Electronic supporting Info

Synthesis and structure of divalent thulium borohydrides, and their application in ε-caprolactone polymerisation.

Aurélien Momin, Fanny Bonnet*, Marc Visseaux*, Laurent Maron, Josef Takats, Michael J. Ferguson, Xavier-Frédéric Le Goff, and François Nief*

Experimental part:

Material. All operations were performed under dry argon by using Schlenk techniques and a glove box. The solvents were dried over sodium/benzophenone ketyl, deoxygenated, and stored over molecular sieves (3A) in a glovebox. ε-caprolactone (99% from Aldrich) was dried over calcium hydride, distilled and stored over molecular sieves (3A) in a glovebox. Dicumylperoxide, di*tert*-butylperoxide, and AIBN (Aldrich) were used as received. ^{1}H spectra of the poly(ε-caprolactone) were recorded on Bruker Avance spectrometers. The chemical shifts were calibrated using the residual resonances of the solvent. NMR spectra of **1** and **2** were measured on Bruker Avance and Varian Inova spectrometers, respectively. Size exclusion chromatography of the polymers was performed in THF as an eluent at 40 °C (1 mL min^{-1}) with a Waters SIS HPLC pump, a Waters 410 refractometer, and Waters Styragel columns (HR2, HR3, HR4, and HR5E) calibrated with polystyrene standards. Molecular weights were corrected by a factor of 0.56 for the determination of true number-average molecular weight of polycaprolactone. Elemental analyses for **1** and **2** were performed at the Universities of Lille and Alberta, respectively.

Synthesis of [Tm(BH$_4$)$_2$(DME)$_2$] (1). First route: A round-bottom flask containing [Tm(BH$_4$)$_3$(THF)$_3$] (701 mg, 1.63 mmol) and KC$_8$ (600 mg, 4.44 mmol) was fitted to a reversible Schlenk filtration apparatus and evacuated. DME (ca. 20 mL) was condensed onto the solids at -78°C. The resulting dark suspension was stirred at this temperature for 30 minutes and filtered under vacuum. The residue was continuously extracted with DME at low temperature, by recondensing DME at -78°C. The dark filtrate was concentrated to ca. 10mL and **1** was obtained as a black microcrystalline solid by crystallisation at -40°C (251 mg, 663 µmol, 41 %). **Second route:** In a helium/argon glove box, DME (20 mL) was added to a mixture of [TmI$_2$(THF)$_3$][1] (500 mg, 782 µmol, 1.0 eq.) and KBH$_4$ (85 mg, 1.6 mmol, 2.0 eq.). The mixture was stirred for 2 h at room temperature. The dark brown supernatant was separated by centrifugation, concentrated to saturation (ca. 3 mL). After two days at -40°C, a black microcrystalline solid precipitated and was washed with pentane. A second batch of crystals was obtained by concentrating the supernatant to ca. 1.5 mL and cooling at -40°C overnight. Global yield of **1**: 258 mg (685 µmol, 88 %). ^{1}H NMR (300 MHz, THF-d^8, 20 °C): δ (ppm) -96.2 (broad s, $w_{1/2}$ = 3.7 kHz, BH_4). μ_{eff} (Evans' method) = 4.8μ_B. Crystals suitable

[1] **[**TmI$_2$(THF)$_3$**]** was obtained by extraction of TmI$_2$ with THF: F. Nief, B. Tayart de Borms, L. Ricard and D. Carmichael, *Eur. J. Inorg. Chem.*, 2005, 637-643. The TmI$_2$ used in the extraction procedure can either be of commercial origin or synthesised by the solid-state direct reaction of Tm powder and I$_2$ according to M. N. Bochkarev and A. A. Fagin, *Chem.–Eur. J.*, 1999, **5**, 2990-2992.

for X-Ray analysis were obtained from DME at -30°C. Anal.: % Calcd. for $C_8H_{28}B_2O_4Tm$ = 378.86, C: 25.36, H: 7.45;.found, C: 24.20, H: 7.75.

