

Supporting Information for
Phosphazene/Triisobutylaluminum-Promoted Anionic Ring-Opening Polymerization of 1,2-Epoxybutane Initiated by Secondary Carbamates

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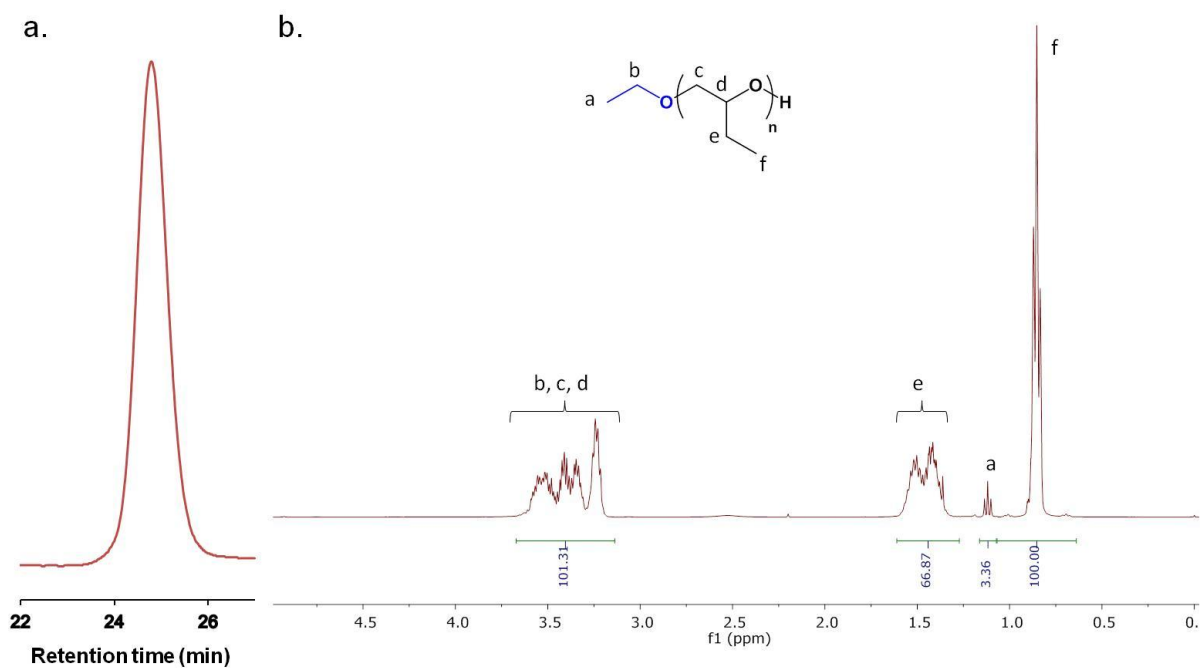


Figure S1. SEC traces (left) and ¹H NMR spectrum in CDCl₃ (right) of a poly(butylene oxide) synthesized with *N*-ethylurethane-*t*BuP₄ as initiating system (Table 1, run 1).

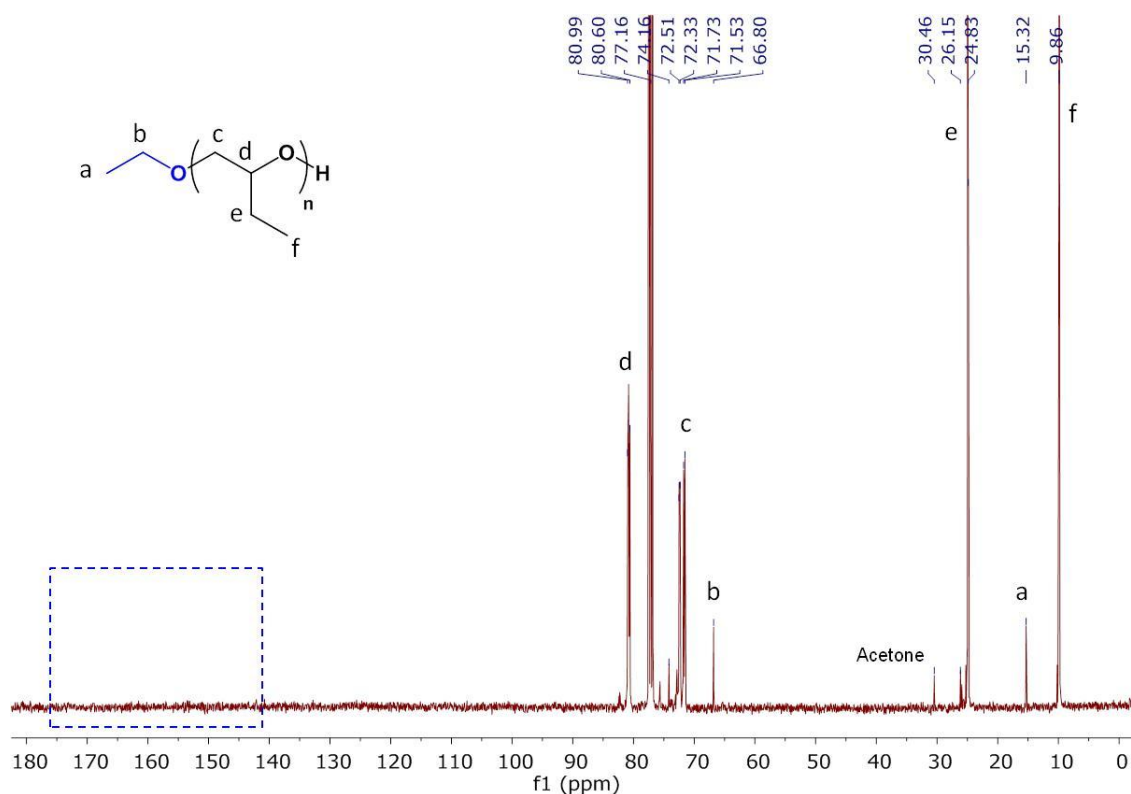
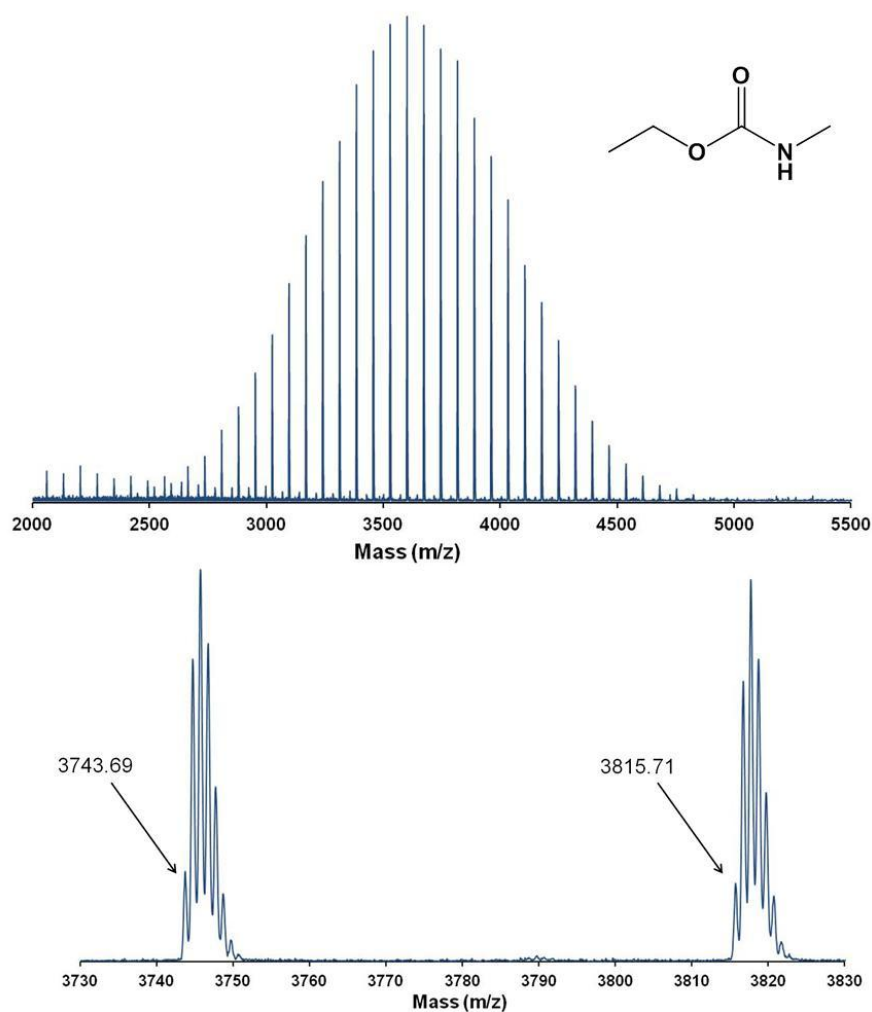


Figure S2. ¹³C NMR spectrum in CDCl₃ of a poly(butylene oxide) synthesized with *N*-ethylurethane-*t*BuP₄ as initiating system (Table 1, run 1).



α -end group	Ω -end group	Cation	DP	Calculated exact mass
		Na ⁺	51	3800.99
		Na ⁺	52	3816.02
		Na ⁺	52	3801.02

Figure S3. MALDI-ToF spectra (top: linear mode; bottom: reflectron mode) of a poly(butylene oxide) synthesized with *N*-Methylurethane-*t*BuP₄ as initiating system (Table 1, run 4).

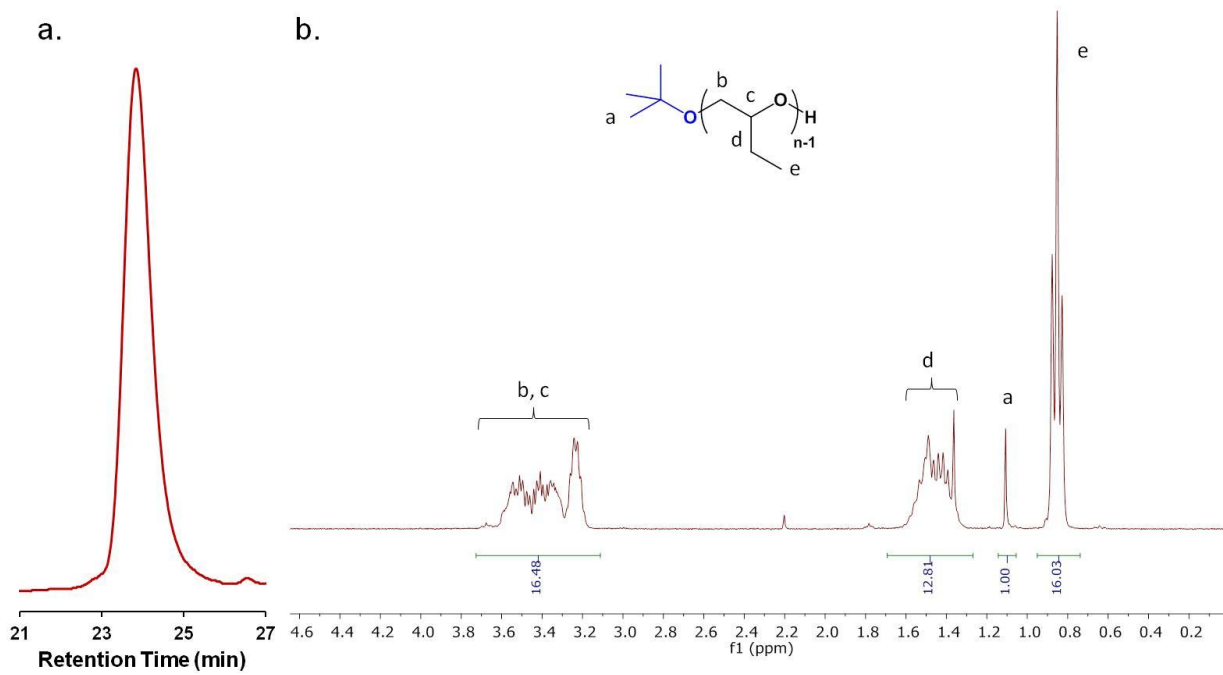


Figure S4. SEC traces (left) and ¹H NMR spectrum in CDCl₃ (right) of a poly(butylene oxide) synthesized with *tert*-butyl *N*-allylcarbamate / *t*BuP₄ as initiating system (Table 1, run 5).

