Electronic Supplementary Material (ESI) for Polymer Chemistry

Supporting Information

Organocatalyzed Controlled ROP of β-Lactones towards Poly(HydroxyAlkanoate)s: From β-Butyrolactone to Benzyl β-Malolactone Polymers

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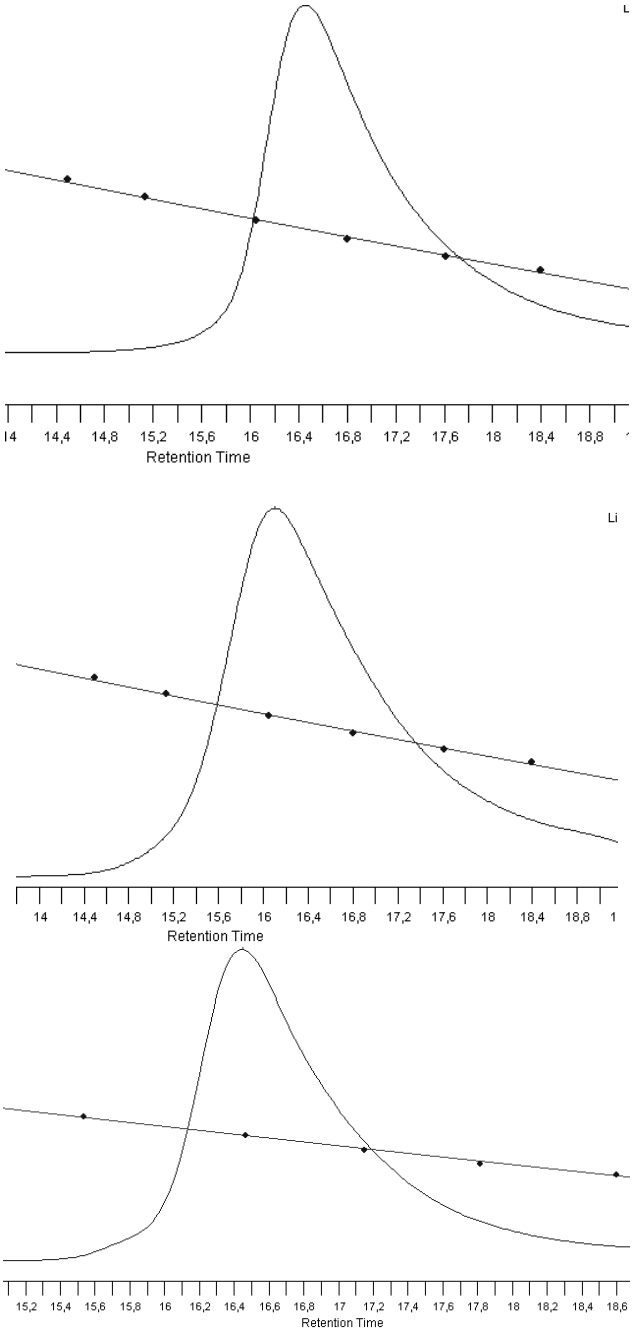

Figure S1. SEC traces of PMLABes produced from the ROP of MLABe mediated by organocatalysts: (top) TBD (Table 1, entry 2); (middle) DBU (Table 1, entry 6); (bottom) BEMP (Table 1, entry 9).

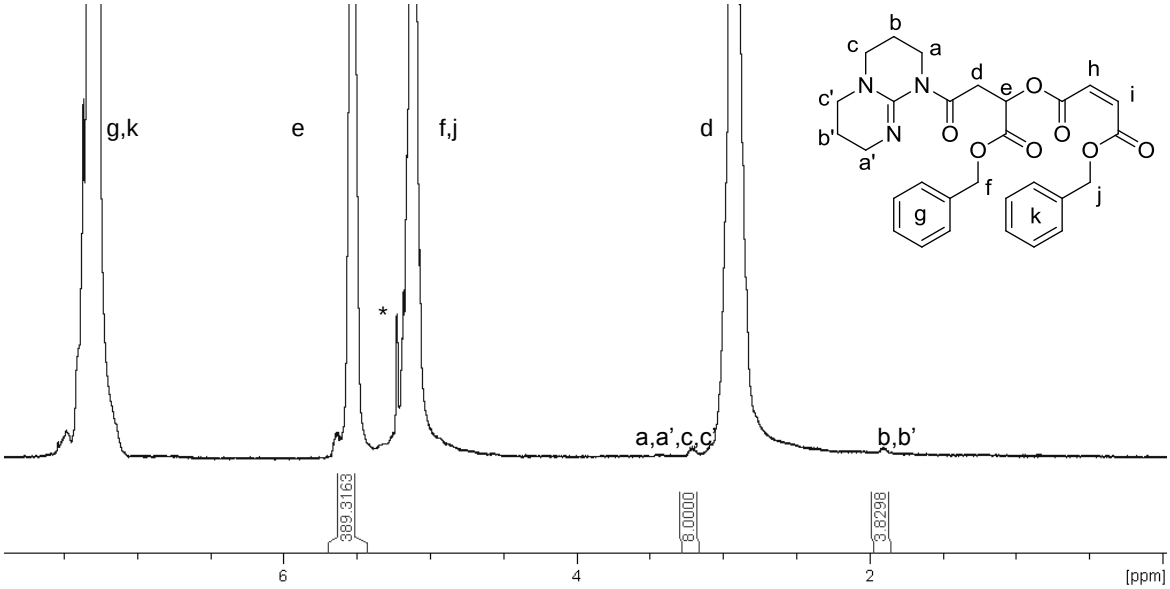

Figure S2. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) spectrum of a high molar mass ($M_{n,NMR}$ = 80 400 g.mol^{-1}), twice-precipitated PMLABe produced in the presence of TBD, illustrating the possibility to reliably evaluate $M_{n,NMR}$ even at such high molar mass polymers (Table 1, entry 4) (* marker stands for residual CH_2Cl_2).

