Living catalyzed-chain-growth polymerization and block copolymerization of isoprene by rare-earth metal allyl precursors bearing CGC ligand

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Experiment Section

General Methods. All reactions were carried out under a dry and oxygen-free argon atmosphere by using Schlenk techniques or under a nitrogen atmosphere in an MBraun glovebox. All solvents were purified from an MBraun SPS system. Organometallic samples for NMR spectroscopic measurements were prepared in the glovebox by use of NMR tubes sealed by paraffin film. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AV400 (FT, 400 MHz for ^{1}H; 100 MHz for ^{13}C) spectrometer. NMR assignments were confirmed by ^{1}H-^{1}H COSY and ^{1}H-^{13}C HMQC experiments when necessary. The molecular weight and molecular weight distribution of the polymers were measured by a TOSOH HLC-8220 GPC. Elemental analyses were performed at National Analytical Research Centre of Changchun Institute of Applied Chemistry (CIAC). C_3H_5MgCl (2.0 M in THF), $AlMe_3$, $AlEt_3$, Al^iBu_3 were purchased from Aldrich or Fluka. Isoprene (99%, Acros) was dried over CaH_2 under stirring for 48 h and distilled before use. $[PhMe_2NH][B(C_6F_5)_4]$ and $[Ph_3C][B(C_6F_5)_4]$ were synthesized according to literature.[1] Ligand (C_5Me_4H-C_6H_4-*o*-NMe_2) was prepared according to the known procedure.[2] The ligand lithium salt, $[C_5Me_4$-C_6H_4-*o*-$NMe_2]Li$, was prepared by treating ligand with *n*BuLi.

X-ray Crystallographic Studies. Crystals for X-ray analysis were obtained as described in the preparations. The crystals were manipulated in a glovebox. Data collections were performed at –86.5 °C on a Bruker SMART APEX diffractometer with a CCD area detector, using graphite-monochromated Mo $K\alpha$ radiation (λ = 0.71073 Å). The determination of crystal class and unit cell parameters was carried out by the SMART program package. The raw frame data were processed using SAINT and SADABS to yield the reflection data file. The structures were solved by using the SHELXTL program. Refinement was performed on F^2 anisotropically for all non-hydrogen atoms by the full-matrix least-squares method. The hydrogen atoms were placed at the calculated positions and were included in the structure calculation without further refinement of the parameters.

Synthesis of complex (C_5Me_4-C_6H_4-*o*-NMe_2)Y(η^3-C_3H_5)$_2$ (1). Under a nitrogen atmosphere, to a THF suspension (20 mL) of $YCl_3(THF)_{3.5}$ (0.448 g, 1.0 mmol), 1 equiv of $[C_5Me_4$-C_6H_4-*o*-$NMe_2]Li$ (0.247 g, 1.0 mmol) was added slowly at room temperature. The mixture was stirred for 4 h to afford a clear solution, to which C_3H_5MgCl (1.0 mL, 2.0 mmol, 2.0 M in THF) was added. The resulting light-yellow solution was stirring overnight. Removal of volatiles, extraction with toluene and dryness gave **1** as pale yellow crystalline solids (0.314 g, 76%). Single crystals suitable for X-ray analysis grew from a mixture of toluene and hexane. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 1.93 (s, 6H, C_5Me_4), 2.13 (s, 6H, C_5Me_4), 2.33 (s, 6H, NMe_2), 3.22 (d, $J_{H–H}$ = 9.0 Hz, 8H, CH_2CHCH_2), 6.37–6.49 (m, 2H, CH_2CHCH_2), 6.90 (d, $J_{H–H}$ = 8.0 Hz, 1H, *o*-NC_6H_4), 7.06 (t, $J_{H–H}$ = 14.0 Hz, 1H, *p*-NC_6H_4), 7.12 (t, $J_{H–H}$ = 8.0 Hz, 1H, *m*-NC_6H_4), 7.19 ppm (d, $J_{H–H}$ = 7.2 Hz, 1H, *m*-NC_6H_4). ^{13}C NMR (100 MHz, C_6D_6, 25 °C): δ 12.49 (s, 2C, C_5Me_4), 12.54 (s, 2C, C_5Me_4), 50.46 (s, 2C, NMe_2), 70.42 (s, 4C, CH_2CHCH_2), 116.53 (s, 2C, C_5Me_4), 117.90 (s, 2C, C_5Me_4), 121.36 (s, 1C, *o*-NC_6H_4), 122.25 (s, 1C, *ipso*-C_5Me_4), 127.32 (s, 1C, *p*-NC_6H_4), 128.26 (s, 1C, *m*-NC_6H_4), 133.95 (s, 1C, *o*-$C_5Me_4C_6H_4$), 135.76 (s, 1C, *ipso*-$C_5Me_4C_6H_4$), 149.81 (s, 2C, CH_2CHCH_2), 156.80 ppm (s, 1C, *ipso*-NC_6H_4). Anal. calcd for $C_{23}H_{32}NY$ (%): C, 67.15; H, 7.84; N, 3.40. Found: C, 66.74; H, 7.66; N, 3.28.

