Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Polymerization of epoxide monomers promoted by *t*BuP$_4$ phosphazene base: A comparative study of kinetic behavior.

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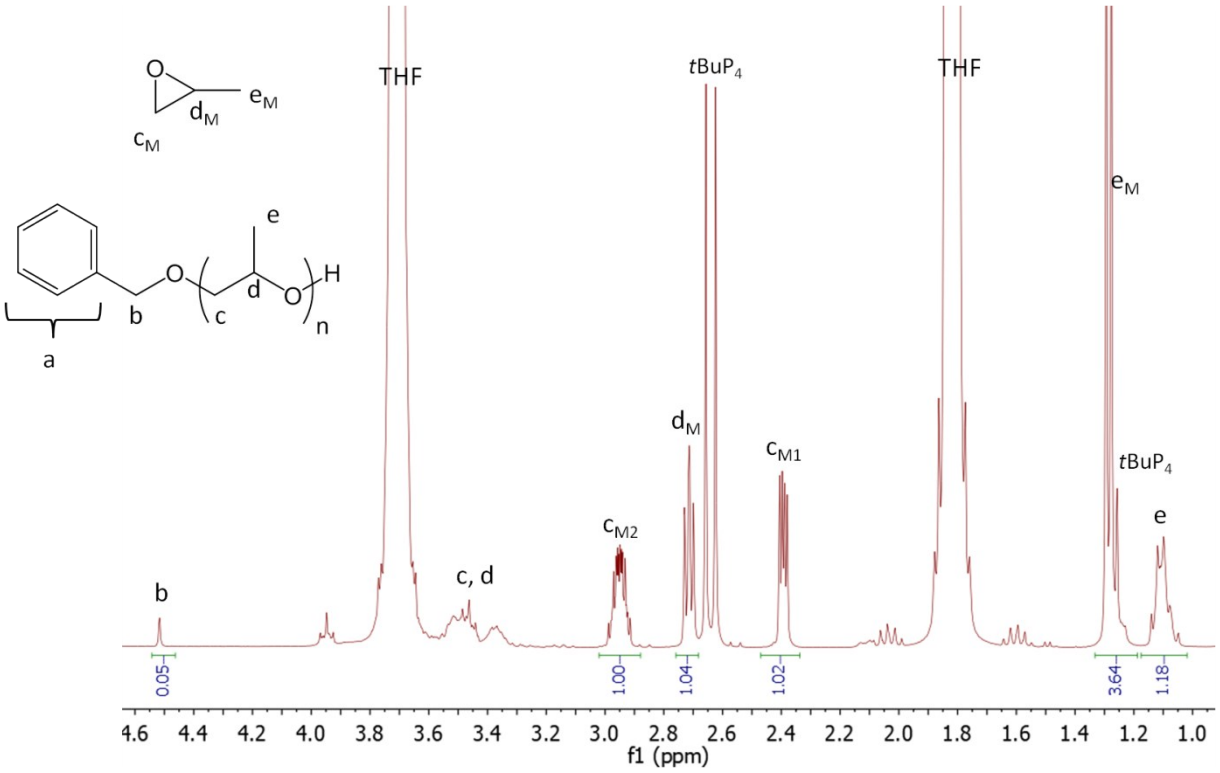
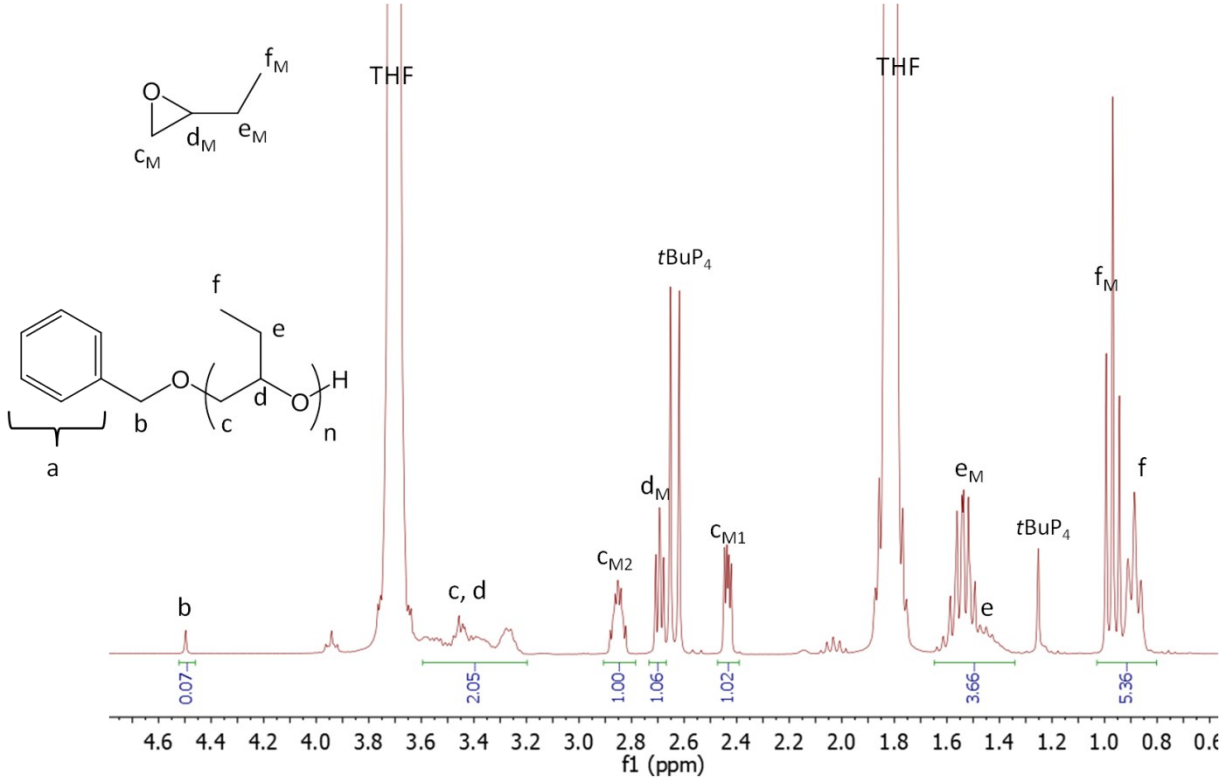