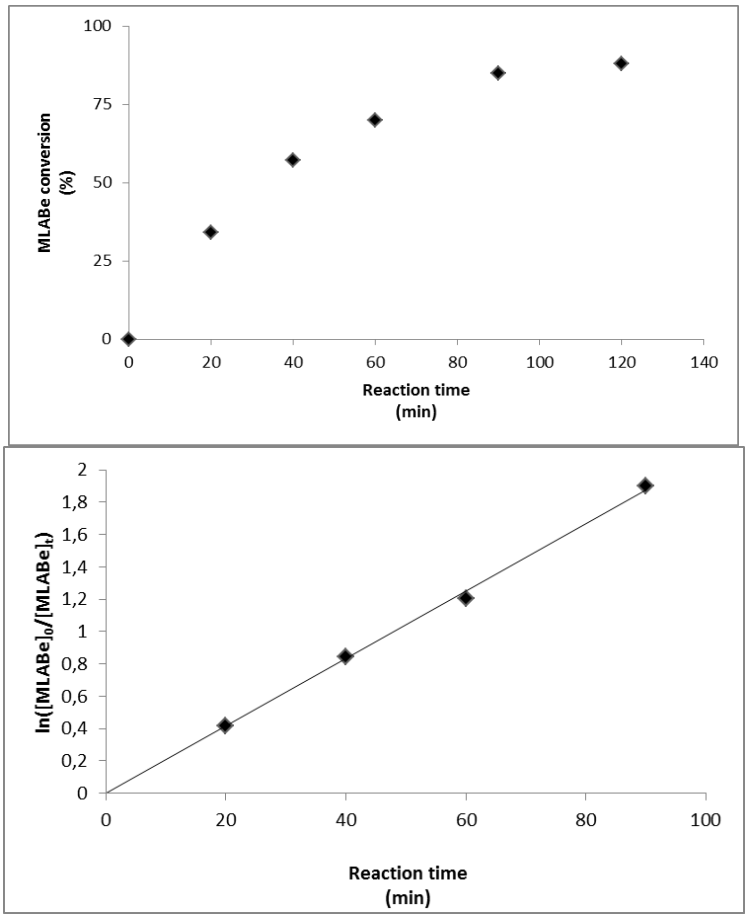

Figure S3. Kinetics of the ROP of bulk MLABe promoted by TBD at 60 °C (Table 1, entry 2); k_{app} = 1.252 (± 2.10^{-3}) h^{-1}, R^2 = 0.999.

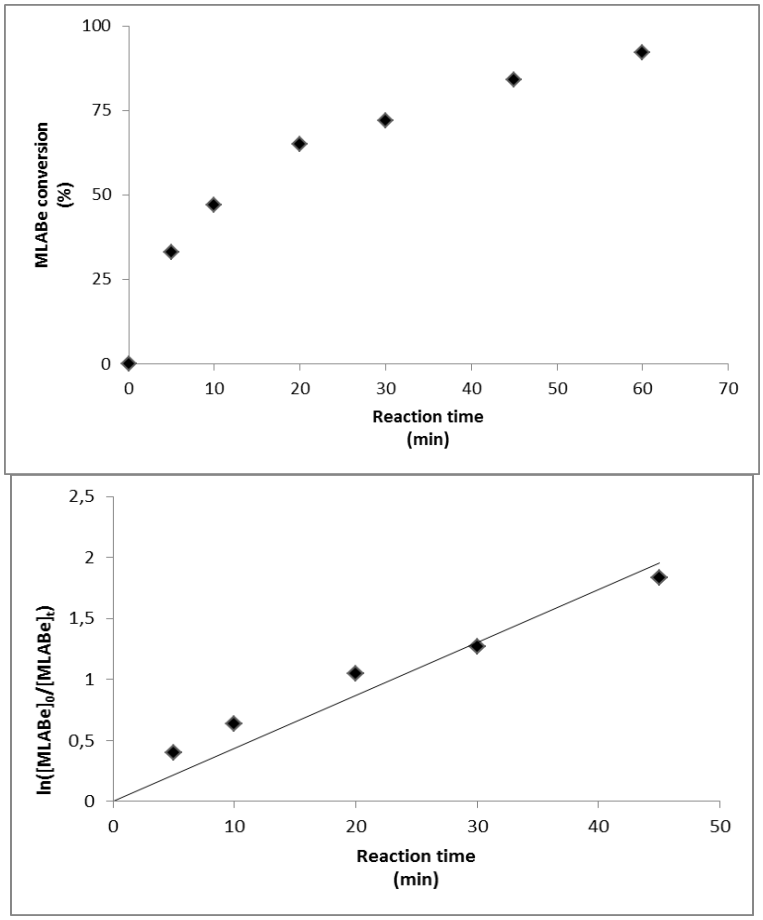

Figure S4. Kinetics of the bulk ROP of MLABe promoted by DBU at 60 °C (Table 1, entry 7; k_{app} = 2.61(± 3.10^{-2}) h^{-1}, R^2 = 0.943).

