Zwitterionic bis(phenolate)amine lanthanide complexes for the ring-opening polymerisation of cyclic esters

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Supporting information

Data for $Sm(O_2N^{OMe})\{N(SiHMe_2)_2\}(THF)$ (2^{OMe}). ^1H NMR (C_7D_8, 299.87 MHz, 353 K): δ 8.25 (2 H, s, ArH), 8.17 (2 H, s, ArH), 6.12 (2 H, br s, CH_2 of NCH_2CH_2O or NCH_2Ar), 3.73 (2 H, d, J^2 = 11.6 Hz, CH_2 of NCH_2CH_2O or NCH_2Ar), 2.98 (18 H, s, ^tBu), 1.79 (18 H, s, ^tBu), 1.16 (2 H, br s, CH_2 of NCH_2CH_2O or NCH_2Ar), 1.02 (12 H, s, $N(SiH\underline{Me_2})_2$), -0.07 (4 H, br s, $OCH_2C\underline{H_2}$), -1.81 (4 H, br s, OCH_2), -1.40 (2 H, br s, CH_2 of NCH_2CH_2O or NCH_2Ar), -1.81 (3 H, br s, OMe), -3.81 (2 H, br s, $N(Si\underline{H}Me_2)_2$). IR (NaCl plates, Nujol mull, cm^{-1}): ν 2079-2067 (br) (Si-H) 1600 (w) 1412 (w) 1362 (m) 1326 (w) 1298 (m) 1277 (w) 1202 (w) 1165 (w) 1071 (s) 1026 (m) 897 (s). Anal. Found (calcd. for $C_{41}H_{73}O_4N_2Si_2Sm$): C, 56.9 (56.9); H, 8.4 (8.5); N, 3.2 (3.2) %.

Data for $Sm(O_2N^{NMe2})\{N(SiHMe_2)_2\}(THF)$ (2^{NMe2}). ^1H NMR (C_6D_6, 299.87 MHz, 333 K): δ 8.49 (2 H, s, ArH), 8.41 (2 H, s, ArH), 4.76 (2 H, br s, CH_2 of NCH_2CH_2N or NCH_2Ar), 3.75 (2H, d, J^2 = 9.60 Hz, CH_2 of NCH_2CH_2N or NCH_2Ar), 3.53 (18 H, s, ^tBu), 1.90 (18 H, s, ^tBu), 1.59 (2 H, br s, CH_2 of NCH_2CH_2N or NCH_2Ar), 1.17 (12 H, s, $N(SiH\underline{Me_2})_2$), -1.72 (4 H, br s, $OCH_2C\underline{H_2}$), -2.01 (4 H, br s, OCH_2), -4.21 (2 H, br s, $N(Si\underline{H}Me_2)_2$), -4.43 (6 H, br s, NMe_2). The remaining CH_2 of NCH_2CH_2N or NCH_2Ar resonance was not observed due to paramagnetic effects. IR (NaCl plates, Nujol mull, cm^{-1}): ν 2084 (br) (Si-H) 1601 (w) 1413 (m) 1360 (m) 1328 (m) 1300 (s) 1279 (s) 1242 (s) 1202 (w) 1165 (w)

1133 (w) 1116 (w) 1065 (m) 1026 (s) 958 (w) 899 (s) 876 (m) 834 (s). Anal. Found (calcd. for $C_{42}H_{76}O_3N_3Si_2Sm$): C, 57.4 (57.8); H, 8.8 (8.8); N, 4.8 (4.8) %.

