Supporting Information

$[(SiMe_3)_2NC(NiPr)_2]_2Ln(\mu\text{-}Me)_2Li(TMEDA)$ (Ln = Nd, Yb) as Effective Single-component Initiators for Styrene Polymerization

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General Procedures and Materials. All manipulations were performed under pure argon with rigorous exclusion of air and moisture using standard Schlenk techniques. THF, toluene, Et_2O and hexane were analytically pure (Shanghai chemical reagent co., Ltd), and were distilled from purple Na/benzophenone ketyl prior to use. $[(SiMe_3)_2NC(NiPr)_2]_2Ln(\mu\text{-}Cl)_2Li(THF)_2$ (Ln = Nd, Yb) were prepared according to the literature.[1] Styrene (analytically pure, Shanghai chemical reagent co., Ltd) was dried by stirring with CaH_2 for 48h, then distilled under reduced pressure. Melting points were determined in argon-filled capillary tubes and are uncorrected. Lanthanide metal analyses were carried out by complexometric titration. The content of lithium was determined on a Hitachi 180-80 polarized Zeeman atomic absorption spectrophotometer. Carbon, hydrogen, and nitrogen analyses were performed by direct combustion on a Carlo-Erba EA-1110 instrument. The IR spectra were recorded on a Nicolet Magna-IR 550 spectrometer. ^1H NMR spectra were measured on a Unity Inova-400 spectrometer in $CDCl_3$ at 25 °C. Molecular weight and molecular weight distributions were determined against polystyrene standard by gel permeation chromatography (GPC) on a Waters 1515 apparatus equipped with a set of Waters Styragel HR columns (HR-1, HR-2 and HR-4 columns, effective molecular-weight range, 100 to 5,000, 500 to

20,000, and 5,000 to 500,000, respectively). THF was used as an eluent at a flow rate of 1.0 mL/min at 30 °C.

Synthesis of $[(SiMe_3)_2NC(N\mathit{i}Pr)_2]Li$ (a). To a hexane (50 mL) solution of N, N'-diisopropylcarbodiimide (1.6 mL, 10 mmol) was added dropwise $LiN(SiMe_3)_2$ (1.7 g, 10 mmol) in 30 mL of hexane at room temperature. The resulting reaction mixture was stirred for half an hour to give a clear pale-yellow solution. After removal of the reaction solvent under reduced pressure, crude **a** was isolated as white powder (2.9 g, 9.8 mmol, 98%). Anal. Calcd for $C_{13}H_{32}LiN_3Si_2$: C, 53.19; H, 11.01; N, 14.32. Found: C, 52.79; H, 11.24; N, 13.82. ^{1}H NMR (benzene-d_6, ppm): 3.78 (m, 2 H, C*H*Me_2), 1.17 (d, 12H, CH(C*H*$_3$)$_2$), 0.35 (s, 18H, Si(C*H*$_3$)$_3$). ^{13}C NMR (benzene-d_6, ppm): 164.36 (*C*N_3), 46.17 (*C*HMe_2), 28.19 ((*C*H$_3$)$_2$CH), 3.03 (CN(Si(*C*H$_3$)$_3$)$_2$). IR (KBr pellets, cm^{-1}): 3449 (s), 2963 (m), 1636 (s), 1450 (m), 1389 (m), 1327 (m), 1258 (m), 1173 (m), 1049 (m), 957 (m), 841 (s), 686 (m).

Synthesis of $[(SiMe_3)_2NC(N\mathit{i}Pr)_2]_2Yb(\mu\text{-}Cl)_2Li(THF)_2$. A hexane (50 mL) solution of **a** (3.9 g, 13.3 mmol) was added into a slurry of $YbCl_3$ (1.9 g, 6.6 mmol) in 30 mL of THF. The reaction mixture was stirred for 24h at room temperature and the solvents were stripped off in vacuo. The residue yellow powder was extracted with diethyl ether (100 mL) and LiCl was separated by centrifugation. The yellow supernatant was then concentrated to 20 mL and cooled to −15 °C overnight to give bright-yellow crystals. Yield: 4.9 g (5.1 mmol, 76%). M.p.165-168 °C. Anal. Calcd for $C_{34}H_{80}Cl_2LiN_6O_2Si_4Yb$: C, 42.17; H, 8.34; N, 8.68; Yb, 17.87; Li, 0.72. Found: C, 41.63; H, 8.26; N, 8.41; Yb, 18.52; Li, 0.81. ^{1}H NMR (benzene-d_6, ppm): 4.15, 3.84 (m,