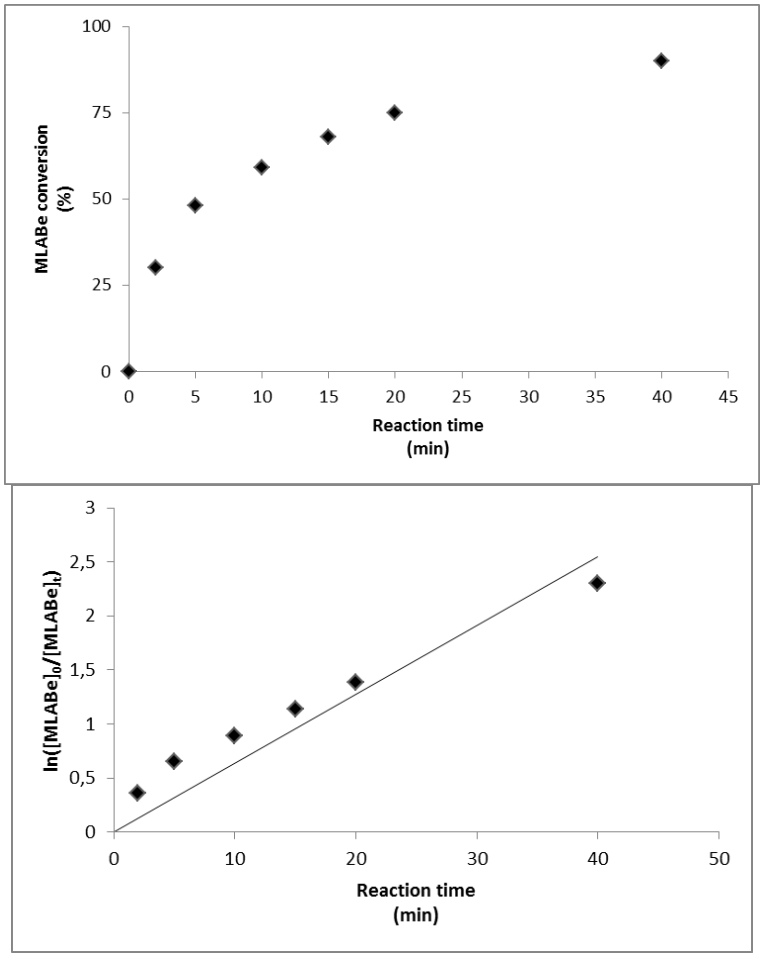

Figure S5. Kinetics of the bulk ROP of MLABe promoted by BEMP at 60 °C (Table 1, entry 10); k_{app} = 3.8 (± 1.10^{-1}) h^{-1}, R^2 = 0.901.

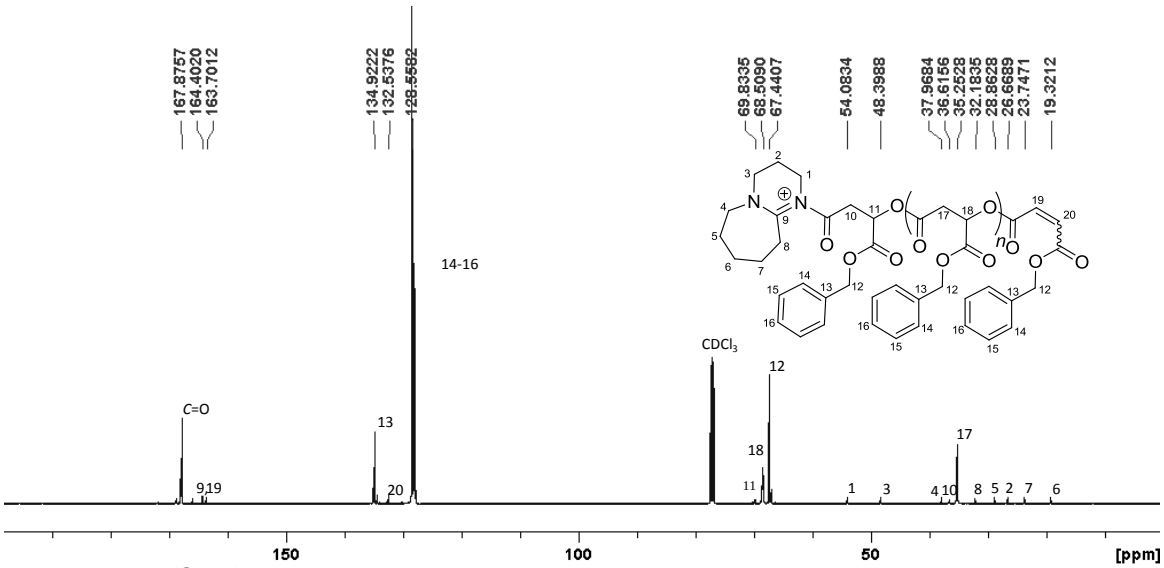

Figure S6. $^{13}C\{^1H\}$ NMR (125 MHz; $CDCl_3$, 25 °C) spectrum of a twice-precipitated PMLABe produced in the presence of DBU (Table 1, entry 6).

