

Supplementary Materials: 1,3-Diene Polymerization Mediated by Homoleptic Tetramethylaluminates of the Rare-Earth Metals

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S1. Polymerization Data

S1.1 Isoprene polymerization at standard conditions

If not mentioned otherwise in the respective table, the polymers shown in this section have been synthesized according to the procedure given in Section 3.4 of the main article (Materials and Methods) or are taken from the literature for comparison.

Table S1.1.1. Comparison of the polyisoprenes obtained applying cocatalyst A^a

entry ^b	precatalyst	cocatalyst ^c	yield [%]	cis-content [%] ^d	trans-content [%] ^d	vinyl content [%] ^d	M _n [10 ⁴ g/mol] ^e	PDI ^e	T _g [°C] ^g	ref.
1 ^h	La(AlMe ₄) ₃ (2 ^{La})	A	>99	46.3	51.4	2.3	5.0	1.29	n.d.	[1]
2	Ce(AlMe ₄) ₃ (2 ^{Ce})	A	>99	44.4	51.8	3.8	3.5	1.25	-62	– ^s
3	Pr(AlMe ₄) ₃ (2 ^{Pr})	A	93	44.7	50.2	5.1	3.9	1.35	-66	– ^s
4	Nd(AlMe ₄) ₃ (2 Nd)	A	86	44.3	50.9	4.9	3.8	1.29	-64	– ^s
5	Gd(AlMe ₄) ₃ (2 ^{Gd})	A	95	62.4	26.4	11.3	5.6	1.76	-59	– ^s
6	Tb(AlMe ₄) ₃ (2 ^{Tb})	A	85	55.1	33.5	11.4	5.2	3.02	-55	– ^s
7	Dy(AlMe ₄) ₃ (2 ^{Dy})	A	92	58.7	29.0	12.3	9.6	1.74	-60	– ^s
8	Ho(AlMe ₄) ₃ (2 ^{Ho})	A	84	63.7	24.2	12.1	5.6	2.15	-56	– ^s
9 ^h	Y(AlMe ₄) ₃ (2 ^Y)	A	>99	69.1	23.6	7.3	9.0	2.09	n.d.	[1]
10	Er(AlMe ₄) ₃ (2 ^{Er})	A	80	70.3	21.5	8.3	7.9	1.91	-56	– ^s
11	Lu(AlMe ₄) ₃ (2 ^{Lu})	A	>99	77.1	17.6	5.3	6.7	1.58	-62	– ^s
12	La(AlMe ₄) ₃ (2 ^{La})	2A	79	69.9	18.2	11.9	5.3 ^r	6.90 ^r	-63	– ^s
13	Ce(AlMe ₄) ₃ (2 ^{Ce})	2A	>99	68.1	18.7	13.3	4.0	1.28	-55	– ^s
14	Pr(AlMe ₄) ₃ (2 ^{Pr})	2A	78	n.d. ^u	n.d. ^u	n.d. ^u	8.0 ^r	2.35 ^r	n.d.	– ^s
15	Nd(AlMe ₄) ₃ (2 Nd)	2A	76	66.2	21.2	12.6	4.7	1.38	-57	– ^s
16	Gd(AlMe ₄) ₃ (2 ^{Gd})	2A	99	75.8	9.0	15.2	2.9	1.63	-51	– ^s
17	Tb(AlMe ₄) ₃ (2 ^{Tb})	2A	77	76.3	8.2	15.5	2.6	1.62	-52	– ^s
18	Dy(AlMe ₄) ₃ (2 ^{Dy})	2A	82	72.1	10.4	17.5	1.5	1.87	-55	– ^s
19	Ho(AlMe ₄) ₃ (2 ^{Ho})	2A	85	77.9	6.5	15.6	3.7	1.57	-55	– ^s
20	Y(AlMe ₄) ₃ (2 ^Y)	2A	77	73.7	11.7	14.5	3.1	1.62	-53	– ^s
21	Er(AlMe ₄) ₃ (2 ^{Er})	2A	79	76.5	5.9	17.7	4.1	1.62	-50	– ^s
22	Lu(AlMe ₄) ₃ (2 ^{Lu})	2A	90	70.3	13.8	15.9	3.4	1.62	-55	– ^s

^a For data sorted by precatalyst, see Section S1.2. ^b Conditions: 0.02 mmol of the resp. Ln precatalyst, 0.02 or 0.04 mmol co-catalyst, in toluene, [Ln]:[isoprene] 1:1000 (n/n), reaction time 1 h, pre-reaction time 0.5 h. ^c A = [Ph₃C][B(C₆F₅)₄]. ^d Determined by ¹H and ¹³C NMR spectroscopy in CDCl₃. ^e Determined by means of size-exclusion chromatography (SEC) against polystyrene standards.

^f Determined by differential scanning calorimetry; heating rate: 20 K/min, cooling rate: 60 K/min. ^h Reaction time 24 h. ^r These data represent only 28.5 mol% (2^{La}) and 75 mol% (2^{Pr}) of the polymer, the rest showed swelling behavior in THF implying crosslinking.

^s This study. ^u Insoluble in CDCl₃.

Table S1.1.2. Comparison of the polyisoprenes obtained applying cocatalyst B^a

entry ^b	precatalyst	cocatalyst ^c	yield [%]	cis-content [%] ^d	trans-content [%] ^d	vinyl content [%] ^d	M _n [10 ⁴ g/mol] ^e	PDI ^e	T _g [°C] ^g	ref.
1 ^h	La(AlMe ₃) ₃ (2 ^{La})	B	>99	49.8	46.8	3.4	6.0	1.23	n.d.	[1]
2	Ce(AlMe ₃) ₃ (2 ^{Ce})	B	92	43.7	53.0	3.3	2.8	1.35	-62	– ^s
3	Pr(AlMe ₃) ₃ (2 ^{Pr})	B	92	45.5	50.2	4.3	3.2	1.55	-67	– ^s
4	Nd(AlMe ₃) ₃ (2 Nd)	B	79	46.8	48.4	4.8	1.6	1.27	-64	– ^s
5	Gd(AlMe ₃) ₃ (2 ^{Gd})	B	89	58.8	30.0	11.2	6.1	1.70	-64	– ^s
6	Tb(AlMe ₃) ₃ (2 ^{Tb})	B	87	58.9	27.6	13.4	7.5	1.97	-57	– ^s
7	Dy(AlMe ₃) ₃ (2 ^{Dy})	B	95	57.5	27.4	15.1	10.0	1.70	-58	– ^s
8	Ho(AlMe ₃) ₃ (2 ^{Ho})	B	93	64.3	20.0	15.7	12.1	1.85	-56	– ^s
9 ^h	Y(AlMe ₃) ₃ (2 ^Y)	B	>99	60.0	26.0	14.0	11.7	1.60	n.d.	[2]
10	Er(AlMe ₃) ₃ (2 ^{Er})	B	81	67.6	19.0	13.5	9.1	2.63	-55	– ^s
11	Lu(AlMe ₃) ₃ (2 ^{Lu})	B	>99	77.2	16.9	5.9	5.2	2.06	-63	– ^s
12	La(AlMe ₃) ₃ (2 ^{La})	2B	88	70.5	19.4	10.1	5.0	1.15	-62	– ^s
13	Ce(AlMe ₃) ₃ (2 ^{Ce})	2B	>99	57.7	33.5	8.8	3.5	1.18	-62	– ^s
14	Pr(AlMe ₃) ₃ (2 ^{Pr})	2B	90	45.9	49.7	4.4	14.1	1.78	-65	– ^s
15	Nd(AlMe ₃) ₃ (2 Nd)	2B	82	62.6	28.5	8.9	4.4	1.26	-57	– ^s
16	Gd(AlMe ₃) ₃ (2 ^{Gd})	2B	94	66.3	21.6	12.0	8.4	1.88	-61	– ^s
17	Tb(AlMe ₃) ₃ (2 ^{Tb})	2B	87	65.6	19.4	15.0	5.6	1.74	-58	– ^s
18	Dy(AlMe ₃) ₃ (2 ^{Dy})	2B	88	65.2	19.9	14.9	6.7	1.79	-57	– ^s
19	Ho(AlMe ₃) ₃ (2 ^{Ho})	2B	93	63.7	20.1	16.2	7.8	2.31	-55	– ^s
20 ^h	Y(AlMe ₃) ₃ (2 ^Y)	2B	>99	67.0	13.0	20.0	26.0	1.50	n.d.	[2]
21	Er(AlMe ₃) ₃ (2 ^{Er})	2B	74	71.4	13.4	15.2	5.9	2.13	-52	– ^s
22	Lu(AlMe ₃) ₃ (2 ^{Lu})	2B	>99	73.1	15.4	11.5	4.2	1.78	-59	– ^s

^a For data sorted by precatalyst, see Section S1.2. ^b Conditions: 0.02 mmol of the resp. Ln precatalyst, 0.02 or 0.04 mmol cocatalyst, in toluene, [Ln]:[isoprene] 1:1000 (n/n), reaction time 1 h, pre-reaction time 0.5 h. ^c **B** = [PhNMe₂H][B(C₆F₅)₄]. ^d Determined by ¹H and ¹³C NMR spectroscopy in CDCl₃. ^e Determined by means of size-exclusion chromatography (SEC) against polystyrene standards. ^f Determined by differential scanning calorimetry; heating rate: 20 K/min, cooling rate: 60 K/min. ^h Reaction time 24 h.

^s This study.

Table S1.1.3. Comparison of the polyisoprenes obtained applying cocatalyst C^a

entry ^b	precatalyst	cocatalyst ^c	yield [%]	cis-content [%] ^d	trans-content [%] ^d	vinyl content [%] ^d	M _n [10 ⁴ g/mol] ^e	PDI ^e	T _g [°C] ^g	ref.
1 ^h	La(AlMe ₃) ₃ (2 ^{La})	C	>99	39.1	59.5	1.4	33.0	1.18	n.d.	[1]
2	Ce(AlMe ₃) ₃ (2 ^{Ce})	C	86	55.4	41.8	2.7	3.3	1.22	-61	- ^s
3	Pr(AlMe ₃) ₃ (2 ^{Pr})	C	87	65.6	30.4	4.0	6.8	1.32	-65	- ^s
4	Nd(AlMe ₃) ₃ (2 Nd)	C	76	68.0	29.2	2.7	7.9	1.16	-63	- ^s
5	Gd(AlMe ₃) ₃ (2 ^{Gd})	C	87	63.4	36.6	0.0	9.6	1.28	-65	- ^s
6	Tb(AlMe ₃) ₃ (2 ^{Tb})	C	83	60.4	35.5	4.1	8.0	1.57	-66	- ^s
7	Dy(AlMe ₃) ₃ (2 ^{Dy})	C	54	63.3	33.0	3.7	8.5	1.33	-65	- ^s
8	Ho(AlMe ₃) ₃ (2 ^{Ho})	C	78	57.0	38.8	4.3	11.6	1.73	-64	- ^s
9 ^h	Y(AlMe ₃) ₃ (2 ^Y)	C	56	62.5	35.1	2.4	12.0	2.03	n.d.	[1]
10	Er(AlMe ₃) ₃ (2 ^{Er})	C	85	74.2	21.4	4.5	15.5	1.86	-59	- ^s
11	Lu(AlMe ₃) ₃ (2 ^{Lu})	C	>99	67.6	28.1	4.3	23.0	1.55	-61	- ^s
12	La(AlMe ₃) ₃ (2 ^{La})	2C	69	77.6	18.8	3.7	16.3	1.40	-63	- ^s
13	Ce(AlMe ₃) ₃ (2 ^{Ce})	2C	84	86.0	8.8	5.2	5.9	1.13	-58	- ^s
14	Pr(AlMe ₃) ₃ (2 ^{Pr})	2C	87	87.9	6.0	6.1	8.7	1.35	-61	- ^s
15	Nd(AlMe ₃) ₃ (2 Nd)	2C	83	92.7	2.9	4.5	17.6	2.48	-61	- ^s
16	Gd(AlMe ₃) ₃ (2 ^{Gd})	2C	87	87.0	7.0	6.0	11.8	1.36	-68	- ^s
17	Tb(AlMe ₃) ₃ (2 ^{Tb})	2C	83	89.7	5.5	4.8	10.6	1.43	-61	- ^s
18	Dy(AlMe ₃) ₃ (2 ^{Dy})	2C	94	91.5	3.9	4.6	13.1	1.40	-61	- ^s
19	Ho(AlMe ₃) ₃ (2 ^{Ho})	2C	90	90.4	4.1	5.5	17.6	1.39	-62	- ^s
20	Y(AlMe ₃) ₃ (2 ^Y)	2C	86	82.2	13.3	4.4	16.1	1.55	-62	- ^s
21	Er(AlMe ₃) ₃ (2 ^{Er})	2C	93	92.6	2.1	5.2	15.5	1.75	-57	- ^s
22	Lu(AlMe ₃) ₃ (2 ^{Lu})	2C	>99	85.9	8.7	5.4	9.2	2.07	-61	- ^s

^a For data sorted by precatalyst, see Section S1.2. ^b Conditions: 0.02 mmol of the resp. Ln precatalyst, 0.02 or 0.04 mmol cocatalyst, in toluene, [Ln]:[isoprene] 1:1000 (n/n), reaction time 1 h, pre-reaction time 0.5 h. ^c C = B(C₆F₅)₃. ^d Determined by ¹H and ¹³C NMR spectroscopy in CDCl₃. ^e Determined by means of size-exclusion chromatography (SEC) against polystyrene standards.

^g Determined by differential scanning calorimetry; heating rate: 20 K/min, cooling rate: 60 K/min. ^h Reaction time 24 h. ^s This study.

