Supporting information

Identification of a transient but key motif in the living coordinative chain transfer *cyclo*copolymerization of ethylene with butadiene

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General experimental information. Under a dry nitrogen atmosphere, all operations and sensitive chemicals were performed in a glovebox or Schlenk techniques. The toluene used as solvent for the polymerization was purified on a SPS800 MBraun system. BOMag 20 mol% solution in heptane was purchased from Chemtura. Deuterated solvents were supplied by Eurisotop. The bisfluorenyl neodymium catalyst was synthesized according to the literature.¹ Butadiene was supplied by Michelin. Ethylene was supplied by Air Liquide.

Copolymerization procedure

Polymerizations were performed in a 250 mL glass reactor, equipped with a stainless steel blade. The alkylating agent BOMag and the neodymium complex were introduced in a flask containing 200 mL of toluene. The mixture was stirred for 10 min and then transferred into the reactor under a stream of argon. Argon was then pumped out, and the reactor was charged with butadiene-ethylene mixture. The pressure is then gradually increased to 4 bars at the same time as the desired temperature is reached and kept constant during the entire reaction. Once the polymerization is complete, the reactor is cooled and degassed. The polymer was then precipitated in 400 mL of methanol, washed, and dried at 70 °C under vacuum.

For kinetic investigations, aliquots were regularly withdrawn from the polymerization medium and weighted. The polymer was recovered and weighted and then analyzed by SEC.

Analytical techniques

NMR spectroscopy. The microstructure of the copolymers were determined by ¹H, ¹³C NMR spectra recorded in CDCl₃ at room temperature or TCE/C₆D₆ mixture (volume ratio 2/1) at 363 K on Bruker spectrometers working at 400 MHz for ¹H and at 101 MHz for ¹³C. The solutions were prepared at 10-15% (w/v) for ¹H and at 60-100% (w/v) for ¹³C. 1D-¹H spectra and 2D-¹H/¹H g-COSY and g-TOCSY, ¹H/¹³C g-HSQC and g-HMBC correlations were recorded with a 5 mm BBFO+ probe. 1D-¹³C spectra were performed with a 10mm ¹H/¹³C Selective probe. Both probes are equipped with a z-gradient coil. Chemical shift values are referenced to the polyethylene peak at 30.06 ppm for TCE/C₆D₆ and the peak of the solvent at 77.0 ppm when CDCl₃ is used as a solvent.

Size exclusion chromatography. For copolymers of ethylene and butadiene with 20 mol% of butadiene in the feed the molar masses are determined by size exclusion chromatography (SEC) in 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). THF was used as the mobile phase at a flow rate of 1 mL min⁻¹. All polymers were injected at a concentration of 3 mg mL⁻¹ after filtration through a 0.45 μ m pore-size membrane. The separation was carried out on a guard column and three columns (SDVB, 5 μ m, 300 \times 7.5 mm I.D.) from Polymer Standard Service. Columns and detectors were

maintained at 40 °C. The OmniSEC 5.02 software was used for data acquisition and data processing. A universal calibration constructed with narrow polystyrene (Polymer Standards Service, Mainz, Germany) was used to calculate average molar masses.

For copolymers of ethylene and butadiene with 5 mol% of butadiene in the feed, HT-SEC analyses were performed using a Viscotek system, from Malvern Instruments, equipped with a combination of three columns (Polefin 300 mm x 8 mm I.D. porosity of 1 000 Å, 100 000 Å and 1 000 000 Å) from Polymer Standards Service. Samples were dissolved in 1,2,4-TCB with a concentration of 5 mg mL⁻¹ by heating the mixture for 1 h at 150 °C. 200 μ L of sample solutions were injected and eluted in 1,2,4-TCB using a flow rate of 1 mL min⁻¹ at 150 °C. 2,6-di-tert-butyl-4-methylphenol (BHT) was added to the eluent (200 mg L⁻¹) in order to stabilize the polymer against oxidative degradation. Online detection was performed with a differential refractive index detector and a viscometer detector. A universal calibration curve, obtained with polystyrene standards (Polymer Standards Service, Mainz, Germany) in the range of 500 to 4.2x10⁶ g mol⁻¹, was used to calculate the molar mass distribution of the samples. Data were acquired and processed with the OmniSEC 5.02 software.