4 H, C*H*Me$_2$), 3.64 (m, 8 H, THF-α-C*H*$_2$), 1.47 (m, 8 H, THF-β-C*H*$_2$), 1.33, 1.09 (d, 24 H, CH(C*H*$_3$)$_2$), 0.23 (s, 36 H, Si(C*H*)$_3$). IR (KBr pellets, cm^{-1}): 3283 (m), 3182 (m), 2966 (m), 1635 (s), 1466 (m), 1388 (m), 1321 (m), 1253 (s), 1172 (m), 1057 (s), 952 (m), 841 (s), 756 (m), 686 (m).

Synthesis of [(SiMe$_3$)$_2$NC(N*i*Pr)$_2$]$_2$Nd(μ-Cl)$_2$Li(THF)$_2$. Followed a procedure similar to the synthesis of [(SiMe$_3$)$_2$NC(N*i*Pr)$_2$]$_2$Yb(μ-Cl)$_2$Li(THF)$_2$, using 11.3 mmol of a.1.4 g of NdCl$_3$ (5.6 mmol), and 60 ml of THF. Recrystallization from toluene yielded blue-purple cubic crystals 4.3 g (4.6 mmol, 82%). M.p.176-178 °C. Anal. Calcd for $C_{34}H_{80}Cl_2LiNdN_6O_2Si_4$: C, 43.46; H, 8.60; N, 8.95; Nd, 15.35; Li, 0.74. Found: C, 42.76; H, 8.78; N, 8.34; Nd, 15.72; Li, 0.71. ^{1}H NMR (benzene-d$_6$, ppm): 4.15, 3.85 (m, 4 H, C*H*Me$_2$), 3.61 (m, 8 H, THF-α-C*H*$_2$), 1.45 (m, 8 H, THF-β-C*H*$_2$), 1.33, 1.09 (d, 24 H, CH(C*H*$_3$)$_2$), 0.23 (s, 36 H, Si(C*H*)$_3$). IR (KBr pellets, cm^{-1}): 3296 (m), 2971 (m), 1636 (s), 1466 (m), 1373 (m), 1327 (m), 1258 (s), 1172 (m), 1057 (s), 941 (s), 833 (s), 756 (m), 686 (m).

Synthesis of [(SiMe$_3$)$_2$NC(N*i*Pr)$_2$]$_2$Nd(μ-Me)$_2$Li(TMEDA) (1). A Schlenk bottle was charged with [(SiMe$_3$)$_2$NC(N*i*Pr)$_2$]$_2$Nd(μ-Cl)$_2$Li(THF)$_2$ (5.3 g, 5.6 mmol) and 100 mL of hexane. The solution was cooled to −78 °C, and MeLi (7.6 mL, 11.3 mmol) was added by syringe. The reaction mixture was kept at −78 °C for one hour, then slowly warmed to room temperature and stirred overnight. After removal of volatiles under vacuum, the yellow residue was extracted with toluene and LiCl was removed by centrifugation. The supernatant was again dried in vacuo, and 20 mL of THF containing 1 mL of TMEDA was added. Cooling to −15 °C overnight gave 1 as blue-purple cubic

crystals. Yield. 3.8 g (4.3 mmol. 76%). M.p.118-120 °C. Anal. Calcd for $C_{34.25}H_{90.50}LiN_8Si_4Nd$: C, 48.26; H, 10.13; N, 12.42; Nd, 15.99; Li, 0.77. Found: C, 47.86; H, 9.90; N, 11.83; Nd, 15.86; Li, 0.75. IR (KBr pellets, cm^{-1}): 3442 (m), 2963 (s), 1636 (s), 1466 (m), 1373 (m), 1327 (m), 1258 (s), 1180 (m), 1049 (s), 957 (s), 918 (m), 841 (s), 756 (m), 686 (m).