Table S1.1.4. Comparison of the polyisoprenes obtained applying cocatalyst D^a

entry ^b	precatalyst	cocatalyst ^c	yield [%]	<i>cis</i> -content [%] ^d	<i>trans</i> -content [%] ^d	vinyl content [%] ^d	<i>M_n</i> [10 ⁴ g/mol] ^e	<i>PDI</i> ^e	<i>T_g</i> [°C] ^g	ref.
1 ^z	La(AlMe ₄) ₃ (2 ^{La})	D	4	— ^f	— ^f	— ^f	1.6	6.28	−61	— ^s
2	Ce(AlMe ₄) ₃ (2 ^{Ce})	D	7	97.1	0.0	2.9	11.7	1.28	−59	— ^s
3	Pr(AlMe ₄) ₃ (2 ^{Pr})	D	27	97.2	0.0	2.8	6.5	2.98	−64	— ^s
4	Nd(AlMe ₄) ₃ (2 Nd)	D	40	98.9	0.0	1.1	9.4	6.77	−60	— ^s
5	Gd(AlMe ₄) ₃ (2 ^{Gd})	D	51	>99.9	0.0	0.0	5.6	5.30	−67	— ^s
6	Tb(AlMe ₄) ₃ (2 ^{Tb})	D	66	85.0	13.5	1.5	4.9	4.44	−66	— ^s
7	Dy(AlMe ₄) ₃ (2 ^{Dy})	D	34	79.3	20.7	0.0	3.0	6.52	−67	— ^s
8	Ho(AlMe ₄) ₃ (2 ^{Ho})	D	7	67.6	31.1	1.3	2.9	2.64	−67	— ^s
9	Y(AlMe ₄) ₃ (2 ^Y)	D	traces	40.6	52.5	6.9	— ^f	— ^f	— ^f	— ^s
10	Er(AlMe ₄) ₃ (2 ^{Er})	D	traces	— ^f	— ^f	— ^f	— ^f	— ^f	— ^f	— ^s
11	Lu(AlMe ₄) ₃ (2 ^{Lu})	D	none	— ^f	— ^f	— ^f	— ^f	— ^f	— ^f	— ^s
12	La(AlMe ₄) ₃ (2 ^{La})	2D	2	91.5	5.6	2.9	— ^f	— ^f	— ^f	— ^s
13	Ce(AlMe ₄) ₃ (2 ^{Ce})	2D	21	97.4	0.0	2.6	3.3	3.73	−60	— ^s
14	Pr(AlMe ₄) ₃ (2 ^{Pr})	2D	42	97.4	0.0	2.6	8.7	3.09	−62	— ^s
15	Nd(AlMe ₄) ₃ (2 Nd)	2D	56	97.9	0.0	2.1	11.3	5.26	−61	— ^s
16	Gd(AlMe ₄) ₃ (2 ^{Gd})	2D	56	96.0	4.0	0.0	6.9	7.00	−67	— ^s
17	Tb(AlMe ₄) ₃ (2 ^{Tb})	2D	67	84.6	13.6	1.9	3.6	6.63	−66	— ^s
18	Dy(AlMe ₄) ₃ (2 ^{Dy})	2D	31	88.7	11.3	0.0	3.2	6.19	−67	— ^s
19	Ho(AlMe ₄) ₃ (2 ^{Ho})	2D	17	68.3	31.7	0.0	3.6	4.87	−66	— ^s
20	Y(AlMe ₄) ₃ (2 ^Y)	2D	6	52.9	46.2	0.9	2.9	2.92	−68	— ^s
21 ^z	Er(AlMe ₄) ₃ (2 ^{Er})	2D	traces	— ^f	— ^f	— ^f	— ^f	— ^f	— ^f	— ^s
22	Lu(AlMe ₄) ₃ (2 ^{Lu})	2D	none	— ^f	— ^f	— ^f	— ^f	— ^f	— ^f	— ^s

^a For data sorted by precatalyst, see Section S1.2. ^b Conditions: 0.02 mmol of the resp. Ln precatalyst, 0.02 or 0.04 mmol cocatalyst, in toluene, [Ln]:[isoprene] 1:1000 (n/n), reaction time 1 h, pre-reaction time 0.5 h. ^c D = Me₂AlCl. ^d Determined by ¹H and ¹³C NMR spectroscopy in CDCl₃. ^e Determined by means of size-exclusion chromatography (SEC) against polystyrene standards. ^f No further evaluation possible due to low yield. ^g Determined by differential scanning calorimetry; heating rate: 20 K/min, cooling rate: 60 K/min. ^h This study. ⁱ For data obtained for a reaction time of 24 h with this active system, see Table S1.4.4.

Table S1.1.5. Comparison of the polyisoprenes obtained applying cocatalyst E^a

entry ^b	precatalyst	cocatalyst ^c	yield [%]	<i>cis</i> -content [%] ^d	<i>trans</i> -content [%] ^d	vinyllic content [%] ^d	<i>M_n</i> [10 ⁴ g/mol] ^e	<i>PDI</i> ^e	<i>T_g</i> [°C] ^g	ref.
1 ^z	La(AlMe ₃) ₃ (2 ^{La})	E	3	89.3	7.6	3.1	— ^f	— ^f	— ^f	— ^s
2	Ce(AlMe ₃) ₃ (2 ^{Ce})	E	19	97.2	0.0	2.8	0.2	3.44	−61	— ^s
3	Pr(AlMe ₃) ₃ (2 ^{Pr})	E	43	97.6	0.0	2.4	4.4	4.84	−61	— ^s
4	Nd(AlMe ₃) ₃ (2 Nd)	E	57	98.2	0.0	1.8	5.6	4.52	−61	— ^s
5	Gd(AlMe ₃) ₃ (2 ^{Gd})	E	77	94.6	4.2	1.2	3.8	7.89	−63	— ^s
6	Tb(AlMe ₃) ₃ (2 ^{Tb})	E	82	88.8	9.7	1.5	2.5	6.36	−67	— ^s
7	Dy(AlMe ₃) ₃ (2 ^{Dy})	E	34	82.6	17.4	0.0	1.9	6.80	−67	— ^s
8	Ho(AlMe ₃) ₃ (2 ^{Ho})	E	15	61.5	37.1	1.4	2.2	2.70	−67	— ^s
9	Y(AlMe ₃) ₃ (2 ^Y)	E	10	48.4	50.6	1.0	2.1	1.43	−67	— ^s
10 ^z	Er(AlMe ₃) ₃ (2 ^{Er})	E	traces	— ^f	— ^f	— ^f	— ^f	— ^f	— ^f	— ^s
11	Lu(AlMe ₃) ₃ (2 ^{Lu})	E	none	— ^f	— ^f	— ^f	— ^f	— ^f	— ^f	— ^s
12 ^z	La(AlMe ₃) ₃ (2 ^{La})	2E	5	92.1	5.0	2.9	2.3	3.27	−62	— ^s
13	Ce(AlMe ₃) ₃ (2 ^{Ce})	2E	34	97.3	0.0	2.7	3.1	3.81	−61	— ^s
14	Pr(AlMe ₃) ₃ (2 ^{Pr})	2E	84	95.4	2.3	2.3	4.1	4.10	−62	— ^s
15	Nd(AlMe ₃) ₃ (2 Nd)	2E	86	98.0	0.0	2.0	5.3	4.66	−62	— ^s
16	Gd(AlMe ₃) ₃ (2 ^{Gd})	2E	89	92.6	5.9	1.5	3.2	5.87	−63	— ^s
17	Tb(AlMe ₃) ₃ (2 ^{Tb})	2E	87	90.2	8.1	1.7	2.1	12.66	−67	— ^s
18	Dy(AlMe ₃) ₃ (2 ^{Dy})	2E	46	86.3	13.7	0.0	1.6	8.95	−67	— ^s
19	Ho(AlMe ₃) ₃ (2 ^{Ho})	2E	4	71.5	28.5	0.0	2.5	4.90	−66	— ^s
20	Y(AlMe ₃) ₃ (2 ^Y)	2E	22	60.1	39.0	0.9	3.2	3.84	−66	— ^s
21 ^z	Er(AlMe ₃) ₃ (2 ^{Er})	2E	2	47.4	51.3	1.3	— ^f	— ^f	−66	— ^s
22 ^z	Lu(AlMe ₃) ₃ (2 ^{Lu})	2E	traces	— ^f	— ^f	— ^f	— ^f	— ^f	— ^f	— ^s

^a For data sorted by precatalyst, see Section S1.2. ^b Conditions: 0.02 mmol of the resp. Ln precatalyst, 0.02 or 0.04 mmol cocatalyst, in toluene, [Ln]:[isoprene] 1:1000 (n/n), reaction time 1 h, pre-reaction time 0.5 h. ^c E = Et₂AlCl. ^d Determined by ¹H and ¹³C NMR spectroscopy in CDCl₃. ^e Determined by means of size-exclusion chromatography (SEC) against polystyrene standards. ^f No further evaluation possible due to low yield. ^g Determined by differential scanning calorimetry; heating rate: 20 K/min, cooling rate: 60 K/min. ^h Reaction time 24 h. ^s This study. ^z For data obtained for a reaction time of 24 h with this active system, see Table S1.4.4.

S1.2 Isoprene polymerization at standard conditions sorted by rare-earth metal

If not mentioned otherwise in the respective table, the polymers shown in this section have been synthesized according to the procedure given in Section 3.4 of the main article (Materials and Methods) or are taken from the literature for comparison.

Table S1.2.1. Comparison of the polyisoprenes obtained applying precatalyst 2^{La}

entry ^b	cocatalyst ^c	yield [%]	cis-content [%] ^d	trans-content [%] ^d	vinyl content [%] ^d	M _n [10 ⁴ g/mol] ^e	PDI ^e	T _g [°C] ^g	ref.
1 ^h	A	>99	46.3	51.4	2.3	5.0	1.29	n.d.	[1]
2	2A	79	69.9	18.2	11.9	5.3	6.90	-63	— ^s
3 ^h	B	>99	49.8	46.8	3.4	6.0	1.23	n.d.	[1]
4	2B	88	70.5	19.4	10.1	5.0	1.15	-62	— ^s
5 ^h	C	>99	39.1	59.5	1.4	33.0	1.18	n.d.	[1]
6	2C	69	77.6	18.8	3.7	16.3	1.40	-63	— ^s
7	D	4	— ^f	— ^f	— ^f	1.6	6.28	-61	— ^s
8	2D	2	91.5	5.6	2.9	— ^f	— ^f	— ^f	— ^s
9	E	3	89.3	7.6	3.1	— ^f	— ^f	— ^f	— ^s
10	2E	5	92.1	5.0	2.9	2.3	3.27	-62	— ^s

^b Conditions: 0.02 mmol of 2^{La}, 0.02 or 0.04 mmol cocatalyst, in toluene, [Ln]:[isoprene] 1:1000 (n/n), reaction time 1 h, pre-reaction time 0.5 h.

^c A = [Ph₃C][B(C₆F₅)₄], B = [PhNMe₂H][B(C₆F₅)₄], C = B(C₆F₅)₃, D = Me₂AlCl, E = Et₂AlCl. ^d Determined by ¹H and ¹³C NMR spectroscopy in CDCl₃. ^e Determined by means of size-exclusion chromatography (SEC) against polystyrene standards. ^g Determined by differential scanning calorimetry; heating rate: 20 K/min, cooling rate: 60 K/min. ^f No further evaluation possible due to low yield. ^h Reaction time 24 h. ^s This study.

Table S1.2.2. Comparison of the polyisoprenes obtained applying precatalyst 2^{Ce}

entry ^b	cocatalyst ^c	yield [%]	cis-content [%] ^d	trans-content [%] ^d	vinyl content [%] ^d	M _n [10 ⁴ g/mol] ^e	PDI ^e	T _g [°C] ^g	ref.
1	A	> 99	44.4	51.8	3.8	3.5	1.25	-62	— ^s
2	2A	> 99	68.1	18.7	13.3	4.0	1.28	-55	— ^s
3	B	92	43.7	53.0	3.3	2.8	1.35	-62	— ^s
4	2B	> 99	57.7	33.5	8.8	3.5	1.18	-62	— ^s
5	C	86	55.4	41.8	2.7	3.3	1.22	-61	— ^s
6	2C	84	86.0	8.8	5.2	5.9	1.13	-58	— ^s
7	D	7	97.1	0.0	2.9	11.7	1.28	-59	— ^s
8	2D	21	97.4	0.0	2.6	3.3	3.73	-60	— ^s
9	E	19	97.2	0.0	2.8	0.2	3.44	-61	— ^s
10	2E	34	97.3	0.0	2.7	3.1	3.81	-61	— ^s

^b Conditions: 0.02 mmol of 2^{Ce}, 0.02 or 0.04 mmol cocatalyst, in toluene, [Ln]:[isoprene] 1:1000 (n/n), reaction time 1 h, pre-reaction time 0.5 h.

^c A = [Ph₃C][B(C₆F₅)₄], B = [PhNMe₂H][B(C₆F₅)₄], C = B(C₆F₅)₃, D = Me₂AlCl, E = Et₂AlCl. ^d Determined by ¹H and ¹³C NMR spectroscopy in CDCl₃. ^e Determined by means of size-exclusion chromatography (SEC) against polystyrene standards. ^g Determined by differential scanning calorimetry; heating rate: 20 K/min, cooling rate: 60 K/min. ^s This study.

Table S1.2.3. Comparison of the polyisoprenes obtained applying pre-catalyst **2^{Pr}**

entry ^b	cocatalyst ^c	yield [%]	cis-content [%] ^d	trans- content [%] ^d	vinyl content [%] ^d	M_n [10 ⁴ g/mol] ^e	PDI^e	T_g [°C] ^g	ref.
1	A	93	44.7	50.2	5.1	3.9	1.35	-66	^{-s}
2	2A	78	n.d. ^u	n.d. ^u	n.d. ^u	8.0	2.35	n.d.	^{-s}
3	B	92	45.5	50.2	4.3	3.2	1.55	-67	^{-s}
4	2B	90	45.9	49.7	4.4	14.1	1.78	-65	^{-s}
5	C	87	65.6	30.4	4.0	6.8	1.32	-65	^{-s}
6	2C	87	87.9	6.0	6.1	8.7	1.35	-61	^{-s}
7	D	27	97.2	0.0	2.8	6.5	2.98	-64	^{-s}
8	2D	42	97.4	0.0	2.6	8.7	3.09	-62	^{-s}
9	E	43	97.6	0.0	2.4	4.4	4.84	-61	^{-s}
10	2E	84	95.4	2.3	2.3	4.1	4.10	-62	^{-s}

^b Conditions: 0.02 mmol of **2^{Pr}**, 0.02 or 0.04 mmol cocatalyst, in toluene, [Ln]:[isoprene] 1:1000 (n/n), reaction time 1 h, pre-reaction time 0.5 h.

