Supporting Information for

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

Lilia Hassouna, Nicolas Illy* and Philippe Guégan

Sorbonne Universités, UPMC Univ Paris 6, CNRS, Institut Parisien de Chimie Moléculaire, Equipe Chimie des Polymères, 4 place Jussieu, F-75005 Paris, France.
Figure S1. SEC traces (left) and $^1$H NMR spectrum in CDCl$_3$ (right) of a poly(butylene oxide) synthesized with N-ethylurethane-tBuP$_4$ as initiating system (Table 1, run 1).

Figure S2. $^{13}$C NMR spectrum in CDCl$_3$ of a poly(butylene oxide) synthesized with N-ethylurethane-tBuP$_4$ as initiating system (Table 1, run 1).
Figure S3. MALDI-ToF spectra (top: linear mode; bottom: reflectron mode) of a poly(butylene oxide) synthesized with N-Methylurethane-\(\tau\)BuP\(_4\) as initiating system (Table 1, run 4).
Figure S4. SEC traces (left) and $^1$H NMR spectrum in CDCl$_3$ (right) of a poly(butylene oxide) synthesized with tert-butyl N-allylcarbamate / $t$BuP$_4$ 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 / tBu4P 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 $^1$H NMR spectrum in CDCl$_3$ (right) of a poly(butylene oxide) synthesized with $N$-methylurethane / iBu$_3$Al / tBuP$_4$ (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 / iBu$_3$Al / tBuP$_4$ (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 / iBu_3Al / tBuP_4 (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 / iBu_3Al / iBuP_4 as initiating system in toluene (Table 2, run 2) at 25 °C in toluene ([I]_0 = 0.06534 mol.L^{-1}, [M]_0 = 3.27 mol.L^{-1}, M:N-methylurethane: iBu_3Al : iBuP_4 = 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 / iBu3Al / tBuP2 (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 / iBu3Al / tBuP2 (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 / iBu$_3$Al / tBuP$_2$ (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 / iBu$_3$Al / tBuP$_2$ (1 / 1 / 1) as initiating system in toluene (Table 2, run 3).
Figure S16. SEC traces (left) and $^1$H NMR spectrum in CDCl$_3$ (right) of a poly(butylene oxide) synthesized with N-methylurethane / iBu$_3$Al / tBuP$_4$ (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 / iBu$_3$Al / tBuP$_4$ (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 / iBu$_3$Al / tBuP$_4$ (1 / 3 / 1) as initiating system in MeTHF (Table 2, run 6).
Figure S19. $^1$H NMR spectrum in CDCl$_3$ of a poly(butylene oxide) synthesized with N-methylurethane / iBu$_3$Al / tBuP$_4$ (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 / \(i\)Bu\(_3\)Al / \(t\)BuP\(_4\) (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 / iBu$_3$Al / tBuP$_4$ (1 / 3 / 1) as initiating system in MeTHF (Table 2, run 8).
**Figure S22.** SEC traces (left) and $^1$H NMR spectrum in CDCl$_3$ (right) of a poly(butylene oxide) synthesized with $N$-methylurethane / $i$Bu$_3$Al / $t$BuP$_2$ (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 / $i$Bu$_3$Al / $t$BuP$_2$ (1 / 3 / 1) as initiating system in MeTHF (Table 2, run 9).
Figure S24. SEC traces (left) and $^1$H NMR spectrum in CDCl$_3$ (right) of a poly(butylene oxide) synthesized with N-methylurethane / iBu$_3$Al / iBuP$_4$ (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 / $i$Bu$_3$Al / $t$BuP$_4$ (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 / iBu₃Al / tBuP₄ as initiating system in MeTHF (Table 2, run 11) at 25°C ([I]₀ = 0.065 mol.L⁻¹, [M]₀ = 3.27 mol.L⁻¹, M:N-methylurethane:iBu₃Al:tBuP₄ = 50:1:1:1): first-order kinetic plot (slope = 0.0032 min⁻¹, R² = 0.986).
Figure S27. SEC traces (left) and $^1$H NMR spectrum in CDCl$_3$ (right) of a poly(butylene oxide) synthesized with N-methylurethane / iBu$_3$Al / tBuP$_2$ (1 / 1 / 1) as initiating system in MeTHF (Table 2, run 12).

Figure S28. $^{13}$C NMR spectrum in CDCl$_3$ of a poly(butylene oxide) synthesized with N-methylurethane / iBu$_3$Al / tBuP$_2$ (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 / iBu$_3$Al / tBuP$_2$ (1 / 1 / 1) as initiating system in MeTHF (Table 2, run 12).