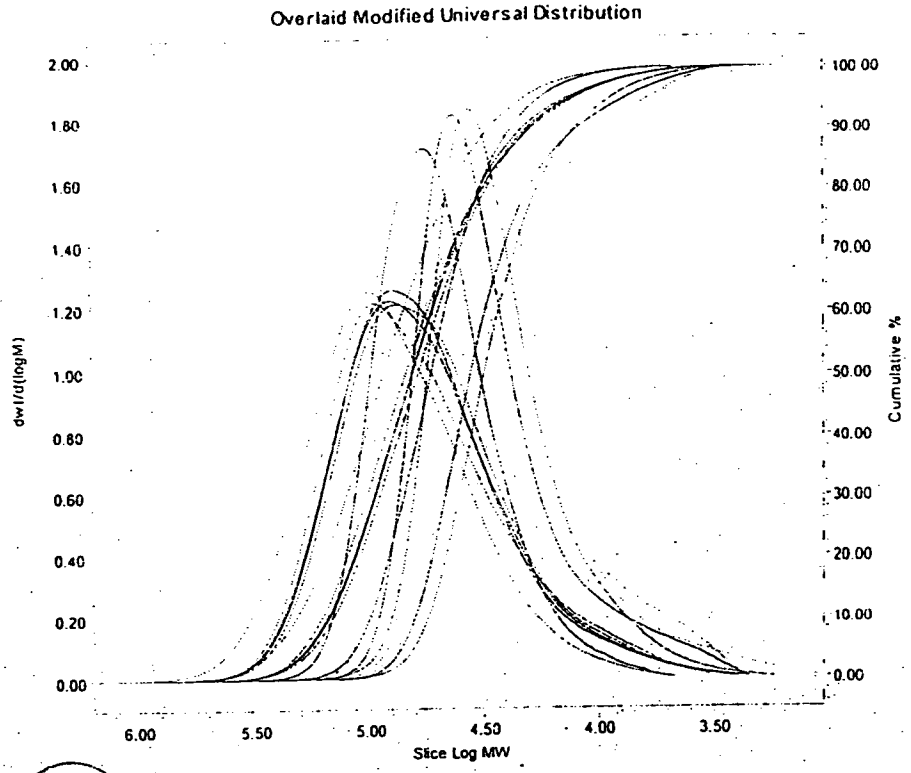
Synthesis of $[(SiMe_3)_2NC(N/Pr)_2]_2Yb(\mu\text{-}Me)_2Li(TMEDA)$ (2). Followed a procedure similar to the synthesis of **1**. This complex was synthesized using $[(SiMe_3)_2NC(N/Pr)_2]_2Yb(\mu\text{-}Cl)_2Li(THF)_2$ (8.2 g, 8.5 mmol), 100 mL of hexane and MeLi (11.4 mL, 17.0 mmol). After workup and cooling to −15 °C overnight gave **2** as bright yellow cubic crystals. Yield. 6.1 g (6.1 mmol, 72%). M.p.100-102 °C. Anal. Calcd for $C_{34.25}H_{90.50}LiN_8Si_4Yb$: C, 44.18; H, 9.82; N, 12.04; Yb, 18.59; Li, 0.75. Found: C, 43.81; H, 9.54; N, 11.98; Yb, 18.32; Li, 0.71. IR (KBr pellets, cm^{-1}): 3449 (m), 2963 (s), 1636 (s), 1466 (m), 1381 (m), 1327 (m), 1258 (s), 1180 (m), 1049 (m), 957 (s), 918 (m), 841 (s), 756 (m), 686 (m).