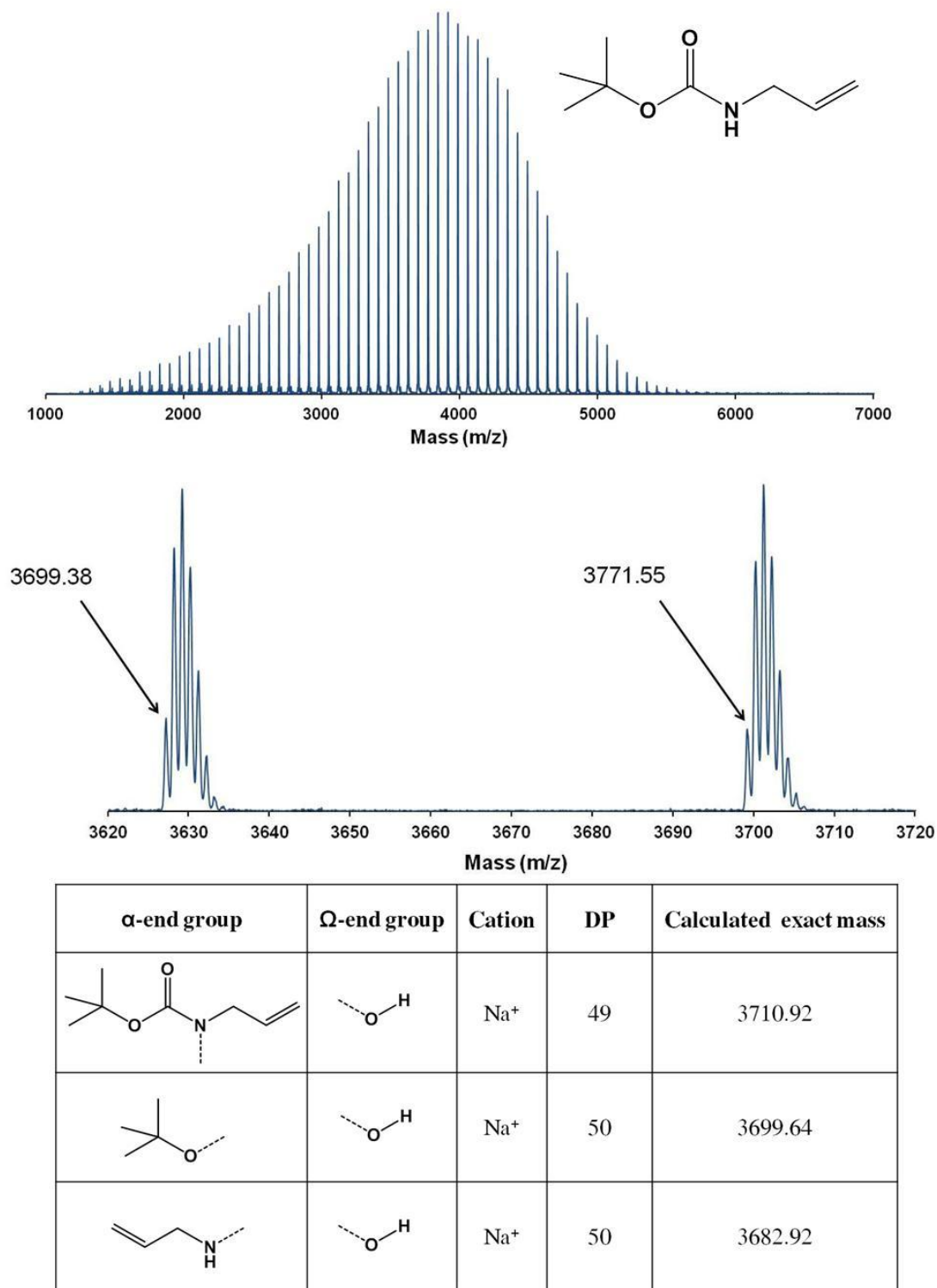


Figure S5. MALDI-ToF spectra (top: linear mode; bottom: reflectron mode) of a poly(butylene oxide) synthesized with *tert*-butyl *N*-allylcarbamate / *t*BuP₄ as initiating system (Table 1, run 5).

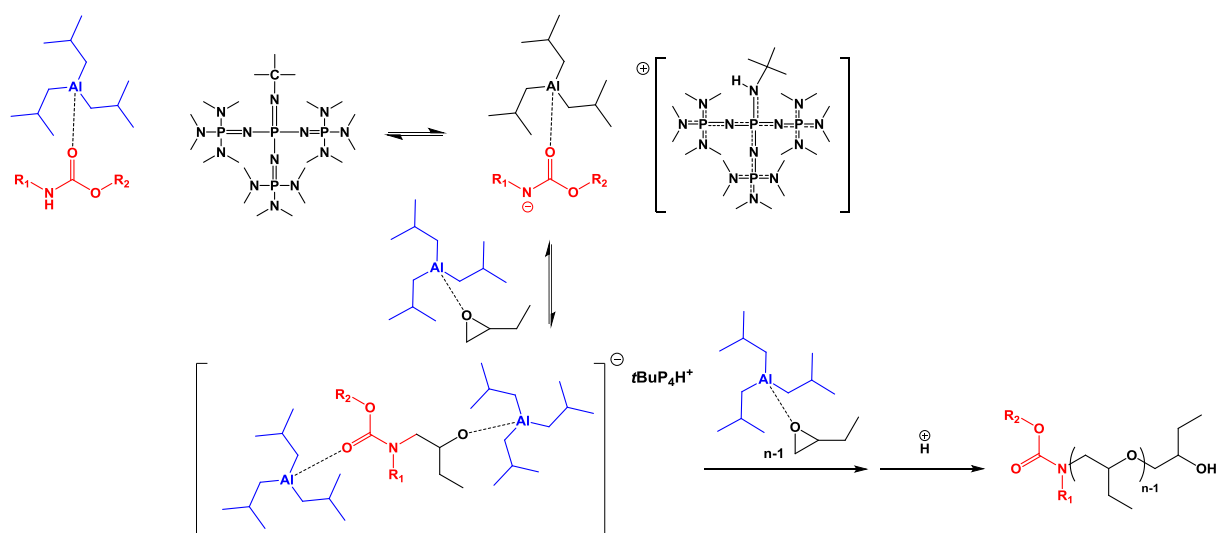


Figure S6. Postulated mechanism for the ROP of 1,2-epoxybutane using secondary urethane-triisobutylaluminum-phosphazene base (1-3-1) as initiating system.

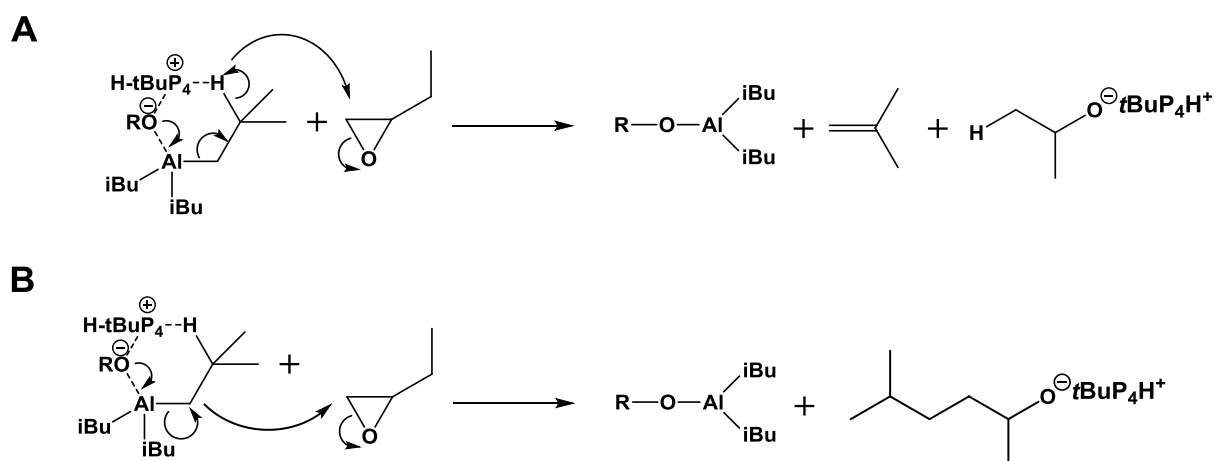


Figure S7. Proposed mechanisms for the transfer reactions during the anionic ring-opening polymerization of 1,2-epoxybutane in presence of triisobutylaluminum.