Synthesis of complex (C_5Me_4-C_6H_4-*o*-NMe_2)Nd(η^3-C_3H_5)$_2$ (2). Following a similar procedure described previously, treatment of [C_5Me_4-C_6H_4-*o*-NMe_2]Li (0.247 g, 1.0 mmol) with 1 equiv of $NdCl_3(THF)_2$ (0.395 g, 1.0 mmol) and 2 equiv of C_3H_5MgCl (1.0 mL, 2.0 mmol, 2.0 M in THF) afforded pale green complex **2** (0.368 g, 78%). Anal. calcd for $C_{23}H_{32}NNd$ (%): C, 59.19; H, 6.91; N, 3.00. Found: C, 58.98; H, 6.82; N, 2.91.

Synthesis of complex (C_5Me_4-C_6H_4-*o*-NMe_2)Gd(η^3-C_3H_5)$_2$ (3). Following a similar procedure described previously, treatment of [C_5Me_4-C_6H_4-*o*-NMe_2]Li (0.247 g, 1.0 mmol) with 1 equiv of $GdCl_3(THF)_4$ (0.552 g, 1.0 mmol) and 2 equiv of C_3H_5MgCl (1.0 mL, 2.0 mmol, 2.0 M in THF) afforded yellow complex **3** (0.342 g, 71%). Recrystallization from toluene and hexane gave single crystals suitable for X-ray analysis. Anal. calcd for $C_{23}H_{32}NGd$ (%): C, 57.58; H, 6.72; N, 2.92. Found: C, 57.26; H, 6.61; N, 2.81.

Synthesis of complex (C_5Me_4-C_6H_4-*o*-NMe_2)Dy(η^3-C_3H_5)$_2$ (4). Following a similar procedure described previously, treatment of [C_5Me_4-C_6H_4-*o*-NMe_2]Li (0.247 g, 1.0 mmol) with 1 equiv of $DyCl_3(THF)_{3.5}$ (0.521 g, 1.0 mmol) and 2 equiv of C_3H_5MgCl (1.0 mL, 2.0 mmol, 2.0 M in THF) afforded yellow complex **4** (0.335 g, 68%). Single crystals for X-ray analysis grew from the mixture of toluene and hexane at –30 °C within 12 h. Anal. calcd for $C_{23}H_{32}NDy$ (%): C, 56.96; H, 6.65; N, 2.89. Found: C, 56.61; H, 6.51; N, 2.80.

Isoprene polymerization. A detailed polymerization procedure is described as following (run 3, Table 1): Under a nitrogen atmosphere and room temperature, complex **3** (4.8 mg, 1.0×10^{-5} mol, 2 mL toluene) and 5 equiv. of Al^iBu_3 (0.05 ml, 5.0×10^{-5} mol, 1.0 M in toluene) were added into a 50 mL Schlenk tube, and the solution turned to pale yellow after several minutes. Then 1 equiv of $[PhMe_2NH][B(C_6F_5)_4]$ (8.0 mg, 1.0×10^{-5} mol) was added under stirring to give a colorless solution. Upon the addition of isoprene (1 mL, 0.01 mol), polymerization was initiated and carried out for 60 min. The reaction mixture was poured into a large quantity of methanol and then dried under vacuum at ambient temperature to a constant weight (0.68 g, 100%).