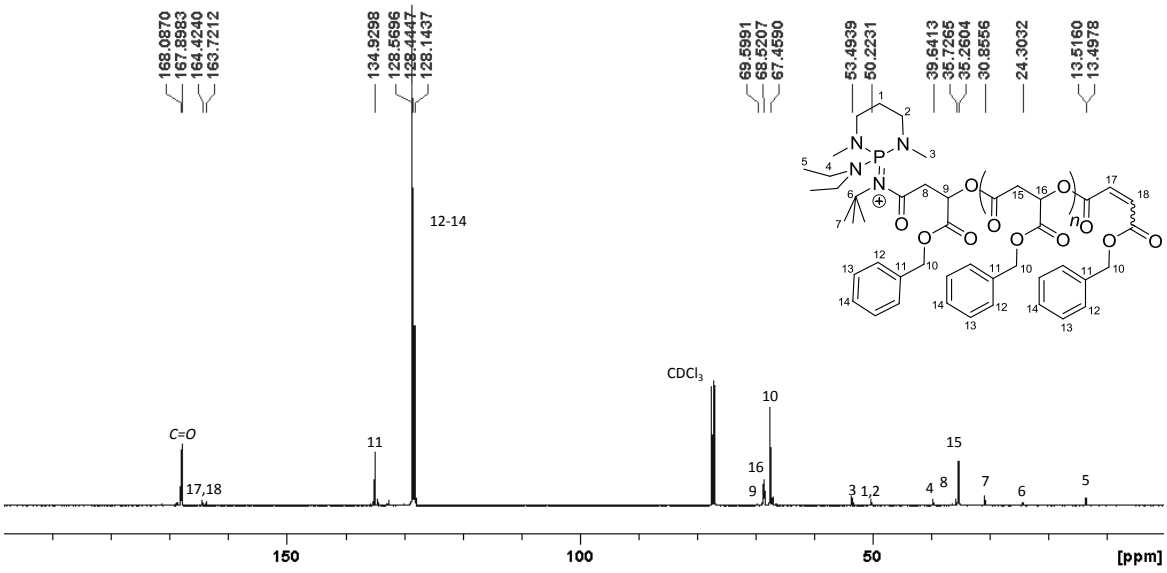

Figure S7. $^{13}C\{^{1}H\}$ NMR (125 MHz; $CDCl_3$, 25 °C) spectrum of a twice-precipitated PMLABe produced in the presence of BEMP (Table 1, entry 9).

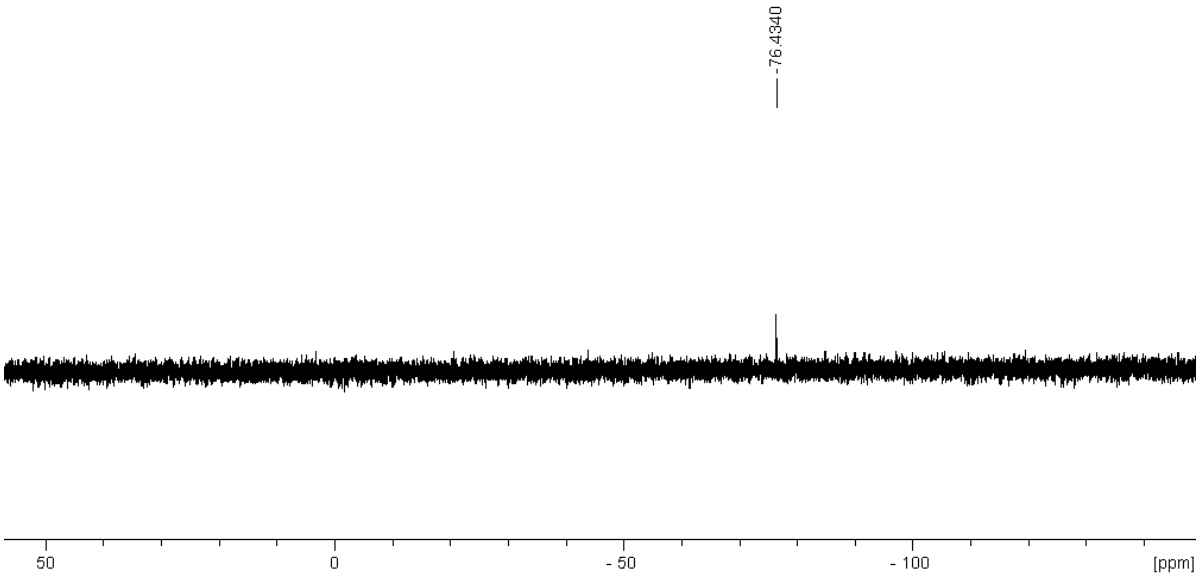

Figure S8. $^{31}P\{^{1}H\}$ NMR (121 MHz, $CDCl_3$, 25 °C) spectrum of a twice-precipitated PMLABe produced in the presence of BEMP (Table 1, entry 10).