Synthesis of [($Tp^{tBu,Me}$)Tm(BH_4)(THF)] (2): In a helium/argon glove box, a solution of $KTp^{tBu,Me}$ (170mg, 367µmol, 1.0 q.) in 8mL of THF was added dropwise over 5 minutes to a solution of [$Tm(BH_4)_2(DME)_2$] (149 mg, 395 µmol, 1.1eq.) in 5mL of THF. The reaction mixture was stirred for 2h at room temperature, resulting in a dark brown suspension. THF was thoroughly removed *in vacuo* and the residue was extracted with three portions of 10 mL of pentane. The residue was separated by centrifugation and the supernatant concentrated to ca. 20 mL. Overnight crystallisation at -40°C yielded a dark brown crystalline solid (138 mg, 203 µmol, 55 %). ^{1}H NMR (400 MHz, C_6D_6, 300 K) (Figure S1): δ (ppm) 26.4 (broad s, $w_{1/2}$ = 500 Hz, 27 H, 3-$^tBu^{pz}$), 5.8 (broad s, $w_{1/2}$ = 600 Hz, 3 H, 4-H^{pz}), -1.2 (broad s, $w_{1/2}$ = 100 Hz, 9 H, 5-*Me*), -10.0 (broad s, $w_{1/2}$ = 285 Hz, 1H, BH^{Tp}), -16.5 (broad s, $w_{1/2}$ = 200 Hz, 4 H, *THF*), -36.6 (broad s, $w_{1/2}$ = 400 Hz, 4 H, *THF*), -89.2 (broad s, $w_{1/2}$ = 875 Hz, 4 H, BH_4). ^{11}B NMR (128 MHz, C_6D_6, 27 °C): δ (ppm) -41.7 (broad s, $w_{1/2}$ = 300 Hz, BH^{Tp}), -216.8 (broad s, $w_{1/2}$ = 285 Hz, BH$_4$); Decomposition products start to appear after a few hours at room temperature. Crystals suitable for X-Ray analysis were obtained from a dilute pentane solution at -40°C. Anal.: % Calcd. for $C_{28}H_{52}B_2N_6OTm$ = 679.31, C: 49.51, H: 7.72, N: 12.37; % Found, C: 49.38, H: 7.82, N: 11.90.

Typical ε-caprolactone polymerisation. In a glove box under argon (H_2O and O_2 < 2 ppm), the initiator is dissolved in the appropriate amount of dry and degassed THF. ε-caprolactone was then added under vigorous stirring. Instant change of colour was observed from dark-brown to colourless. The reaction was then stirred at room temperature for a given time. The reaction was quenched by addition of some methanol drops. The polymer was dissolved in wet THF, poured in a large excess of ethanol, filtered and dried under vacuum. ^{1}H and ^{13}C NMR analysis of the polymers was performed in $CDCl_3$ at room temperature. NMR data of a poly(ε-caprolactone) prepared *via* ring-opening polymerisation of ε-CL initiated by 1 in THF with [ε-CL]$_0$ / [Tm]$_0$ = 100, $M_{n\ (RMN)}$ = 5100 g/mol (run 1): ^{1}H NMR (300 MHz, $CDCl_3$, 293 K) (Figure S2): HO(CH_2)$_5$C(O){O(CH_2)$_5$C(O)}$_n$O(CH_2)$_6$OH, δ (ppm): 4.05 (OCH_2); 3.64 (HOCH_2); 2.30 (CH_2C(O)); 1.64 (*C*H_2CH$_2$*C*H_2); 1.37 (CH$_2$*C*H_2CH$_2$). ^{13}C NMR data in $CDCl_3$, 293 K (Figure S3): HO(CH_2)$_5$C(O){O(CH_2)$_5$C(O)}$_n$O(CH_2)$_6$OH, δ (ppm): 173.6 (CH$_2$*C*O); 64.2 (O*C*H$_2$); 62.7 (HO*C*H$_2$); 34.2 (*C*H$_2$CO); 28.4, 25.6, 24.7 (*C*H$_2$*C*H$_2$*C*H$_2$).

NMR scale reaction of 1 with ^{t}BuOO^{t}Bu: In the glove box, 0.5 equiv of di-*tert*-butylperoxide was added to 5 mg of **1** in anhydrous THF-d_8 at room temperature. The initial dark-brown solution turned instantly colourless. A new large signal at -145ppm was attributed to O^{t}Bu bonded to Tm^{III} (See manuscript for details).