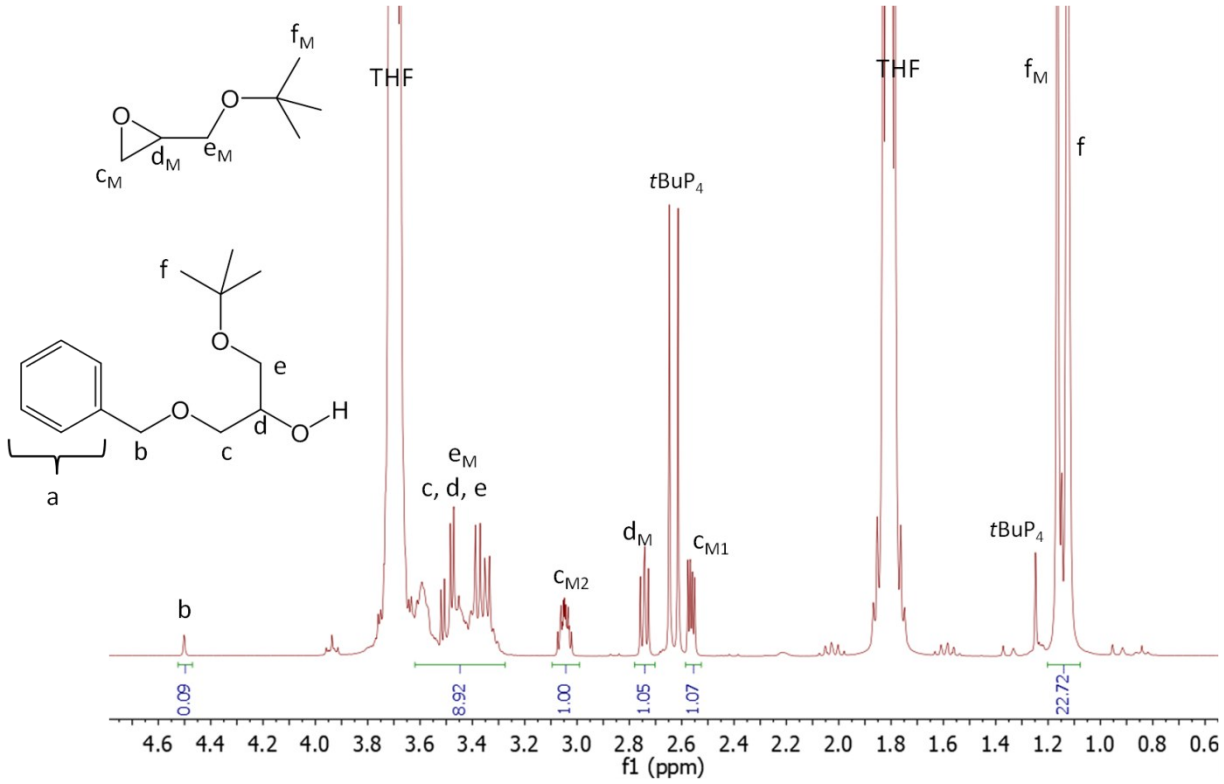
$$p = \frac{I_e/_3}{I_e/_3 + I_{C_{M2}}} = \frac{1.18/_3}{1.18/_3 + 1} = 0.28$$

Figure S1. ^{1}H NMR spectrum in $CDCl_3$ of the reaction mixture of PO polymerization initiated by benzyl alcohol-*t*BuP$_4$ at 25°C in THF (Table 2, run 1) after 3 hours and the equation use to determine the monomer conversion.



