Electronic Supplementary Material (ESI) for Chemical Communications

Facile Synthesis of Pendant- and *α, ω*-Chain-End-Functionalized Polycarbonates by Salan Lutetium Alkyl Precursor

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Supporting information

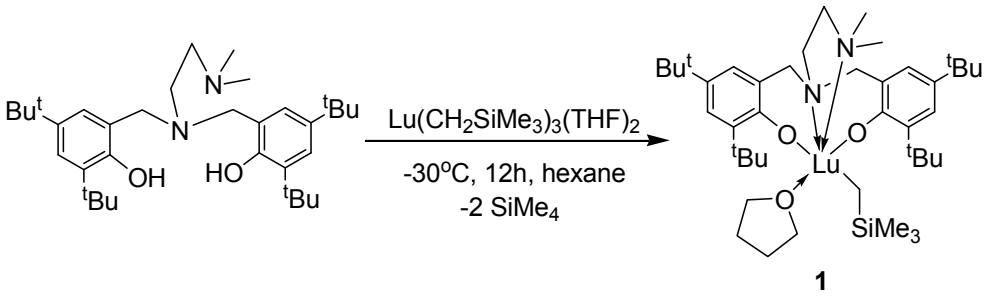
General Methods. All reactions were carried out under a dry and oxygen-free argon atmosphere by using Schlenk techniques or under a nitrogen atmosphere in an MBraun glovebox. Solvents were purified by an MBraun SPS system. Ligands were synthesized according to modified literature procedures.[1] The phenols and amines were purchased from Aldrich or Fluka. All liquids were dried over 4 Å molecular sieves for a week and distilled before use, and solid materials were used without purification. The synthesis of Salan lutetium complex **1** and complex **2** followed our previously established method.[2] 5-Methyl-5-allyloxycarbonyl-1,3-dioxan-2-one (MAC) was synthesized as reported, recrystallized three times before use and dried over CaH_2 in dry THF.[3]

Instruments and Measurements. Organometallic samples for NMR spectroscopic measurements were prepared in a glove box by use of NMR tubes and then sealed by paraffin film. ^1H, ^{13}C NMR spectra were recorded on a Bruker AV400 (FT, 400 MHz for ^1H; 100 MHz for ^{13}C) spectrometer. NMR assignments were confirmed by ^1H-^1H (COSY), ^1H-^{13}C (HMQC), and ^{13}C NMR (DEPT) experiments when necessary. Polymer characterizations were carried out by combining a Waters 515 GPC instrument with multiangle laser light scattering (MALLS) apparatus at 25 °C. The system included Styragel HMW6E column, a 515 HPLC pump, an OPTILAB DSP RI detector, and a DAWN EOS multiangle laser-light scattering (MALLS) detector at a laser wavelength of 690 nm (from Wyatt Technology). One guard column and three 30 cm columns were used for polymer fractionation. HPLC-grade DMF was used as the mobile phase at a flow rate of 0.5 mL/min. The whole system, including columns and detectors, was maintained at 25 °C. Polymers solutions with a concentration between 8.0

and 10.0 mg/mL were injected into the columns at an injection volume of 200 μL. Astra software from Wyatt Technology was used to collect and analyze the data from the detectors. The differential refractive index (DRI) increment (dn/dc) value of 0.051 mL/g was used for all obtained star polylactide.