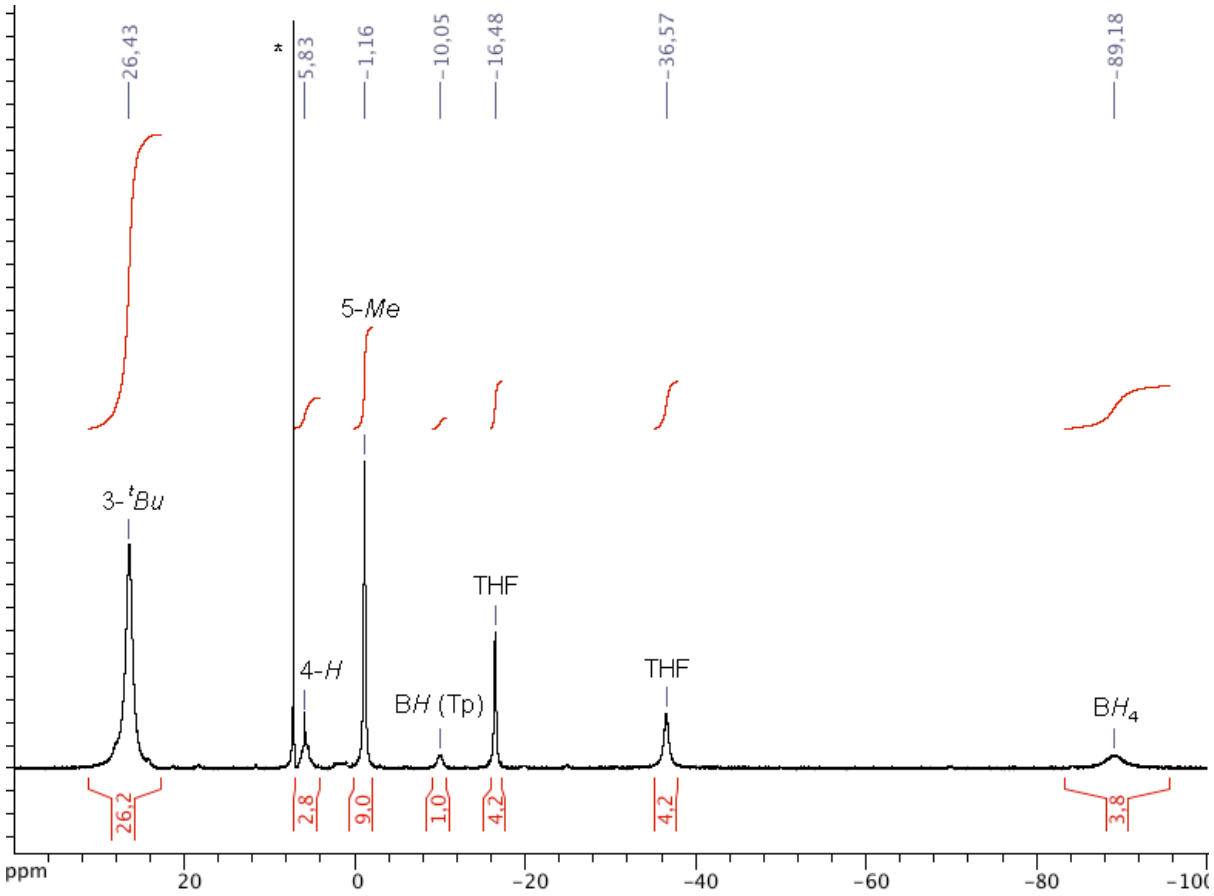

Figure S1 ^{1}H NMR spectrum of [(Tp^{tBu,Me})Tm(BH$_4$)(THF)] (2) in C_6D_6 at 300 K. The starred peak denotes residual C_6D_5H.