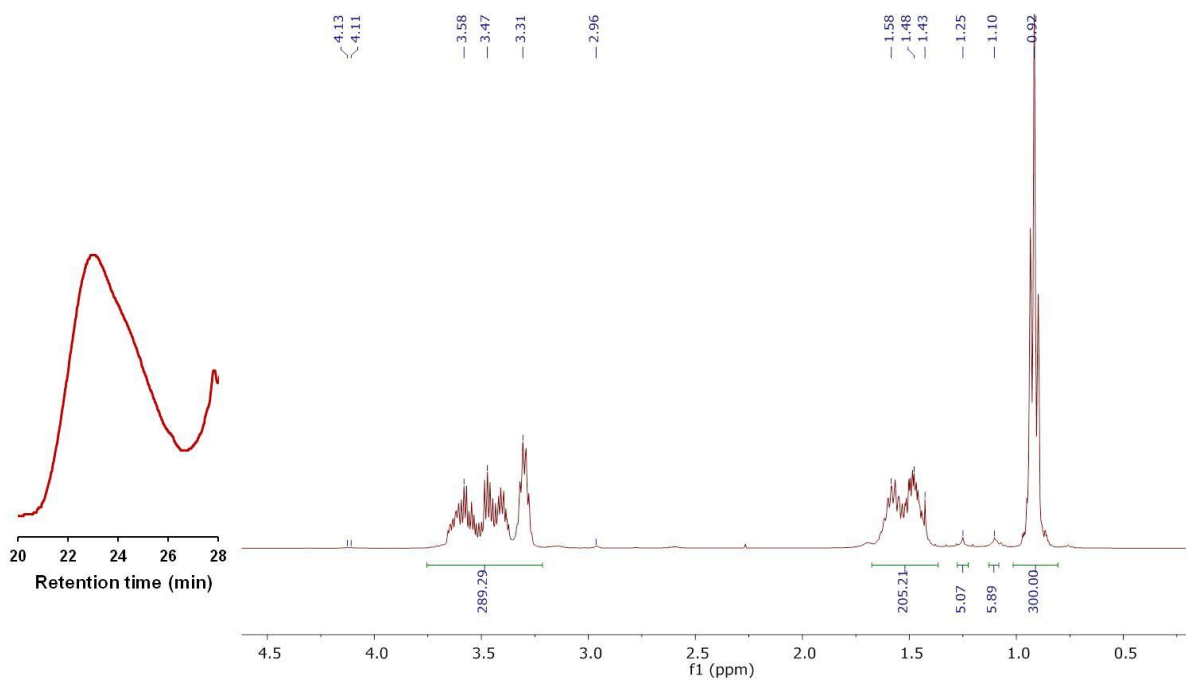


Figure S8. SEC traces (left) and ¹H NMR spectrum in CDCl₃ (right) of a poly(butylene oxide) synthesized with *N*-methylurethane / *i*Bu₃Al / *t*BuP₄ (1 / 3 / 1) as initiating system (Table 2, run 1).

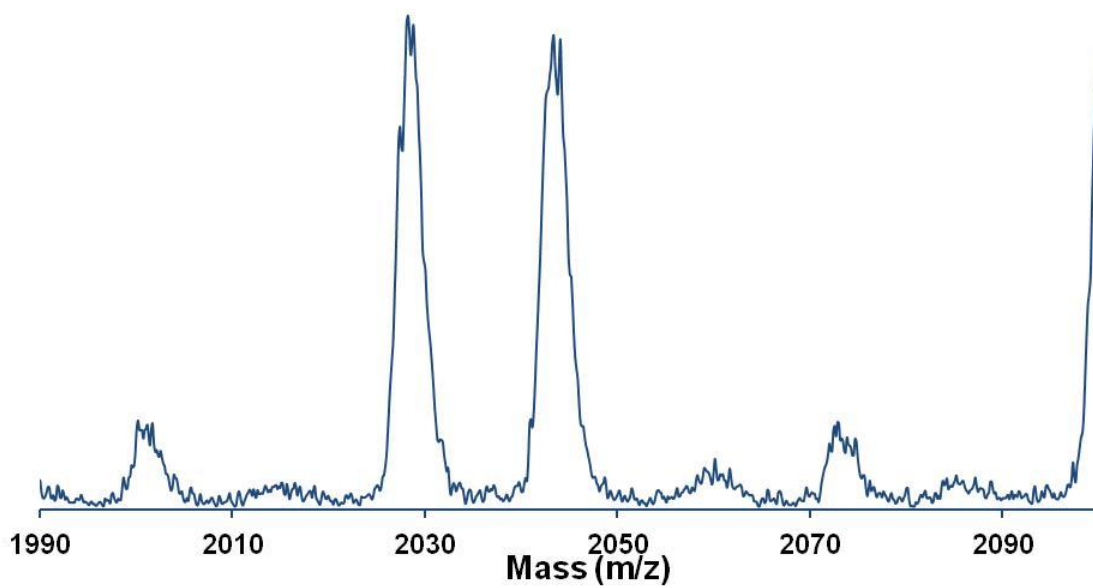
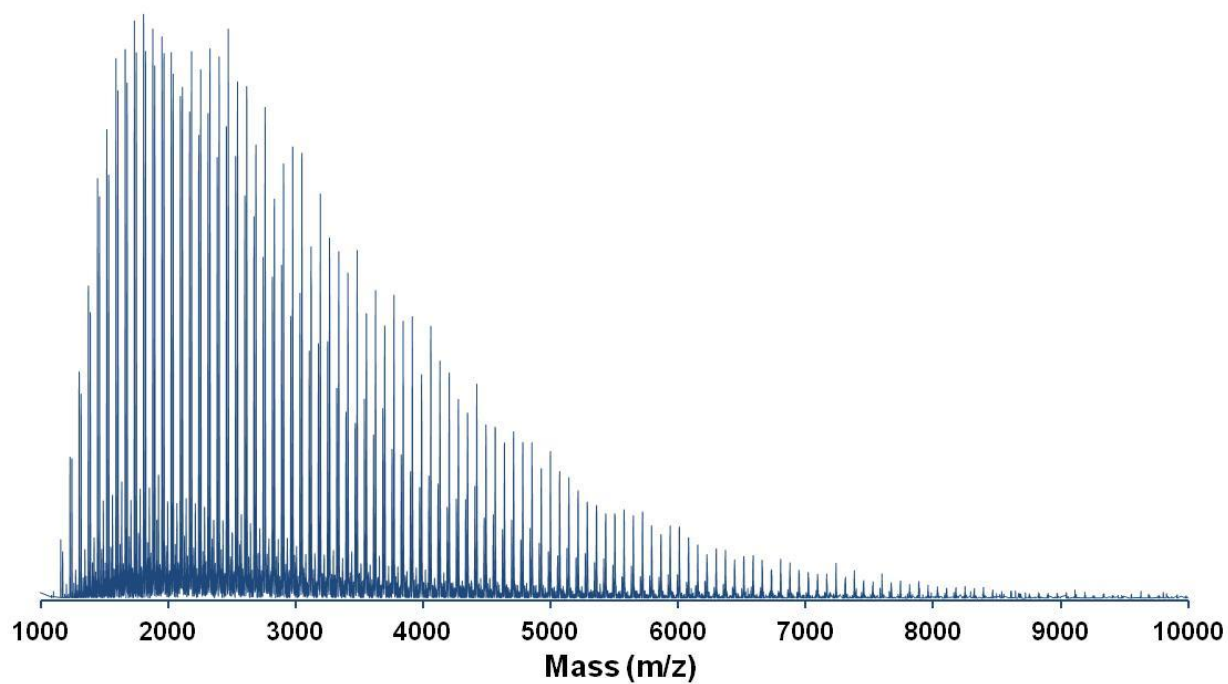


Figure S9. MALDI-ToF spectra (linear mode) of a poly(butylene oxide) synthesized with *N*-methylurethane / *i*Bu₃Al / *t*BuP₄ (1 / 3 / 1) as initiating system in toluene (Table 2, run 1).

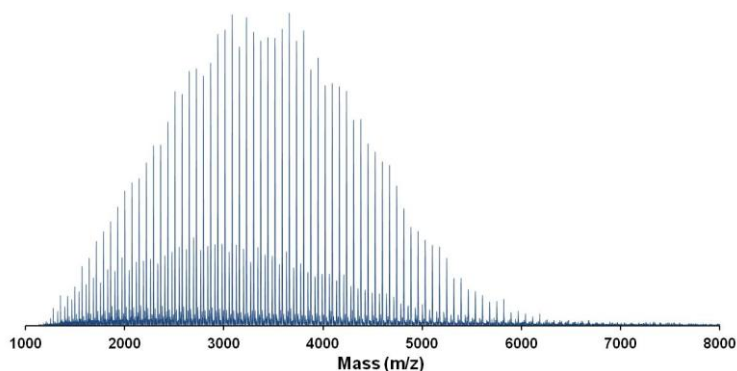


Figure S10. MALDI-ToF spectra (linear mode) of a poly(butylene oxide) synthesized with *N*-methylurethane / *i*Bu₃Al / *t*BuP₄ (1 / 1 / 1) as initiating system in toluene (Table 2, run 2).

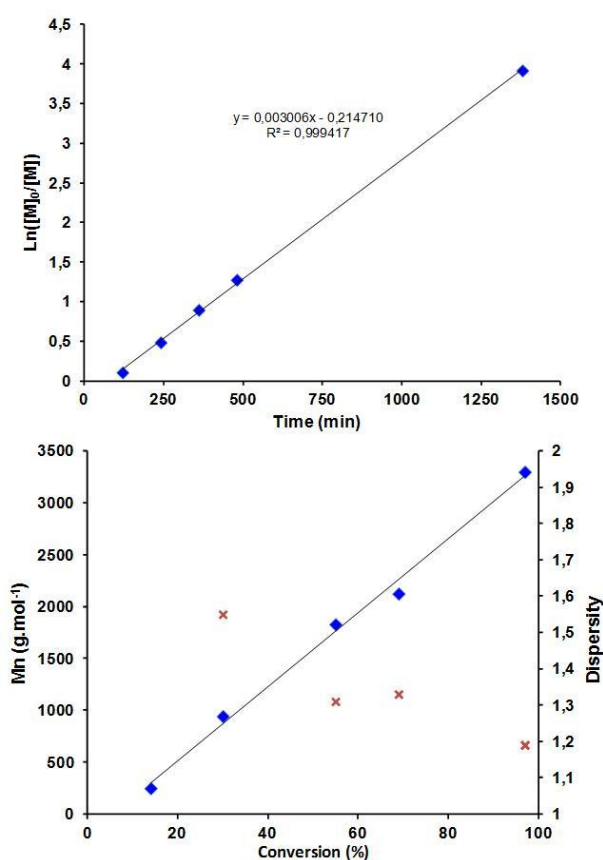


Figure S11. Anionic ring-opening polymerization of 1,2-epoxybutane synthesized with *N*-methylurethane / *i*Bu₃Al / *t*BuP₄ as initiating system in toluene (Table 2, run 2) at 25 °C in toluene ($[I]_0 = 0.06534 \text{ mol.L}^{-1}$, $[M]_0 = 3.27 \text{ mol.L}^{-1}$, M:*N*-methylurethane:*i*Bu₃Al:*t*BuP₄ = 50:1:1:1:1): (a) first-order kinetic plot ; (b) relationship observed between number-average molar mass (squares; linear trend is indicated by the dashed line) or dispersity (crosses) and monomer conversion.

