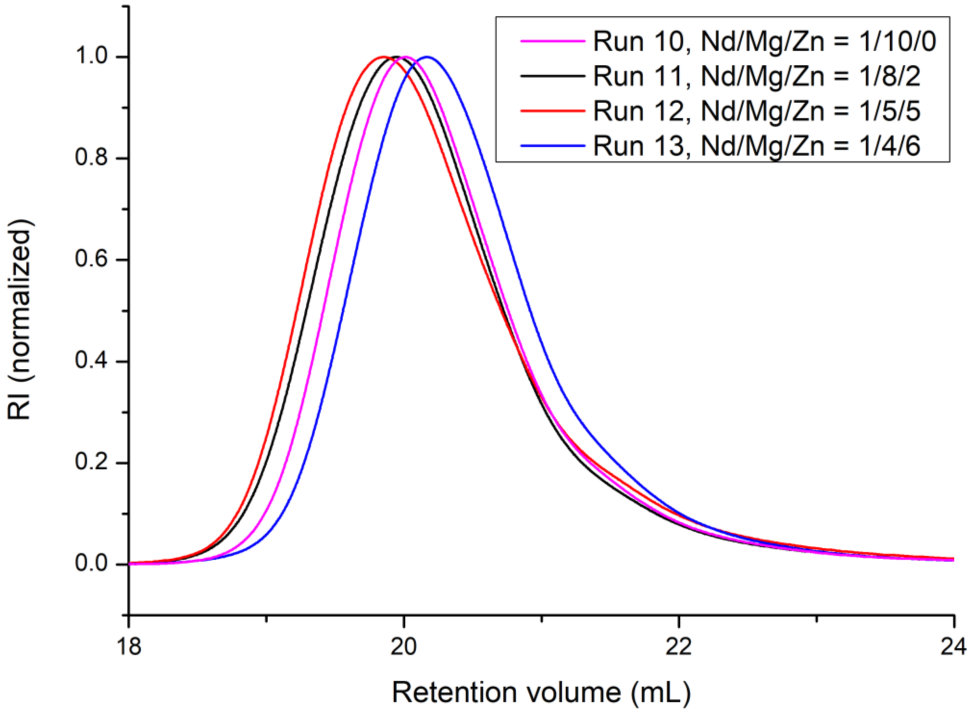


**Figure S9**. SEC chromatograms of EBR obtained with **1** / BOMAG / $ZnEt_2$ using various [Zn]/[Mg] ratios.

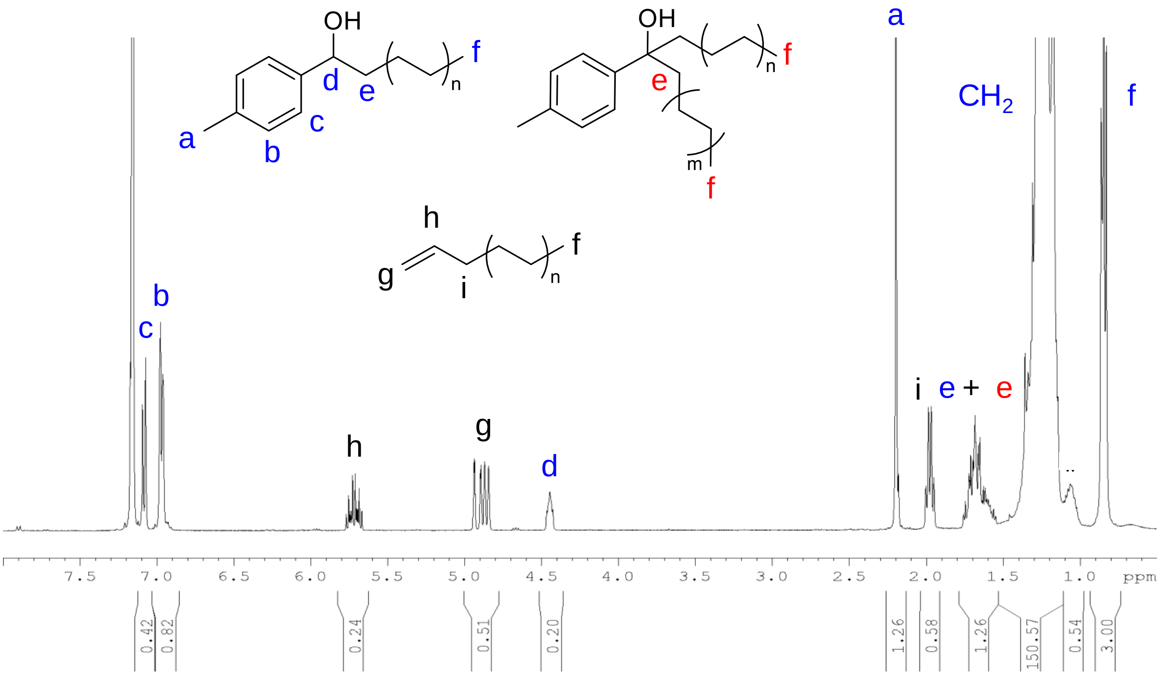


**Figure S10**. $^1$H NMR spectrum of the product formed by reaction of MgPE$_2$ with with p-toluoyl chloride recorded in TCE/$C_6D_6$ (2/1) at 363K.