Experiments

Synthesis of Complex 1. To a hexane (5 mL) solution of $Lu(CH_2SiMe_3)_3(THF)_2$ (0.2 g, 0.34 mmol) was added an equimolar amount of *N,N,O,O*-multidentate Salan ligands (0.18 g, 0.37 mmol, in 10 mL of hexane). The reaction mixture was stirred at -30 °C for 12 h. Removal of the volatiles afforded a residue, which was carefully washed with cold hexane to remove non reacted lanthanide tris(alkyl)s and then cooled to -30 °C again. White solids of complex **1** deposited on the bottom of the flask in 1 day (0.22 g, 75%). ^{1}H NMR (300 MHz, Tol-d_8, 25 °C): δ_H 7.54 (2 H, d, J_{HH} = 2.4, C_6H_2), 7.08 (2 H, d, J_{HH} = 2.4, C_6H_2), 3.92 (4 H, br, THF), 3.76 (2 H, d, J_{HH} = 12.4, $ArCH_2N$), 2.89 (2 H, d, J_{HH} = 12.4, $ArCH_2N$), 2.31 (2 H, br, $N(CH_2)_2N$), 1.74 (18 H, s, $C(CH_3)_3$), 1.72 (6 H, s, $N(CH_3)_3$), 1.57 (2 H, br, $N(CH_2)_2N$), 1.44 (18 H, s, $C(CH_3)_3$), 1.28 (4 H, br, THF), 0.43 (9 H, s, $CH_2Si\mathit{Me}_3$), -0.54 (2 H, d, J_{LuH} = 3.0, $C\mathit{H}_2SiMe_3$).



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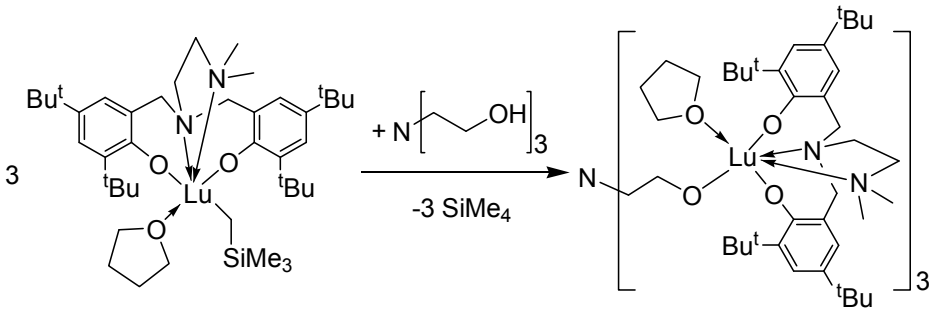
Synthesis of Complex 2. To a THF (2.5ml) solution of complex **1** (0.50g, 0.58 mmol) was dropwise added 1/3 equivalent TEA (0.029g, 0.19 mmol, in 2.5ml THF) slowly. After being stirred at 25 °C for 10 minutes, volatiles were then removed *in vacuo* to give complex **2** in a quantitative yield (0.47g). ^{1}H NMR (300 MHz, THF-d_8, 25 °C) δ_H 7.20 (6H, d, J_{HH} = 3.0 Hz, C_6H_2), 7.00 (6H, d, J_{HH} = 3.0 Hz, C_6H_2), 4.29 (6H, brs, $NCH_2C\mathit{H}_2O$), 4.23–3.89 (6H, m, $ArCH_2N$), 3.48 (6H, brs, $NC\mathit{H}_2CH_2O$), 3.23–2.86 (6H, m, $ArCH_2N$), 2.54 (6H, brs, $N(CH_2)_2N$), 2.00 (18H, s, $N(CH_3)_2$), 1.93 (6H, brs, $N(CH_2)_2N$), 1.49 (54H, s, $C(CH_3)_3$), 1.22 (54H, s, $C(CH_3)_3$). ^{13}C NMR (100 MHz, THF-d_8, 25 °C): δ_C 164.0 (6C, *ipso*-2,4-*t*Bu_2-C_6H_2), 135.0 (6C, *ipso*-2,4-*t*Bu_2-C_6H_2), 136.8 (6C, *ipso*-2,4-*t*Bu_2-C_6H_2), 126.2 (6C, 2,4-*t*Bu_2-C_6H_2), 126.5(6C, 2,4-*t*Bu_2-C_6H_2), 122.2 (6C, *ipso*-2,4-*t*Bu_2-C_6H_2), 66.0 (6C, $ArCH_2N$), 62.1 (3C, NCH_2CH_2O), 59.4 (3C, $N(CH_2)_2N$), 49.0 (3C, $N(CH_2)_2N$), 47.2 (3C, NCH_2CH_2O), 46.1 (6C, $N(CH_3)_2$), 34.8 (6C, $C(CH_3)_3$), 33.4 (6C, $C(CH_3)_3$), 30.3 (18C, $C(CH_3)_3$), 31.6 (18C, $C(CH_3)_3$).