Di-(tri-)block copolymerization of isoprene and butadiene. Under a nitrogen atmosphere and room temperature, complex **3** (4.8 mg, 1.0×10^{-5} mol, 2 mL toluene), 10 equiv. of $\mathrm{Al}^i\mathrm{Bu}_3$ (0.1 ml, 10×10^{-5} mol, 1.0 M in toluene) were added into a 50 mL Schlenk tube with vigorous stirring and reacted for several minutes. Then 1 equiv. of $[\mathrm{PhMe_2NH}][\mathrm{B(C_6F_5)_4}]$ (8.0 mg, 1.0×10^{-5} mol) was added and kept stirring for several minutes until a colorless solution was obtained. Addition of isoprene (0.5 mL, 5.0×10^{-3} mol) initiated the polymerization that was carried out for 30 min to reach a 100% conversion. Then butadiene (0.23 g, 4.25×10^{-3} mol, 35% in toluene) was added and kept reaction for another 40 min. The reaction mixture was poured into a large quantity of methanol to give di-block copolymer of PIP-*b*-PBD (0.57 g, 100%). Following the similar procedure, sequential addition of isoprene, butadiene and isoprene would give tri-block copolymer PIP-*b*-PBD-*b*-PIP with a total of 100% conversion.

1 (*a*) E. B. Tjaden, D. C. Swenson and R. F. Jordan, *Organometallics*, 1995, **14**, 371; (*b*) J. Chein, W. Tsai and M. Rausch, *J. Am. Chem. Soc.*, 1991, **113**, 8570.

2 M. Ender, G. Ludwig and H. Pritzkow, *Organometallics*, 2001, **20**, 827.

STable 1 Summary of crystallographic data for complexes **1, 3** and **4**

	1	**3**	**4**
formula	$C_{23}H_{32}NY$	$C_{23}H_{32}NGd$	$C_{23}H_{32}NDy$
crystal size, mm	0.20 x 0.18 x 0.09	0.17 x 0.15 x 0.12	0.21 x 0.18 x 0.17
Fw	411.41	479.75	485.00
cryst syst	Monoclinic	Monoclinic	Monoclinic
space group	P2(1)/ c	P2(1)/ c	P2(1)/ c
a (Å)	8.7801(6)	8.7876(6)	8.7688(4)
b (Å)	18.6736(13)	18.6815(12)	18.6646(9)
c (Å)	12.9685(9)	13.0273(8)	12.9847(6)
α (deg)	90	90	90
β (deg)	98.4000(10)	98.3860(10)	98.3560(10)
γ (deg)	90	90	90
V (Å^3)	2103.5(3)	2115.8(2)	2102.60(17)
Z	4	4	4
D_{calcd} (g/cm^3)	1.299	1.506	1.532
radiation (λ), Å	Mo Kα (0.71073)	Mo Kα (0.71073)	MoKα (0.71073)
$2\theta_{max}$, deg	52.04	52.04	52.10
μ (cm^{-1})	27.77	31.39	35.58
F(000)	864	964	972
no. of obsd reflns	4122	4145	4140
no. of params refnd	232	232	232
GOF	1.029	1.058	1.067
R_1	0.0301	0.0322	0.0223
wR_2	0.0798	0.0697	0.0578

STable 2 Selected bond distances (Å) and angles (deg) for complexes **1, 3** and **4**