^c A = [Ph₃C][B(C₆F₅)₄], B = [PhNMe₂H][B(C₆F₅)₄], C = B(C₆F₅)₃, D = Me₂AlCl, E = Et₂AlCl. ^d Determined by ¹H and ¹³C NMR spectroscopy in CDCl₃. ^e Determined by means of size-exclusion chromatography (SEC) against polystyrene standards. ^f No further evaluation possible due to low yield. ^g Determined by differential scanning calorimetry; heating rate: 20 K/min, cooling rate: 60 K/min. ^h This study. ^u Insoluble in CDCl₃.

Table S1.2.4. Comparison of the polyisoprenes obtained applying precatalyst **2Nd**

entry ^b	cocatalyst ^c	yield [%]	cis-content [%] ^d	trans- content [%] ^d	vinyl content [%] ^d	M_n [10 ⁴ g/mol] ^e	PDI^e	T_g [°C] ^g	ref.
1	A	86	44.3	50.9	4.9	3.8	1.29	-64	^{-s}
2	2A	76	66.2	21.2	12.6	4.7	1.38	-57	^{-s}
3	B	79	46.8	48.4	4.8	1.6	1.27	-64	^{-s}
4	2B	82	62.6	28.5	8.9	4.4	1.26	-57	^{-s}
5	C	76	68.0	29.2	2.7	7.9	1.16	-63	^{-s}
6	2C	83	92.7	2.9	4.5	17.6	2.48	-61	^{-s}
7	D	40	98.9	0.0	1.1	9.4	6.77	-60	^{-s}
8	2D	56	97.9	0.0	2.1	11.3	5.26	-61	^{-s}
9	E	57	98.2	0.0	1.8	5.6	4.52	-61	^{-s}
10	2E	86	98.0	0.0	2.0	5.3	4.66	-62	^{-s}

^b Conditions: 0.02 mmol of **2Nd**, 0.02 or 0.04 mmol cocatalyst, in toluene, [Ln]:[isoprene] 1:1000 (n/n), reaction time 1 h, pre-reaction time 0.5 h.

^c A = [Ph₃C][B(C₆F₅)₄], B = [PhNMe₂H][B(C₆F₅)₄], C = B(C₆F₅)₃, D = Me₂AlCl, E = Et₂AlCl. ^d Determined by ¹H and ¹³C NMR spectroscopy in CDCl₃.

^e Determined by means of size-exclusion chromatography (SEC) against polystyrene standards. ^g Determined by differential scanning calorimetry; heating rate: 20 K/min, cooling rate: 60 K/min. ^h This study.

Table S1.2.5. Comparison of the polyisoprenes obtained applying precatalyst **2^{Gd}**

entry ^b	cocatalyst ^c	yield [%]	cis-content [%] ^d	trans-content [%] ^d	vinyl content [%] ^d	M_n [10 ⁴ g/mol] ^e	PDI^e	T_g [°C] [§]	ref.
1	A	95	62.4	26.4	11.3	5.6	1.76	-59	– [§]
2	2A	99	75.8	9.0	15.2	2.9	1.63	-51	– [§]
3	B	89	58.8	30.0	11.2	6.1	1.70	-64	– [§]
4	2B	94	66.3	21.6	12.0	8.4	1.88	-61	– [§]
5	C	87	63.4	36.6	0.0	9.6	1.28	-65	– [§]
6	2C	87	87.0	7.0	6.0	11.8	1.36	-66	– [§]
7	D	51	>99.9	0.0	0.0	5.6	5.30	-67	– [§]
8	2D	56	96.0	4.0	0.0	6.9	7.00	-67	– [§]
9	E	77	94.6	4.2	1.2	3.8	7.89	-63	– [§]
10	2E	89	92.6	5.9	1.5	3.2	5.87	-63	– [§]

^b Conditions: 0.02 mmol of **2^{Gd}**, 0.02 or 0.04 mmol cocatalyst, in toluene, [Ln]:[isoprene] 1:1000 (n/n), reaction time 1 h, pre-reaction time 0.5 h.

^c **A** = [Ph₃C][B(C₆F₅)₄], **B** = [PhNMe₂H][B(C₆F₅)₄], **C** = B(C₆F₅)₃, **D** = Me₂AlCl, **E** = Et₂AlCl. ^d Determined by ¹H and ¹³C NMR spectroscopy in CDCl₃.

^e Determined by means of size-exclusion chromatography (SEC) against polystyrene standards. [§] Determined by differential scanning calorimetry; heating rate: 20 K/min, cooling rate: 60 K/min. [§] This study.

Table S1.2.6. Comparison of the polyisoprenes obtained applying precatalyst **2^{Tb}**

entry ^b	cocatalyst ^c	yield [%]	cis-content [%] ^d	trans-content [%] ^d	vinyl content [%] ^d	M_n [10 ⁴ g/mol] ^e	PDI^e	T_g [°C] [§]	ref.
1	A	85	55.1	33.5	11.4	5.2	3.02	-55	– [§]
2	2A	77	76.3	8.2	15.5	2.6	1.62	-52	– [§]
3	B	87	58.9	27.6	13.4	7.5	1.97	-57	– [§]
4	2B	87	65.6	19.4	15.0	5.6	1.74	-58	– [§]
5	C	83	60.4	35.5	4.1	8.0	1.57	-66	– [§]
6	2C	83	89.7	5.5	4.8	10.6	1.43	-61	– [§]
7	D	66	85.0	13.5	1.5	4.9	4.44	-66	– [§]
8	2D	67	84.6	13.6	1.9	3.6	6.63	-66	– [§]
9	E	82	88.8	9.7	1.5	2.5	6.36	-67	– [§]
10	2E	87	90.2	8.1	1.7	2.1	12.66	-67	– [§]

^b Conditions: 0.02 mmol of **2^{Tb}**, 0.02 or 0.04 mmol cocatalyst, in toluene, [Ln]:[isoprene] 1:1000 (n/n), reaction time 1 h, pre-reaction time 0.5 h.

^c **A** = [Ph₃C][B(C₆F₅)₄], **B** = [PhNMe₂H][B(C₆F₅)₄], **C** = B(C₆F₅)₃, **D** = Me₂AlCl, **E** = Et₂AlCl. ^d Determined by ¹H and ¹³C NMR spectroscopy in CDCl₃.

^e Determined by means of size-exclusion chromatography (SEC) against polystyrene standards. [§] Determined by differential scanning calorimetry; heating rate: 20 K/min, cooling rate: 60 K/min. [§] This study.

Table S1.2.7. Comparison of the polyisoprenes obtained applying precatalyst **2^{Dy}**

entry ^b	cocatalyst ^c	yield [%]	cis-content [%] ^d	trans-content [%] ^d	vinyl content [%] ^d	M_n [10 ⁴ g/mol] ^e	PDI^e	T_g [°C] ^g	ref.
1	A	92	58.7	29.0	12.3	9.6	1.74	-60	^{-s}
2	2A	82	72.1	10.4	17.5	1.5	1.87	-55	^{-s}
3	B	95	57.5	27.4	15.1	10.0	1.70	-58	^{-s}
4	2B	88	65.2	19.9	14.9	6.7	1.79	-57	^{-s}
5	C	54	63.3	33.0	3.7	8.5	1.33	-65	^{-s}
6	2C	94	91.5	3.9	4.6	13.1	1.40	-61	^{-s}
7	D	34	79.3	20.7	0.0	3.0	6.52	-67	^{-s}
8	2D	31	88.7	11.3	0.0	3.2	6.19	-67	^{-s}
9	E	34	82.6	17.4	0.0	1.9	6.80	-67	^{-s}
10	2E	46	86.3	13.7	0.0	1.6	8.95	-67	^{-s}

^b Conditions: 0.02 mmol of **2^{Dy}**, 0.02 or 0.04 mmol cocatalyst, in toluene, [Ln]:[isoprene] 1:1000 (n/n), reaction time 1 h, pre-reaction time 0.5 h.

^c **A** = [Ph₃C][B(C₆F₅)₄], **B** = [PhNMe₂H][B(C₆F₅)₄], **C** = B(C₆F₅)₃, **D** = Me₂AlCl, **E** = Et₂AlCl. ^d Determined by ¹H and ¹³C NMR spectroscopy in CDCl₃.

^e Determined by means of size-exclusion chromatography (SEC) against polystyrene standards. ^g Determined by differential scanning calorimetry; heating rate: 20 K/min, cooling rate: 60 K/min. ^s This study.

Table S1.2.8 Comparison of the polyisoprenes obtained applying precatalyst **2^{Ho}**

entry ^b	cocatalyst ^c	yield [%]	cis-content [%] ^d	trans-content [%] ^d	vinyl content [%] ^d	M_n [10 ⁴ g/mol] ^e	PDI^e	T_g [°C] ^g	ref.
1	A	84	63.7	24.2	12.1	5.6	2.15	-56	^{-s}
2	2A	85	77.9	6.5	15.6	3.7	1.57	-55	^{-s}
3	B	93	64.3	20.0	15.7	12.1	1.85	-56	^{-s}
4	2B	93	63.7	20.1	16.2	7.8	2.31	-55	^{-s}
5	C	78	57.0	38.8	4.3	11.6	1.73	-64	^{-s}
6	2C	90	90.4	4.1	5.5	17.6	1.39	-62	^{-s}
7	D	7	67.6	31.1	1.3	2.9	2.64	-67	^{-s}
8	2D	17	68.3	31.7	0.0	3.6	4.87	-66	^{-s}
9	E	15	61.5	37.1	1.4	2.2	2.7	-67	^{-s}
10	2E	4	71.5	28.5	0.0	2.5	4.9	-66	^{-s}

^b Conditions: 0.02 mmol of **2^{Ho}**, 0.02 or 0.04 mmol cocatalyst, in toluene, [Ln]:[isoprene] 1:1000 (n/n), reaction time 1 h, pre-reaction time 0.5 h.

^c **A** = [Ph₃C][B(C₆F₅)₄], **B** = [PhNMe₂H][B(C₆F₅)₄], **C** = B(C₆F₅)₃, **D** = Me₂AlCl, **E** = Et₂AlCl. ^d Determined by ¹H and ¹³C NMR spectroscopy in CDCl₃.

^e Determined by means of size-exclusion chromatography (SEC) against polystyrene standards. ^g Determined by differential scanning calorimetry; heating rate: 20 K/min, cooling rate: 60 K/min. ^s This study.

Table S1.2.9. Comparison of the polyisoprenes obtained applying pre-catalyst **2^Y**^a

entry ^b	cocatalyst ^c	yield [%]	cis-content [%] ^d	trans-content [%] ^d	vinyl content [%] ^d	<i>M_n</i> [10 ⁴ g/mol] ^e	<i>PDI</i> ^e	<i>T_g</i> [°C] ^g	ref.
1 ^h	A	>99	69.1	23.6	7.3	9.0	2.09	n.d.	[1]
2	2A	77	73.7	11.7	14.5	3.1	1.62	-53	— ^s
3 ^h	B	>99	60.0	26.0	14.0	11.7	1.60	n.d.	[2]
4 ^h	2B	> 99	67.0	13.0	20.0	26.0	1.50	n.d.	[2]
5 ^h	C	56	62.5	35.1	2.4	12.0	2.03	n.d.	[1]
6	2C	86	82.2	13.3	4.4	16.1	1.55	-62	— ^s
7	D	traces	40.6	52.5	6.9	— ^f	— ^f	— ^f	— ^s
8	2D	6	52.9	46.2	0.9	2.9	2.92	-68	— ^s
9	E	10	48.4	50.6	1.0	2.1	1.43	-67	— ^s
10	2E	22	60.1	39.0	0.9	3.2	3.84	-66	— ^s

^a For data produced by systems of **2^Y/B** and **2^Y/2B** in the presence of Al*i*Bu₃, see ref. [2]. ^b Conditions 0.02 mmol of **2^Y**, 0.02 or 0.04 mmol cocatalyst, in toluene, [Ln]:[isoprene] 1:1000 (n/n), reaction time 1 h, pre-reaction time 0.5 h. ^c **A** = [Ph₃C][B(C₆F₅)₄], **B** = [PhNMe₂H][B(C₆F₅)₄], **C** = B(C₆F₅)₃, **D** = Me₂AlCl, **E** = Et₂AlCl. ^d Determined by ¹H and ¹³C NMR spectroscopy in CDCl₃. ^e Determined by means of size-exclusion chromatography (SEC) against polystyrene standards. ^f No further evaluation possible due to low yield. ^g Determined by differential scanning calorimetry; heating rate: 20 K/min, cooling rate: 60 K/min. ^h This study.

Table S1.2.10. Comparison of the polyisoprenes obtained applying precatalyst **2^{Er}**

entry ^b	cocatalyst ^c	yield [%]	cis-content [%] ^d	trans-content [%] ^d	vinyl content [%] ^d	<i>M_n</i> [10 ⁴ g/mol] ^e	<i>PDI</i> ^e	<i>T_g</i> [°C] ^g	ref.
1	A	80	70.3	21.5	8.3	7.9	1.91	-56	— ^s
2	2A	79	76.5	5.9	17.7	4.1	1.62	-50	— ^s
3	B	81	67.6	19.0	13.5	9.1	2.63	-55	— ^s
4	2B	74	71.4	13.4	15.2	5.9	2.13	-52	— ^s
5	C	85	74.2	21.4	4.5	15.5	1.86	-59	— ^s
6	2C	93	92.6	2.1	5.2	15.5	1.75	-57	— ^s
7	D	traces	— ^f	— ^f	— ^f	— ^f	— ^f	— ^f	— ^s
8	2D	traces	— ^f	— ^f	— ^f	— ^f	— ^f	— ^f	— ^s
9	E	traces	— ^f	— ^f	— ^f	— ^f	— ^f	— ^f	— ^s
10	2E	2	47.4	51.3	1.3	— ^f	— ^f	— ^f	— ^s

^b Conditions 0.02 mmol of **2^{Er}**, 0.02 or 0.04 mmol cocatalyst, in toluene, [Ln]:[isoprene] 1:1000 (n/n), reaction time 1 h, pre-reaction time 0.5 h.

^c **A** = [Ph₃C][B(C₆F₅)₄], **B** = [PhNMe₂H][B(C₆F₅)₄], **C** = B(C₆F₅)₃, **D** = Me₂AlCl, **E** = Et₂AlCl. ^d Determined by ¹H and ¹³C NMR spectroscopy in CDCl₃.

^e Determined by means of size-exclusion chromatography (SEC) against polystyrene standards. ^f No further evaluation possible due to low yield. ^g Determined by differential scanning calorimetry; heating rate: 20 K/min, cooling rate: 60 K/min. ^h This study.