1 **2**

Typical Polymerization of MAC in the presence of TEA. A typical procedure for polymerization of MAC in the presence of TEA was performed in a 25 mL round flask under an N_2 atmosphere. To a vigorously stirred solution of complex **1** in 3 mL THF was added TEA in 2 mL THF. After 10 minutes, MAC was added quickly. The polymerization took place immediately at room temperature. After a specified polymerization time, an aliquot was withdrawn and quenched quickly with 1.0 mL $HCl/CH_3OH/CHCl_3$ (0.1/10/60 v/v) solution, and then 1.0 mL THF was added to obtain a clear solution. Several drops of the quenched solution were taken, removed volatiles and subjected to monomer conversion determination using ^{1}HNMR ($CDCl_3$). The residue solution was quenched by an excess amount of ethanol, filtered, washed with ethanol, and then dried at 40°C for 24 h *in vacuo* to give polymer product. The molecular weight and the molecular weight distribution of the resulting polymer were determined by SEC-MALLS.

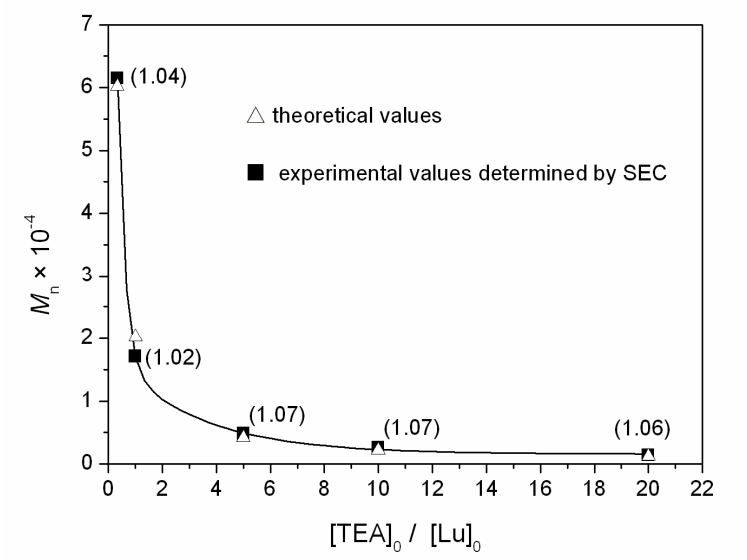


Figure S1. Dependence of the molar mass M_n (PDI indicated in parentheses) on $[TEA]_0/[Lu]_0$ ratio. Conditions: $[MAC]_0$-to-$[Lu]_0$ ratio = 100, $[MAC]_0$ = 0.33M, Solvent, THF, Tp = 25 ^oC.