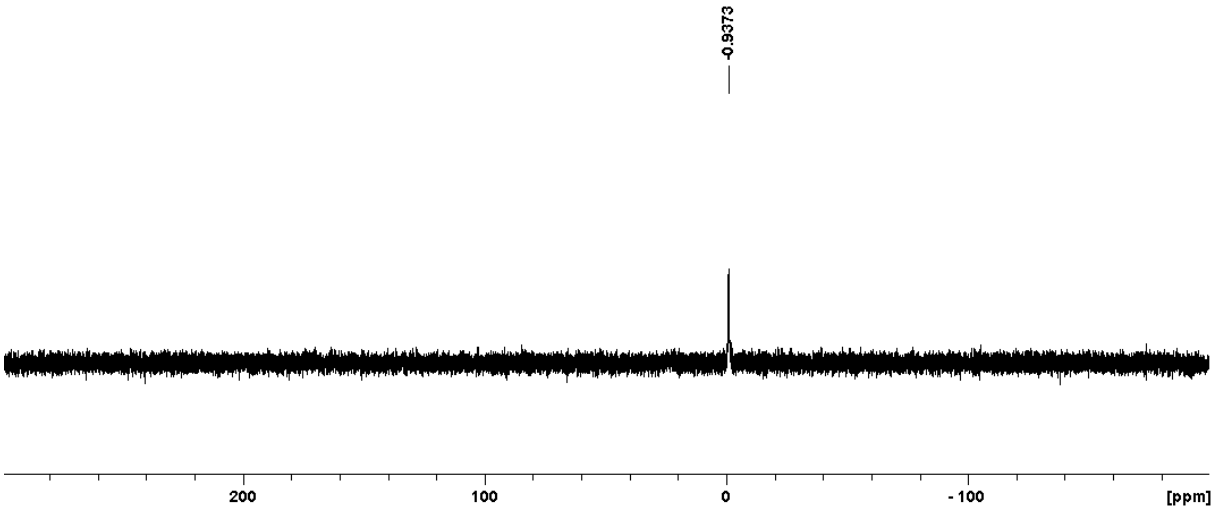

Figure S9. $^{31}P\{^{1}H\}$ NMR (121 MHz, $CDCl_3$, 25 °C) spectrum of BEMP.

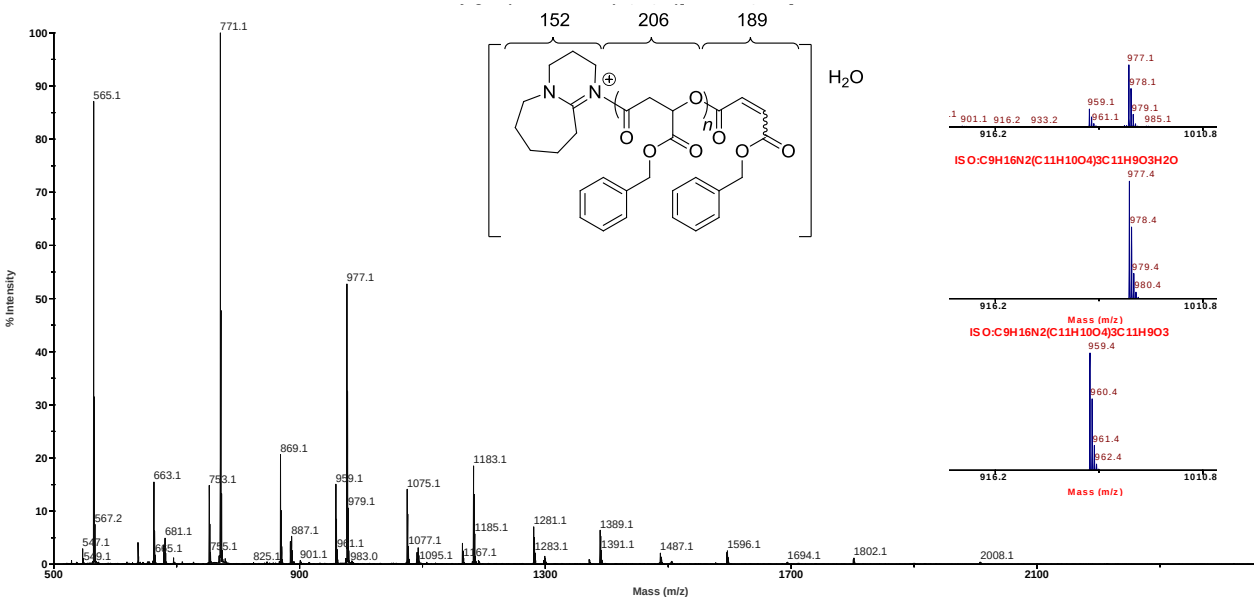

Figure S10. MALDI-ToF mass spectrum of a freshly synthesized PMLABe sample produced from DBU, using CHCA as matrix (Table 1, entry 6). The major population corresponds to $[DBU\{MLABe\}_nC(O)CH{=}CH(CO_2Be)]^+.H_2O$ macromolecules ($[M]^+{\cdot}H_2O$), with *m/z* = 771.1 g.mol^{-1} for *n* = 3 (isotopic simulation for $[DBU\{MLABe\}_3C(O)CH{=}CH(CO_2Be)]^+.H_2O$, $^{12}C_{42}{}^{1}H_{47}{}^{16}O_{12}{}^{14}N_2$, *m/z* = 771.4 g.mol^{-1}). The minor populations correspond to *m/z*: $[M]^+$ = 753.1 g.mol^{-1} and *m/z* : $[M]^+{\cdot}H_2O$ – OCH_2Ph (107) – H = 663.1 g.mol^{-1}.