Pyrolysis-GC-MS. GC–MS were a 7890B GC, equipped with a capillary GC column, and a 5977A mass selective detector from Agilent Technologies. The Multi-Shot Pyrolyzer EGA/PY-3030D is joined to the system. The polymer sample is placed in a sample cup which is then attached to the sampler of the Multi-Shot pyrolyzer. Pyrolysis occurs when the cup is released and "free falls" into the pyrolyzer furnace which is at the pre-selected pyrolysis temperature of 600 °C (this method is also called flash pyrolysis). The gases generated in the furnace are swept into the splitter by the Helium as carrier gas. GC/MSD ChemStation Software is used for the data treatment.

Computational details

Geometry optimization of the reactants, and transition states were carried out at a DFT level of theory using the hybrid functional B3PW91^{2,3} without any symmetry restrictions. Neodymium was represented by a Stuttgart-Dresden-Bonn quasi-relativistic large effective core potential, that includes the 4*f* electrons in the core, and the associated basis set^{4,5} completed with a polarization *f* function (ζ_f = 1.0). Silicon was represented by a Stuttgart-Dresden-Bonn pseudopotential and its adapted basis set⁶ augmented by a *d* function (ζ_f = 0.284). Magnesium was represented by a polarized all electron triple- ζ 6-311G(d,p) basis set and supplemented by a 6 diffuse function.⁷⁻¹⁰ Carbon and hydrogen atoms were represented by a polarized all electron triple- ζ 6-311G(d,p) basis set.⁷⁻⁹ Solvation by toluene was implicitly represented during optimization using the SMD method.¹¹ The Grimme empirical

correction with the original D3 damping function was used to include the dispersion correction as a single point calculation.^{12,13} Analytical frequency calculations were carried out to verify the nature of the extrema (minimum or transition state). Gibbs energy have computed within the harmonic approximation and estimated at 298.15 K, 1 atm. Criteria for SCF convergence and geometry optimization, and integration grids are set to default values. All these computations have been performed with the gaussian09 suite of programs.¹⁴

Cartesian coordinates of optimized structures and associated energies

The Cartesian coordinates of optimized structures and associated energies are in ESI.xyz. These data are readable with Mercury, CCDC. Each structure contains associated energies in a.u, visible in its title with its name. When the precoordination structure is not presented, it means that the adduct is dissociative.

Time	Productivity	$M_{ m n}{}^{ m a}$	D		
(min)	(kg mol ⁻¹)	(g mol ⁻¹)	Ð	Chains/lvig	
11	134	18 670	1.4	1.4	
26	262	28 490	1.5	1.8	
39	357	34 750	1.5	2.0	
59	416	41 690	1.9	2.0	
200 mL	toluene, [Mg] ₀ =	: 1.23 mmol	L-1, []	$Mg]_{0}/[Nd]_{0} = 5$	
6	59	7 220	1.3	0.8	
23	231	16 300	1.5	1.4	
55	453	23 300	1.6	1.9	
92	588	29 650	1.8	2.0	
200 mL	toluene, $[Mg]_0 =$	2.42 mmol	L ⁻¹ , [N	$[Mg]_0/[Nd]_0 = 10$	
7	44	3 970	1.4	0.6	
15	85	5 800	1.3	0.7	
30	167	9 160	1.5	0.9	
60	317	14 500	1.4	1.1	
102	519	17 300	1.5	1.5	
160	740	20 040	1.6	1.8	
200 mL	toluene, $[Mg]_0 =$	5.10 mmol	L ⁻¹ , [N	$[Mg]_0/[Nd]_0 = 20$	
24	89	2 820	1.4	0.8	
53	176	3 950	1.4	1.1	
105	285	5 460	1.4	1.2	
161	413	71 640	1.4	1.4	
208	525	9 070	1.3	1.4	
252	652	10 830	1.3	1.4	
330	878	13 190	1.3	1.6	
200 mL toluene, $[Mg]_0 = 9.68 \text{ mmol } L^{-1}$, $[Mg]_0/[Nd]_0 = 40$					

Table S1. Kinetics and evolution of molar masses versus productivity with 5 mol% of butadiene