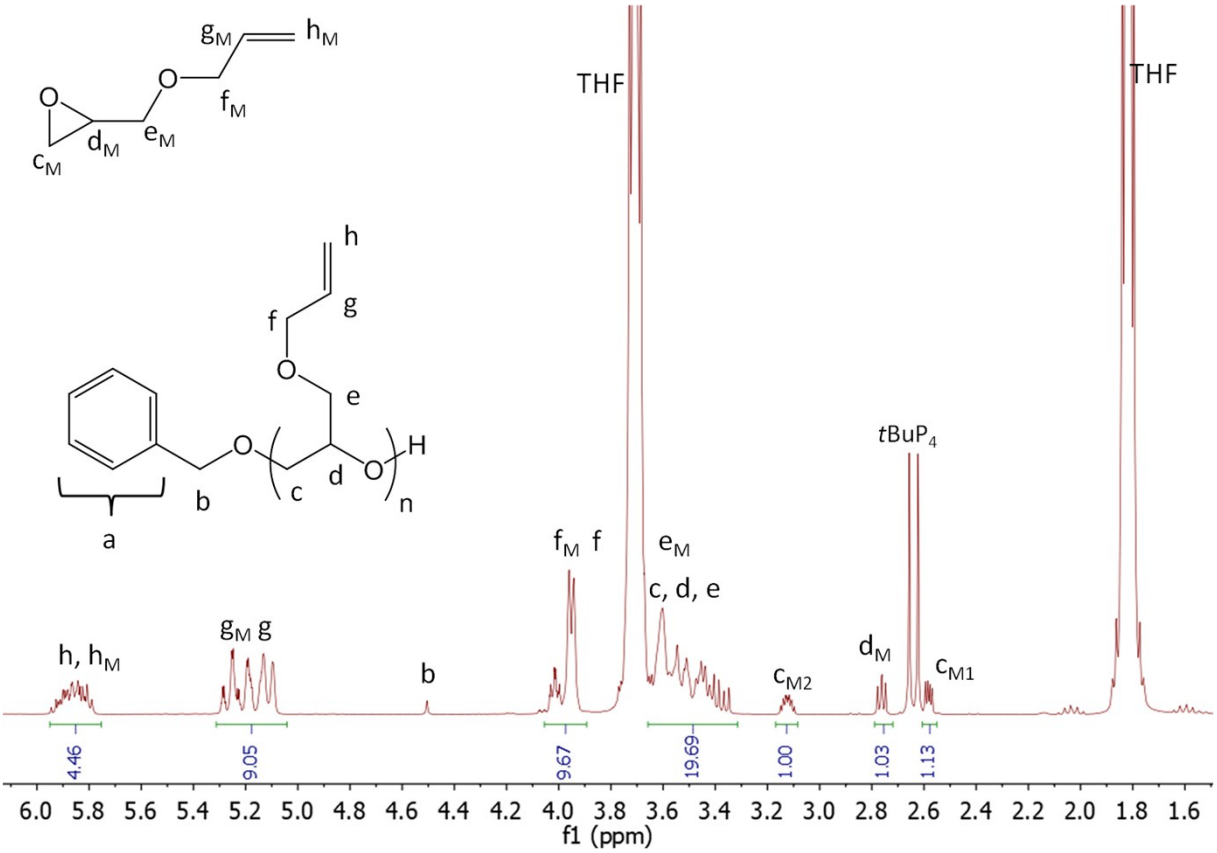
$$p = 1 - \frac{I_{C_{M2}}}{\left(I_e + I_{e_M}\right)/_2} = 1 - \frac{1}{3.66/_2} = 0.45$$

Figure S2. ^{1}H NMR spectrum in $CDCl_3$ of the reaction mixture of BO polymerization initiated by benzyl alcohol-*t*BuP_4 at 25°C in THF (Table 2, run 2) after 6 hours and the equation use to determine the monomer conversion.



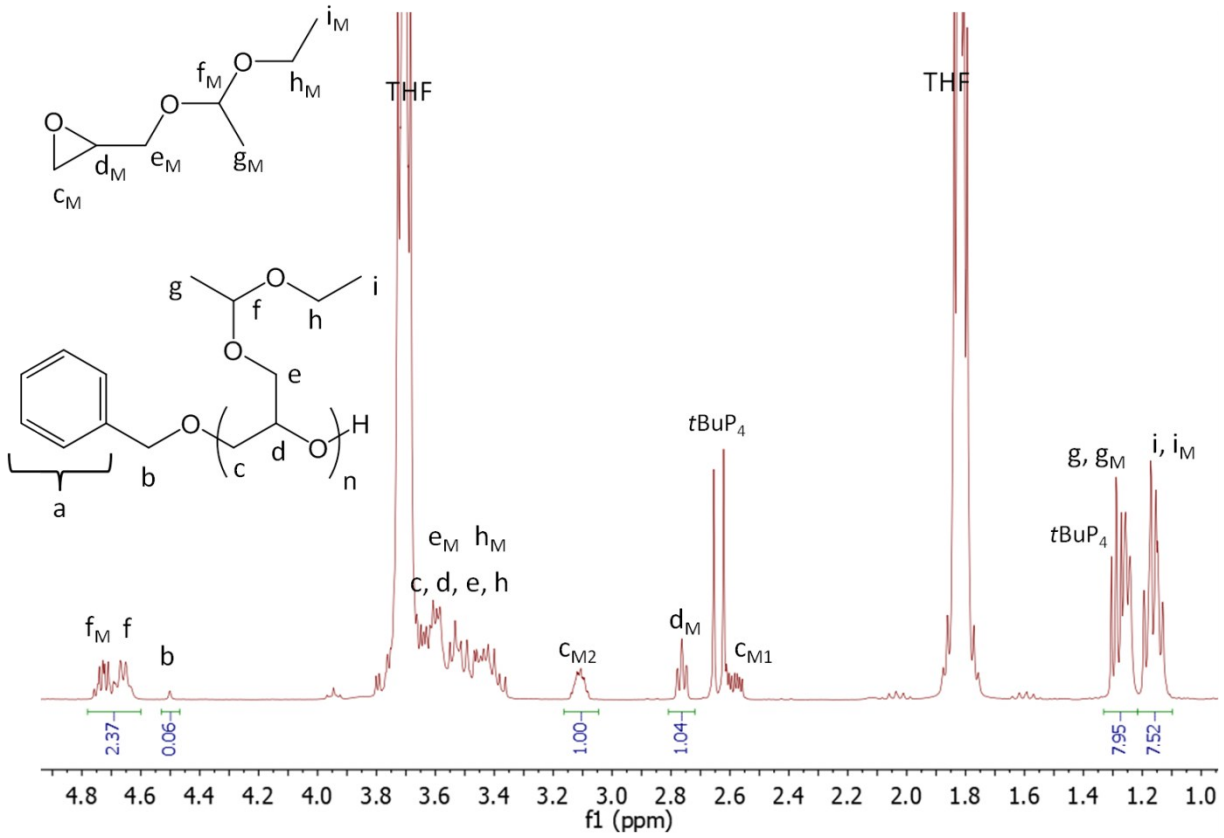
$$p = 1 - \frac{I_{C_{M2}}}{(I_f + I_{f_M})/_9} = 1 - \frac{1}{22.72/_9} = 0.60$$

Figure S3. ^{1}H NMR spectrum in $CDCl_3$ of the reaction mixture of *t*BuGE polymerization initiated by benzyl alcohol-*t*BuP_4 at 25°C in THF (Table 2, run 3) after 9 hours and the equation use to determine the monomer conversion.