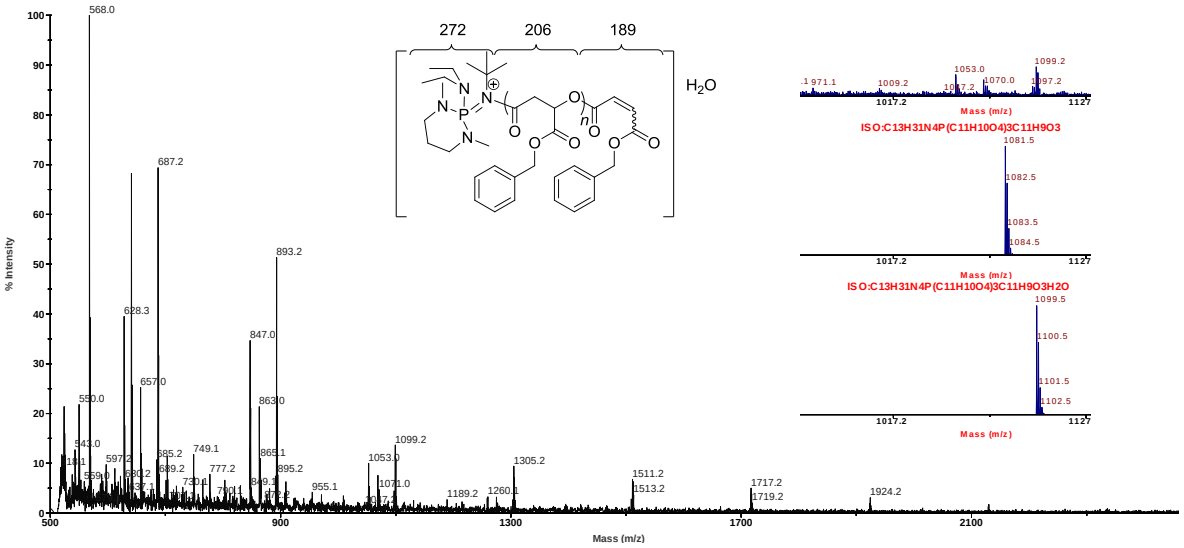

Figure S11. MALDI-ToF mass spectrum of a freshly synthesized PMLABe sample produced from BEMP, using CHCA as matrix (Table 1, entry 9). The major population corresponds to $[BEMP\{MLABe\}_nC(O)CH=CH(CO_2Be)]^+.H_2O$ macromolecules ($[M]^+.H_2O$) with *m/z* = 893.2 g.mol^{-1} for *n* = 2 (isotopic simulation for $[BEMP\{MLABe\}_2C(O)CH=CH(CO_2Be)]^+.H_2O$, $^{12}C_{46}{}^{1}H_{62}{}^{16}O_{12}{}^{14}N_4{}^{31}P_1$, *m/z* = 893.4 g.mol^{-1}). The minor populations correspond to $[M]^+$ – Et + H= = 847.0 g.mol^{-1} and to $[M]^+.H_2O$ – Et – H = 863.0 g.mol^{-1}.

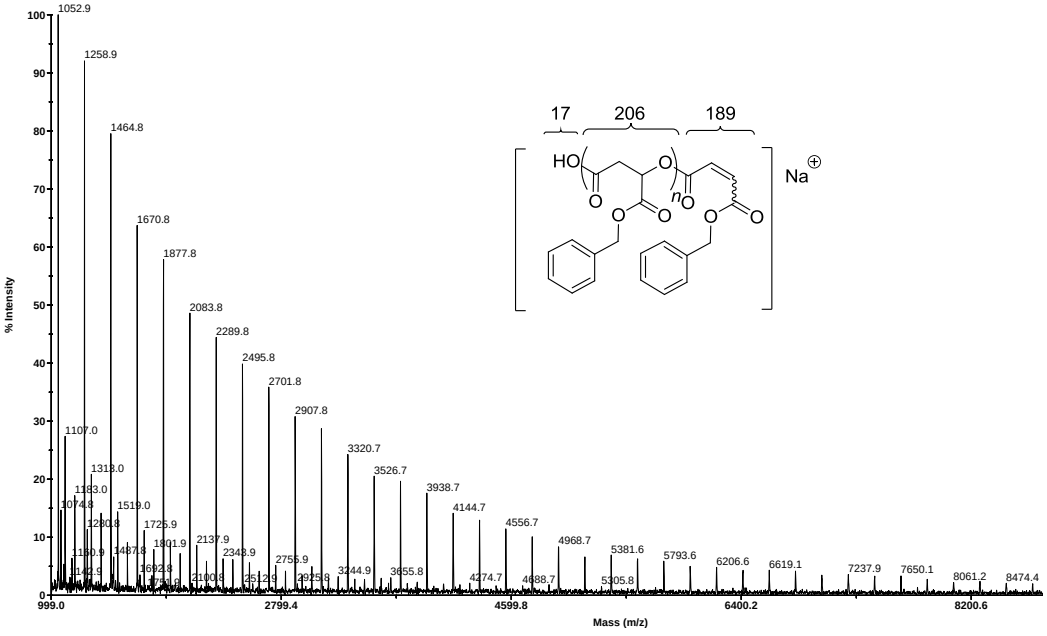

Figure S12. MALDI-ToF mass spectrum of a *non-freshly* synthesized PMLABe sample, initially produced from DBU, using IAA as matrix (Table 1, entry 6). The major population corresponds to $[HO\{MLABe\}_nC(O)CH=CH(CO_2Be)]Na^+$ macromolecules ($[M]^+\cdot Na$), with *m/z* = 1053.2 g.mol^{-1} for *n* = 4 (isotopic simulation for $[HO\{MLABe\}_4C(O)CH=CH(CO_2Be)]Na^+$, $^{12}C_{55}{}^{1}H_{50}{}^{16}O_{20}{}^{3}Na_1$, *m/z* = 1053.2 g.mol^{-1}).