 $T = 70^{\circ}C$, P = 4 bars, 5 mol% butadiene.^a SEC in TCB at 150^oC

Time (min)	Productivity (kg mol ⁻¹)	<i>M</i> _n ^a (g mol ⁻¹)	Ð	Chains/Mg		
15	47	9 374	1.5	1.0		
30	86	14 147	1.7	1.2		
60	177	29 660	1.7	1.2		
92	278	42 672	2.3	1.3		
200 mL	toluene, [Mg] ₀ =	= 1.14 mmol	L ⁻¹ , [N	$[g]_0/[Nd]_0 = 5$		
15	65	4 500	1.5	1.5		
30	112	7 020	1.5	1.6		
73	295	16 620	1.4	1.8		
108	437	23 470	1.5	1.9		
137	552	28 590	1.6	1.9		
307	1 1 3 0	49 360	2.2	2.3		
200mL	toluene, $[Mg]_0 =$	2.29 mmol L	⁻¹ , [M	$g_{0}/[Nd]_{0} = 10$		
26	86	1 690	1.6	1.3		
47	211	2 630	1.6	2.0		
93	362	4 455	1.7	2.0		
162	600	7 580	1.6	2.0		
215	714	9 660	1.7	1.8		
253	793	10 580	1.6	1.9		
324	947	15 660	1.5	1.5		
200mL	toluene, $[Mg]_0 =$	9.24 mmol L	. ⁻¹ , [M	$g_0/[Nd]_0 = 40$		
34	64	1 420	1.7	0.5		
55	102	1 740	1.6	0.7		
100	222	1 520	1.7	1.8		
120	275	2 040	1.7	1.7		
180	424	3 110	1.7	1.7		
240	579	3 500	1.7	2.0		
300	745	5 200	1.7	1.8		
390	1 004	6 500	1.6	1.9		
200 mL toluene, $[Mg]_0 = 21.89 \text{ mmol } L^{-1}$, $[Mg]_0/[Nd]_0 = 81$						

Table S2. Kinetics and evolution of molar masses versus productivity with 20 mol% of butadiene

 $\overline{T = 70^{\circ}C}$, P = 4 bars, 20 mol% butadiene.^a SEC in THF at $40^{\circ}C$

	[Nd]	[Mø]	%B in polym	I ₂ fonction	nalisation	SEC	2
copolymer	(μmol L ⁻¹)	(mmol L ⁻¹)	(%mol)	I/Mg	time (min)	<i>M</i> _n (g mol ⁻¹)	Ð
Copolymer 1	235	18.8	18.8	-	-	1700	1.9
Copolymer 2	235	18.8	19.8	4	60	2000	1.7

Table S3. Copolymerization of ethylene and butadiene with the catalytic system $[Me_2Si(C_{13}H_8)_2Nd(BH_4)_2Li(thf)]_2/BOMag$ and functionalization with iodine

200 mL toluene, $[Mg]_0/[Nd]_0 = 80$, T = 70°C, P = 4 bars, 75 min, 20 mol% butadiene



Figure S1. 13 C NMR (CDCl₃, 300 K) spectrum of a low molar mass poly(ethylene-*co*-butadiene)prepared with {Me₂Si(C₁₃H₈)₂Nd(BH₄)₂Li(thf)}₂/BOMag (*Copolymer 1*) (E stands for inserted ethyleneunits,Tfor1,4-transinsertedbutadieneunits,Vbutadieneunits, inserted in 2,1 manner and Cy for the cycles)



Figure S2. ¹³C NMR (CDCl₃, 300 K) spectrum of a low molar mass iodo functionalized poly(ethylene*co*-butadiene) prepared with {Me₂Si(C₁₃H₈)₂Nd(BH₄)₂Li(thf)}₂/BOMag (*Copolymer 2*)



Figure S3. ¹H NMR (TCE/C₆D₆, 300 K) spectrum of a high molar mass poly(ethylene-*co*-butadiene) $(M_n = 10\ 600\ \text{g mol}^{-1})$ prepared with $\{\text{Me}_2\text{Si}(\text{C}_{13}\text{H}_8)_2\text{Nd}(\text{BH}_4)_2\text{Li}(\text{thf})\}_2/\text{BOMag}$



Figure S4. Two-dimensional NMR correlations ${}^{1}H/{}^{13}C$ g-HSQC (CDCl₃, 300 K) of the iodo functionalized poly(ethylene-*co*-butadiene) prepared with {Me₂Si(C₁₃H₈)₂Nd(BH₄)₂Li(thf)}₂/BOMag (*Copolymer 2*)



Figure S5. Two-dimensional NMR correlations ${}^{1}H/{}^{1}H$ g-COSY (CDCl₃, 300 K) of the iodo functionalized poly(ethylene-*co*-butadiene) prepared with {Me₂Si(C₁₃H₈)₂Nd(BH₄)₂Li(thf)}₂/BOMag (*Copolymer 2*)



Figure S6. Two-dimensional heteronuclear NMR correlations ${}^{1}H/{}^{13}C$ g-HSQC (CDCl₃, 300 K) of theiodofunctionalizedpoly(ethylene-co-butadiene)preparedwithMe_2Si(C_{13}H_8)_2Nd(BH_4)_2Li(thf)}_2/BOMag (Copolymer 2) $(C_{13}H_{13})_{12}$ $(C_{13}H_{13})_{12}$ $(C_{13}H_{13})_{12}$