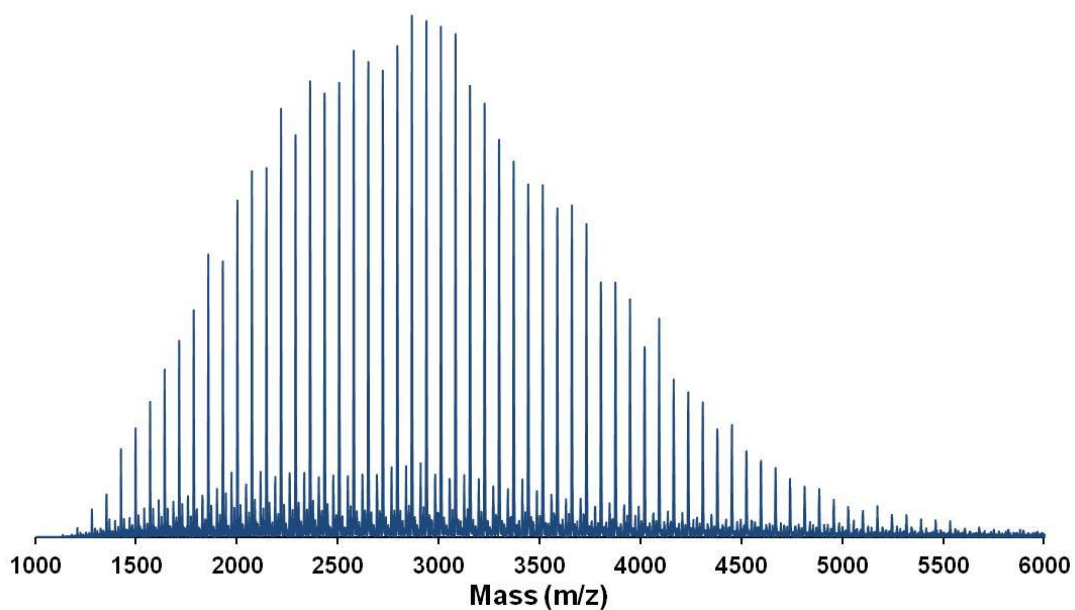


Figure S12. MALDI-ToF spectra (linear mode) of a poly(butylene oxide) synthesized with *N*-methylurethane / $i\text{Bu}_3\text{Al}$ / $t\text{BuP}_2$ (1 / 1 / 1) as initiating system in toluene (Table 2, run 3).

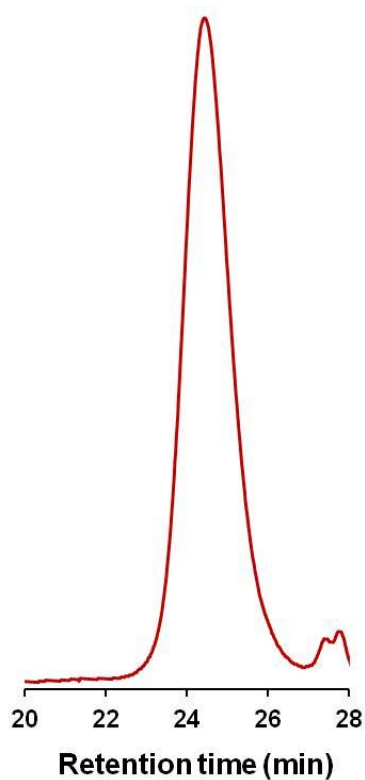


Figure S13. SEC trace of a poly(butylene oxide) synthesized with *N*-methylurethane / $i\text{Bu}_3\text{Al}$ / $t\text{BuP}_2$ (1 / 1 / 1) as initiating system in toluene (Table 2, run 3).

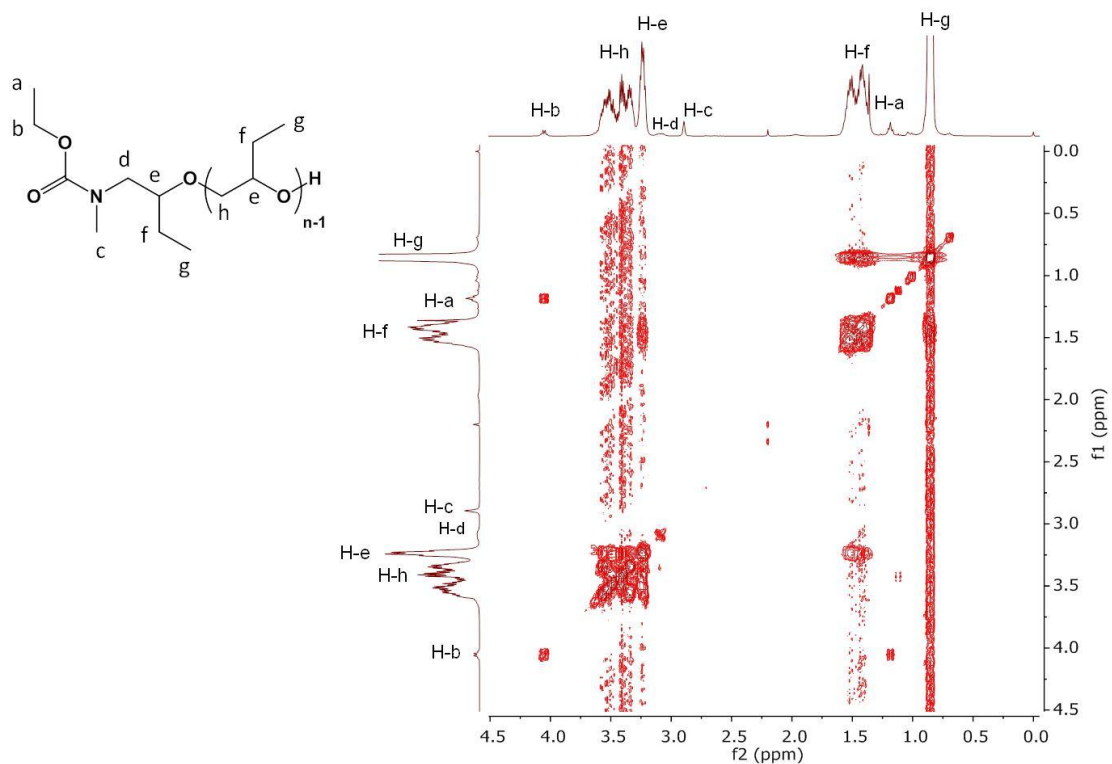


Figure S14. 2D COSY-NMR spectrum in CDCl_3 at room temperature of a poly(butylene oxide) synthesized with *N*-methylurethane / $i\text{Bu}_3\text{Al}$ / *t*BuP₂ (1 / 1 / 1) as initiating system in toluene (Table 2, run 3).

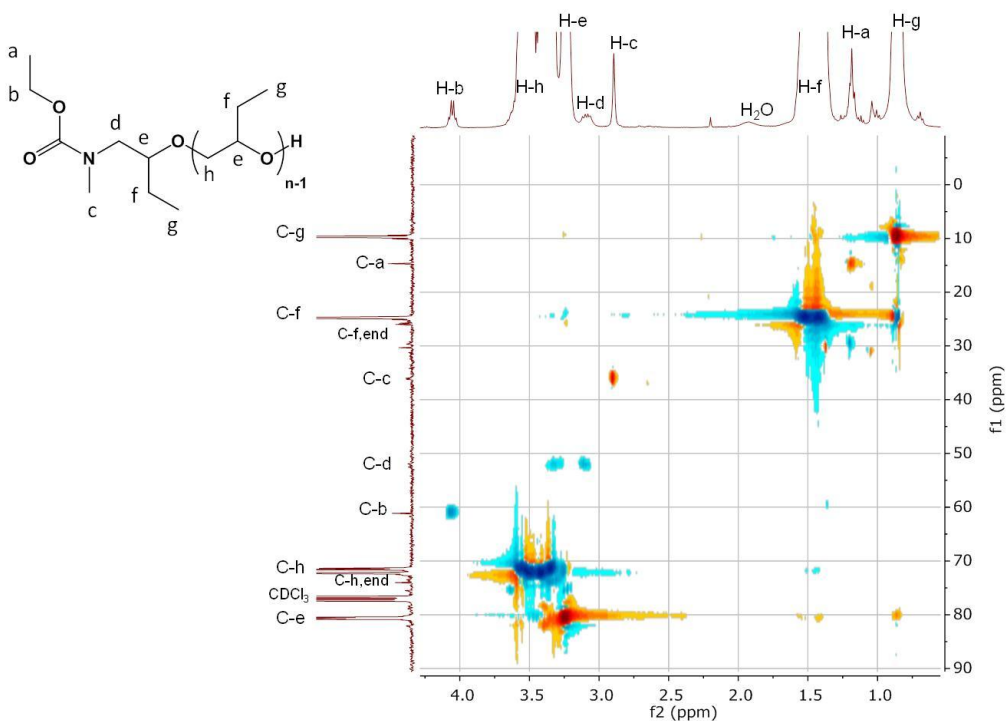


Figure S15. 2D HSQC-NMR spectrum in CDCl_3 at room temperature of a poly(butylene oxide) synthesized with *N*-methylurethane / $i\text{Bu}_3\text{Al}$ / *t*BuP₂ (1 / 1 / 1) as initiating system in toluene (Table 2, run 3).

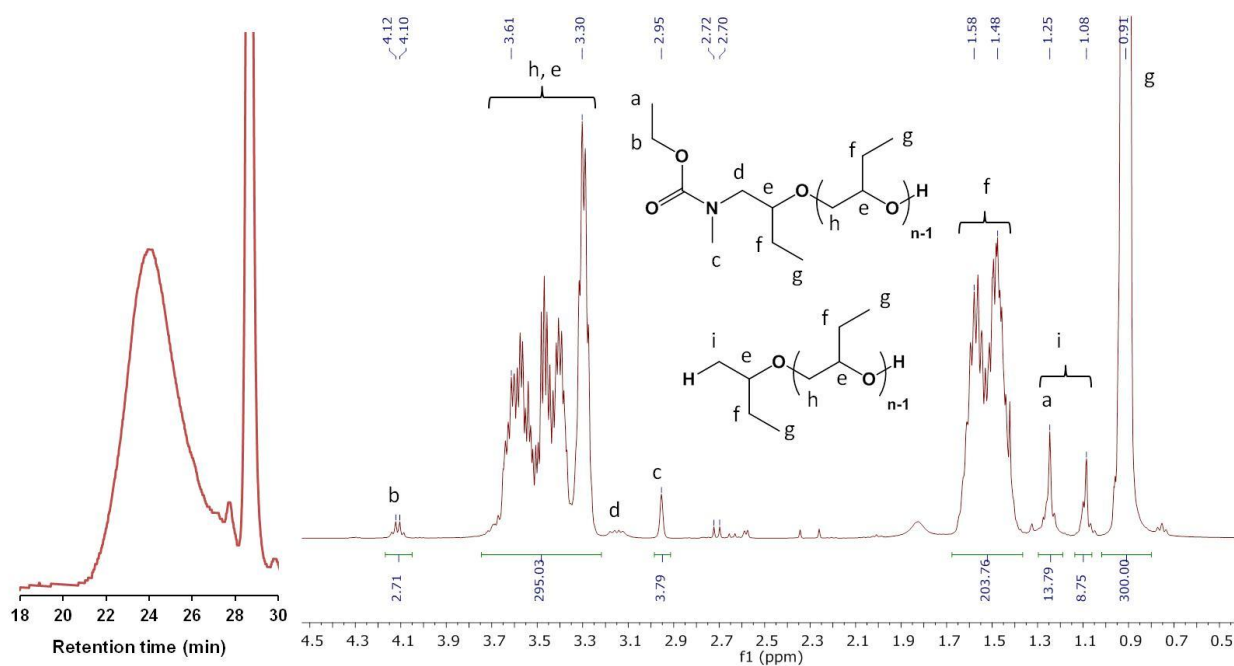


Figure S16. SEC traces (left) and ^1H NMR spectrum in CDCl_3 (right) of a poly(butylene oxide) synthesized with *N*-methylurethane / *i*Bu₃Al / *t*BuP₄ (1 / 3 / 1) as initiating system in MeTHF (Table 2, run 4).