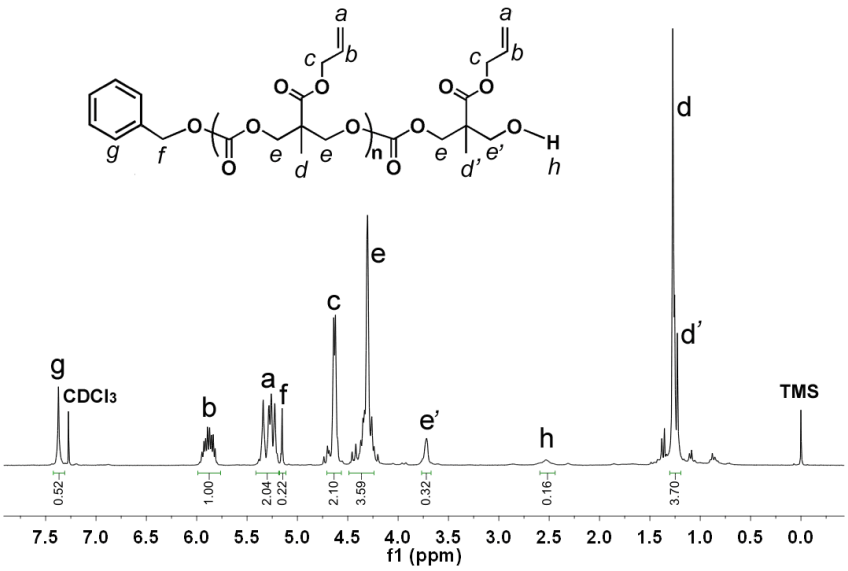


Figure S2. ^1H NMR (300MHz, $CDCl_3$, 25 °C) spectrum of PMAC. Conditions: $[MAC]_0$ = 0.33 M, $[MAC]_0$:$[BnOH]_0$:$[Lu]_0$ = 100:10:1, THF, 100% conversion, T_p = 25 °C.

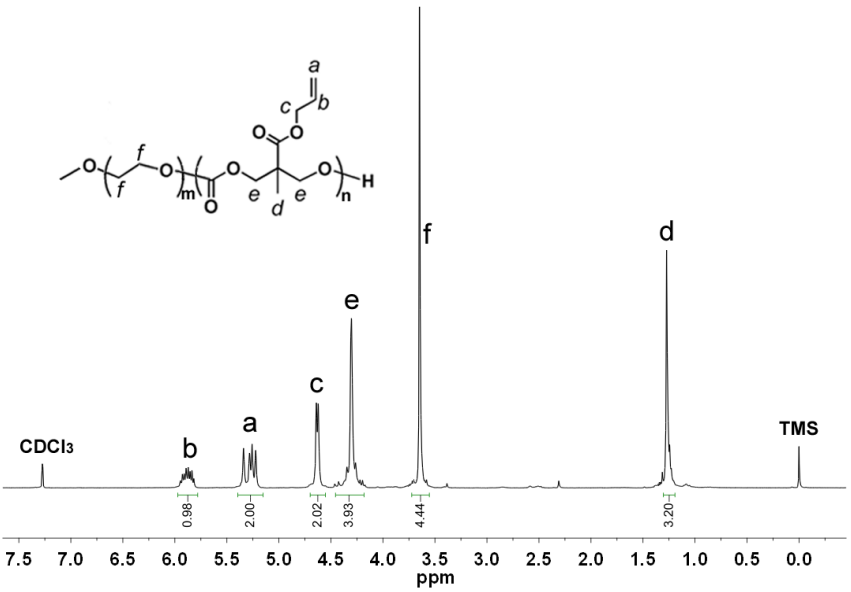


Figure S3. ^1H NMR (300MHz, $CDCl_3$, 25 °C) spectrum of amphiphilic diblock copolymers MPEG-*b*-PMAC. Conditions: $[MAC]_0$ = 0.33 M, $[MAC]_0$:$[MPEG5K]_0$:$[Lu]_0$ = 100:1:1, THF, 100% conversion, T_p = 25 °C.