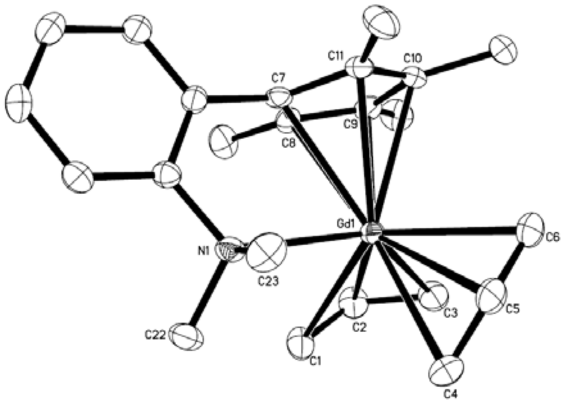
Parameter	**3 (Gd)**	**4 (Dy)**
Ln(1)–C(Cp) (av.)	2.670(4)	2.643(3)
Ln(1)–C_{cent1}[a]	2.382(4)	2.353(4)
Ln(1)–C_{AT} (av.)[b]	2.648(4)	2.612(3)
Ln(1)–C_{AC} (av.)[c]	2.674(4)	2.637(3)
Ln(1)–N(1)	2.645(3)	2.627(2)
C_{AT}–C_{AC}–C_{AT}	125.8(5)	127.2(4)
C_{cent1}–Ln(1)–C_{cent2}	109.2(4)	109.3(4)
C_{cent1}–Ln(1)–C_{cent3}	132.1(5)	131.9(5)
C_{cent2}–Ln(1)–C_{cent3}	107.0(4)	106.9(4)
C_{cent1}–Ln(1)–N(1)	94.5(4)	95.3(4)

[a] C_{Cent1}, C_{Cent2}, and C_{Cent3} are the centroids of the cyclopentadienyl ring and the two allyl ligands, respectively. [b] C_{AT} = terminal allylic carbon atom. [c] C_{AC} = central allylic carbon atom.

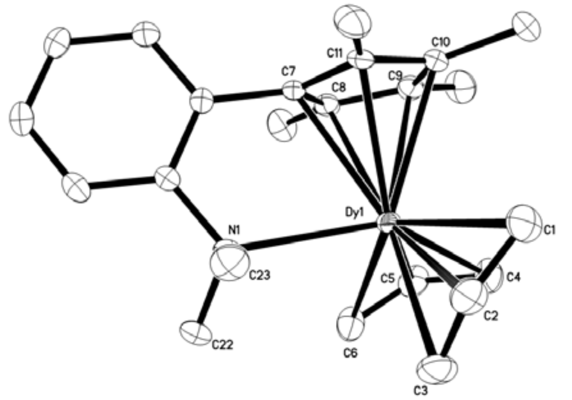
STable 3 Isoprene polymerization by rare-earth metal allyl precursors **1**–**4** under various conditions[a]