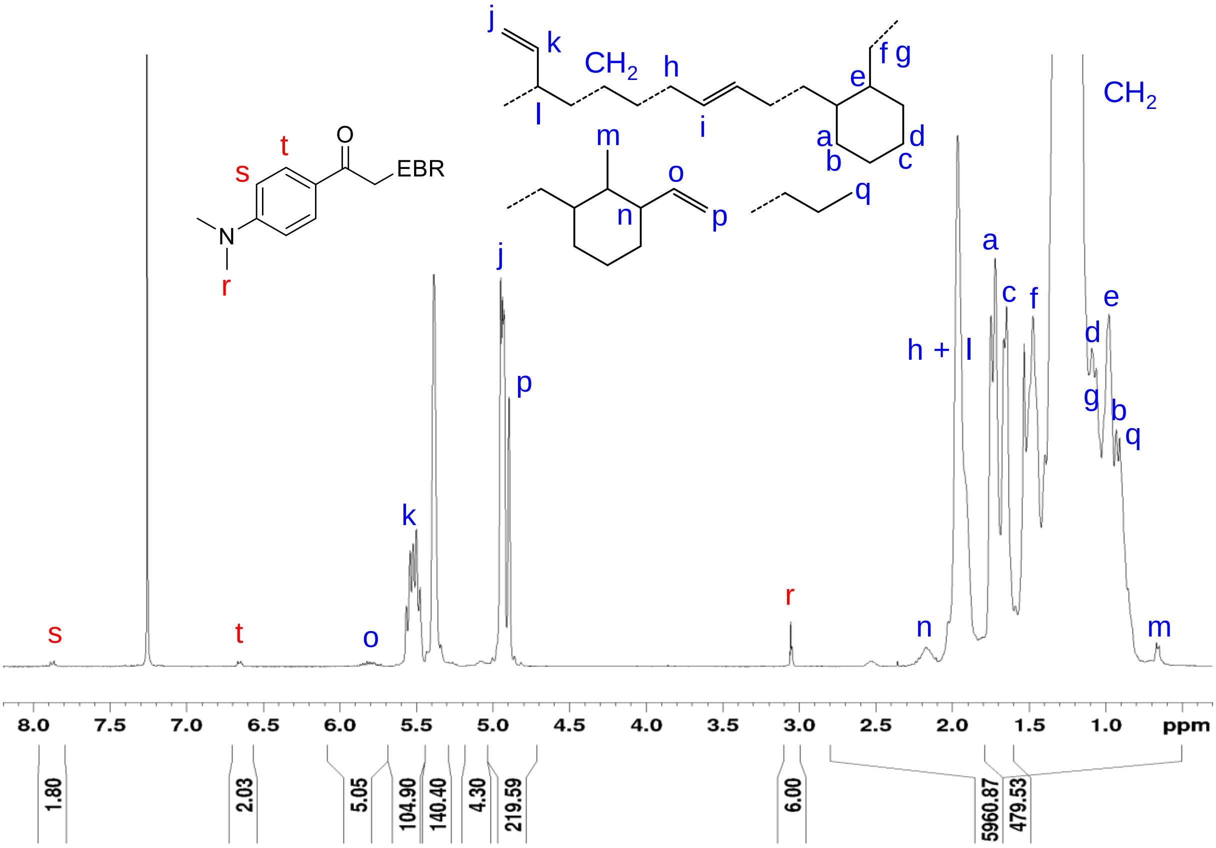


**Figure S11**. $^1$H NMR spectrum of *p*-dimethylaminophenone-EBR (run 17) recorded in $CDCl_3$ at 298K.

# Computational chemistry

### Computational Details

The computational level is based on that defined in the studies published in 2016, 2018, 2019 and 2021.[1-5] The Gaussian 09 revision D01 software was used, rated G09.[6] The B3PW91 functional[7,8] is used considering an implicit solvent model (SMD= toluene).[9] The contribution of dispersion effects is added by a single-point correction at the D3-BJ level.[10] Hydrogen, carbon and oxygen atoms are represented by polarized Pople bases with triple-ζ valences (6-311(d,p)). Magnesium and lithium atoms are represented by the same base augmented by a diffuse function (6-311++(d,p)). For silicon and chlorine atoms, the quasi-relativistic pseudo-potentials of Stuttgart-Dresden-Bonn and their associated basis are used.[11] These bases are supplemented by a polarization *d* orbital ($\alpha_d^{Si}$= 0.284 and $\alpha_d^{Cl}$ = 0.643).[12] Neodymium is described by a quasi-relativistic Stuttgart-Dresden-Bonn pseudopotential with a large core of 49 electrons and its associated base augmented by a *f*-function ($\alpha_f^{Nd}$ = 1.0). Zinc is represented by a quasi-relativistic Stuttgart-Dresden-Bonn pseudopotential with a small core of 10 electrons and its associated base.[13]