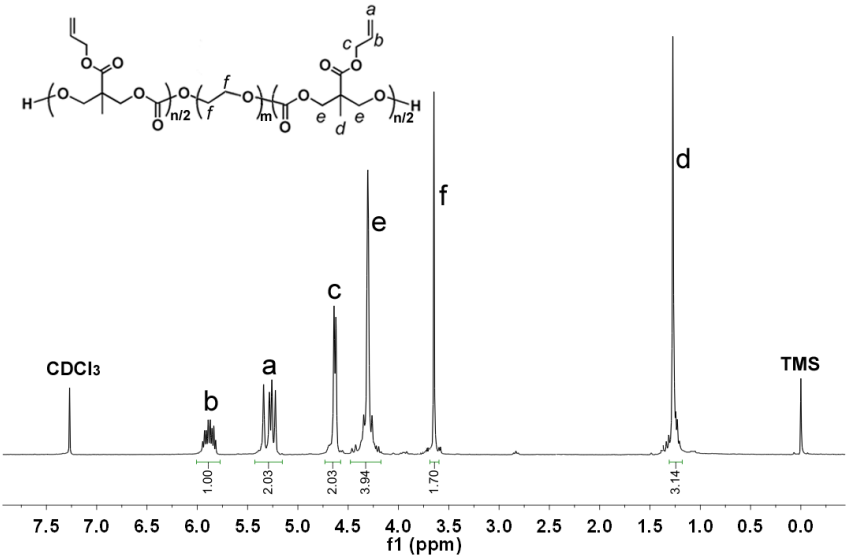


Figure S4. ^{1}H NMR spectrum (300MHz, $CDCl_3$, 25 °C) of an amphiphilic triblock copolymer PMAC-*b*-PEG-*b*-PMAC. Conditions: $[MAC]_0$ = 0.33 M, $[MAC]_0$:$[PEG2K]_0$:$[Lu]_0$ = 100:1:1, THF, 100% conversion, T_p = 25 °C.

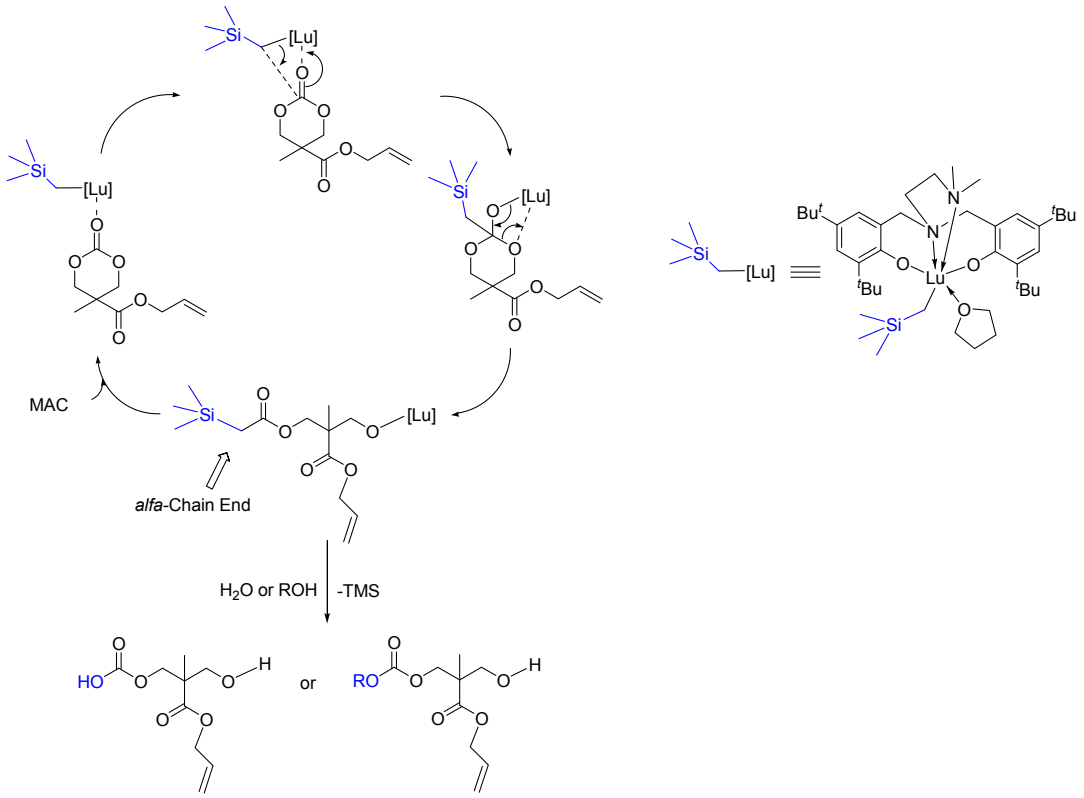


Figure S5. Coordination-insertion mechanism for the ROP of MAC using complex **1** in absence of alcohols.