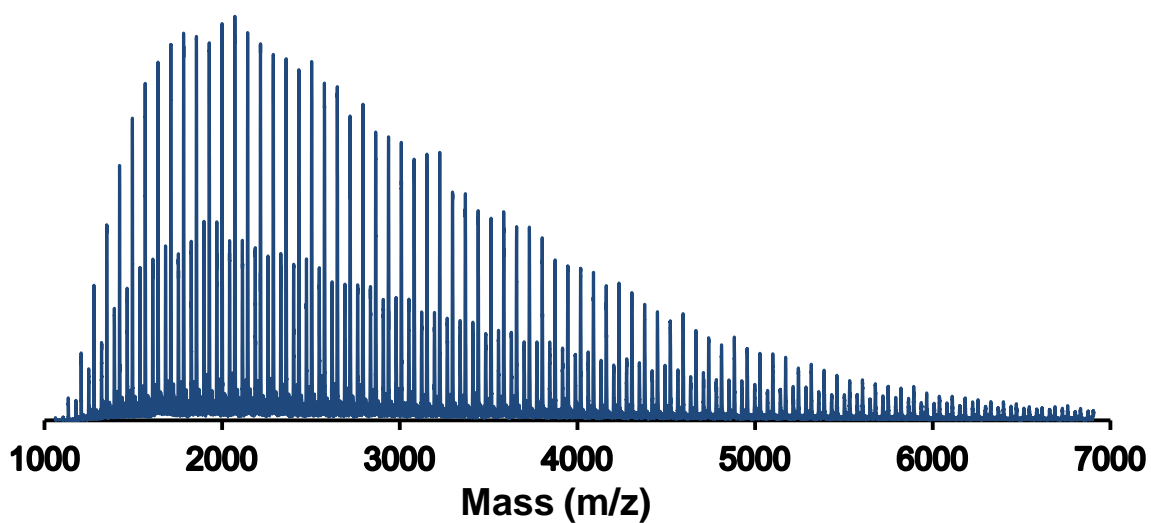


Figure S17. MALDI-ToF spectra (linear mode) of a poly(butylene oxide) synthesized with *N*-methylurethane / *i*Bu₃Al / *t*BuP₄ (1 / 3 / 1) as initiating system in MeTHF (Table 2, run 4).

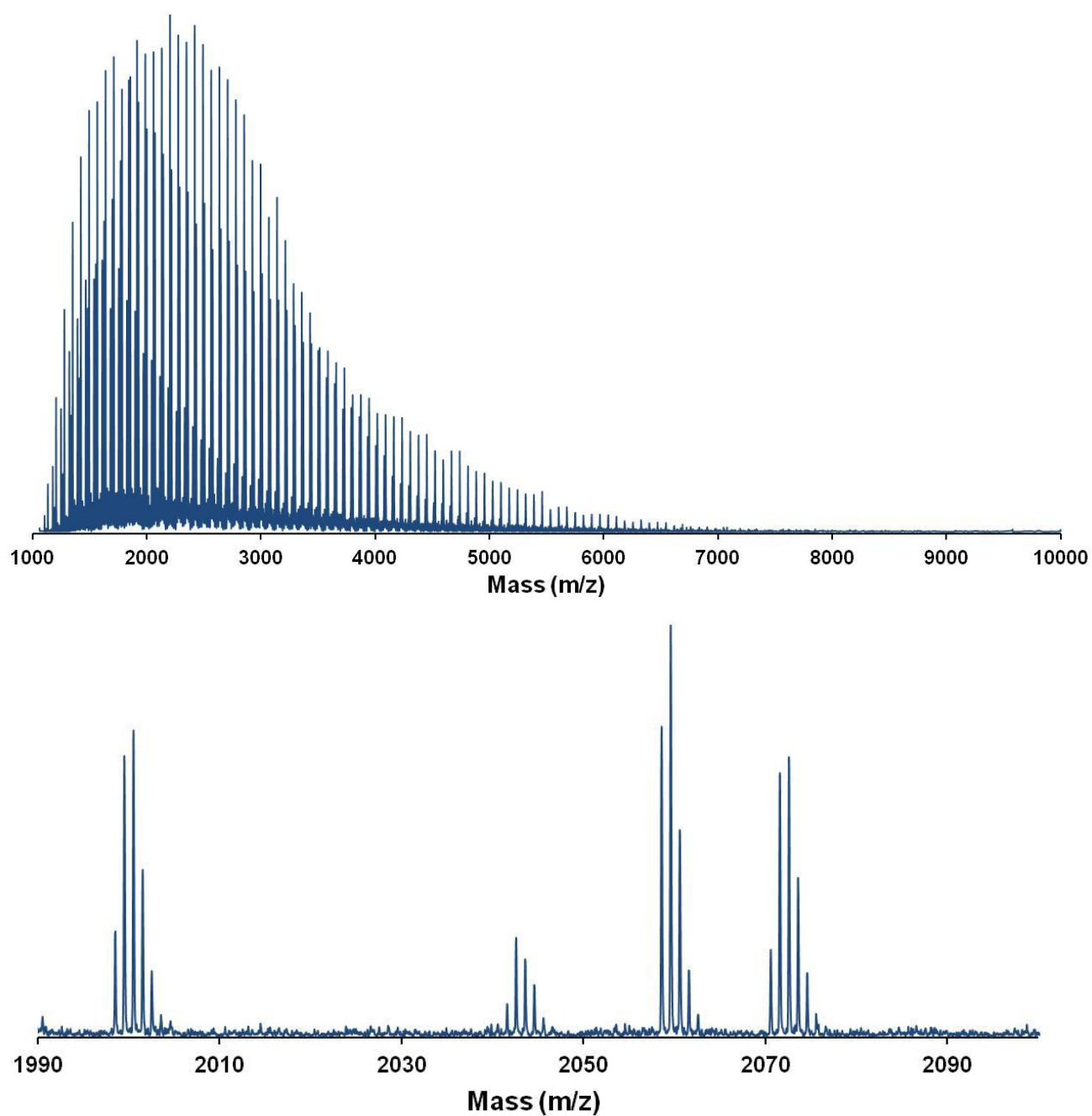


Figure S18. MALDI-ToF spectra (top: linear mode; bottom: reflectron mode) of a poly(butylene oxide) synthesized with *N*-methylurethane / *i*Bu₃Al / *t*BuP₄ (1 / 3 / 1) as initiating system in MeTHF (Table 2, run 6).

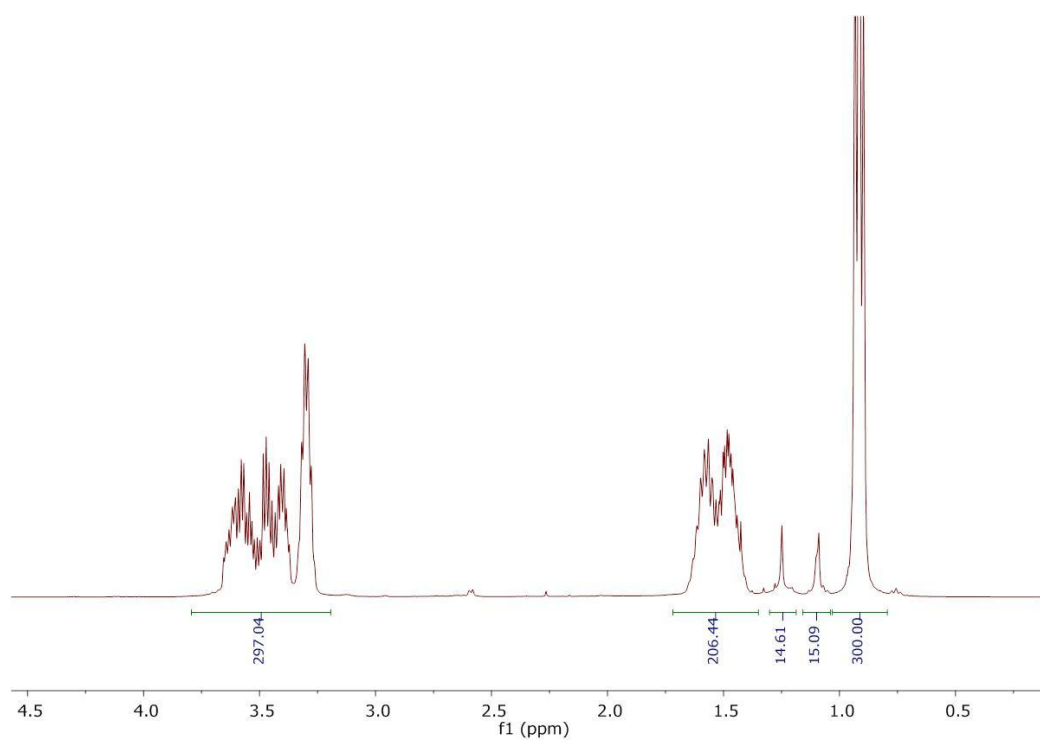


Figure S19. ^1H NMR spectrum in CDCl_3 of a poly(butylene oxide) synthesized with *N*-methylurethane / *i*Bu₃Al / *t*BuP₄ (1 / 3 / 1) as initiating system in MeTHF (Table 2, run 7).