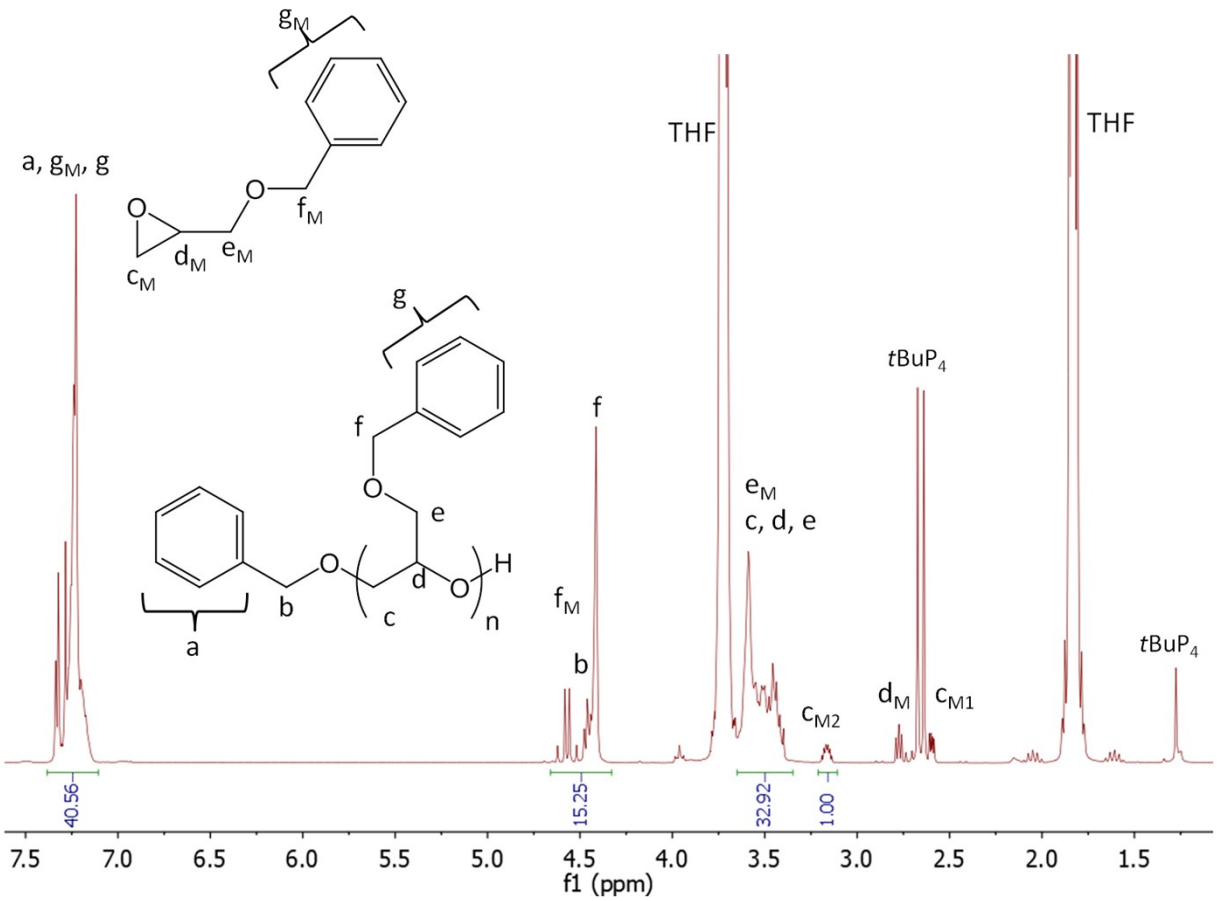
$$p = 1 - \frac{I_{C_{M2}}}{(I_h + I_{h_M})} = 1 - \frac{1}{4.46} = 0.78$$

Figure S4. ^{1}H NMR spectrum in $CDCl_3$ of the reaction mixture of AGE polymerization initiated by benzyl alcohol-*t*BuP_4 at 25°C in THF (Table 2, run 4) after 2 hours and the equation use to determine the monomer conversion.