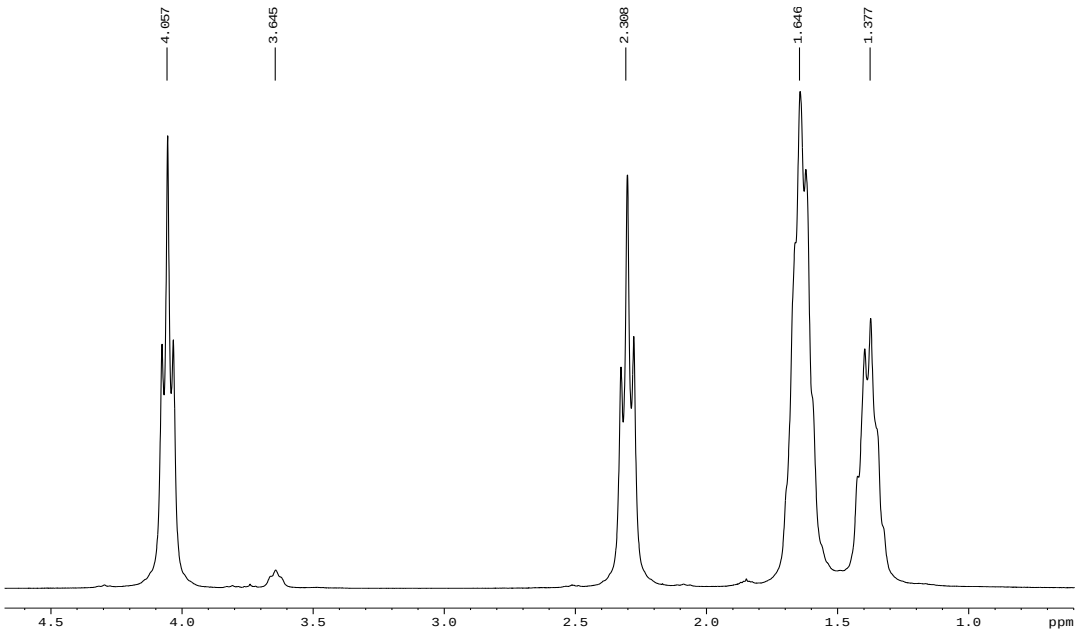

Figure S2 ^{1}H NMR spectrum of poly(ε-caprolactone) in $CDCl_3$ at 293 K, $M_{n\ (NMR)}$ = 5100 g/mol

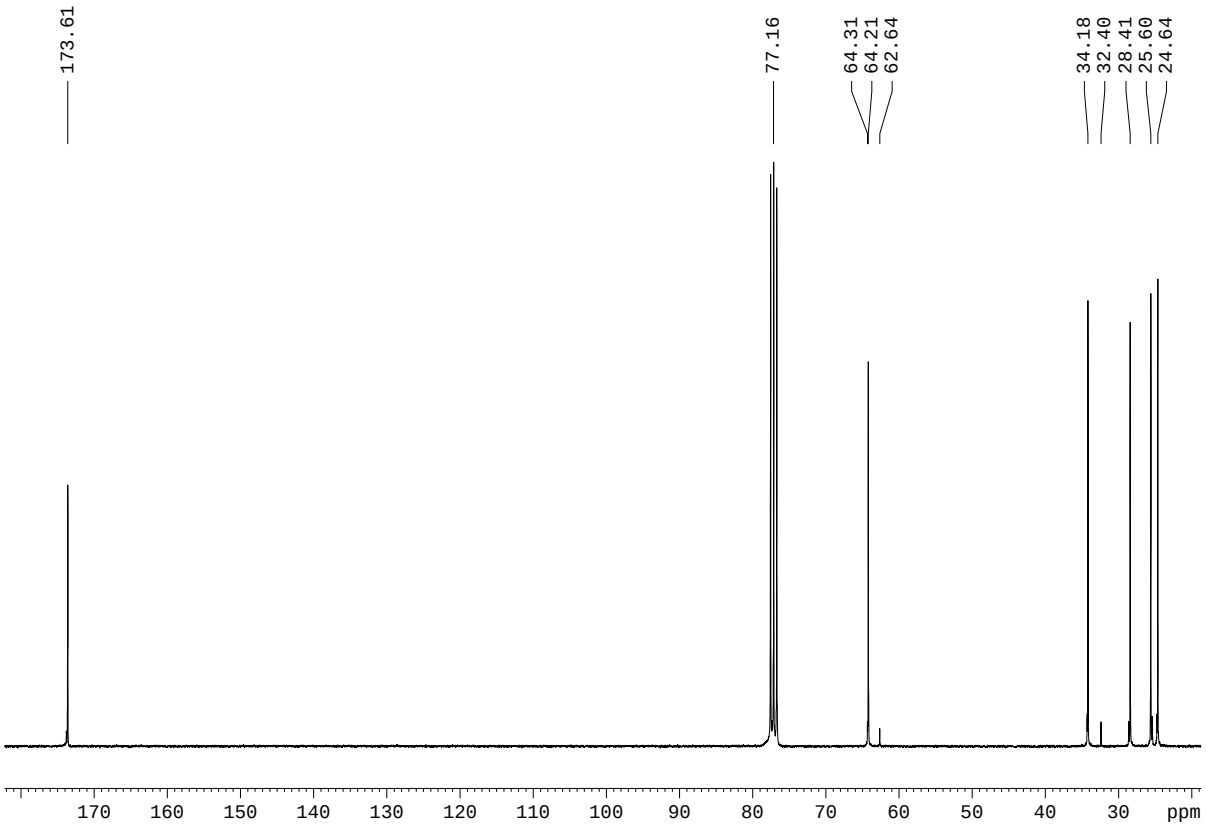

Figure S3 ^{13}C NMR spectrum of poly(ε-caprolactone) in $CDCl_3$ at 293 K, $M_{n\,(NMR)}$ = 5100 g/mol