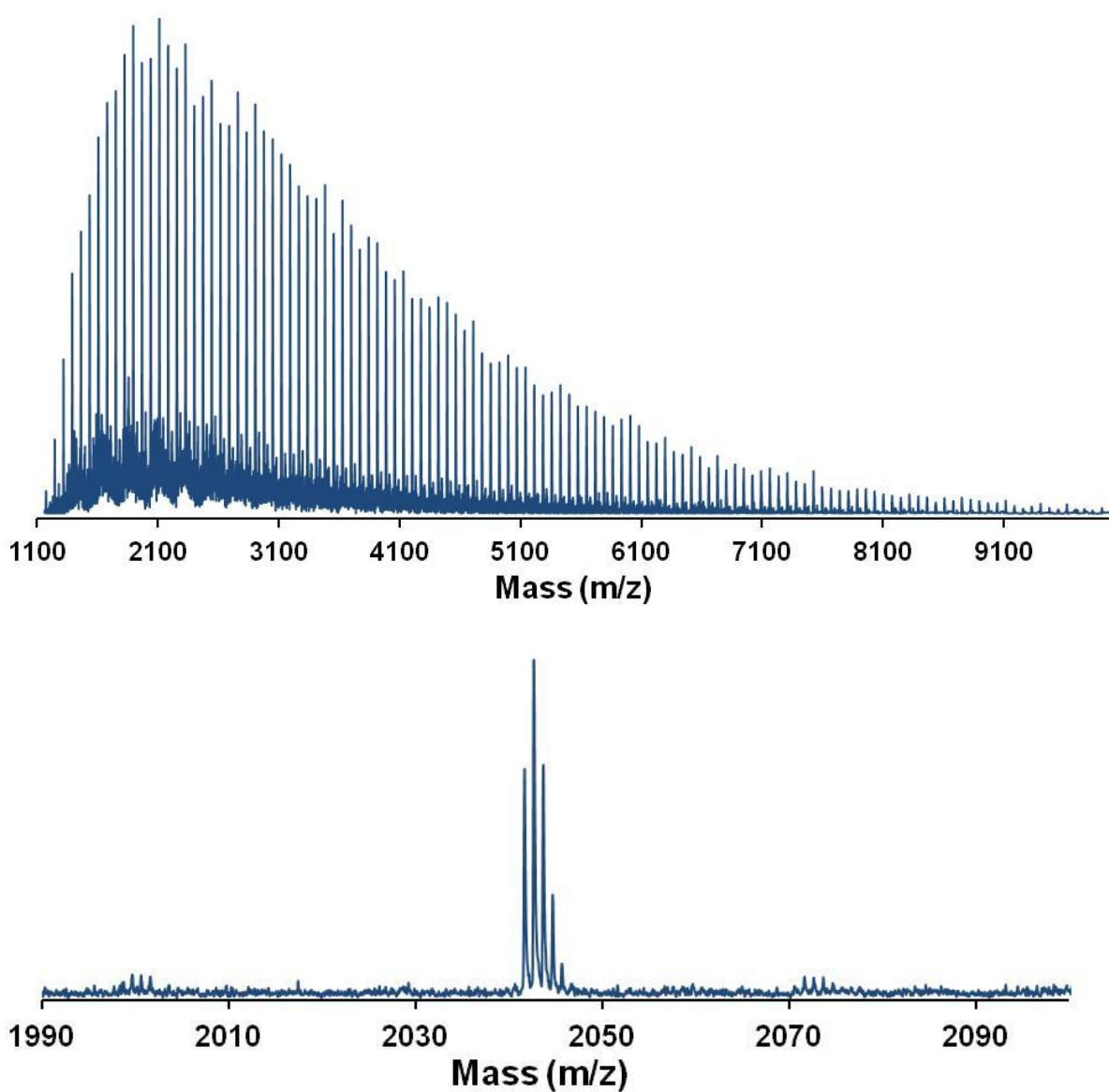


Figure S20. MALDI-ToF spectra (top: linear mode; bottom: reflectron mode) of a poly(butylene oxide) synthesized with *N*-methylurethane / *i*Bu₃Al / *t*BuP₄ (1 / 3 / 1) as initiating system in MeTHF (Table 2, run 7).

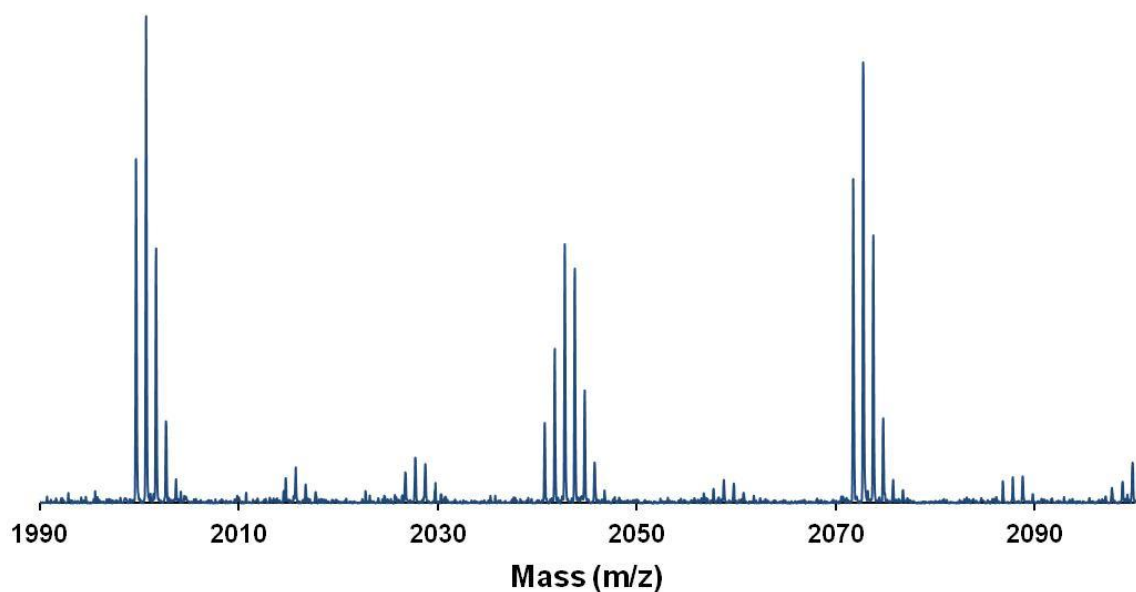
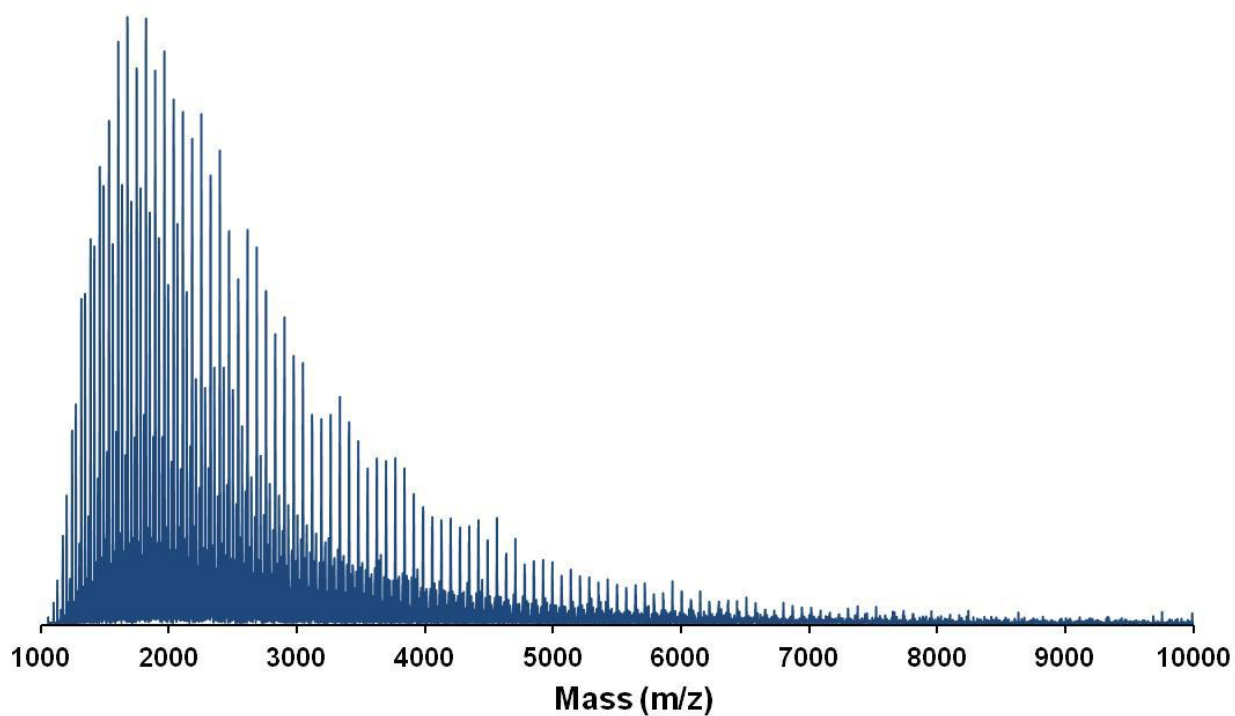


Figure S21. MALDI-ToF spectra (top: linear mode; bottom: reflectron mode) of a poly(butylene oxide) synthesized with *N*-methylurethane / *i*Bu₃Al / *t*BuP₄ (1 / 3 / 1) as initiating system in MeTHF (Table 2, run 8).

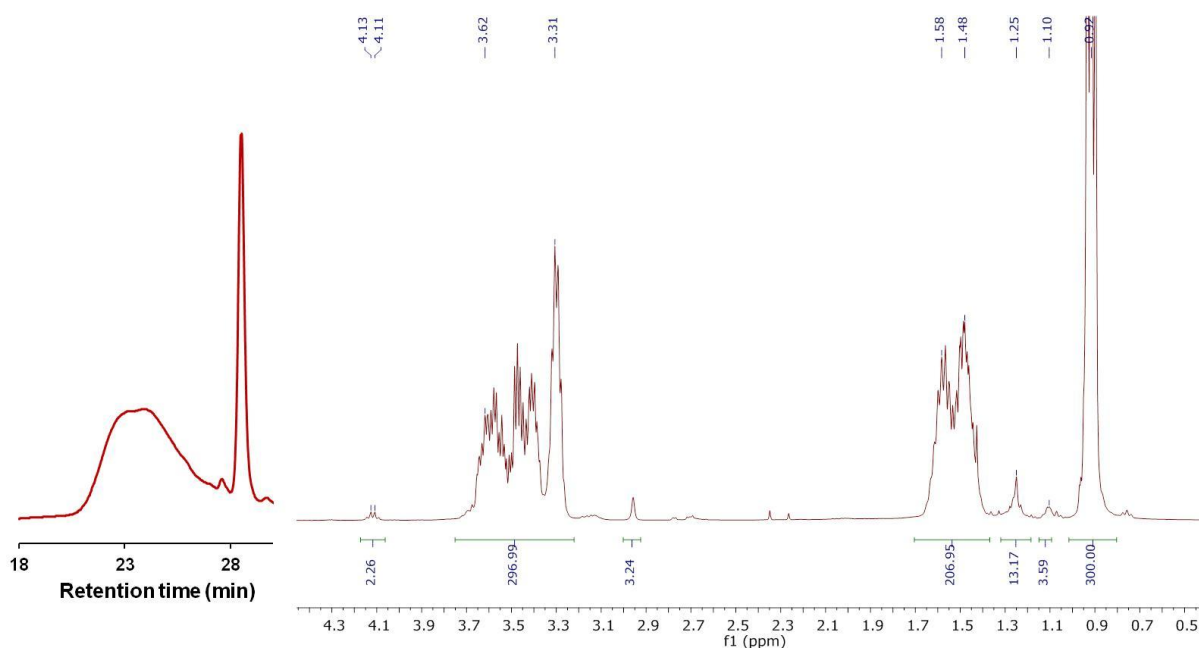


Figure S22. SEC traces (left) and ¹H NMR spectrum in CDCl₃ (right) of a poly(butylene oxide) synthesized with *N*-methylurethane / *i*Bu₃Al / *t*BuP₂ (1 / 3 / 1) as initiating system in MeTHF (Table 2, run 9).