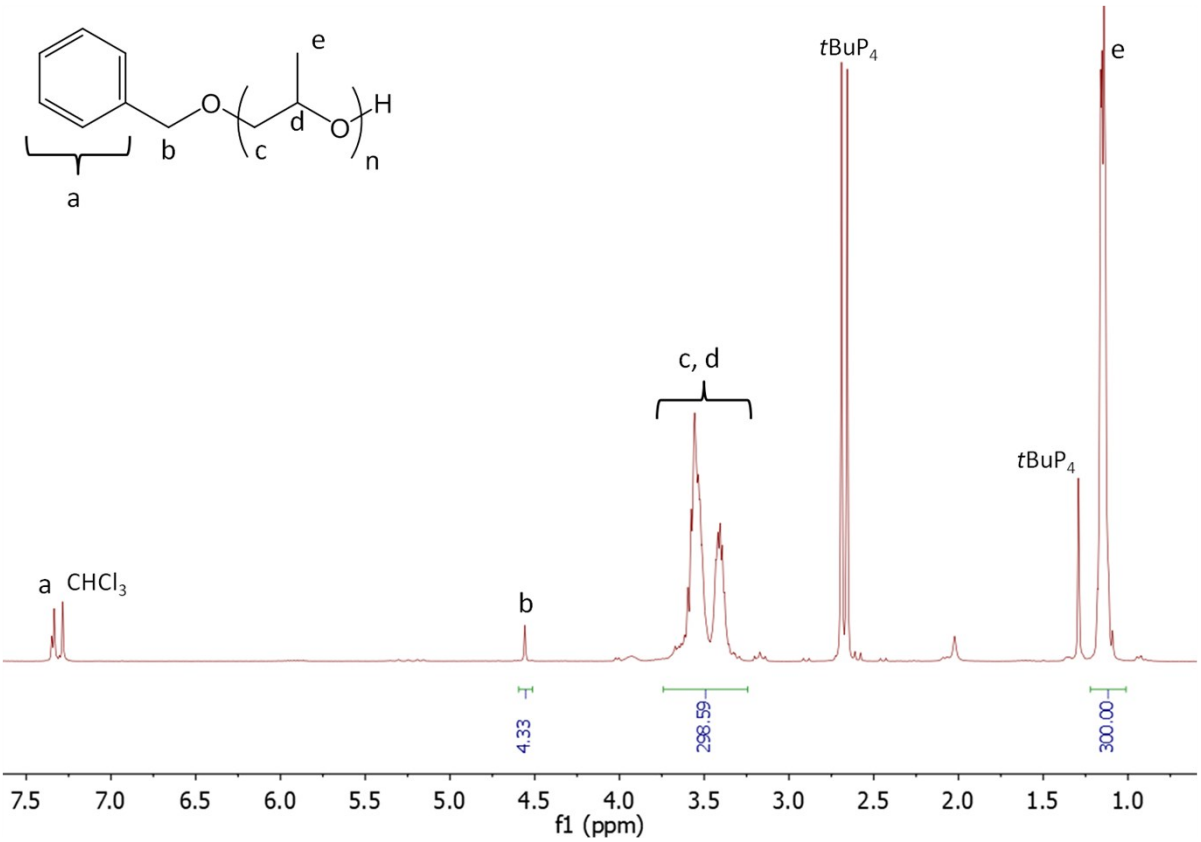
$$p = 1 - \frac{I_{C_{M2}}}{(I_f + I_{f_M})} = 1 - \frac{1}{2.37} = 0.58$$

Figure S5. ^{1}H NMR spectrum in $CDCl_3$ of the reaction mixture of EEGE polymerization initiated by benzyl alcohol-*t*BuP$_4$ at 25°C in THF (Table 2, run 5) after 1.5 hours and the equation use to determine the monomer conversion.



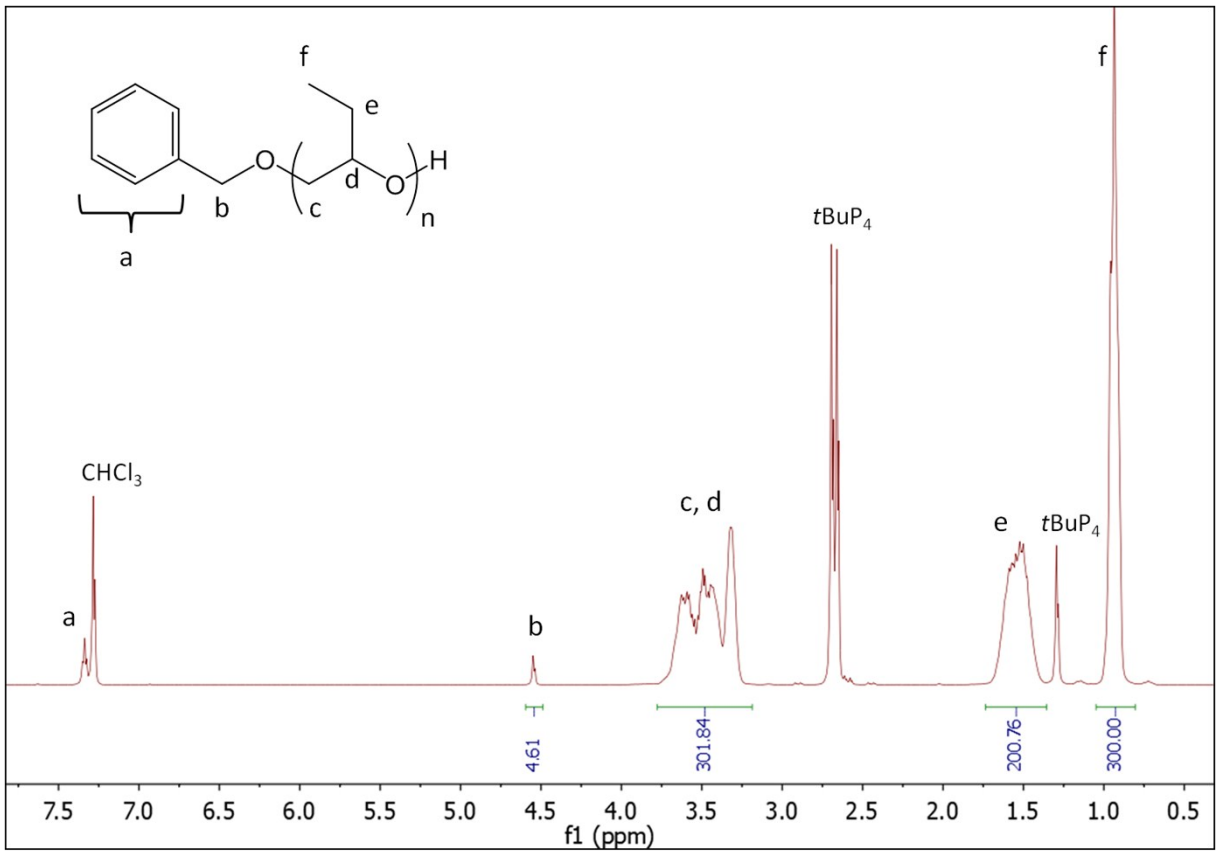
$$p = 1 - \frac{I_{C_{M2}}}{\left(I_f + I_{f_M}\right)/_2} = 1 - \frac{1}{15.25/_2} = 0.87$$

Figure S6. ^{1}H NMR spectrum in $CDCl_3$ of the reaction mixture of BnGE polymerization initiated by benzyl alcohol-*t*BuP$_4$ at 25°C in THF (Table 2, run 6) after 6 hours and the equation use to determine the monomer conversion.