Data for $Sm(O_2N^{NMe2})(HO_2N^{NMe2})$ (3^{NMe2}). ^1H NMR (C_7D_8, 299.87 MHz, 298 K): δ 22.09 (br s, CH_2 of NCH_2CH_2N, NCH_2Ar or CH_3 of NMe_2), 17.51 (br s, CH_2 of NCH_2CH_2N, NCH_2Ar or CH_3 of NMe_2), 9.69 (br s, CH_2 of NCH_2CH_2N, NCH_2Ar or CH_3 of NMe_2), 9.07 (br s, CH_2 of NCH_2CH_2N, NCH_2Ar or CH_3 of NMe_2), 8.63 (br s, ArH), 8.35 (br s, ArH), 8.08 (br s, 2 x ArH), 7.15 – 6.9 (2 x ArH obscured by residual protio solvent resonances), 6.61 (br s, ArH), 6.50 (br s, ArH), 4.60 (br s, CH_2 of NCH_2CH_2N, NCH_2Ar or CH_3 of NMe_2), 4.17 (br s, CH_2 of NCH_2CH_2N, NCH_2Ar or CH_3 of NMe_2), 3.71 (br s, CH_2 of NCH_2CH_2N, NCH_2Ar or CH_3 of NMe_2), 3.52 (br s, CH_2 of NCH_2CH_2N, NCH_2Ar or CH_3 of NMe_2), 3.08 (br s, ^tBu), 2.32 (br s, ^tBu), 2.02 (br s, ^tBu), 1.61 (br s, ^tBu), 1.44 (br s, ^tBu), 1.14 (br s, ^tBu), 0.99 (br s, ^tBu), -0.51 (br s, CH_2 of NCH_2CH_2N, NCH_2Ar or CH_3 of NMe_2), -1.98 (br s, ^tBu), -2.34 (br s, CH_2 of NCH_2CH_2N, NCH_2Ar or CH_3 of NMe_2), -4.33 (br s, CH_2 of NCH_2CH_2N, NCH_2Ar or CH_3 of NMe_2). IR (NaCl plates, Nujol mull, cm^{-1}): ν 1605 (w) 1413 (s) 1361 (s) 1325 (m) 1298 (s) 1273 (s) 1238 (s) 1204 (m) 1171 (m) 1134 (w) 1118 (w) 1043 (w) 1026 (w) 990 (w) 911(w) 876 (w) 833 (s) 755 (m) 742 (s).Anal. Found (calcd. for $C_{68}H_{109}O_4N_4Sm$): C, 68.3 (68.2); H, 9.1 (9.1); N, 4.7 (4.7) %.

Data for $Sm(O_2N^{OMe})(HO_2N^{OMe})$ (3^{OMe}). ^1H NMR spectra were extremely broad due to the paramagnetic and fluctional nature of the compound. As a result meaningful interpretation was not possible. IR (NaCl plates, Nujol mull, cm^{-1}): ν 1604 (w) 1411 (s) 1361 (s) 1322 (m) 1297 (s) 1274 (s) 1260 (s) 1243 (m) 1203 (m) 1183 (w) 1164 (m) 1134 (m) 1121 (w) 1072 (w) 1061 (m) 1032 (w) 1024 (w) 998 (w) 976 (w) 964(w) 910 (w) 879 (m) 872 (s) 866 (m) 833 (s) 742 (s) Anal. Found (calcd. for $C_{66}H_{103}O_6N_2Sm$): C, 68.1 (68.0); H, 9.2 (9.0); N, 3.4 (3.5) %.

Data for $Sm(O_2N^{Me})(HO_2N^{Me})$ (3^{Me}). ^1H NMR spectra were extremely broad due to the paramagnetic and fluctional nature of the compound. As a result meaningful interpretation was not possible. IR (NaCl plates, Nujol mull, cm^{-1}): ν 1605 (w) 1413 (s) 1361 (s) 1299(s) 1263 (s) 1237 (s) 1202 (m) 1166 (m) 1132 (m) 1096 (w) 1025 (w) 997 (w) 911 (w) 877 (m) 833 (s) 741 (s). Anal. Found (calcd. for $C_{66}H_{103}O_4N_2Sm$): C, 69.5 (69.6); H, 9.1 (9.1); N, 2.4 (2.4) %.