# References

1. Deciphering the Mechanism of Coordinative Chain Transfer Polymerization of Ethylene Using Neodymocene Catalysts and Dialkylmagnesium. R. Ribeiro, R. Ruivo, H. Nsiri, S. Norsic, F. D'Agosto, L. Perrin, C. Boisson, *ACS Catal.,* **2016**, *6*(2), 851-860. DOI: 10.1021/acscatal.5b02316

2. Ethylene–Butadiene Copolymerization by Neodymocene Complexes: A Ligand Structure/Activity/Polymer Microstructure Relationship Based on DFT Calculations. H. Nsiri, I. Belaid, P. Larini, J. Thuilliez, C. Boisson, and L. Perrin**,** *ACS Catal.,* **2016**, *6*(2), 1028-1036. DOI: 10.1021/acscatal.5b02317

3. Dialkenylmagnesium Compounds in Coordinative Chain Transfer Polymerization of Ethylene. Reversible Chain Transfer Agents and Tools To Probe Catalyst Selectivities toward Ring Formation. I. Belaid, M.-N. Poradowski, S. Bouaouli, J. Thuilliez, L. Perrin, F. D'Agosto, and C. Boisson**,** *Organometallics,* **2018**, *37*(10), 1546-1554. DOI: 10.1021/acs.organomet.8b00127

4. Identification of a Transient but Key Motif in the Living Coordinative Chain Transfer Cyclocopolymerization of Ethylene with Butadiene. I. Belaid, B. Macqueron, M.-N. Poradowski, S. Bouaouli, J. Thuilliez, F. Da Cruz-Boisson, V. Monteil, F. D'Agosto, L. Perrin, and C. Boisson, *ACS Catal.,* **2019**, *9*(10), 9298-9309. DOI: 10.1021/acscatal.9b02620

5. Design of selective divalent chain transfer agents for coordinative chain transfer polymerization of ethylene and its copolymerization with butadiene. N. Baulu, M.-N. Poradowski, L. Verrieux, J. Thuilliez, F. Jean-Baptiste-dit-Dominique, L. Perrin, F. D'Agosto, and C. Boisson, *Polym. Chem.*, **2022**, 13, 1970-1977. DOI: 10.1039/d2py00155a

6. Gaussian 09, Revision A.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.

7. Atoms, molecules, solids, and surfaces: Applications of the generalized gradient approximation for exchange and correlation. J. P. Perdew, J. A. Chevary, S. H. and Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh, and C. Fiolhais, *Phys. Rev. B*, **1992**, 46(11), 6671-6687. DOI: 10.1103/PhysRevB.46.6671

8. Density-functional thermochemistry. III. The role of exact exchange. A. D. Becke, *J. Chem. Phys.,* **1993**, 98(7), 5648-5652. DOI 10.1063/1.464913

9. Universal Solvation Model Based on Solute Electron Density and on a Continuum Model of the Solvent Defined by the Bulk Dielectric Constant and Atomic Surface Tensions. A. V. Marenich, C. J. Cramer, and D. G. Truhlar, *J. Phys. Chem. B,* **2009**, *113*(18), 6378-6396. DOI: 10.1021/jp810292n

10. Effect of the damping function in dispersion corrected density functional theory. S. Grimme, S. Ehrlich, and L. Goerigk, *J. Comput. Chem.*, **2011**, *32*, 1456-1465. DOI 10.1002/jcc.21759

11. Ab-initio energy-adjusted pseudopotentials for elements of groups 13-17. A. Bergner, M. Dolg, W. Kuechle, H. Stoll, and H. Preuss, *Mol. Phys.*, **1993**, *80*, 1431-1441. DOI: 10.1080/00268979300103121

12. On the accuracy of averaged relativistic shape-consistent pseudopotentials. L. Maron, and C. Teichteil, *Chem. Phys.*, **1998**, *237*(1), 105-122. DOI 10.1016/S0301-0104(98)00243-2

13. M. Dolg, U. Wedig, H. Stoll, H. Preuss; Energy-adjusted *ab initio* pseudopotentials for the first row transition elements. *J. Chem. Phys.* 15 January 1987; 86 (2): 866–872.