Run	Cat.	$\mathrm{AlR_3}$	[Al]/[Ln]	Borate[b]	*t* (min)	Conv. (%)	M_n^c (10^4)	M_w/M_n^c	*cis*-1,4 / *trans*-1,4 /3,4[d](%)
1	**1**	$\mathrm{AlMe_3}$	10	A	240	>99	5.4	1.33	3.7/70.2/26.1
2	**1**	$\mathrm{AlEt_3}$	10	A	420	>99	3.1	1.36	69.4/14.3/16.3
3	**1**	$\mathrm{Al^{i}Bu_3}$	10	A	60	81	3.1	1.64	75.2/5.4/19.4
4	**1**	$\mathrm{Al^{i}Bu_3}$	10	B	540	trace	-	-	-
5	**1**	$\mathrm{Al^{i}Bu_3}$	10	C	540	trace	-	-	-
6	**2**	$\mathrm{Al^{i}Bu_3}$	5	A	25	>99	6.1	1.23	87.2/11.3/1.5
7	**2**	$\mathrm{Al^{i}Bu_3}$	10	A	25	>99	4.4	1.22	86.3/11.4/2.3
8	**2**	$\mathrm{Al^{i}Bu_3}$	20	A	60	>99	2.7	1.19	85.8/11.9/2.3
9	**2**	$\mathrm{AlMe_3}$	5	B	15	>99	8.8	1.31	88.6/10.0/1.4
10	**2**	$\mathrm{AlEt_3}$	5	B	30	>99	7.9	1.34	90.4/7.6/2.0
11	**2**	$\mathrm{Al^{i}Bu_3}$	5	B	20	>99	12.8	1.36	95.2/3.0/1.8
12	**2**	$\mathrm{Al^{i}Bu_3}$	10	B	30	>99	7.9	1.32	95.0/3.3/1.7
13	**2**	$\mathrm{Al^{i}Bu_3}$	20	B	60	>99	4.0	1.33	94.9/3.6/1.5
14	**2**	$\mathrm{Al^{i}Bu_3}$	30	B	360	>99	3.0	1.31	94.9/3.7/1.4
15	**2**	$\mathrm{Al^{i}Bu_3}$	35	B	360	>99	2.5	1.36	94.8/3.7/1.5
16	**2**	$\mathrm{Al^{i}Bu_3}$	40	B	360	>99	2.1	1.28	94.7/3.8/1.5
17	**2**	$\mathrm{Al^{i}Bu_3}$	50	B	360	>99	1.6	1.30	94.6/3.8/1.6
18	**2**	$\mathrm{Al^{i}Bu_3}$	70	B	360	>99	1.3	1.34	94.5/3.9/1.6
19	**3**	$\mathrm{AlMe_3}$	10	A	40	>99	10.3	1.23	41.0/45.4/13.6
20	**3**	$\mathrm{AlEt_3}$	10	A	90	>99	6.1	1.60	61.4/34.4/4.2
21	**3**	$\mathrm{Al^{i}Bu_3}$	5	A	60	>99	5.0	1.40	96.8/1.4/1.8
22	**3**	$\mathrm{Al^{i}Bu_3}$	10	A	60	>99	3.5	1.26	94.6/3.5/1.9
23	**3**	$\mathrm{Al^{i}Bu_3}$	20	A	60	>99	2.3	1.23	93.6/4.0/2.4
24[e]	**3**	$\mathrm{Al^{i}Bu_3}$	10	A	900	45	7.4	1.89	99.0/0/1.0
25[f]	**3**	$\mathrm{Al^{i}Bu_3}$	10	B	20	>99	6.6	1.66	93.4/4.3/2.3
26	**3**	$\mathrm{Al^{i}Bu_3}$	5	C	840	>99	4.1	1.69	97.7/0.7/1.6
27	**3**	$\mathrm{Al^{i}Bu_3}$	10	C	420	88	3.1	1.50	97.0/1.3/1.7
28	**3**	$\mathrm{Al^{i}Bu_3}$	20	C	840	54	1.4	1.40	96.7/1.8/1.5
29	**4**	$\mathrm{AlMe_3}$	10	A	60	>99	4.9	1.21	43.3/30.0/26.7
30	**4**	$\mathrm{AlEt_3}$	10	A	120	88	1.2	1.42	50.9/20.0/29.1
31	**4**	$\mathrm{Al^{i}Bu_3}$	10	A	120	>99	2.8	1.53	90.7/6.6/2.7
32	**4**	$\mathrm{AlMe_3}$	5	B	90	81	9.3	1.31	95.7/1.9/2.4
33	**4**	$\mathrm{AlEt_3}$	5	B	450	82	2.3	1.40	97.2/1.5/1.3
34	**4**	$\mathrm{Al^{i}Bu_3}$	5	B	450	85	4.9	1.60	98.0/0.7/1.3
35	**4**	$\mathrm{Al^{i}Bu_3}$	10	B	720	>99	4.0	1.38	97.8/0.7/1.5
36	**4**	$\mathrm{Al^{i}Bu_3}$	20	B	720	44	1.7	1.22	97.4/0.8/1.8