Table S1.2.11. Comparison of the polyisoprenes obtained applying precatalyst **2^{Lu}**

entry ^b	cocatalyst ^c	yield [%]	<i>cis</i> -content [%] ^d	<i>trans</i> - content [%] ^d	vinyl content [%] ^d	<i>M_n</i> [10 ⁴ g/mol] ^e	<i>PDI</i> ^e	<i>T_g</i> [°C] ^g	ref.
1	A	>99	77.1	17.6	5.3	6.7	1.58	-62	— ^h
2	2A	90	70.3	13.8	15.9	3.4	1.62	-55	— ^h
3	B	>99	77.2	16.9	5.9	5.2	2.06	-63	— ^h
4	2B	>99	73.1	15.4	11.5	4.2	1.78	-59	— ^h
5	C	>99	67.6	28.1	4.3	23	1.55	-61	— ^h
6	2C	>99	85.9	8.7	5.4	9.2	2.07	-61	— ^h
7	D	none	— ⁱ	— ⁱ	— ⁱ	— ⁱ	— ⁱ	— ⁱ	— ^h
8	2D	none	— ⁱ	— ⁱ	— ⁱ	— ⁱ	— ⁱ	— ⁱ	— ^h
9	E	none	— ⁱ	— ⁱ	— ⁱ	— ⁱ	— ⁱ	— ⁱ	— ^h
10	2E	traces	— ⁱ	— ⁱ	— ⁱ	— ⁱ	— ⁱ	— ⁱ	— ^h

^b Conditions: 0.02 mmol of **2^{Lu}**, 0.02 or 0.04 mmol cocatalyst, in toluene, [Ln]:[isoprene] 1:1000 (n/n), reaction time 1 h, pre-reaction time 0.5 h.

^c **A** = [Ph₃C][B(C₆F₅)₄], **B** = [PhNMe₂H][B(C₆F₅)₄], **C** = B(C₆F₅)₃, **D** = Me₂AlCl, **E** = Et₂AlCl. ^d Determined by ¹H and ¹³C NMR spectroscopy in CDCl₃.

^e Determined by means of size-exclusion chromatography (SEC) against polystyrene standards. ^f No further evaluation possible due to low yield. ^g Determined by differential scanning calorimetry; heating rate: 20 K/min, cooling rate: 60 K/min. ^h This study.

S1.3 Isoprene polymerization at standard conditions by results

If not mentioned otherwise in the respective table, the polymers shown in this section have been synthesized according to the procedure given in Section 3.4 of the main article (Materials and Methods) or are taken from the literature for comparison.

Table S1.3.1. Comparison of the yields obtained for the polyisoprenes^a

entry ^b	precatalyst	cocatalyst ^c									
		A	2A	B	2B	C	2C	D	2D	E	2E
1	La(AlMe ₃) ₃ (2 ^{La})	>99 ^h	79	>99 ^h	88	>99 ^h	69	4	2	3	5
2	Ce(AlMe ₃) ₃ (2 ^{Ce})	>99	>99	92	100	86	84	7	21	19	34
3	Pr(AlMe ₃) ₃ (2 ^{Pr})	93	78	92	90	87	87	27	42	43	84
4	Nd(AlMe ₃) ₃ (2 Nd)	86	76	79	82	76	83	40	56	57	86
5	Gd(AlMe ₃) ₃ (2 ^{Gd})	95	99	89	94	87	87	51	56	77	89
6	Tb(AlMe ₃) ₃ (2 ^{Tb})	85	77	87	87	83	83	66	67	82	87
7	Dy(AlMe ₃) ₃ (2 ^{Dy})	92	82	95	88	54	94	34	31	34	46
8	Ho(AlMe ₃) ₃ (2 ^{Ho})	84	85	93	93	78	90	7	17	15	4
9	Y(AlMe ₃) ₃ (2 ^Y)	>99 ^h	77	>99 ^h	>99 ^h	56 ^h	86	tr ^d	6	10	22
10	Er(AlMe ₃) ₃ (2 ^{Er})	80	79	81	74	85	93	tr ^d	tr ^d	tr ^d	2
11	Lu(AlMe ₃) ₃ (2 ^{Lu})	>99	90	>99	>99	>99	>99	0	0	0	tr ^d

^a For detailed information on polymerization data and origin of the values (literature or this study), see sections S1.1 and S1.2. The values in this table are given in [%]. ^b Conditions: 0.02 mmol of the resp. Ln precatalyst, 0.02 or 0.04 mmol cocatalyst, in toluene, [Ln]:[isoprene] 1:1000 (n/n), reaction time 1 h, pre-reaction time 0.5 h. ^c A = [Ph₃C][B(C₆F₅)₄], B = [PhNMe₂H][B(C₆F₅)₄], C = B(C₆F₅)₃, D = Me₂AlCl, E = Et₂AlCl. ^h Reaction time 24 h. ^d This study. ^e tr. = traces.

Table S1.3.2. Comparison of the *cis*-1,4-contents obtained for the polyisoprenes^{ad}

entry ^b	precatalyst	cocatalyst ^c									
		A	2A	B	2B	C	2C	D	2D	E	2E
1	La(AlMe ₃) ₃ (2 ^{La})	46.3 ^h	69.9	49.8 ^h	70.5	39.1 ^h	77.6	- ^f	91.5	89.3	92.1
2	Ce(AlMe ₃) ₃ (2 ^{Ce})	44.4	68.1	43.7	57.7	55.4	86.0	97.1	97.4	97.2	97.3
3	Pr(AlMe ₃) ₃ (2 ^{Pr})	44.7	0.0	45.5	45.9	65.6	87.9	97.2	97.4	97.6	95.4
4	Nd(AlMe ₃) ₃ (2 Nd)	44.3	66.2	46.8	62.6	68.0	92.7	98.9	97.9	98.2	98.0
5	Gd(AlMe ₃) ₃ (2 ^{Gd})	62.4	75.8	58.8	66.3	63.4	87.0	100.0	96.0	94.6	92.6
6	Tb(AlMe ₃) ₃ (2 ^{Tb})	55.1	76.3	58.9	65.6	60.4	89.7	85.0	84.6	88.8	90.2
7	Dy(AlMe ₃) ₃ (2 ^{Dy})	58.7	72.1	57.5	65.2	63.3	91.5	79.3	88.7	82.6	86.3
8	Ho(AlMe ₃) ₃ (2 ^{Ho})	63.7	77.9	64.3	63.7	57.0	90.4	67.6	68.3	61.5	71.5
9	Y(AlMe ₃) ₃ (2 ^Y)	69.1 ^h	73.7	60.0 ^h	67.0 ^h	62.5 ^h	82.2	40.6	52.9	48.4	60.1
10	Er(AlMe ₃) ₃ (2 ^{Er})	70.3	76.5	67.6	71.4	74.2	92.6	- ^f	- ^f	- ^f	47.4
11	Lu(AlMe ₃) ₃ (2 ^{Lu})	77.1	70.3	77.2	73.1	67.6	85.9	- ^f	- ^f	- ^f	- ^f

^a For detailed information on polymerization data and origin of the values (literature or this study), see sections S1.1 and S1.2. The values in this table are given in [%]. Selectivities of >99.9 % are represented by 100. ^b Conditions: 0.02 mmol of the resp. Ln precatalyst, 0.02 or 0.04 mmol cocatalyst, in toluene, [Ln]:[isoprene] 1:1000 (n/n), reaction time 1 h, pre-reaction time 0.5 h. ^c A = [Ph₃C][B(C₆F₅)₄], B = [PhNMe₂H][B(C₆F₅)₄], C = B(C₆F₅)₃, D = Me₂AlCl, E = Et₂AlCl. ^d Determined by ¹H and ¹³C NMR spectroscopy in CDCl₃. ^e No further evaluation possible due to low yield. ^h Reaction time 24 h.

Table S1.3.3. Comparison of the *trans*-1,4-contents obtained for the polyisoprenes^{a,d}

entry ^b	precatalyst	cocatalyst ^c									
		A	2A	B	2B	C	2C	D	2D	E	2E
1	La(AlMe ₃) ₃ (2 ^{La})	51.4 ^h	18.2	46.8 ^h	19.4	59.5 ^h	18.8	– ^f	5.6	7.6	5.0
2	Ce(AlMe ₃) ₃ (2 ^{Ce})	51.8	18.7	53.0	33.5	41.8	8.8	0.0	0.0	0.0	0.0
3	Pr(AlMe ₃) ₃ (2 ^{Pr})	50.2	0.0	50.2	49.7	30.4	6.0	0.0	0.0	0.0	2.3
4	Nd(AlMe ₃) ₃ (2 Nd)	50.9	21.2	48.4	28.5	29.2	2.9	0.0	0.0	0.0	0.0
5	Gd(AlMe ₃) ₃ (2 ^{Gd})	26.4	9.0	30.0	21.6	36.6	7.0	0.0	4.0	4.2	5.9
6	Tb(AlMe ₃) ₃ (2 ^{Tb})	33.5	8.2	27.6	19.4	35.5	5.5	13.5	13.6	9.7	8.1
7	Dy(AlMe ₃) ₃ (2 ^{Dy})	29.0	10.4	27.4	19.9	33.0	3.9	20.7	11.3	17.4	13.7
8	Ho(AlMe ₃) ₃ (2 ^{Ho})	24.2	6.5	20.0	20.1	38.8	4.1	31.1	31.7	37.1	28.5
9	Y(AlMe ₃) ₃ (2 ^Y)	23.6 ^h	11.7	26.0 ^h	13.0 ^h	35.1 ^h	13.3	52.5	46.2	50.6	39.0
10	Er(AlMe ₃) ₃ (2 ^{Er})	21.5	5.9	19.0	13.4	21.4	2.1	– ^f	– ^f	– ^f	51.3
11	Lu(AlMe ₃) ₃ (2 ^{Lu})	17.6	13.8	16.9	15.4	28.1	8.7	– ^f	– ^f	– ^f	– ^f

^a For detailed information on polymerization data and origin of the values (literature or this study), see sections S1.1 and S1.2. The values in this table are given in [%]. Selectivities of >99.9 % are represented by 100.0. ^b Conditions: 0.02 mmol of the resp. Ln precatalyst, 0.02 or 0.04 mmol cocatalyst, in toluene, [Ln]:[isoprene] 1:1000 (n/n), reaction time 1 h, pre-reaction time 0.5 h. ^c **A** = [Ph₃C][B(C₆F₅)₄], **B** = [PhNMe₂H][B(C₆F₅)₄], **C** = B(C₆F₅)₃, **D** = Me₂AlCl, **E** = Et₂AlCl. ^d Determined by ¹H and ¹³C NMR spectroscopy in CDCl₃. ^e No further evaluation possible due to low yield. ^h Reaction time 24 h.

Table S1.3.4. Comparison of the vinylic 3,4-contents obtained for the polyisoprenes^{a,d}

entry ^b	precatalyst	cocatalyst ^c									
		A	2A	B	2B	C	2C	D	2D	E	2E
1	La(AlMe ₃) ₃ (2 ^{La})	2.3 ^h	11.9	3.4 ^h	10.1	1.4 ^h	3.7	– ^f	2.9	3.1	2.9
2	Ce(AlMe ₃) ₃ (2 ^{Ce})	3.8	13.3	3.3	8.8	2.7	5.2	2.9	2.6	2.8	2.7
3	Pr(AlMe ₃) ₃ (2 ^{Pr})	5.1	0.0	4.3	4.4	4.0	6.1	2.8	2.6	2.4	2.3
4	Nd(AlMe ₃) ₃ (2 Nd)	4.9	12.6	4.8	8.9	2.7	4.5	1.1	2.1	1.8	2.0
5	Gd(AlMe ₃) ₃ (2 ^{Gd})	11.3	15.2	11.2	12.0	0.0	6.0	0.0	0.0	1.2	1.5
6	Tb(AlMe ₃) ₃ (2 ^{Tb})	11.4	15.5	13.4	15.0	4.1	4.8	1.5	1.9	1.5	1.7
7	Dy(AlMe ₃) ₃ (2 ^{Dy})	12.3	17.5	15.1	14.9	3.7	4.6	0.0	0.0	0.0	0.0
8	Ho(AlMe ₃) ₃ (2 ^{Ho})	12.1	15.6	15.7	16.2	4.3	5.5	1.3	0.0	1.4	0.0
9	Y(AlMe ₃) ₃ (2 ^Y)	7.3 ^h	14.5	14.0 ^h	20.0 ^h	2.4 ^h	4.4	6.9	0.9	1.0	0.9
10	Er(AlMe ₃) ₃ (2 ^{Er})	8.3	17.7	13.5	15.2	4.5	5.2	– ^f	– ^f	– ^f	1.3
11	Lu(AlMe ₃) ₃ (2 ^{Lu})	5.3	15.9	5.9	11.5	4.3	5.4	– ^f	– ^f	– ^f	– ^f

^a For detailed information on polymerization data and origin of the values (literature or this study), see sections S1.1 and S1.2. The values in this table are given in [%]. Selectivities of >99.9 % are represented by 100.0. ^b Conditions: 0.02 mmol of the resp. Ln precatalyst, 0.02 or 0.04 mmol cocatalyst, in toluene, [Ln]:[isoprene] 1:1000 (n/n), reaction time 1 h, pre-reaction time 0.5 h. ^c **A** = [Ph₃C][B(C₆F₅)₄], **B** = [PhNMe₂H][B(C₆F₅)₄], **C** = B(C₆F₅)₃, **D** = Me₂AlCl, **E** = Et₂AlCl. ^d Determined by ¹H and ¹³C NMR spectroscopy in CDCl₃. ^e No further evaluation possible due to low yield. ^h Reaction time 24 h.