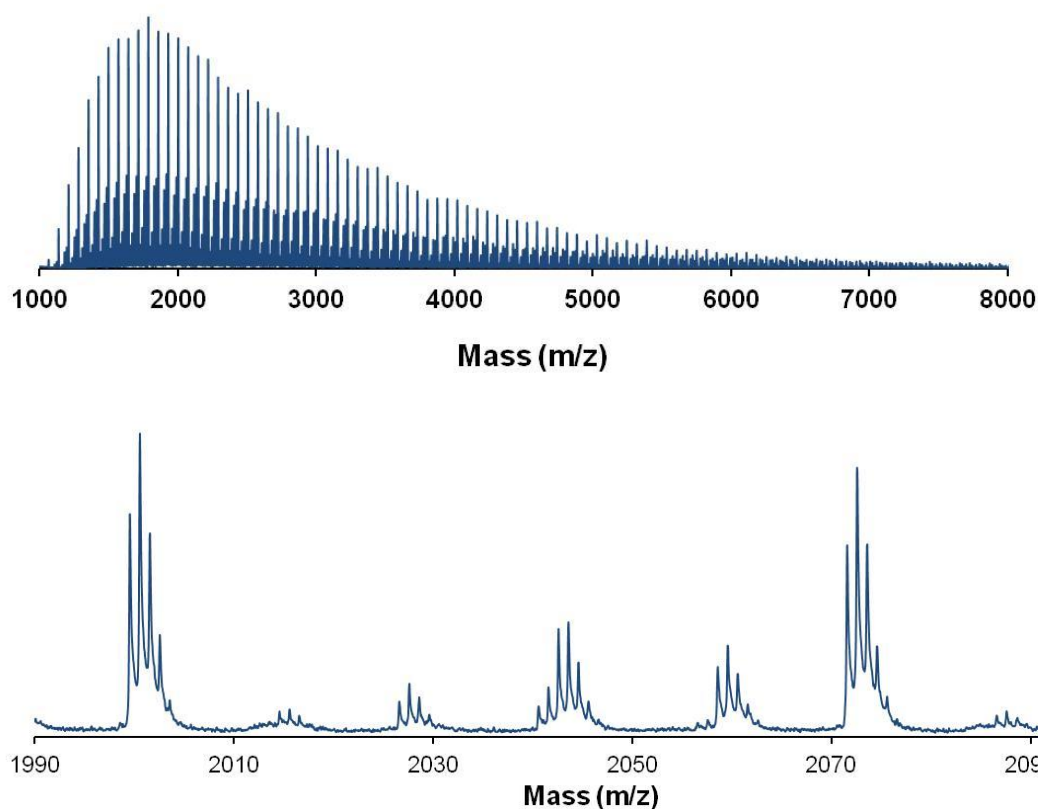


Figure S23. MALDI-ToF spectra (top: linear mode; bottom: reflectron mode) of a poly(butylene oxide) synthesized with *N*-methylurethane / *i*Bu₃Al / *t*BuP₂ (1 / 3 / 1) as initiating system in MeTHF (Table 2, run 9).

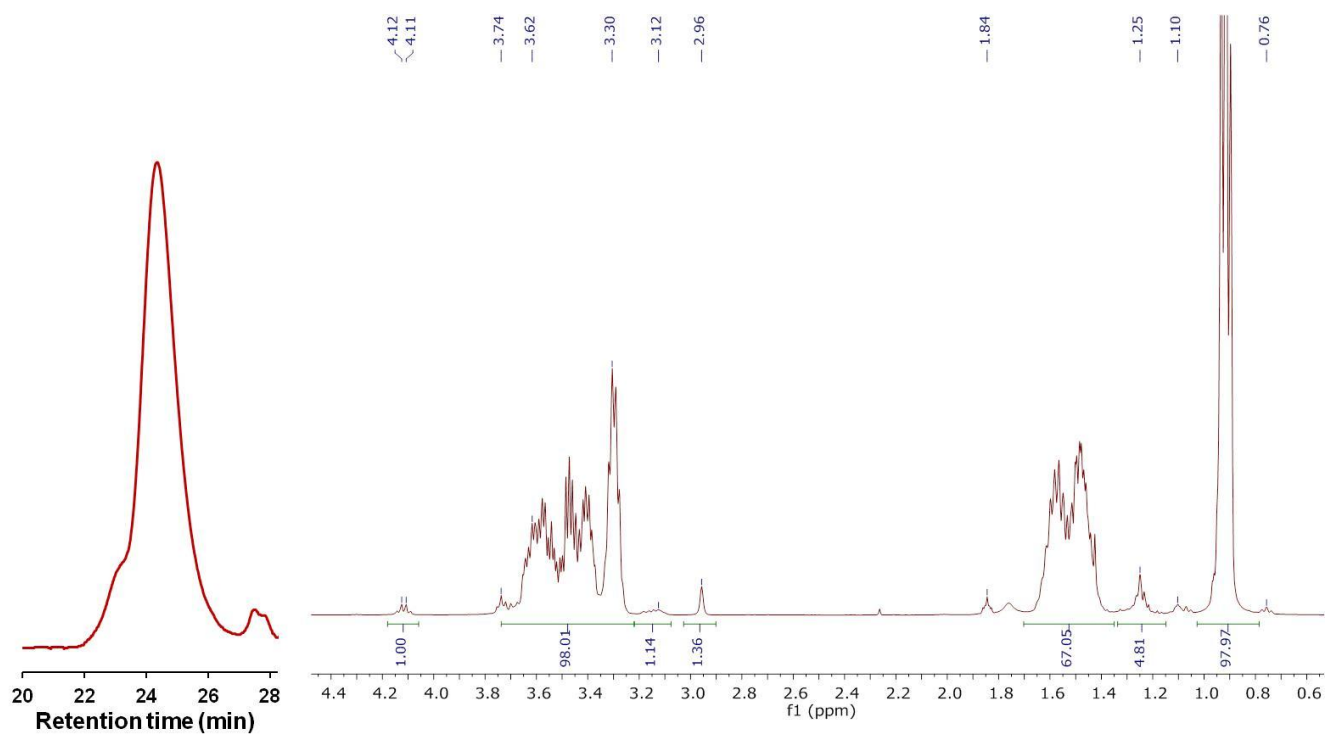


Figure S24. SEC traces (left) and ¹H NMR spectrum in CDCl₃ (right) of a poly(butylene oxide) synthesized with *N*-methylurethane / *i*Bu₃Al / *t*BuP₄ (1 / 1 / 1) as initiating system in MeTHF (Table 2, run 11).

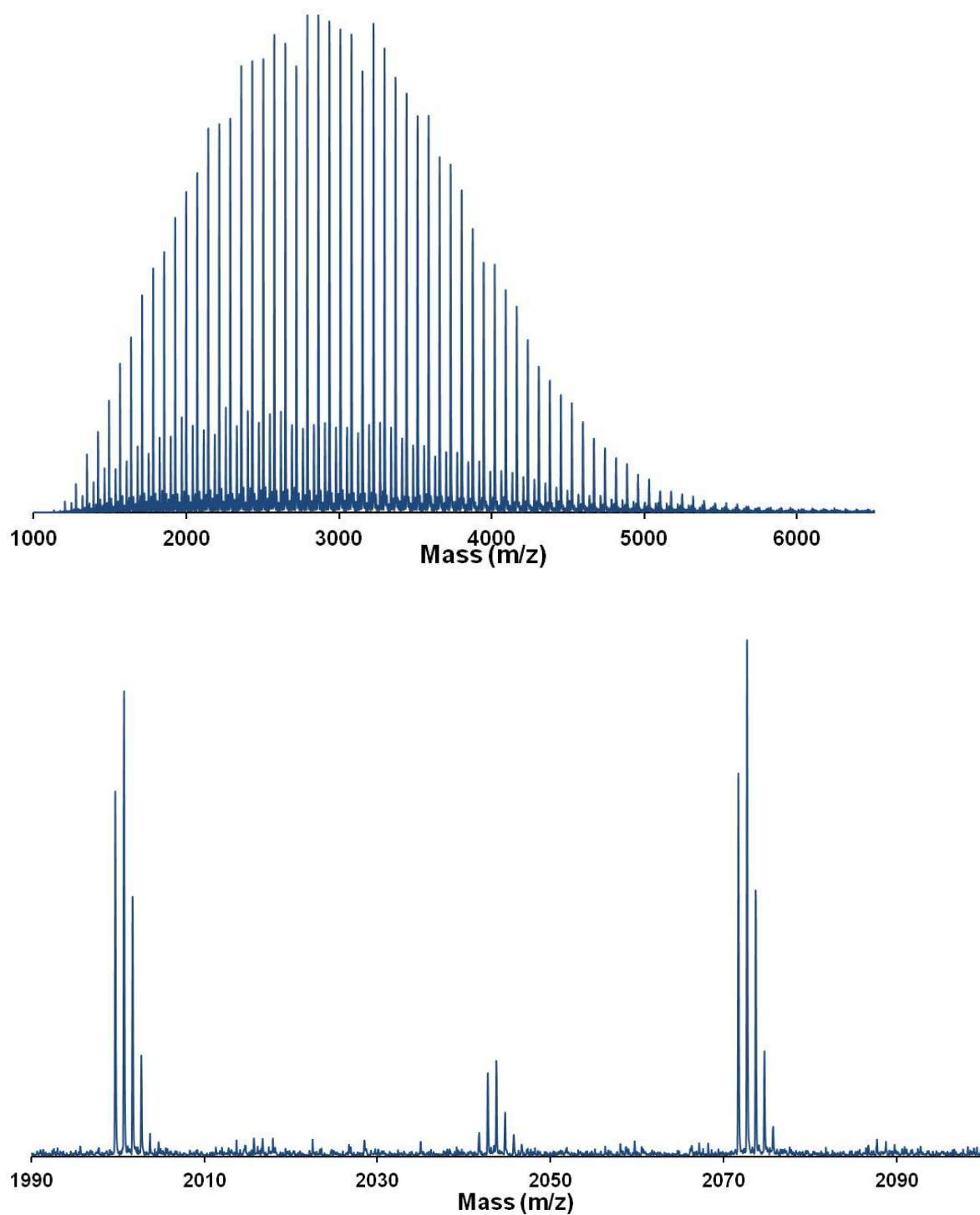


Figure S25. MALDI-ToF spectra (top: linear mode; bottom: reflectron mode) of a poly(butylene oxide) synthesized with *N*-methylurethane / *i*Bu₃Al / *t*BuP₄ (1 / 1 / 1) as initiating system in MeTHF (Table 2, run 11).