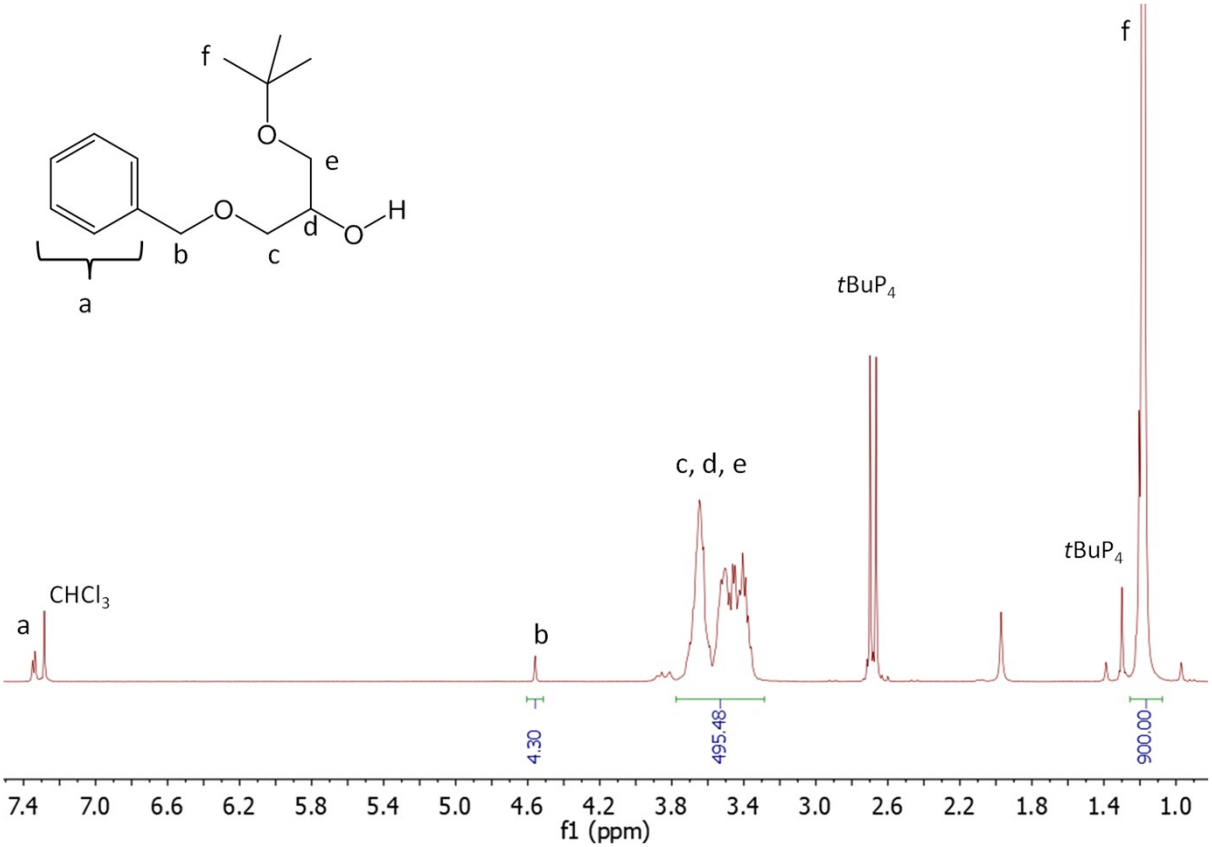
$$M_n = M_0 \times \frac{I_e/3}{I_b/2} + M_{BnOH} = 58.1 \times \frac{300/3}{4.33/2} + 108.14 = 2792\ g.mol^{-1} \approx 2800\ g.mol^{-1}$$

Figure S7. ^{1}H NMR spectrum in $CDCl_3$ of polyPO polymerization initiated by benzyl alcohol-*t*BuP$_4$ (Table 2, run 1) and the equation use to determine its number-average molar mass.