Table S1.3.5. Comparison of the number average molar weights obtained for the polyisoprenes^{ae}

entry ^b	precatalyst	cocatalyst ^c									
		A	2A	B	2B	C	2C	D	2D	E	2E
1	La(AlMe ₃) ₃ (2^{La})	5.0 ^h	5.3	6.0 ^h	5.0	33.0 ^h	16.3	1.6	– ^f	– ^f	2.3
2	Ce(AlMe ₃) ₃ (2^{Ce})	3.5	4.0	2.8	3.5	3.3	5.9	11.7	3.3	0.2	3.1
3	Pr(AlMe ₃) ₃ (2^{Pr})	3.9	8.0	3.2	14.1	6.8	8.7	6.5	8.7	4.4	4.1
4	Nd(AlMe ₃) ₃ (2Nd)	3.8	4.7	1.6	4.4	7.9	17.6	9.4	11.3	5.6	5.3
5	Gd(AlMe ₃) ₃ (2^{Gd})	5.6	2.9	6.1	8.4	9.6	11.8	5.6	6.9	3.8	3.2
6	Tb(AlMe ₃) ₃ (2^{Tb})	5.2	2.6	7.5	5.6	8.0	10.6	4.9	3.6	2.5	2.1
7	Dy(AlMe ₃) ₃ (2^{Dy})	9.6	1.5	10.0	6.7	8.5	13.1	3.0	3.2	1.9	1.6
8	Ho(AlMe ₃) ₃ (2^{Ho})	5.6	3.7	12.1	7.8	11.6	17.6	2.9	3.6	2.2	2.5
9	Y(AlMe ₃) ₃ (2^Y)	9.0 ^h	3.1	11.7 ^h	26.0 ^h	12.0 ^h	16.1	– ^f	2.9	2.1	3.2
10	Er(AlMe ₃) ₃ (2^{Er})	7.9	4.1	9.1	5.9	15.5	15.5	– ^f	– ^f	– ^f	– ^f
11	Lu(AlMe ₃) ₃ (2^{Lu})	6.7	3.4	5.2	4.2	23.0	9.2	– ^f	– ^f	– ^f	– ^f

^a For detailed information on polymerization data and origin of the values (literature or this study), see sections S1.1 and S1.2. The values in this table are given in [10⁴ g/mol]. ^b Conditions: 0.02 mmol of the resp. Ln precatalyst, 0.02 or 0.04 mmol co-catalyst, in toluene, [Ln]:[isoprene] 1:1000 (n/n), reaction time 1 h, pre-reaction time 0.5 h. ^c **A** = [Ph₃C][B(C₆F₅)₄], **B** = [PhNMe₂H][B(C₆F₅)₄], **C** = B(C₆F₅)₃, **D** = Me₂AlCl, **E** = Et₂AlCl. ^e Determined by means of size-exclusion chromatography (SEC) against polystyrene standards.

^f No further evaluation possible due to low yield. ^h Reaction time 24 h.

Table S1.3.6. Comparison of the polydispersity indices obtained for the polyisoprenes^{ae}

entry ^b	precatalyst	cocatalyst ^c									
		A	2A	B	2B	C	2C	D	2D	E	2E
1	La(AlMe ₃) ₃ (2^{La})	1.29 ^h	6.90	1.23 ^h	1.15	1.18 ^h	1.40	6.28	– ^f	– ^f	3.27
2	Ce(AlMe ₃) ₃ (2^{Ce})	1.25	1.28	1.35	1.18	1.22	1.13	1.28	3.73	3.44	3.81
3	Pr(AlMe ₃) ₃ (2^{Pr})	1.35	2.35	1.55	1.78	1.32	1.35	2.98	3.09	4.84	4.10
4	Nd(AlMe ₃) ₃ (2Nd)	1.29	1.38	1.27	1.26	1.16	2.48	6.77	5.26	4.52	4.66
5	Gd(AlMe ₃) ₃ (2^{Gd})	1.76	1.63	1.70	1.88	1.28	1.36	5.30	7.00	7.89	5.87
6	Tb(AlMe ₃) ₃ (2^{Tb})	3.02	1.62	1.97	1.74	1.57	1.43	4.44	6.63	6.36	12.66
7	Dy(AlMe ₃) ₃ (2^{Dy})	1.74	1.87	1.70	1.79	1.33	1.40	6.52	6.19	6.80	8.95
8	Ho(AlMe ₃) ₃ (2^{Ho})	2.15	1.57	1.85	2.31	1.73	1.39	2.64	4.87	2.70	4.90
9	Y(AlMe ₃) ₃ (2^Y)	2.09 ^h	1.62	1.60 ^h	1.50 ^h	2.03 ^h	1.55	– ^f	2.92	1.43	3.84
10	Er(AlMe ₃) ₃ (2^{Er})	1.91	1.62	2.63	2.13	1.86	1.75	– ^f	– ^f	– ^f	– ^f
11	Lu(AlMe ₃) ₃ (2^{Lu})	1.58	1.62	2.06	1.78	1.55	2.07	– ^f	– ^f	– ^f	– ^f

^a For detailed information on polymerization data and origin of the values (literature or this study), see sections S1.1 and S1.2. ^b Conditions: 0.02 mmol of the resp. Ln precatalyst, 0.02 or 0.04 mmol co-catalyst, in toluene, [Ln]:[isoprene] 1:1000 (n/n), reaction time 1 h, pre-reaction time 0.5 h. ^c **A** = [Ph₃C][B(C₆F₅)₄], **B** = [PhNMe₂H][B(C₆F₅)₄], **C** = B(C₆F₅)₃, **D** = Me₂AlCl, **E** = Et₂AlCl. ^e Determined by means of size-exclusion chromatography (SEC) against polystyrene standards. ^f No further evaluation possible due to low yield.

^h Reaction time 24 h.

Table S1.3.7. Comparison of the glass transition temperatures obtained for the polyisoprenes^{a,g}

entry ^b	precatalyst	cocatalyst ^c									
		A	2A	B	2B	C	2C	D	2D	E	2E
1	La(AlMe ₃) ₃ (2^{La})	n.d. ^h	-63	n.d. ^h	-62	n.d. ^h	-63	-61	- ^f	- ^f	-62
2	Ce(AlMe ₃) ₃ (2^{Ce})	-62	-55	-62	-62	-61	-58	-59	-60	-61	-61
3	Pr(AlMe ₃) ₃ (2^{Pr})	-66	n.d.	-67	-65	-65	-61	-64	-62	-61	-62
4	Nd(AlMe ₃) ₃ (2Nd)	-64	-57	-64	-57	-63	-61	-60	-61	-61	-62
5	Gd(AlMe ₃) ₃ (2^{Gd})	-59	-51	-64	-61	-65	-66	-67	-67	-63	-63
6	Tb(AlMe ₃) ₃ (2^{Tb})	-55	-52	-57	-58	-66	-61	-66	-66	-67	-67
7	Dy(AlMe ₃) ₃ (2^{Dy})	-60	-55	-58	-57	-65	-61	-67	-67	-67	-67
8	Ho(AlMe ₃) ₃ (2^{Ho})	-56	-55	-56	-55	-64	-62	-67	-66	-67	-66
9	Y(AlMe ₃) ₃ (2^Y)	n.d. ^h	-53	n.d. ^h	n.d. ^h	n.d. ^h	-62	- ^f	-68	-67	-66
10	Er(AlMe ₃) ₃ (2^{Er})	-56	-50	-55	-52	-59	-57	- ^f	- ^f	- ^f	- ^f
11	Lu(AlMe ₃) ₃ (2^{Lu})	-62	-55	-63	-59	-61	-61	- ^f	- ^f	- ^f	- ^f

^a For detailed information on polymerization data and origin of the values (literature or this study), see sections S1.1 and S1.2. The values in this table are given in [°C]. ^b Conditions: 0.02 mmol of the resp. Ln precatalyst, 0.02 or 0.04 mmol co-catalyst, in toluene, [Ln]:[isoprene] 1:1000 (n/n), reaction time 1 h, pre-reaction time 0.5 h. ^c **A** = [Ph₃C][B(C₆F₅)₄], **B** = [PhNMe₂H][B(C₆F₅)₄], **C** = B(C₆F₅)₃, **D** = Me₂AlCl, **E** = Et₂AlCl. ^f No further evaluation possible due to low yield. ^g Determined by differential scanning calorimetry; heating rate: 20 K/min, cooling rate: 60 K/min. ^h Reaction time 24 h.

S1.4 Isoprene polymerization screenings

In order to gain more insight into the polymerization-active species, the standard conditions given in Section 3.4 of the main article (Materials and Methods) have been augmented as presented in the respective tables. Besides the obtained data, our group has reported on isoprene polymerization in *n*-hexane applying combinations of $\text{Ln}(\text{AlMe}_4)_3/\text{E}$ ($\text{Ln} = \text{La}$ [4,5], Pr [6], Gd [4,5]) resulting in high yields after 24 h and nearly quantitative *cis*-selectivity. Moderate yields and selectivity were obtained for $\text{Ln} = \text{Y}$ [4,5] and low yields (<7%) but high *cis*-contents after 24 h reaction time for $\text{Sm}(\text{AlMe}_4)_3$ [4,5]. Polymerization attempts with $\text{Nd}(\text{AlMe}_4)_3$ applying Me_3SiCl as a chlorine source did not reveal any polyisoprene formation, nor is $\text{Nd}(\text{AlMe}_4)_3$ active as a single component catalyst. Furthermore, polymerizations with some of the low yielding systems at standard conditions have been repeated with a reaction time of 24 h (results can be found in Table S1.4.4).

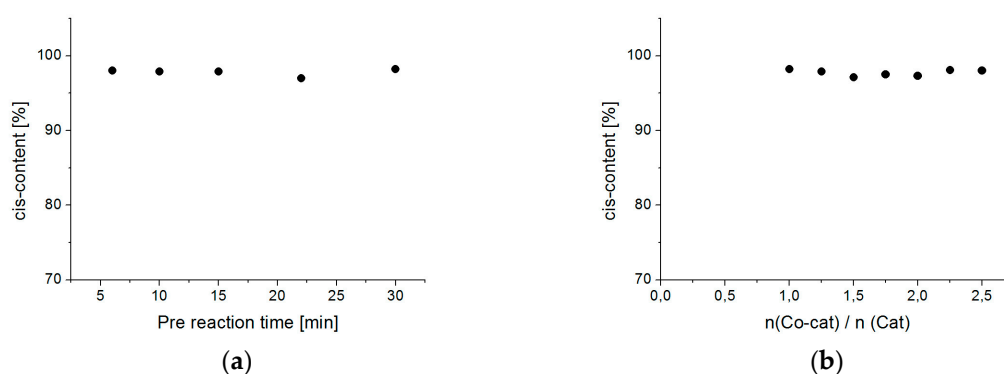


Figure S1.4.1. Overview on the *cis*-contents obtained by screening the pre-reaction time (a) and cocatalyst concentration (b) of the isoprene polymerization applying $\text{Nd}(\text{AlMe}_4)_3$ (2^{Nd})/ Et_2AlCl (E).

Table S1.4.1. Influence of pre-reaction time on isoprene polymerization by $2^{\text{Nd}}/\text{E}^{\text{a}}$

entry ^b	pre-reaction time [min]	yield [%]	<i>cis</i> -content [%] ^d	<i>trans</i> -content [%] ^d	vinyllic content [%] ^d	M_n [10^4 g/mol] ^e	<i>PDI</i> ^e	ref.
1	30	57	98.2	0	1.8	5.6	4.52	^a
2	22	87	97.0	0.8	2.2	6.2	4.11	^a
3	15	83	97.9 ⁱ	0	2.1 ⁱ	7.0	3.71	^a
4	10	83	97.9 ⁱ	0	2.1 ⁱ	6.3	3.86	^a
5	6	65	98.0	0	2.0	6.2	3.45	[3]

^a For data produced at standard conditions, see Table S1.2.4 as well. ^b Conditions: 0.02 mmol 2^{Nd} , 0.02 mmol cocatalyst, 8 mL toluene, $[\text{Ln}]:[\text{isoprene}]$ 1:1000 (n/n), reaction time 1 h. ^c $\text{E} = \text{Et}_2\text{AlCl}$. ^d Determined by ^1H and ^{13}C NMR spectroscopy in CDCl_3 . ^e Determined by means of size-exclusion chromatography (SEC) against polystyrene standards. ⁱ For entries 3 and 4 identical microstructures were obtained. ^{*} This study.

Table S1.4.2. Influence of cocatalyst concentration on isoprene polymerization by **2Nd/E^a**

entry ^b	cocatalyst ^c	yield [%]	cis-content [%] ^d	trans-content [%] ^d	vinyl content [%] ^d	M _n [10 ⁴ g/mol] ^e	PDI ^e	ref.
1	E	57	98.2	0.0	1.8	5.6	4.52	– ^s
2	1.25 E	77	97.9	0.0	2.1	5.9	4.65	– ^s
3	1.5 E	80	97.1	0.9	2.0	6.7	4.28	– ^s
4	1.75 E	83	97.5	0.4	2.1	8.8	3.40	– ^s
5	2 E	86	97.3	0.9	1.8	5.3	4.66	– ^s
6	2.25 E	87	98.1	0.0	1.9	6.1	4.11	– ^s
7	2.5 E	91	98.0	0.0	2.0	5.5	4.58	– ^s

^a For data produced standard conditions, see Table S1.6.2. ^b Conditions: 0.02 mmol **2Nd**, 8 mL toluene, reaction time 1 h, pre-reaction time 0.5 h. ^c E = Et₂AlCl. ^d Determined by ¹H and ¹³C NMR spectroscopy in CDCl₃. ^e Determined by means of size-exclusion chromatography (SEC) against polystyrene standards. ^s This study.

Table S1.4.3. Influence of solvent on isoprene polymerization applying **2Nd/E^a**

entry ^b	solvent	yield [%]	cis-content [%] ^d	trans-content [%] ^d	vinyl content [%] ^d	M _n [10 ⁴ g/mol] ^e	PDI ^e	ref.
1	toluene	57	98.2	0.0	1.8	5.6	4.52	– ^s
2	toluene: <i>n</i> -hexane (1:7)	73	98.0	0.0	2.0	5.9	3.61	– ^s
3	<i>n</i> -hexane	52	94.6	3.2	2.2	7.2	7.07	– ^s

^a For data produced standard conditions, see Table S1.1.5. ^b Conditions: 0.02 mmol **2Nd**, 0.02 mmol cocatalyst, 25 mL solvent, pre-reaction time: 0.5 h, reaction time 1 h. ^c E = Et₂AlCl. ^d Determined by ¹H and ¹³C NMR spectroscopy in CDCl₃. ^e Determined by means of size-exclusion chromatography (SEC) against polystyrene standards. ^s this study.