Data for $Sm(O_2N^{NMe_2})\{N(SiMe_3)_2\}$ (4^{NMe2}). ^1H NMR (C_6D_6, 299.87 MHz, 333 K): δ 8.75 (2 H, s, ArH), 8.30 (2 H, s, ArH), 3.42 (4 H, br s, CH_2 of $O(CH_2CH_3)_2$), 2.89 (18 H, br s, ^tBu), 2.05 (18 H, br s, ^tBu), 1.36 (6 H, br s, CH_3 of $O(CH_2CH_3)_2$), -0.29 (4 H, br, 2 x CH_2 of NCH_2CH_2N or NCH_2Ar), -3.80 (18 H, br s, $N(SiMe_3)$). Remaining resonances are not observed due to paramagnetic effects. Satisfactory elemental analysis was not obtained.

Experimental details for the polymerisation experiments

In the glovebox, ε-caprolactone (0.51 g) was weighed into a vial and dissolved in 2 mL toluene. A sufficient quantity of catalyst ($[\varepsilon\text{-CL}]_0/[\text{Sm}]_0 = 275$) was weighed into another vial and dissolved in 0.2 mL THF and 2 mL toluene. The ε-caprolactone solution was added to the catalyst solution at room temperature and with vigourous stirring. The polymerisation mixure was observed to become extremely viscous until stiring was no longer be possible. After 2 minutes the polymerisation was quenched by addition of a few drops of wet toluene. Polymers were precipitated in ethanol, filtered and dried to constant weight *in vacuo*.

Polymer samples for MALDI-ToF analysis, where $[\varepsilon\text{-CL}]_0/[\text{Sm}]_0 = 30$, were prepared as follows. In the glovebox, ε-caprolactone (56 μL) was weighed into a vial and dissolved in 1mL toluene. A sufficient quantity of catalyst was weighed into another vial and dissolved in 0.1 mL THF and 1 mL toluene. The ε-caprolactone solution was added to the catalyst solution at room temperature and with vigourous stirring. The polymerisation mixure was observed to become viscous. After 2 minutes the polymerisation was quenched by addition of a few drops of wet toluene. Polymers were not precipitated. The crude polymerisation mixtures were concentrated *in vacuo* and analysed.

Table S1. Selected data for ε-CL polymerisation experiment ($[\varepsilon\text{-CL}]_0/[\text{Sm}]_0 = 275$)

Catalyst	Isolated Yield (%)	*M*n (GPC)	*M*n (calcd)	*M*w/*Mn*
$\mathbf{3}^{\mathbf{OMe}}$	71	91,575	31,390	2.7
$\mathbf{3}^{\mathbf{NMe2}}$	73	51,750	31,390	3.3
$\mathbf{4}^{\mathbf{NMe2}}$	67	30,060	31,390	2.0

MALDI-ToF-MS Analysis. MALDI-ToF-MS analysis was performed on a Voyager DE-STR from Applied Biosystems equipped with a 337 nm nitrogen laser. An accelerating voltage of 25 kV was applied. Mass spectra of 1000 shots were accumulated. The polymer samples were dissolved in THF at a concentration of 1 mg mL^{-1}. The cationization agent used was potassium trifluoroacetate (Fluka, >99%) dissolved in THF at a concentration of 5 mg mL^{-1}. The matrix used was *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) (Fluka) and was dissolved in THF at a concentration of 40 mg mL^{-1}. Solutions of matrix, salt and polymer were mixed in a volume ratio of 4:1:4, respectively. The mixed solution was hand-spotted on a stainless steel MALDI target and left to dry. The spectra were recorded in the reflectron mode.

Figure S1. Displacement ellipsoid plot (25 %) of $\mathrm{Sm(O_2N^{NMe2})\{N(SiMe_3)_2\}}$ ($\mathbf{4}^{\mathbf{NMe2}}$). H atoms and second orientation of the $\mathrm{CH_2CH_2NMe_2}$ side arm omitted for clarity.