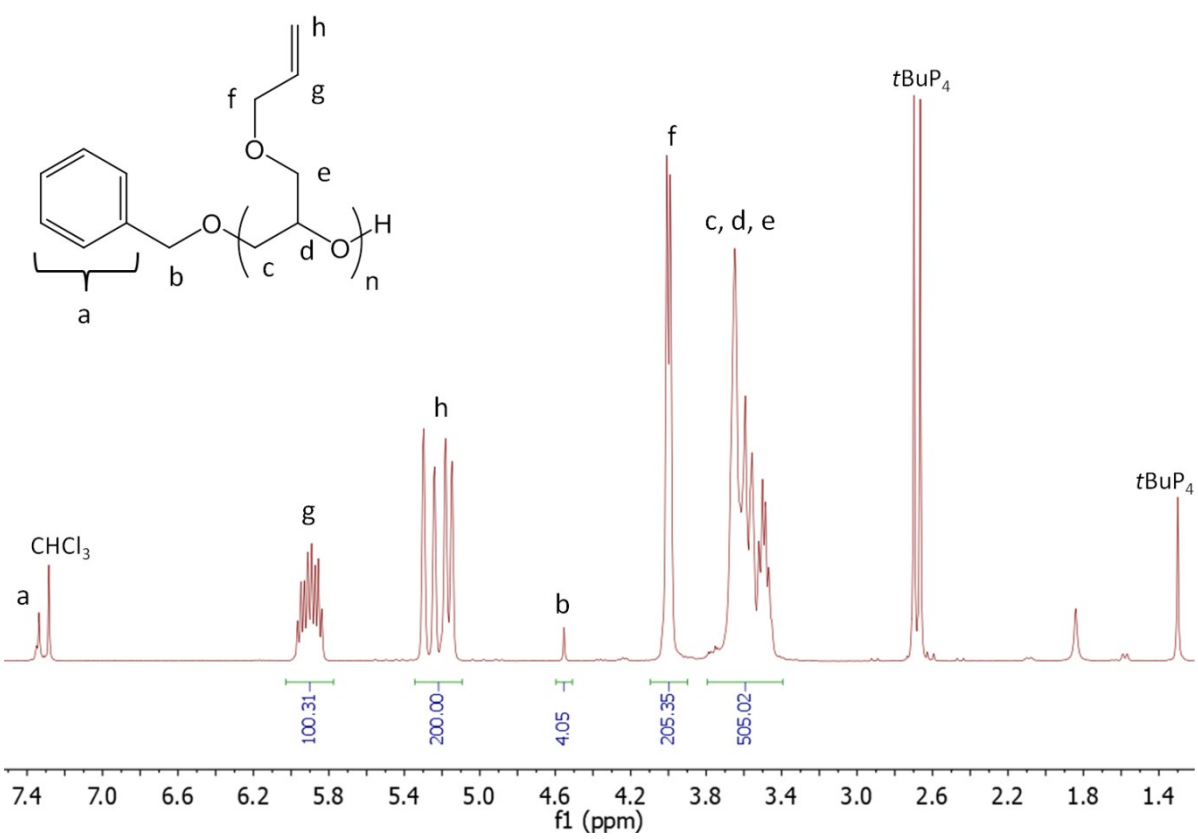
$$M_n = M_0 \times \frac{I_f/_3}{I_b/_2} + M_{BnOH} = 72.11 \times \frac{300/_3}{4.61/_2} + 108.14 = 3236\ g.mol^{-1} \approx 3200\ g.mol^{-1}$$

Figure S8. ^{1}H NMR spectrum in $CDCl_3$ of polyBO polymerization initiated by benzyl alcohol-*t*BuP_4 (Table 2, run 2) and the equation use to determine its number-average molar mass.



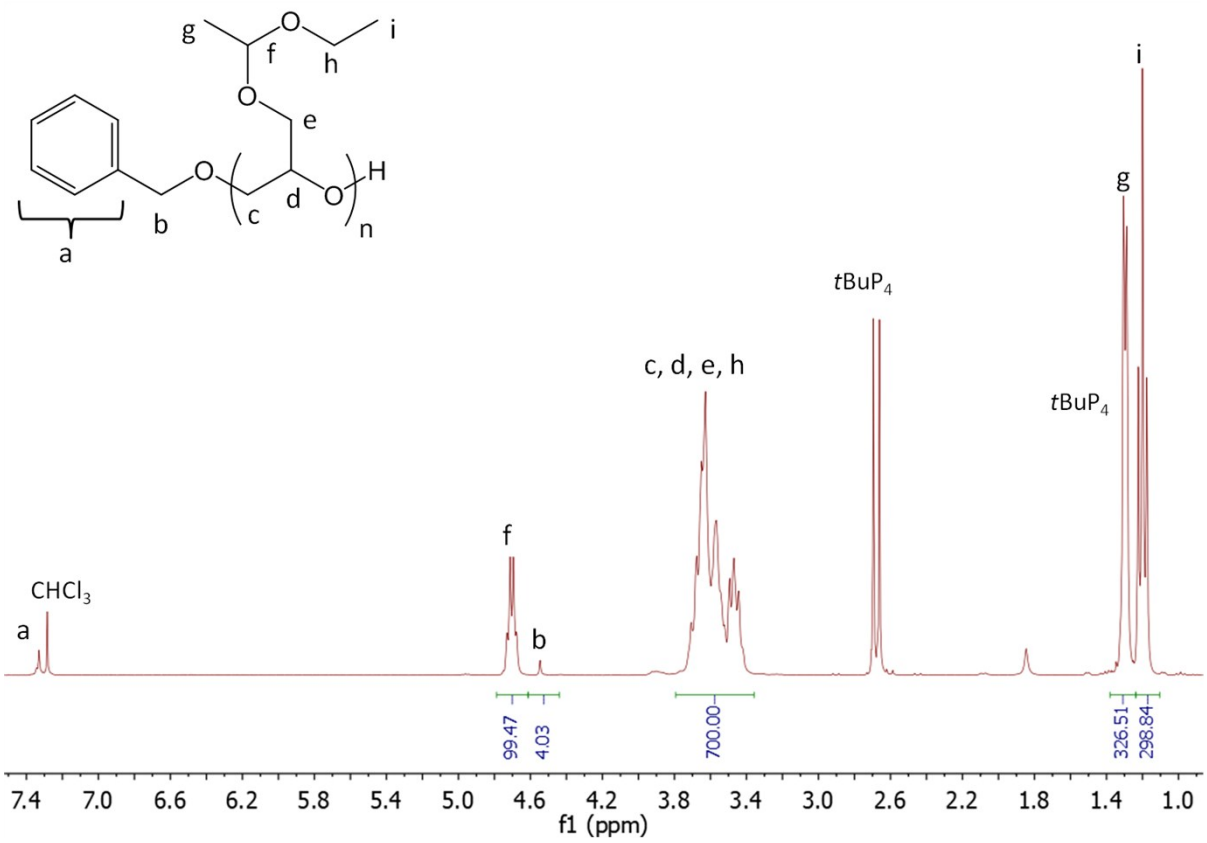
$$M_n = M_0 \times \frac{I_f/_9}{I_b/_2} + M_{BnOH} = 130.18 \times \frac{900/_9}{4.29/_2} + 108.14 = 6163\ g.mol^{-1} \approx 6200\ g.mol^{-1}$$