Figure S7. Two-dimensional heteronuclear NMR correlations ${}^{1}H/{}^{13}C$ g-HSQC (CDCl₃, 300 K) of the poly(ethylene-*co*-butadiene) prepared with {Me₂Si(C₁₃H₈)₂Nd(BH₄)₂Li(thf)}₂/BOMag (*Copolymer 1*)



Figure S8. Two-dimensional NMR correlations ${}^{1}H/{}^{13}C$ g-HMBC (CDCl₃, 300 K) of the poly(ethyleneco-butadiene) prepared with {Me₂Si(C₁₃H₈)₂Nd(BH₄)₂Li(thf)}₂/BOMag (*Copolymer 1*)



Potential energy surface scan of the Bu/Allyl exchange reaction starting from the bimetallic species BM^1 . The reaction coordinate was set to be the distance Nd-C³. Some corresponding reaction intermediates and transition states, obtained from the calculated free energy profile reported in the main text, are identified.

Figure S9. Potential energy surface of the chain exchange reaction.



Figure S10. Representation of the 3D structures of the transition states for ethylene insertion into the trisubstituted cyclohexylmethyl site ${}^{21}BEBC^{12t}E^*$. Distances in Å.



Figure S11. Simulated ¹³C NMR spectrum and corresponding chemical shifts in ppm (ChemDraw Professional 15.1) of a disubstituted decalin unit.



Figure S12. Pyrolysis-GC-MS of a high molar mass poly(ethylene-*co*-butadiene) ($M_n = 50\ 000\ \text{g mol}^-$ ¹, D = 1.50) prepared with {Me₂(C₁₃H₈)₂Nd(BH₄)₂Li(thf)}₂/BOMag.

Table S4. Assignment o	f represent	tative	peaks of	the	gas chr	omatogra	am of a	high molar	mass
poly(ethylene-co-butadien	e) $(M_n$	=	50 000	g	mol ⁻¹ ,	Đ=	1.50)	prepared	with
${Me_2(C_{13}H_8)_2Nd(BH_4)_2Li($	thf)}2/BON	/lag.							

Peak	Retention time (min)	Analyte	Molar mass (g mol ⁻¹)
1	1.51	propene	42
2	1.80	1,3-pentadiene	68
3	2.36	1-hexene	84
4	3.64	cyclohexene	82
5	3.89	1-heptene	98
6	4.71	methylcyclohexane	98
7	6.63	1-methylcyclohexene	96
8	7.13	1,3,5-heptatriene	94
9	12.01	1-ethylcyclohexene	110
10	12.63	1-nonene	126
11	12.89	1-ethenylcyclohexene	108
12	13.80	1-propylcyclohexene	124
13	14.28	1-decene	140
14	14.51	3-methylcyclohexene	96
15	14.56	1-methyl, 2-propyl cyclohexane	140
16	14.66	1-butylcyclohexene	138
17	15.38	1-undecene	154
18	16.08	Decalin cis or trans	138
19	16.29	1-dodecene	168
20	1704	1-tridecene	182
21	17.73	1-tetradecene	196
22	18.29	1-octylcyclohexene	194
23	18.39	1-pentadecene	210
24	18.94	1-nonylcyclohexene	208
25	19.55	1-decylcyclohexene	222



 ${Me_2(C_{13}H_8)_2Nd(BH_4)_2Li(thf)}_2/BOMag.$

Table S5. Assignment of representative peaks of the gas chromatogram of a polyethylene ($M_n = 1$ 150)
g mol ⁻¹ , <i>D</i> = 1.17)

	Retention time		Molar mass
Peak	(min)	Analyte	(g mol ⁻¹)
1	1.49	1-propene	42
2	1.81	1,4-pentadiene	68
3	2.35	1-hexene	84
4	3.87	1-heptene	98
5	4.08	heptane	100
6	7.94	1-octene	112
7	8.51	octane	114
8	12.60	1-nonene	126
9	14.27	1-decene	140
10	15.38	1-undecene	154
11	16.27	1-dodecene	168
12	17.05	1-tridecene	182
13	17.74	1-tetradecene	196
14	18.39	1-pentadecene	210
15	19.01	1-hexadecene	224
16	19.58	1-heptadecene	230
17	20.14	1-octadecene	252
18	20.67	1-nonadecene	266
19	21.18	1-eicosene	280

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