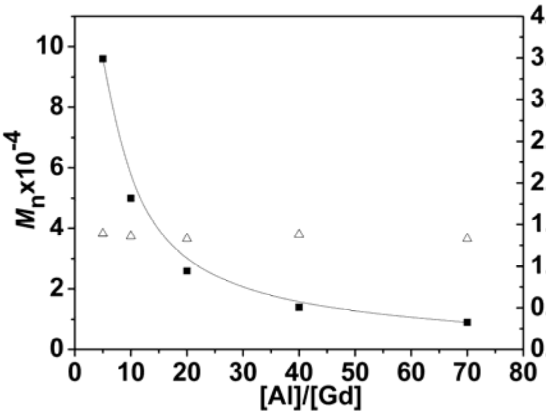
[a] General condition: 20 °C, toluene (2.0 ml), Ln (10 μmol), Borate (10 μmol), [Ip]/[Ln] = 1000. [b] A = $[\mathrm{Ph_3C}][\mathrm{B(C_6F_5)_4}]$, B = $[\mathrm{PhMe_2NH}][\mathrm{B(C_6F_5)_4}]$, C = $\mathrm{B(C_6F_5)_3}$. [c] Measured by GPC calibrated with standard polystyrene samples. [d] Determined by ^{1}H NMR and ^{13}C NMR spectroscopy in $\mathrm{CDCl_3}$. [e] T_p = –20 °C. [f] T_p = 50 °C.



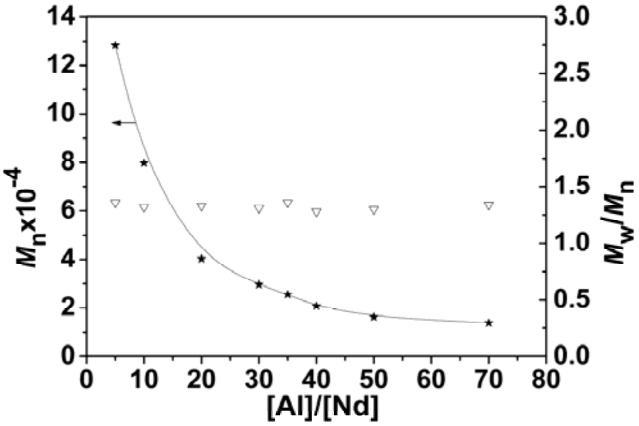
SFigure 1 X-ray structure of **3** with 35% probability of thermal ellipsoids. Hydrogen atoms are omitted for clarity.



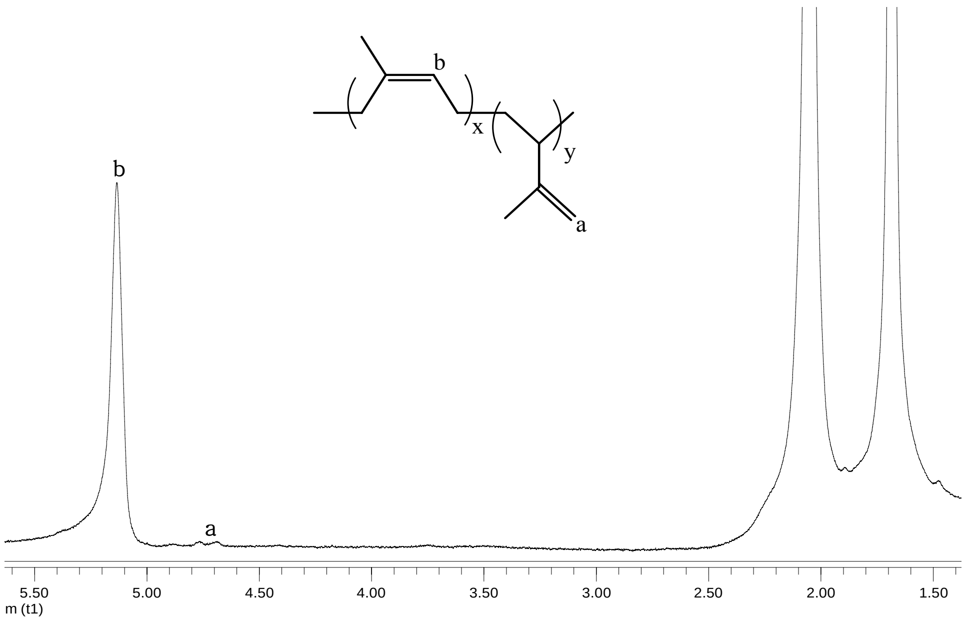
SFigure 2 X-ray structure of **4** with 35% probability of thermal ellipsoids. Hydrogen atoms are omitted for clarity.