Table S1.4.4. 24 h-Reaction time for selected low-yielding systems in Tables S1.1.1 – S1.3.7 ^a

entry ^b	precatalyst	cocatalyst ^c	yield [%]	cis-content [%] ^d	trans-content [%] ^d	vinyl content [%] ^d	M _n [10 ⁴ g/mol] ^e	PDI ^e	ref.
1	La(AlMe ₄) ₃ (2^{La})	D	38	77.6	18.8	2.8/0.8 ^q	3.3	3.62	– ^s
2	La(AlMe ₄) ₃ (2^{La})	E	43	87.0	10.0	2.9	2.7	2.71	– ^s
3	La(AlMe ₄) ₃ (2^{La})	2E	83	87.2	10.1	2.8	5.1	2.73	– ^s
4	Er(AlMe ₄) ₃ (2^{Er})	2D	37	34.6	64.0	1.4	3.4	2.65	– ^s
5	Er(AlMe ₄) ₃ (2^{Er})	E	14	35.8	63.0	1.1	1.4	2.11	– ^s
6	Er(AlMe ₄) ₃ (2^{Er})	2E	54	24.3	74.1	1.5	2.2	1.91	– ^s
7	Lu(AlMe ₄) ₃ (2^{Lu})	2E	4	14.1	81.8	4.1	6.0	2.46	– ^s

^a For data produced at standard conditions, see Tables S1.2.1, S1.2.10 and S1.2.11. ^b Conditions: 0.02 mmol of the resp. precatalyst, 0.02 or 0.04 mmol cocatalyst, 8 mL toluene, reaction time 24 h, pre-reaction time 0.5 h. ^c D = Me₂AlCl, E = Et₂AlCl. ^d Determined by ¹H and ¹³C NMR spectroscopy in CDCl₃. ^e Determined by means of size-exclusion chromatography (SEC) against polystyrene standards. ^q 3,4-Content / 1,2-content. ^s This study.

S1.5 Polyisoprene data on UV-light irradiated samples

Polymer data reported in this section were obtained from samples produced according to the standard conditions given in Sections 3.4 and 3.5 of the main article (Materials and Methods) and thereafter irradiated applying UV-light of 254 nm for 48 h under air. Data obtained before radiation are presented for comparison.

Table S1.5.1. Polymer data of polyisoprenes applying **2Nd** after exposure to UV-light of 254 nm^a

entry ^b	cocatalyst ^c	cis-content [%] ^d	trans-content [%] ^d	vinyl content [%] ^d	M _n [10 ⁴ g/mol] ^e	PDI ^e	ref.
1	A	43.9	51.9	4.3	3.3	1.25	– ^s
2	B	39.9	55.8	4.3	5.6	1.14	– ^s
3	C	57.0	40.7	2.3	6.7	1.13	– ^s
4	D	97.9	0.0	2.1	8.9	6.66	– ^s
5	E	98.0	0.0	2.0	4.2	5.50	– ^s

^a For data of the original polymers, see Table S1.2.4, for ATR-IR data of the polymers, see Table S2.5.1. ^b 48 h Exposure to UV-light of 254 nm. ^c A = [Ph₃C][B(C₆F₅)₄], B = [PhNMe₂H][B(C₆F₅)₄], C = B(C₆F₅)₃, D = Me₂AlCl, E = Et₂AlCl. ^d Determined by ¹H and ¹³C NMR spectroscopy in CDCl₃. ^e Determined by means of size-exclusion chromatography (SEC) against polystyrene standards. ^s This study.

S1.6 Polymerization of 1,3-butadiene at standard conditions by precatalyst

If not mentioned otherwise in the respective table, the polybutadienes shown in this section have been synthesized according to the procedure given in Section 3.5 of the main article (Materials and Methods) or taken from the literature for comparison.

Table S1.6.1. Polybutadiene applying Y(AlMe₄)₃ (**2^Y**)^a

entry ^b	cocatalyst ^c	pre-reaction time [h]	reaction time [h]	yield [%]	cis-content [%] ^d	trans-content [%] ^d	vinyl content [%] ^d	M _n [10 ⁴ g/mol] ^e	PDI ^e	ref.
1	B	0.5	0.5	<5	– ^f	– ^f	– ^f	– ^f	– ^f	[2]
2	B	4	0.5	73	n.d.	n.d.	n.d.	18.6	4.4	[2]
3	2B	0.5	0.5	26	95	3	2	14.0	2.0	[2]
4	2B	4	0.5	93	n.d.	n.d.	n.d.	31.2	2.6	[2]

^a For data produced by systems of **2^Y/B** and **2^Y/2B** in the presence of Al*i*Bu₃, see [2]. ^b Conditions: 0.02 mmol **2^Y**, 0.02 or 0.04 mmol resp. co-catalyst, 8 mL toluene, [9]:[1,3-butadiene] 1:1000 (n/n). ^c B = [PhNMe₂H][B(C₆F₅)₄]. ^d Determined by ¹H and ¹³C NMR spectroscopy in CDCl₃. ^e Determined by means of size-exclusion chromatography (SEC) against polystyrene standards. ^f No further evaluation possible due to low yield.

Table S1.6.2. Polybutadiene applying $\text{Nd}(\text{AlMe}_4)_3$ (2^{Nd})^a

entry ^b	cocatalyst ^c	BD [mmol]	yield [%]	cis-content [%] ^d	trans- content [%] ^d	vinyl content [%] ^d	M_n [10 ⁴ g/mol] ^e	PDI ^e	ref.
1	D	53.5	28	99.7	0.0	0.3	40.7	2.39	– ^s
2	E	22.4	41	96.7	2.9	0.4	8.3	3.47	– ^s

^a For data produced by optimization screenings, see Section S1.7; Polymerization attempts with $\text{Nd}(\text{AlMe}_4)_3$ applying Me_2SiCl as a chlorine source did not reveal any polyisoprene formation, nor is $\text{Nd}(\text{AlMe}_4)_3$ active as a single component catalyst. ^b Conditions: 0.02 mmol 2^{Nd} , 0.02 mmol cocatalyst, 25 mL toluene, 100 rpm, 1 bar of BD pressure, reaction time 1 h, pre-reaction time 0.5 h. ^c D = Me_2AlCl , E = Et_2AlCl . ^d Determined by ^1H and ^{13}C NMR spectroscopy in CDCl_3 . ^e Determined by means of size-exclusion chromatography (SEC) against polystyrene standards. ^s This study.

Table S1.6.3 Polybutadiene applying $\text{Pr}(\text{AlMe}_4)_3$ (2^{Pr})

entry ^a	cocatalyst ^b	yield [%]	cis-content [%] ^c	trans-content [%] ^c	vinyl content [%] ^c	M_n [10 ⁴ g/mol] ^d	PDI ^d	ref.
1	A	60	30.2	67.2	1.8	10.8	2.52	– ^s
2	B	54	28.8	69.2	2.0	11.8	3.60	– ^s
3	C	54	59.7	39.2	1.0	12.1	1.15	– ^s
4	D	22	92.2	7.1	0.7	10.0	5.07	– ^s
5	E	34	94.3	5.0	0.7	9.8	4.22	– ^s

^a Conditions: 0.02 mmol 2^{Pr} , 0.02 mmol cocatalyst, 25 mL toluene, [3]:[1,3-butadiene] 1:3000 (n/n), 100 rpm, reaction time 1 h, pre-reaction time 0.5 h. ^b A = $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$, B = $[\text{PhNMMe}_2\text{H}][\text{B}(\text{C}_6\text{F}_5)_4]$, C = $\text{B}(\text{C}_6\text{F}_5)_3$, D = Me_2AlCl , E = Et_2AlCl . ^c Determined by ^1H and ^{13}C NMR spectroscopy in CDCl_3 . ^d Determined by means of size-exclusion chromatography (SEC) against polystyrene standards. ^s This study.

Okuda *et al.* used $\text{La}(\text{AlMe}_4)_3$ (2^{La}) and $\text{Gd}(\text{AlMe}_4)_3$ (2^{Gd}) along with co-catalyst A in the presence of $\text{Al}i\text{Bu}_3$ for 1,3-butadiene polymerization[7].

S1.7 1,3-Butadiene polymerization screenings

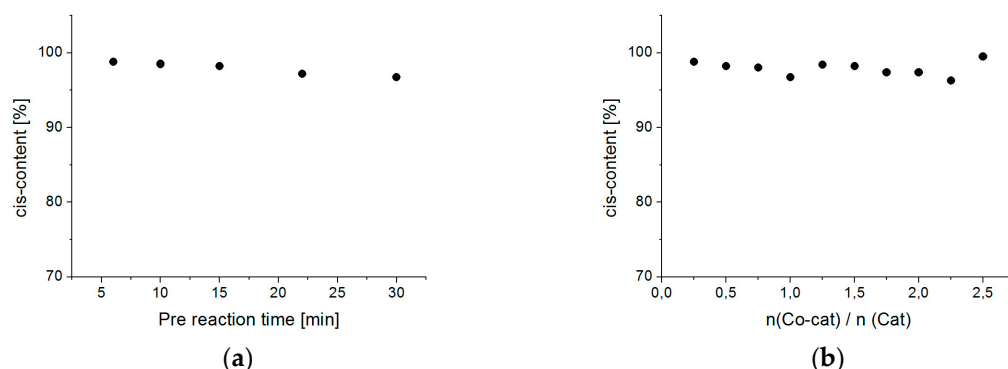


Figure S1.7.1. Overview on the *cis*-contents obtained by screening the pre-reaction time (a) and co-catalyst concentration (b) of the 1,3-butadiene polymerization applying Nd(AlMe₄)₃ (2Nd)/Et₂AlCl (E).

Table S1.7.1. Influence of pre-reaction time on 1,3-butadiene polymerization applying 2Nd/E^a

entry ^b	pre-reaction time [min]	BD [mmol]	yield [%]	<i>cis</i> -content [%] ^d	<i>trans</i> -content [%] ^d	vinyl content [%] ^d	<i>M_n</i> [10 ⁴ g/mol] ^e	<i>PDI</i> ^e	ref.
1	30	22.4	41	96.7	2.9	0.4	8.3	3.47	^s
2	22	21.6	57	97.2	2.7	0.1	12.2	3.90	^s
3	15	42.9	76	98.2	1.6	0.2	11.3	4.02	^s
4	10	51.3	67	98.5	1.3	0.2	13.6	2.51	^s
5	6	36.9	52	98.8	0.9	0.3	10.3	4.24	^s

^a For data produced at standard conditions, see Table S1.6.2. ^b Conditions: 0.02 mmol 2Nd, 0.02 mmol cocatalyst, 25 mL toluene, 100 rpm, 1 bar of BD pressure, reaction time 1h. ^c E = Et₂AlCl. ^d Determined by ¹H and ¹³C NMR spectroscopy in CDCl₃. ^e Determined by means of size-exclusion chromatography (SEC) against polystyrene standards. ^s This study.

Table S1.7.2. Influence of cocatalyst concentration on 1,3-butadiene polymerization applying 2Nd/E^a

entry ^b	cocatalyst ^c	BD [mmol]	yield [%]	cis-content [%] ^d	trans- content [%] ^d	vinyl content [%] ^d	M _n [10 ⁴ g/mol] ^e	PDI ^e	ref.
1	0.25 E	35.6	5	98.8	1.0	0.2	14.5	4.62	– ^s
2	0.5 E	35.4	18	98.2	1.5	0.3	11.9	4.76	– ^s
3	0.75 E	34.1	39	98.0	1.9	0.1	8.3	5.12	– ^s
4	E	22.4	41	96.7	2.9	0.4	8.3	3.47	– ^s
5	1.25 E	38.0	59	98.4	1.5	0.1	11.9	3.72	– ^s
6	1.5 E	39.9	46	98.2	1.6	0.2	16.5	3.57	– ^s
7	1.75 E	38.8	85	97.4 ^l	2.5 ^l	0.1 ^l	10.9	3.92	– ^s
8	2 E	25.9	76	97.4 ^l	2.5 ^l	0.1 ^l	16.6	3.50	– ^s
9	2.25 E	43.7	3	96.3	3.6	0.1	20.5	2.72	– ^s
10	2.5 E	56.6	41	99.5	0.4	0.1	18.8	3.31	– ^s

^a For data produced at standard conditions, see Table S1.6.2. ^b Conditions: 0.02 mmol 2Nd, 25 mL toluene, 100 rpm, 1 bar of BD pressure, reaction time 1 h, pre-reaction time 0.5 h. ^c E = Et₂AlCl. ^d Determined by ¹H and ¹³C NMR spectroscopy in CDCl₃. ^e Determined by means of size-exclusion chromatography (SEC) against polystyrene standards. ^l These polymerizations resulted in identical microstructures. ^s This study.

Table S1.7.3. Influence of reaction time on 1,3-butadiene polymerization applying 2Nd/E^a

entry ^b	reaction time [h]	BD [mmol]	yield [%]	cis-content [%] ^d	trans-content [%] ^d	vinyl content [%] ^d	M _n [10 ⁴ g/mol] ^e	PDI ^e	ref.
1	1	22.4	41	96.7	2.9	0.4	8.3	3.47	– ^s
2	2	30.9	78	97.6	2.2	0.2	11.3	3.85	– ^s

^a For data produced at standard conditions, see Table S1.6.2. ^b Conditions: 0.02 mmol 2Nd, 0.02 mmol co-catalyst, 25 mL toluene, 100 rpm, 1 bar of BD pressure, pre-reaction time 0.5 h. ^c E = Et₂AlCl. ^d Determined by ¹H and ¹³C NMR spectroscopy in CDCl₃. ^e Determined by means of size-exclusion chromatography (SEC) against polystyrene standards. ^s This study.

Table S1.7.4. Influence of solvent on 1,3-butadiene polymerization applying 2Nd/E^a

entry ^b	solvent	BD [mmol]	yield [%]	cis- content [%] ^d	trans- content [%] ^d	vinyl content [%] ^d	M _n [10 ⁴ g/mol] ^e	PDI ^e	ref.
1	toluene	22.4	41	96.7	2.9	0.4	8.3	3.47	– ^s
2	n-hexane	60.0	49	99.3	0.0	0.7	25.5	3.66	– ^s

^a For data produced at standard conditions, see Table S1.6.2. ^b Conditions: 0.02 mmol 2Nd, 0.02 mmol cocatalyst, 25 mL solvent, pre-reaction time: 0.5 h, reaction time 1 h, 100 rpm. ^c E = Et₂AlCl. ^d Determined by ¹H and ¹³C NMR spectroscopy in CDCl₃. ^e Determined by means of size-exclusion chromatography (SEC) against polystyrene standards. ^s This study.