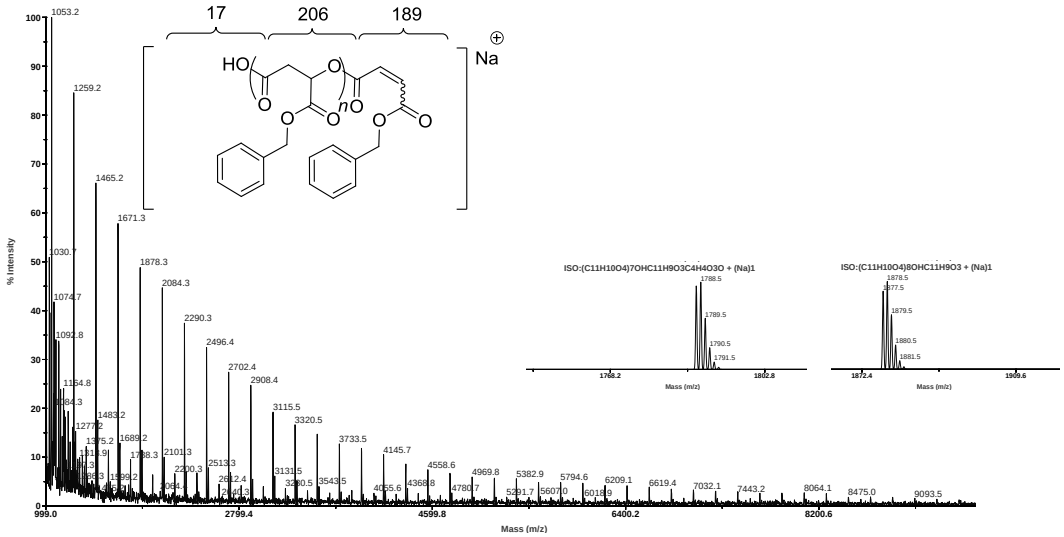

Figure S13. MALDI-ToF mass spectrum of a *non-freshly* synthesized PMLABe sample, initially produced from BEMP, using IAA as matrix (Table 1, entry 9). The major population corresponds to $[HO\{MLABe\}_nC(O)CH=CH(CO_2Be)]Na^+$ macromolecules ($[M]\cdot Na^+$) with *m/z* = 1053.2 g.mol^{-1} for *n* = 4 (isotopic simulation for $[HO\{MLABe\}_4C(O)CH=CH(CO_2CH_2Ph)]Na^+$, $^{12}C_{55}{}^{1}H_{50}{}^{16}O_{20}{}^{3}Na_1$, *m/z* = 1053.2 g.mol^{-1}). The minor populations correspond to $[M]\cdot K^+$, *m/z* +16 g.mol^{-1}, $[M]\cdot Na^+$–CH_2Ph , *m/z* – 91 g.mol^{-1} and $[M]\cdot K^+$–CH_2Ph: *m/z* +16 – 91 g.mol^{-1}.

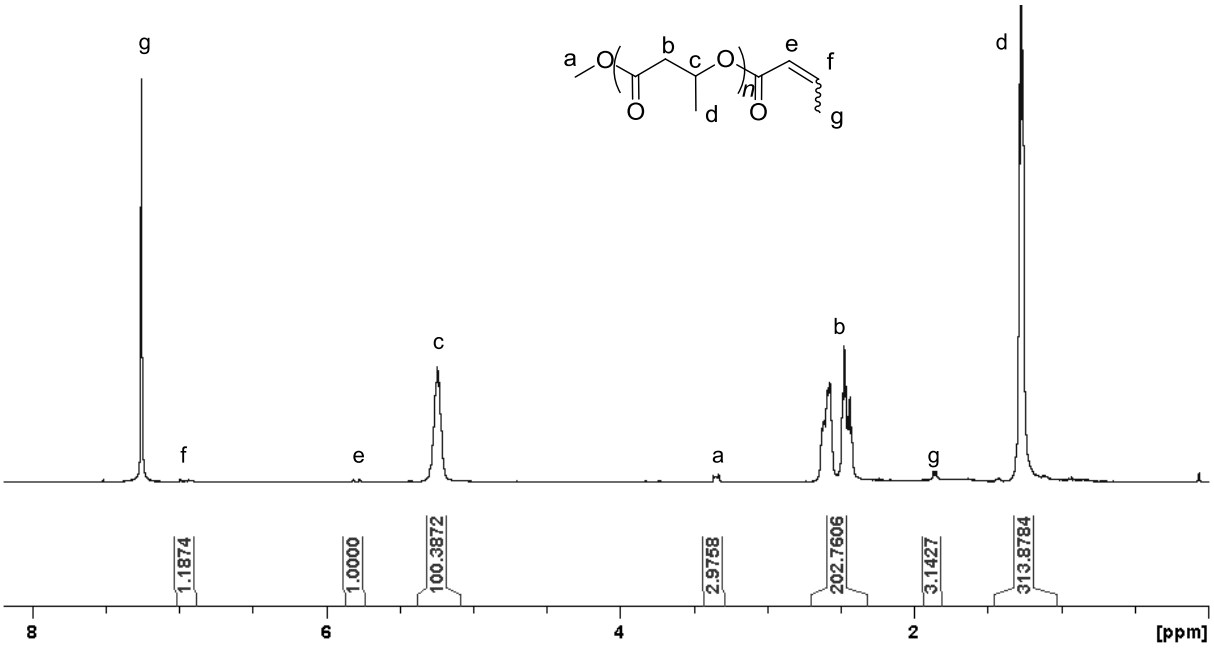

Figure S14. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) spectrum of an α-TBD-ω-crotonate PHB sample left in the presence of wet methanol for 1 h at 23 °C ($M_{n,\,SEC}$ = 7 200 g.mol^{-1}, $Đ_M$ = 1.25).