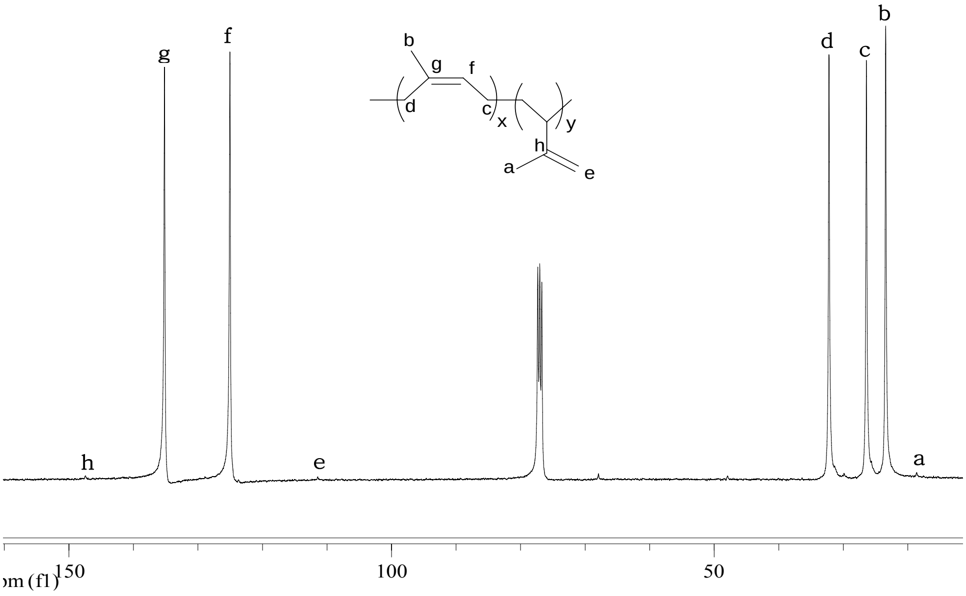
SFigure 3 Catalyzed chain growth (CCG) polymerization of isoprene (IP) with a system **3**/Al^{i}Bu$_3$/[PhMe$_2$NH][B(C$_6$F$_5$)$_4$]: molecular weight vs the ratios of [Al]/[Gd] (runs 3, 7–10, Table 1).



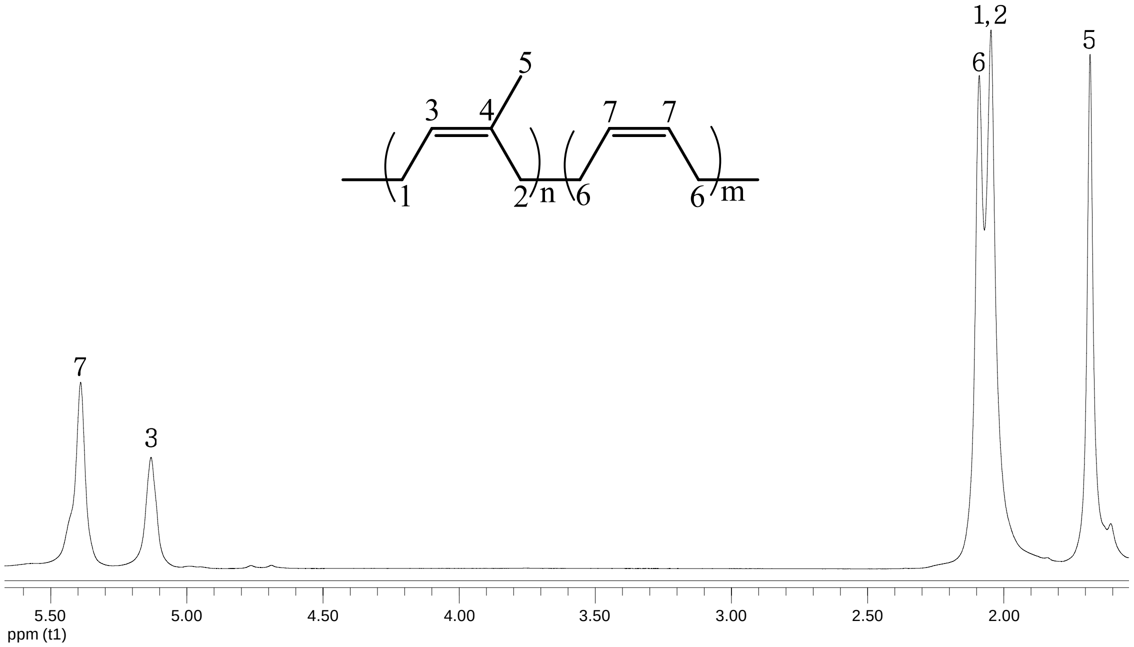
SFigure 4 Catalyzed chain growth (CCG) polymerization of IP with the system **2**/Al^{i}Bu$_3$/[PhMe$_2$NH][B(C$_6$F$_5$)$_4$]: molecular weight vs the ratios of [Al]/[Nd] (runs 11–18, STable 3).