S1.8 Polymerization of ethylene

Table S1.8.1. Results of ethylene polymerization applying $2^{Nd}/E$ and $2^{Nd}/2E$

entry ^b	precatalyst	cocatalyst ^c	yield [%]	M_n [10 ⁴ g/mol] ^e	PDI ^e	T_m^g [°C]	ref.
1	Nd(AlMe ₃) ₃ (2^{Nd})	E	8	16.3	3.4	138	– ^s
2	Nd(AlMe ₃) ₃ (2^{Nd})	2E	58	13.2	4.0	130	– ^s

^b Conditions: 0.06 mmol 2^{Nd} , 0.06 or 0.12 mmol cocatalyst, 125 mL toluene, 60 mmol of ethylene, pre-reaction time: 0.5 h, 60 °C, 50 rpm, reaction time 1 h. ^c E = Et₂AlCl. ^e Determined by means of high temperature size-exclusion chromatography (SEC) against polystyrene standards. ^g Determined by differential scanning calorimetry; heating rate: 20 K/min, cooling rate: 60 K/min. ^s This study.

S2. Comparison of Microstructure Data Obtained from ATR-IR and NMR Spectroscopic Analyses

The data obtained from the prescreening of the microstructure by ATR-IR spectroscopy is plotted versus the microstructure data calculated from the NMR spectra according to section 3.5 in the main article.

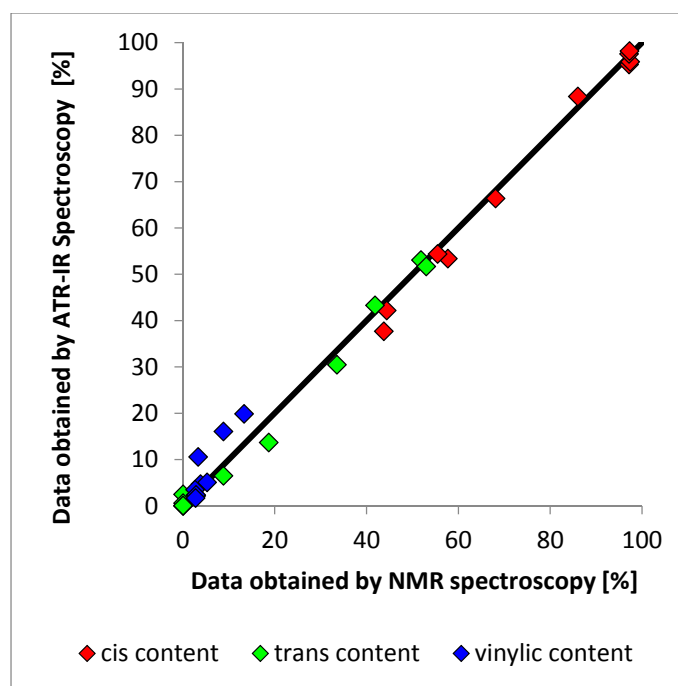
S2.1 Polyisoprene applying precatalyst Ce(AlMe₃)₃ (2^{Ce})

Figure S2.1.1. Comparison of the microstructure results obtained by NMR and ATR-IR spectroscopy, applying 2^{Ce} and cocatalysts A-E (A = [Ph₃C][B(C₆F₅)₄], B = [PhNMe₂H][B(C₆F₅)₄], C = B(C₆F₅)₃, D = Me₂AlCl, E = Et₂AlCl) in both one and two equivalents. For detailed polymerization data see Tables S1.2.2 and S2.1.1.

Table S2.1.1. Comparison of the microstructure results by NMR and ATR-IR spectroscopy, data from isoprene polymerization applying **2**^{ce} ^a

entry ^b	cocatalyst ^c	NMR			ATR-IR			ref.
		<i>cis</i> -content [%] ^d	<i>trans</i> -content [%] ^d	vinyl content [%] ^d	<i>cis</i> -content [%] ^e	<i>trans</i> -content [%] ^e	vinyl content [%] ^e	
1	A	42.2	53.1	4.7	44.4	51.8	3.8	– ^s
2	2A	66.4	13.7	19.9	68.1	18.7	13.3	– ^s
3	B	37.7	51.7	10.6	43.7	53.0	3.3	– ^s
4	2B	53.4	30.5	16.1	57.7	33.5	8.8	– ^s
5	C	54.4	43.3	2.3	55.4	41.8	2.7	– ^s
6	2C	88.4	6.5	5.1	86.0	8.8	5.2	– ^s
7	D	95.3	2.5	2.2	97.1	0.0	2.9	– ^s
8	2D	95.9	0.6	3.5	97.4	0.0	2.6	– ^s
9	E	97.6	0.0	2.4	97.2	0.0	2.8	– ^s
10	2E	98.2	0.1	1.7	97.3	0.0	2.7	– ^s

^a For detailed data on the respective chain properties, see Table S1.2.2. ^b Conditions: 0.02 mmol **2**^{ce}, 0.02 or 0.04 mmol resp. cocatalyst, 8 mL solvent, pre-reaction time: 0.5 h, reaction time 1 h. ^c **A** = [Ph₃C][B(C₆F₅)₄], **B** = [PhNMe₂H][B(C₆F₅)₄], **C** = B(C₆F₅)₃, **D** = Me₂AlCl, **E** = Et₂AlCl. ^d Determined by ¹H and ¹³C NMR spectroscopy in CDCl₃. ^e Determined by ATR-IR spectroscopy. ^s This study.

S2.2 Polyisoprene applying precatalyst Nd(AlMe₄)₃ (**2**Nd)

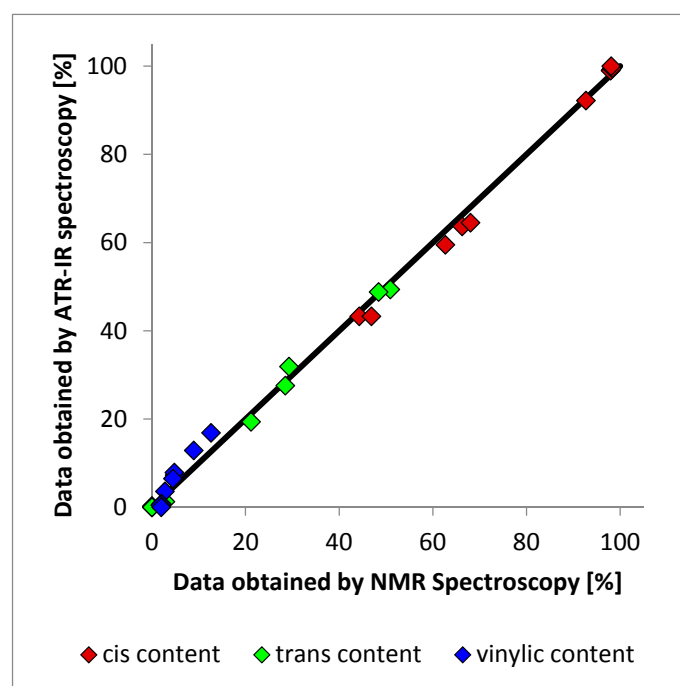


Figure S2.2.1. Comparison of the microstructure results obtained by NMR and ATR-IR spectroscopy, applying Nd(AlMe₄)₃ (**2**Nd) and cocatalysts **A**–**E** (**A** = [Ph₃C][B(C₆F₅)₄], **B** = [PhNMe₂H][B(C₆F₅)₄], **C** = B(C₆F₅)₃, **D** = Me₂AlCl, **E** = Et₂AlCl) in both one and two equivalents. For detailed polymerization data see Tables S1.2.4 and S2.2.1.

Table S2.2.1. Comparison of the microstructure results by NMR and ATR-IR spectroscopy, data from isoprene polymerization applying 2^{Nd} ^a

entry ^b	co-catalyst ^c	NMR			ATR-IR			ref.
		<i>cis</i> -content [%] ^d	<i>trans</i> -content [%] ^d	vinyllic content [%] ^d	<i>cis</i> -content [%] ^e	<i>trans</i> -content [%] ^e	vinyllic content [%] ^e	
1	A	44.3	50.9	4.9	43.3	49.4	7.3	– ^s
2	2A	66.2	21.2	12.6	63.7	19.4	16.9	– ^s
3	B	46.8	48.4	4.8	43.3	48.8	7.9	– ^s
4	2B	62.6	28.5	8.9	59.5	27.6	12.9	– ^s
5	C	68.0	29.2	2.7	64.5	31.9	3.6	– ^s
6	2C	92.7	2.9	4.5	92.2	1.3	6.5	– ^s
7	D	98.0	0.0	2.0	99.2	0.0	0.8	– ^s
8	2D	97.9	0.0	2.1	99.0	0.3	0.7	– ^s
9	E	98.2	0.0	1.8	99.5	0.0	0.5	– ^s
10	2E	98.0	0.0	2.0	99.9	0.0	0.0	– ^s

^a For detailed data on the respective chain properties, see Table S1.2.4. ^b Conditions: 0.02 mmol 2^{Nd} , 0.02 or 0.04 mmol resp. co-catalyst, 8 mL solvent, pre-reaction time: 0.5 h, reaction time 1 h. ^c A = [Ph₃C][B(C₆F₅)₄], B = [PhNMe₂H][B(C₆F₅)₄], C = B(C₆F₅)₃, D = Me₂AlCl, E = Et₂AlCl. ^d Determined by ¹H and ¹³C NMR spectroscopy in CDCl₃. ^e Determined by ATR-IR spectroscopy. ^s This study.

S2.3 Polyisoprene applying precatalyst Tb(AlMe₄)₃ (2^{Tb})

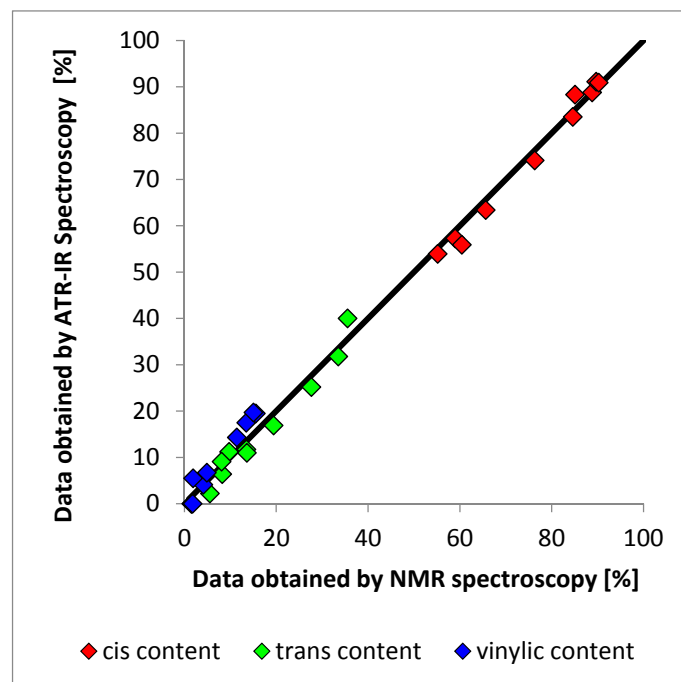


Figure S2.3.1. Comparison of the microstructure results obtained by NMR and ATR-IR spectroscopy, applying Tb(AlMe₄)₃ (2^{Tb}) and cocatalysts A-E (A = [Ph₃C][B(C₆F₅)₄], B = [PhNMe₂H][B(C₆F₅)₄], C = B(C₆F₅)₃, D = Me₂AlCl, E = Et₂AlCl) in both one and two equivalents. For detailed polymerization data see Tables S1.2.6 and S2.3.1.

Table S2.3.1. Comparison of the microstructure results by NMR and ATR-IR spectroscopy, data from isoprene polymerization applying 2^{Tb} ^a

entry ^b	cocatalyst ^c	<i>cis</i> -content [%] ^d	NMR	vinyl content [%] ^d	<i>cis</i> - content [%] ^e	ATR-IR	vinyl content [%] ^e	ref.
			<i>trans</i> - content [%] ^d			<i>trans</i> - content [%] ^e		
1	A	55.1	33.5	11.4	53.9	31.8	14.3	– ^s
2	2A	58.9	27.6	13.4	57.3	25.2	17.5	– ^s
3	B	60.4	35.5	4.1	55.9	40.0	4.1	– ^s
4	2B	85.0	13.5	1.5	88.3	11.7	0.0	– ^s
5	C	88.8	9.7	1.5	88.8	11.2	0.0	– ^s
6	2C	76.3	8.2	15.5	74.1	6.4	19.5	– ^s
7	D	65.6	19.4	15.0	63.4	16.9	19.7	– ^s
8	2D	89.7	5.5	4.8	91.1	2.2	6.7	– ^s
9	E	84.6	13.6	1.9	83.5	11.0	5.5	– ^s
10	2E	90.2	8.1	1.7	90.9	9.1	0.0	– ^s

^a For detailed data on the respective chain properties, see Table S1.2.6. ^b Conditions: 0.02 mmol 2^{Tb} , 0.02 or 0.04 mmol resp. cocatalyst, 8 mL solvent, pre-reaction time: 0.5 h, reaction time 1 h. ^c A = [Ph₃C][B(C₆F₅)₄], B = [PhNMe₂H][B(C₆F₅)₄], C = B(C₆F₅)₃, D = Me₂AlCl, E = Et₂AlCl. ^d Determined by ¹H and ¹³C NMR spectroscopy in CDCl₃. ^e Determined by ATR-IR spectroscopy. ^s This study.