Styrene polymerization. Polymerizations were carried out in a previously flamed and argon-purged glass reactor, and a typical polymerization reaction is given below (entry 5, Table 1). In a 10 mL reactor, initiator **1** (20 mg, 22 μmol) and toluene (1.0 mL) were added at room temperature. After the reactor had been kept at 70 °C with vigorous stirring for half an hour, styrene (1.0 mL) was charged via a syringe. The color of reaction mixture quickly became dark and the magnetic stirring was ceased within a few minutes due to the viscosity. After 5 min, 1 mL of ethanol containing 5 % HCl was added into the reactor to terminate the polymerization, then the reaction mixture was

poured into a large excess of ethanol (100 mL) to precipitate the polymer. The polymer was collected by filtration, washed with ethanol, and dried under vacuum to constant weight (0.83 g, 92%).

Crystallographic Data for 1. Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center. CCDC no. 192648 for complex **1**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

GPC profiles of polystyrenes



THF

GPC Results

	Distribution Name	Elution Volume (ml)	RT (min)	Adjusted RT (min)	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mv (Daltons)	Mz+1 (Daltons)	Polydispersity
1	2	17.907	17.907	17.907	23274	37242	43692		56945	1.600163
2	3	17.250	17.250	17.250	41864	58413	63226		94014	1.395303
3	4	17.817	17.817	17.817	20196	37325	45874		66179	1.848139
4	6	16.441	16.441	16.441	40760	82001	107491		170331	2.011807
5	1	18.457	18.457	18.457	17269	27642	31397		42681	1.600712
6	5	18.100	18.100	18.100	22689	33205	37624		54958	1.463451
7	7	16.303	16.303	16.303	58914	106412	114447		260954	1.806213
8	8	16.633	16.633	16.633	38771	73727	89737		158374	1.901582
9	9	16.633	16.633	16.633	41165	77510	92930		163905	1.882907
10	10	16.600	16.600	16.600	39906	77859	95147		171382	1.951061

GPC Results

	Mz/Mw	Mz+1/Mw	K (dl/g)	alpha	Intrinsic Viscosity (dl/g)	Area (µV*sec)	% Area	Height (µV)	% Height	Integration Type	Peak Codes	Points Across Peak
1	1.286919	1.529031				792154	100.00	5562	100.00	BB		541
2	1.288825	1.609469				611366	100.00	4394	100.00	BB	108	467
3	1.418641	1.773025				452577	100.00	2427	100.00	BB	108	557
4	1.537921	2.077193				515569	100.00	3210	100.00	BV		537
5	1.279801	1.544054				842207	100.00	5939	100.00	BB		602
6	1.297524	1.655130				981654	100.00	6702	100.00	BB		578
7	1.605772	2.452301				1015707	100.00	6908	100.00	BB		500
8	1.542680	2.148118				1974256	100.00	11701	100.00	Bb		560
9	1.524957	2.114522				1332163	100.00	8190	100.00	BB		556
10	1.553709	2.201172				1527343	100.00	9218	100.00	BB		595

GPC Results

	Start Time (min)	End Time (min)	Baseline Start (min)	Baseline End (min)	Slope (µV/sec)	Offset (µV)
1	15.867	24.883	15.867	24.883	4.983579e-002	-1.113722e+000
2	14.883	22.683	14.883	22.683	2.400436e-003	-2.557265e-001
3	15.633	24.933	15.633	24.933	1.811942e-002	-2.364585e-001
4	14.733	23.683	14.733	23.683	8.140610e-003	-1.246192e-001
5	16.000	26.050	16.000	26.050	4.191807e-003	-9.515402e-002
6	15.250	24.900	15.250	24.900	-1.891743e-002	2.463631e-001
7	14.117	22.467	14.117	22.467	7.287552e-003	-1.637270e-001
8	14.567	23.917	14.567	23.917	1.902378e-002	-3.941343e-001
9	14.667	23.933	14.667	23.933	2.525639e-003	-1.353406e-001
10	14.300	24.233	14.300	24.233	3.110096e-002	-5.243181e-001

References

(1) Luo, Y. J.; Yao, Y. M.; Shen, Q.; Yu, K. B.; Weng, L. H. Manuscript accepted for publication in *European Journal of Inorganic Chemistry*.