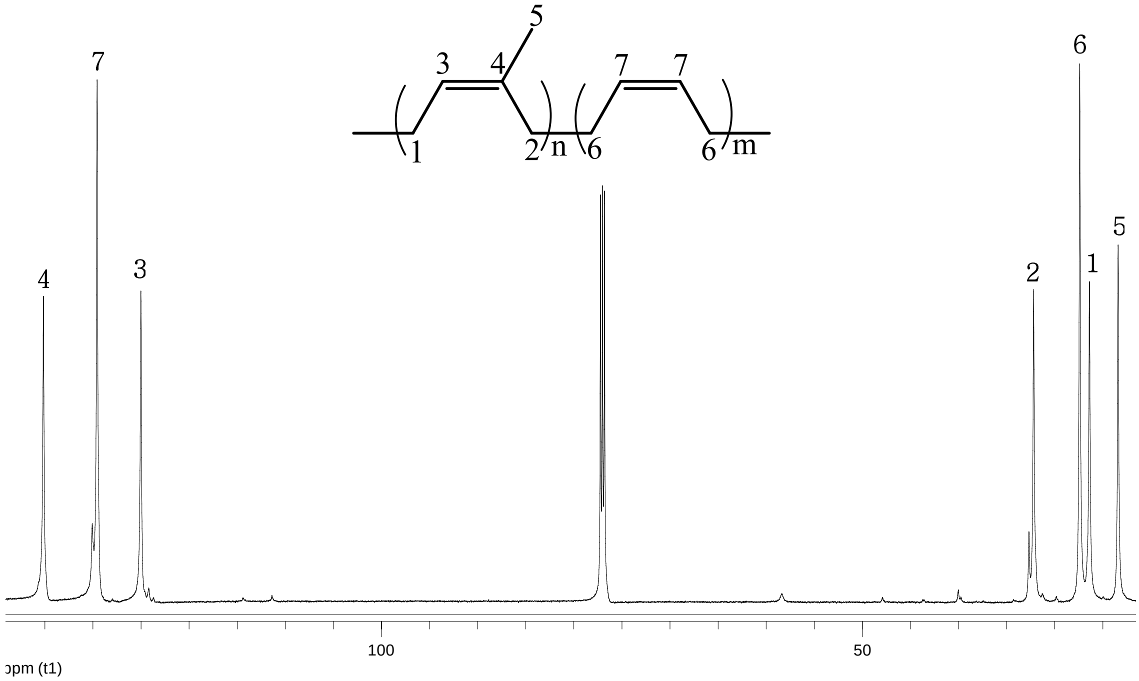
SFigure 5 ^{1}H NMR ($CDCl_3$, 25 °C) spectrum of PIP (run 11, Table 1, 99.2% *cis*-1,4).



SFigure 6 ^{13}C NMR ($CDCl_3$, 25 °C) spectrum of PIP (run 11, Table 1, 99.2% *cis*-1,4).



SFigure 7 ^{1}H NMR (CDCl$_3$, 25 ^{o}C) spectrum of a diblock copolymer PIP-*b*-PBD (Fig. 3b, C$_1$).



SFigure 8 ^{13}C NMR (CDCl$_3$, 25 ^{o}C) spectrum of a diblock copolymer PIP-*b*-PBD (Fig. 3b, C$_1$).