S2.4 Polyisoprene applying precatalyst Er(AlMe₄)₃ (2^{Er})

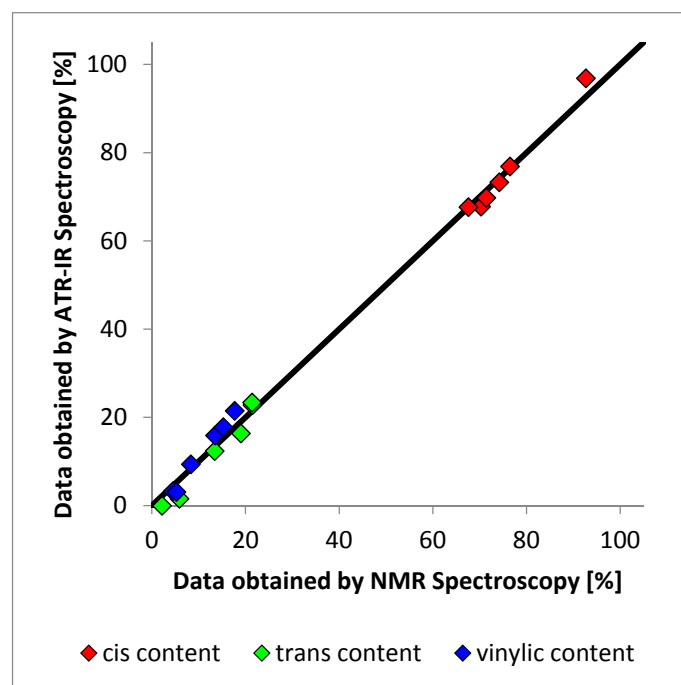
**Figure S2.4.1.** Comparison of the microstructure results obtained by NMR and ATR-IR spectroscopy, applying Er(AlMe₄)₃ (2^{Er}) and cocatalysts A–E (A = [Ph₃C][B(C₆F₅)₄], B = [PhNMe₂H][B(C₆F₅)₄], C = B(C₆F₅)₃, D = Me₂AlCl, E = Et₂AlCl) in both one and two equivalents. For detailed polymerization data see Tables S1.2.10 and S2.4.1.

Table S2.4.1. Comparison of the microstructure results by NMR and ATR-IR spectroscopies, data from isoprene polymerization applying **2^{Er}**^a

entry ^b	cocatalyst ^c	NMR			ATR-IR			ref.
		<i>cis</i> -content [%] ^d	<i>trans</i> -content [%] ^d	vinyl content [%] ^d	<i>cis</i> -content [%] ^e	<i>trans</i> -content [%] ^e	vinyl content [%] ^e	
1	A	67.8	22.8	9.4	70.3	21.5	8.3	– ^s
2	2A	76.9	1.6	21.5	76.5	5.9	17.7	– ^s
3	B	67.7	16.4	15.9	67.6	19.0	13.5	– ^s
4	2B	69.8	12.4	17.8	71.4	13.4	15.2	– ^s
5	C	73.3	23.4	3.3	74.2	21.4	4.5	– ^s
6	2C	96.9	0.0	3.1	92.6	2.1	5.2	– ^s

^a For detailed data on the respective chain properties, see Table S1.2.10. ^b Conditions: 0.02 mmol **2^{Er}**, 0.02 or 0.04 mmol resp. cocatalyst, 8 mL solvent, pre-reaction time: 0.5 h, reaction time 1 h. ^c **A** = [Ph₃C][B(C₆F₅)₄], **B** = [PhNMe₂H][B(C₆F₅)₄], **C** = B(C₆F₅)₃, **D** = Me₂AlCl, **E** = Et₂AlCl. ^d Determined by ¹H and ¹³C NMR spectroscopy in CDCl₃. ^e Determined by ATR-IR spectroscopy. ^s This study.

S2.5 Polyisoprene irradiated by UV-light at 254 nm

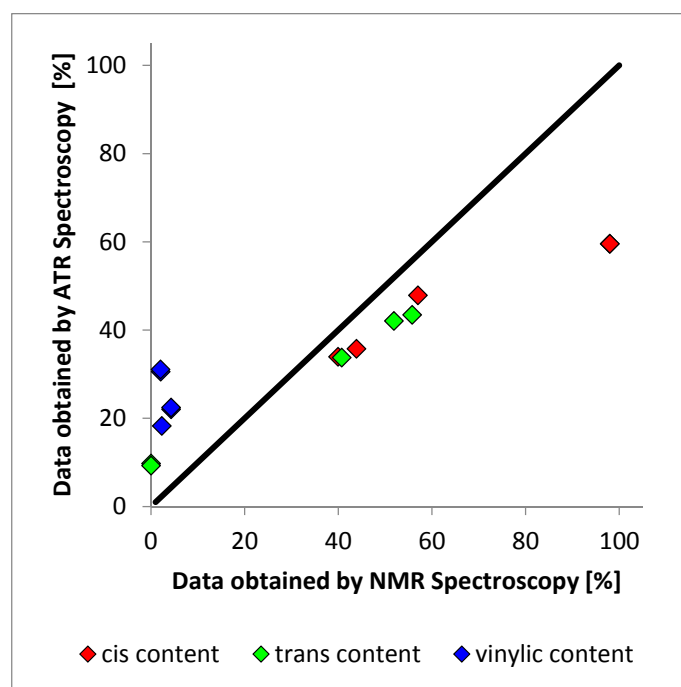


Figure S2.5.1. Comparison of the microstructure results obtained by NMR and ATR-IR spectroscopy, applying Nd(AlMe₄)₃ (**2Nd**) and cocatalysts **A-E** (**A** = [Ph₃C][B(C₆F₅)₄], **B** = [PhNMe₂H][B(C₆F₅)₄], **C** = B(C₆F₅)₃, **D** = Me₂AlCl, **E** = Et₂AlCl) in one equivalent and 48 h of UV radiation at 254 nm. For detailed polymerization data see Tables S1.2.4, S1.5.1 and S2.5.1.

Table S2.5.1 Comparison of the microstructure results by NMR and ATR-IR spectroscopy, data from UV-irradiated samples of isoprene polymerization applying 2^{Na}

entry ^b	cocatalyst ^c	NMR			ATR-IR			ref.
		<i>cis</i> -content [%] ^d	<i>trans</i> -content [%] ^d	vinyl content [%] ^d	<i>cis</i> -content [%] ^e	<i>trans</i> -content [%] ^e	vinyl content [%] ^e	
1	A	43.9	51.9	4.3	35.8	42.1	22.1	– ^s
2	B	39.9	55.8	4.3	34.0	43.5	22.5	– ^s
3	C	57.0	40.7	2.3	47.9	33.8	18.3	– ^s
4	D	97.9	0.0	2.1	59.6	9.8	30.6	– ^s
5	E	98.0	0.0	2.0	59.6	9.3	31.1	– ^s

^a For detailed data on the respective chain properties, see Tables S1.2.4 and S1.5.1. ^b Conditions: samples obtained from isoprene polymerization were exposed to UV-light of 254 nm for 48 h. ^c A = [Ph₃C][B(C₆F₅)₄], B = [PhNMe₂H][B(C₆F₅)₄], C = B(C₆F₅)₃, D = Me₂AlCl, E = Et₂AlCl. ^d Determined by ¹H and ¹³C NMR spectroscopy in CDCl₃. ^e Determined by ATR-IR spectroscopy. ^s This study.

Values reported for the 3,4 contents in Table and Figure S2.5.1 are given, as obtained from the algorithm. As a shift towards vinyl linkage by UV radiation does not seem likely, it is assumed, that UV-induced crosslinking creates oscillations in the IR spectrum that are misinterpreted by the algorithm.

S3. Extrapolation of the Ratio n(Chains) / n(Ln Centers)

In order to obtain the ratio of polymer chains per lanthanide center, the assumption is made, that if the polymerization would not be stopped after 1 h of reaction time, it would continue in the same fashion until all monomer is consumed.

The extrapolated number average molecular mass is then given by

$$M_{n,ext}(c_M = 0) = \frac{M_n(1\text{ h})}{\text{yield}(1\text{ h})} \quad (1)$$

where c_M is the concentration of the monomer. Due to the assumption discussed above, errors occur, as the system, investigated in this study, is intended to set free a chain transfer agent AlMe₃, that could cause the initiation of new chains at all times. As the chain transfer capability of AlMe₃ is known to be low, and chain termination plays only a minor role in catalyzed polymerization, these errors are assumed to be low enough to be neglected.

The respective degree of polymerization is given by equation (2).

$$P_{n,ext} = \frac{M_{n,ext}}{M_M} \quad (2)$$

where M_M is the molecular mass of the monomer.

For 100% monomer consumption, equation (3) applies.

$$P_n = \frac{n_M}{n_{act\ Ln}} = \frac{n_M}{n(chains)} \quad (3)$$

where n_M is the amount of monomer fed [mol] and therefore constant during the whole reaction. $n_{act\ Ln}$ is the amount of active lanthanide centers [mol], and $n(chains)$ the amount of polymer chains formed during the reaction [mol].

$P_{n,exp}$, the expected degree of polymerization if all Ln centers grow polymer chains is given by

$$P_{n,exp} = \frac{n_M}{n_{Ln}} = \frac{n_M}{n(chains)_{exp}} \quad (4)$$

where n_{Ln} is the total amount of Ln centers. Therefore,

$$\frac{P_{n,exp}}{P_{n,ext}} = \frac{n(chains)}{n_{Ln}} = \frac{n_{act} Ln}{n_{Ln}} \quad (5)$$

Applying this extrapolation to the isoprene polymerizations discussed in Sections S1.1 - S1.3 led to the matrix shown as Table S3.1.

Table S3.1 Comparison of the ratios of the amounts of polymer chains and lanthanide centers obtained for the polyisoprenes^a

entry ^b	cocatalyst ^c	precatalyst [Ln(AlMe ₄) ₃] (2 ^{Ln})										
		2 ^{La}	2 ^{Ce}	2 ^{Pr}	2 Nd	2 ^{Gd}	2 ^{Tb}	2 ^{Dy}	2 ^{Ho}	2 ^Y	2 ^{Er}	2 ^{Lu}
1	A	1.36 ^h	1.94	1.62	1.54	1.15	1.11	0.65	1.02	0.76 ^h	0.69	1.01
2	2A	1.01	1.70	0.66	1.09	2.32	2.01	3.72	1.56	0.18	1.31	1.80
3	B	1.13 ^h	2.23	1.96	3.37	0.99	0.79	0.65	0.52	0.58 ^h	0.61	1.31
4	2B	1.20	1.94	0.43	1.25	0.76	1.06	0.89	0.81	0.17 ^h	0.85	1.62
5	C	0.16 ^h	1.78	0.87	0.65	0.62	0.71	0.43	0.46	0.32 ^h	0.37	0.30
6	2C	0.29	0.97	0.68	0.32	0.50	0.53	0.49	0.35	0.36	0.41	— ^f
7	D	0.17	0.04	0.28	0.29	0.62	0.92	0.77	0.16	— ^f	— ^f	— ^f
8	2D	— ^f	0.44	0.33	0.34	0.55	1.27	0.66	0.32	0.14	— ^f	— ^f
9	E	— ^f	6.53	0.66	0.69	1.38	2.23	1.22	0.46	0.32	— ^f	— ^f
10	2E	0.15	0.75	1.39	1.11	1.89	2.82	1.96	0.11	0.47	— ^f	— ^f

^a For detailed information on polymerization data and origin of the values (literature or this study), see sections S1.1 and S1.2. For information on the color code, *vide infra*. ^b Conditions: 0.02 mmol of the resp. Ln precatalyst, 0.02 or 0.04 mmol cocatalyst, in toluene, [Ln]:[isoprene] 1:1000 (n/n), reaction time 1 h, pre-reaction time 0.5 h. ^c A = [Ph₃C][B(C₆F₅)₄], B = [PhNMMe₂H][B(C₆F₅)₄], C = B(C₆F₅)₃, D = Me₂AlCl, E = Et₂AlCl. ^f No further evaluation possible due to low yield. ^h Reaction time 24 h.

Table S3.1 shows the values implying multinary active species or low initiation rates (as $n(chains) / n(n \text{ Ln centers}) < 1$) in green color. Those, which grow more than one chain per metal center or imply chain transfer or termination are given in blue and red; red highlights those active systems, that grow more than two chains per Ln center.

S4. Crystal Structure Data

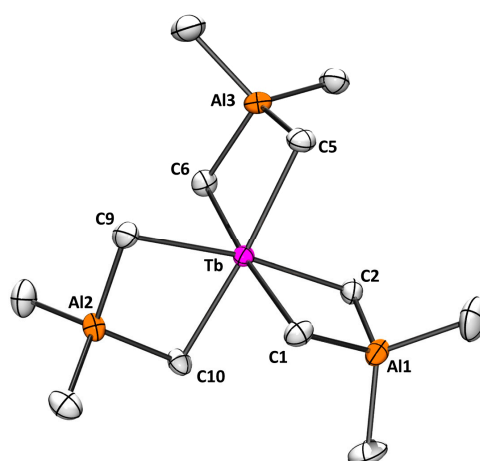


Figure S4.1. ORTEP view of one of two individuals in the unit cell of 2^{Tb}. Atoms are represented by atomic displacement ellipsoids at the 50% level. Hydrogen atoms are omitted for clarity. Selected distances (Å) and angles (deg): Tb1—C1 2.537(4), Tb1—C2 2.520(4), Tb1—C5 2.536(4), Tb1—C6 2.519(4), Tb1—C9 2.522(4), Tb1—C10 2.544(4), average Tb1—CX (X = 1, 2, 5, 6, 9, 10) 2.536, Al1—C1, 2.089(4), Al1—C2, 2.083(4); C1—Tb1—C2 84.27(12), C1—Tb1—C5 92.14(13), C1—Tb1—C6 175.02(13), C1—Al1—C2 108.81(15).

Table S4.1. Crystal data and structure refinement for **2^{Gd}** and **2^{Tb}**

	2^{Gd}	2^{Tb}
CCDC Deposition	1817853	1817852
Empirical formula	C ₁₂ H ₃₆ Al ₃ Gd	C ₁₂ H ₃₆ Al ₃ Tb
Mw [g mol ⁻¹]	418.60	420.27
T[K]	100(2)	100(2)
Wavelength	0.71073 Å	0.71073 Å
Crystal system	monoclinic	monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>
a [Å]	7.3841(4)	7.3790(18)
b [Å]	17.7049(10)	17.703(5)
c [Å]	32.1650(18)	32.277(8)
α [°]	90	90
β [°]	92.4360(10)	92.552(4)
γ [°]	90	90
Volume [Å ³]	4201.3(4)	4205.7 (19)
Z	8	8
density (calculated) [mg mm ⁻³]	1.324	1.327
Absorption coefficient μ [mm ⁻¹]	3.265	3.417
Theta range	2.222 to 27.103°	1.313 to 28.281°
Reflections collected	60729	65817
Independent reflections	9286 [R _(int) = 0.0762]	10430 [R _(int) = 0.061]
Data / restraints / parameters	9286 / 0 / 445	10430 / 0 / 445
R ₁ (obs) ^a	0.0388	0.0306
wR ₂ (all) ^b	0.0689	0.0670

^a Final R indices [I > 2σ(I)]; ^b R indices (all data).

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