As shown in Figure S5, the polymerization mechanism is a coordinating-insertion process. In the case of polymerization using complex **1** without alcohols, $–CH_2SiMe_3$ is the initiating group of the Lu-based catalyst ([Lu]–CH_2SiMe_3), so during the polymerization, the initiation chain ends (alfa-chain ends) of obtained PMAC are $–CH_2SiMe_3$. When the polymerization was terminated with protic compounds such as H_2O, ROH, the chain end may turn out to be –COOH or –COOR by releasing TMS.

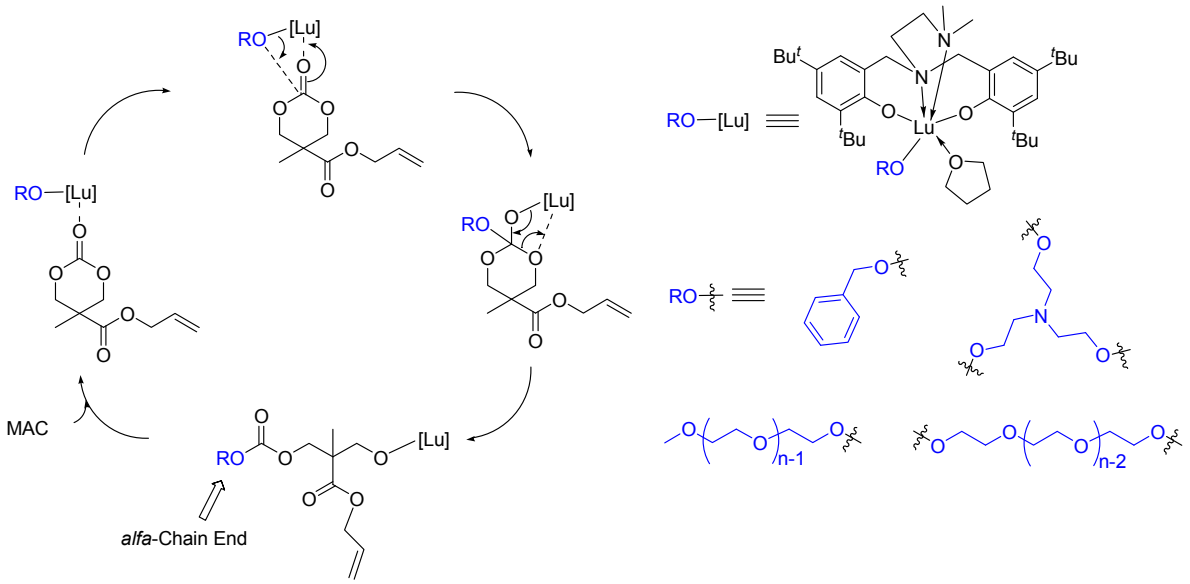


Figure S6. Coordination-insertion mechanism for the ROP of MAC using complex **1** in presence of alcohols.

As shown in Figure S6, the polymerization mechanism is a coordinating-insertion process, which has been supported experimentally by end group analysis through ^{1}H NMR (Figure 1) and MALDI-TOF mass spectrum (Figure 2) in the manuscript. According to the mechanism the Lewis acidic metal center loosely binds and activates the carbonate to attack by the metal alkoxide group. The intermediate undergoes acyl–oxygen bond cleavage of the carbonate ring to generate a new metal alkoxide species and a growing chain end capped with an ester group. The new metal-alkoxide species is capable of further monomer insertion.

References

1. E. Y. Tshuva, I. Goldberg, Z. Goldschmidt and M. Kol, *Organometallics*, 2001, **20**, 3017..

2. (a) X. Liu, X. Shang, T. Tang, N. Hu, F. Pei, D. Cui, X. Chen and X. Jing, *Organometallics*, 2007, **26**, 2747.

3. Hu, X.; Chen, X.; Xie, Z.; Liu, S.; Jing, X. *J. Polym. Sci., Part A: Polym. Chem.* 2007, 45, 5518.