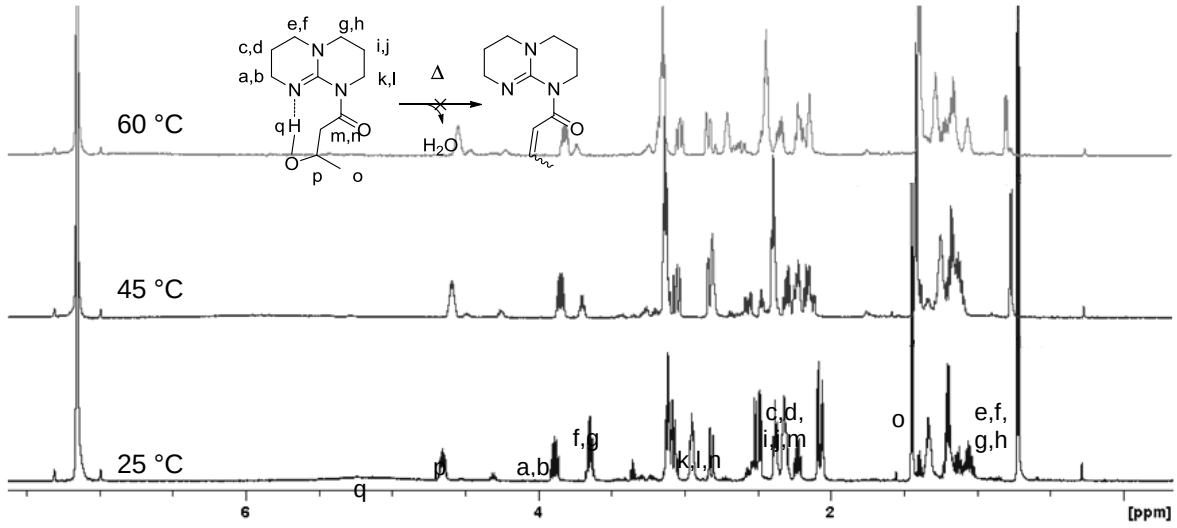

Figure S15. ^{1}H NMR (500 MHz, toluene-d_8) spectra of 1:1 TBD:BL (0.05 mol.L^{-1}) mixture at (bottom) 25 °C, (middle) 45 °C, and (top) 60 °C.

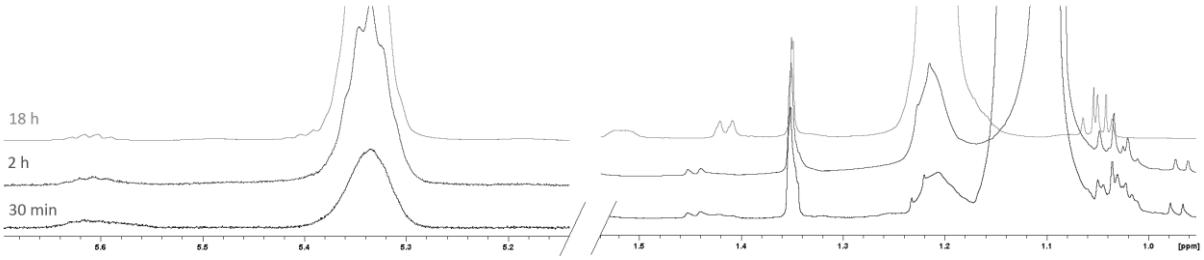

Figure S16. Detail of the region of the ^{1}H NMR (500 MHz, toluene-d_8, 60 °C) spectra of PHB produced from BEMP, showing the evolution as a function of time of the signals of crotonic (δ = 5.69 ppm) and methine (δ = 5.41 ppm) hydrogens of PHB, and of the one corresponding to the N(CH_3)$_3$ hydrogens of BEMP (δ = 1.33 ppm).

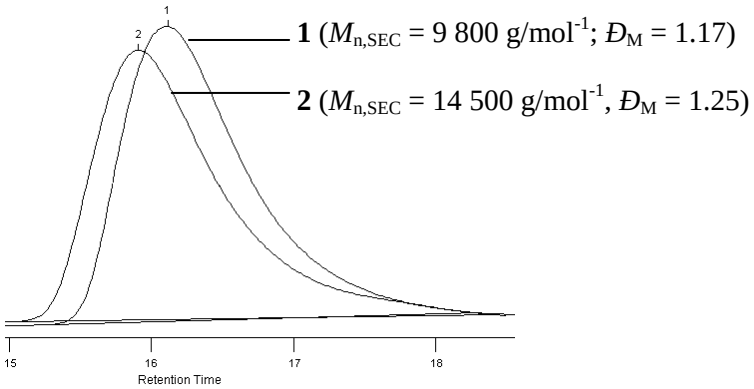

Figure S17. SEC traces of PHB produced from the ROP of BL mediated by TBD: (right) first loading of BL (113 equiv.; $M_{n,SEC}$ = 9 800 g.mol^{-1}; $Đ_M$ = 1.17), (left) second loading of BL (168 equiv.; M_{nSEC} = 14 500 g.mol^{-1}, $Đ_M$ = 1.25).