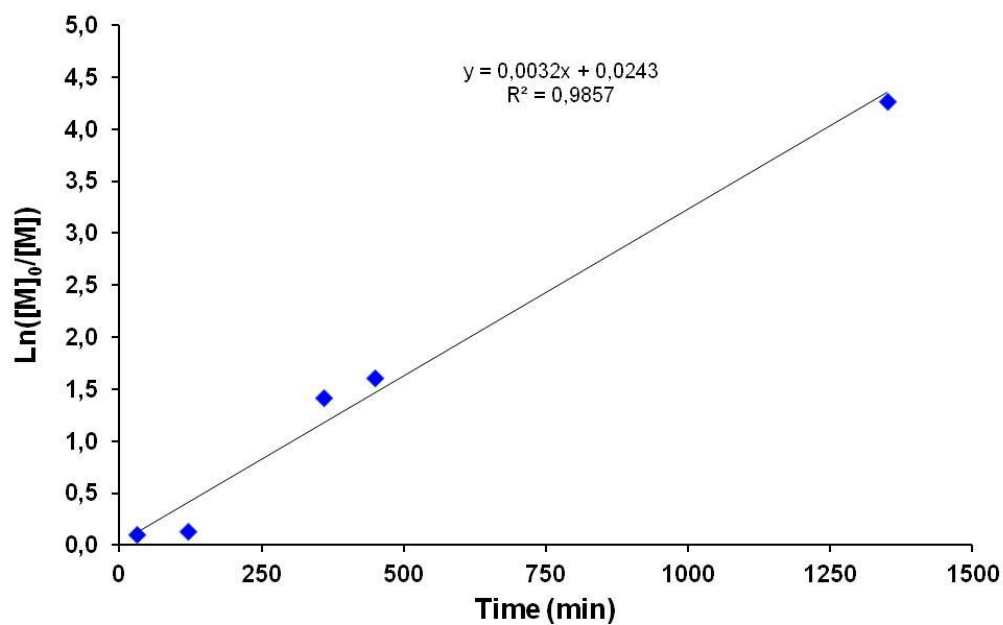


Figure S26. Anionic ring-opening polymerization of 1,2-epoxybutane synthesized with *N*-methylurethane / *i*Bu₃Al / *t*BuP₄ as initiating system in MeTHF (Table 2, run 11) at 25°C ($[I]_0 = 0.065 \text{ mol.L}^{-1}$, $[M]_0 = 3.27 \text{ mol.L}^{-1}$, M:*N*-methylurethane:*i*Bu₃Al:*t*BuP₄ = 50:1:1:1): first-order kinetic plot (slope = 0.0032 min^{-1} , $R^2 = 0.986$).

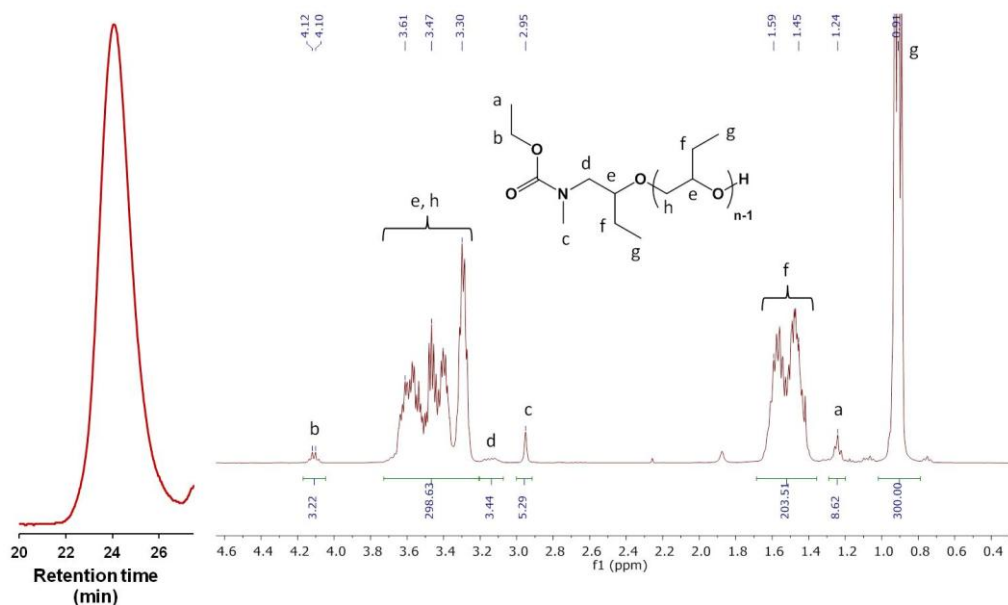


Figure S27. SEC traces (left) and ¹H NMR spectrum in CDCl₃ (right) of a poly(butylene oxide) synthesized with *N*-methylurethane / *i*Bu₃Al / *t*BuP₂ (1 / 1 / 1) as initiating system in MeTHF (Table 2, run 12).

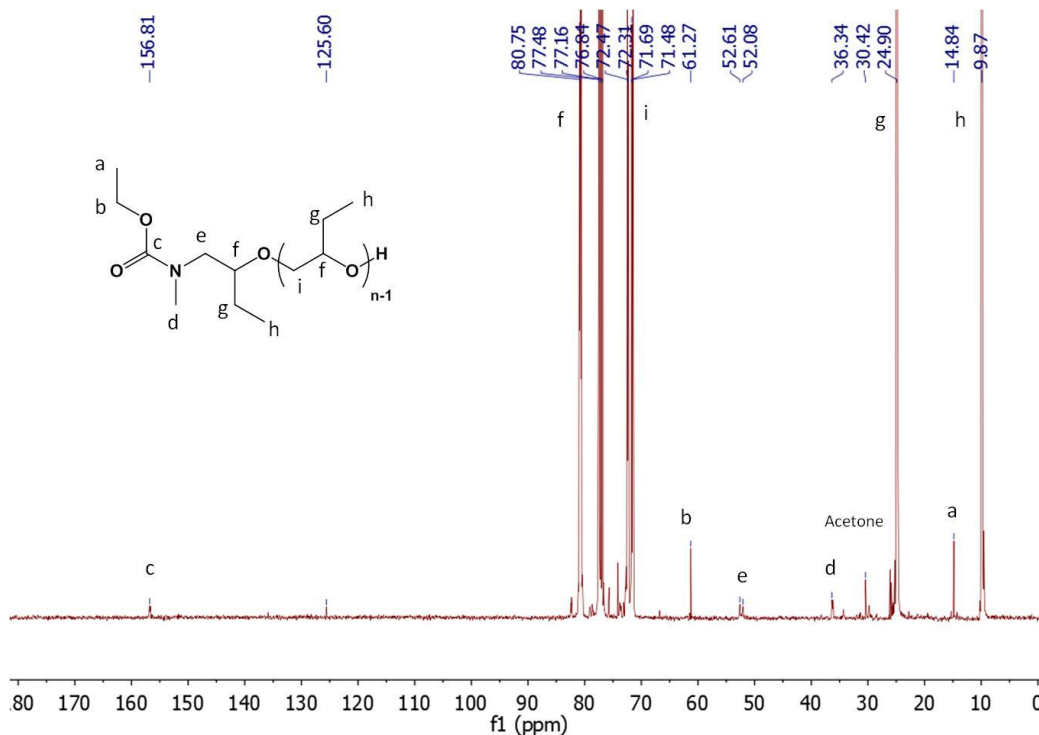


Figure S28. ¹³C NMR spectrum in CDCl₃ of a poly(butylene oxide) synthesized with *N*-methylurethane / *i*Bu₃Al / *t*BuP₂ (1 / 1 / 1) as initiating system in MeTHF (Table 2, run 12).

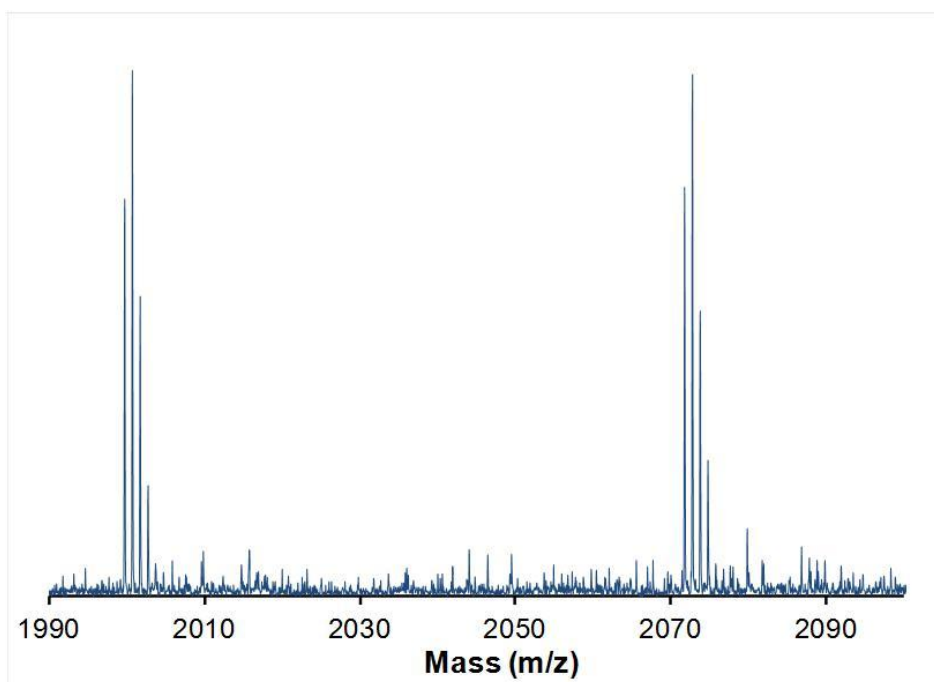
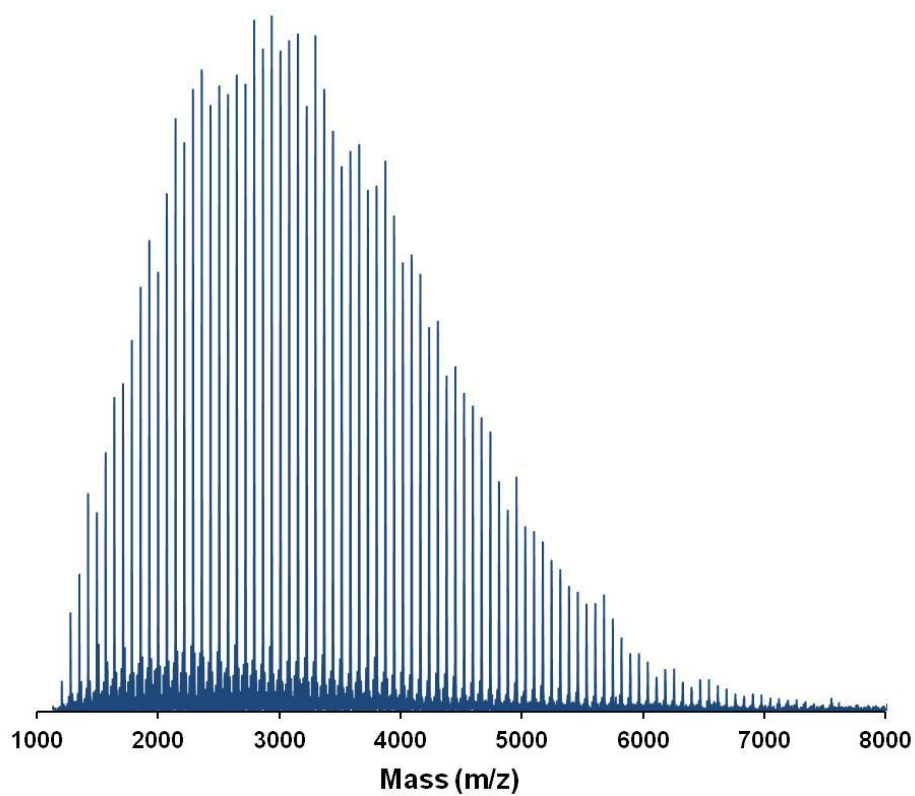


Figure S29. MALDI-ToF spectra (top: linear mode; bottom: reflectron mode) of a poly(butylene oxide) synthesized with *N*-methylurethane / *i*Bu₃Al / *t*BuP₂ (1 / 1 / 1) as initiating system in MeTHF (Table 2, run 12).