Figure S9. ^{1}H NMR spectrum in $CDCl_3$ of polytBuGE polymerization initiated by benzyl alcohol-*t*BuP_4 (Table 2, run 3) and the equation use to determine its number-average molar mass.



$$M_n = M_0 \times \frac{I_h/_2}{I_b/_2} + M_{BnOH} = 114.14 \times \frac{200/_2}{4.05/_2} + 108.14 = 5745\ g.mol^{-1} \approx 5700\ g.mol^{-1}$$

Figure S10. ^{1}H NMR spectrum in $CDCl_3$ of polyAGE polymerization initiated by benzyl alcohol-*t*BuP_4 (Table 2, run 4) and the equation use to determine its number-average molar mass.



$$M_n = M_0 \times \frac{I_{c,d,e,h}/_7}{I_b/_2} + M_{BnOH} = 146.19 \times \frac{700/_7}{4.03/_2} + 108.14 = 7363\ g.mol^{-1} \approx 7400\ g.mol^{-1}$$

Figure S11. ^{1}H NMR spectrum in $CDCl_3$ of polyEEGE polymerization initiated by benzyl alcohol-*t*BuP_4 (Table 2, run 5) and the equation use to determine its number-average molar mass.

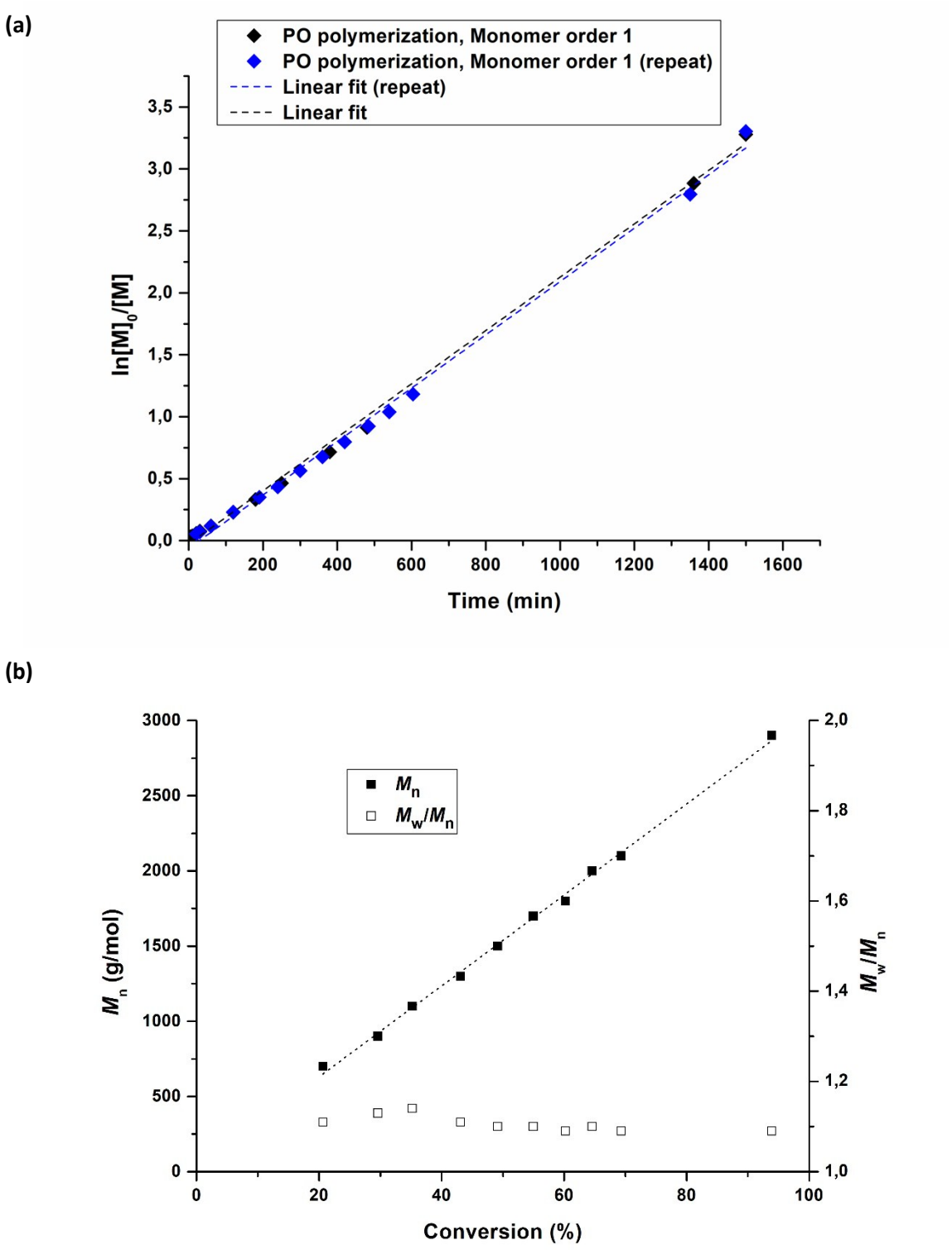


Figure S12. AROP of PO initiated by benzyl alcohol-*t*BuP$_4$ in THF at 25°C ([M]$_0$ = 2 M; [I]$_0$ = 4 x 10^{-2} mol.L^{-1}): (a) First order plot ($k_{p,\ app}$(black) = 5.38 x 10^{-2} L.mol^{-1}.min^{-1}; $k_{p,\ app}$(blue) = 5.38 x 10^{-2} L.mol^{-1}.min^{-1}; average value $k_{p,\ app}$ = 5.38 x 10^{-2} L.mol^{-1}.min^{-1}); relationship observed between number-average molar mass (full squares; linear trend curve is indicated by the dashed line) or dispersity (empty squares) and monomer conversion.

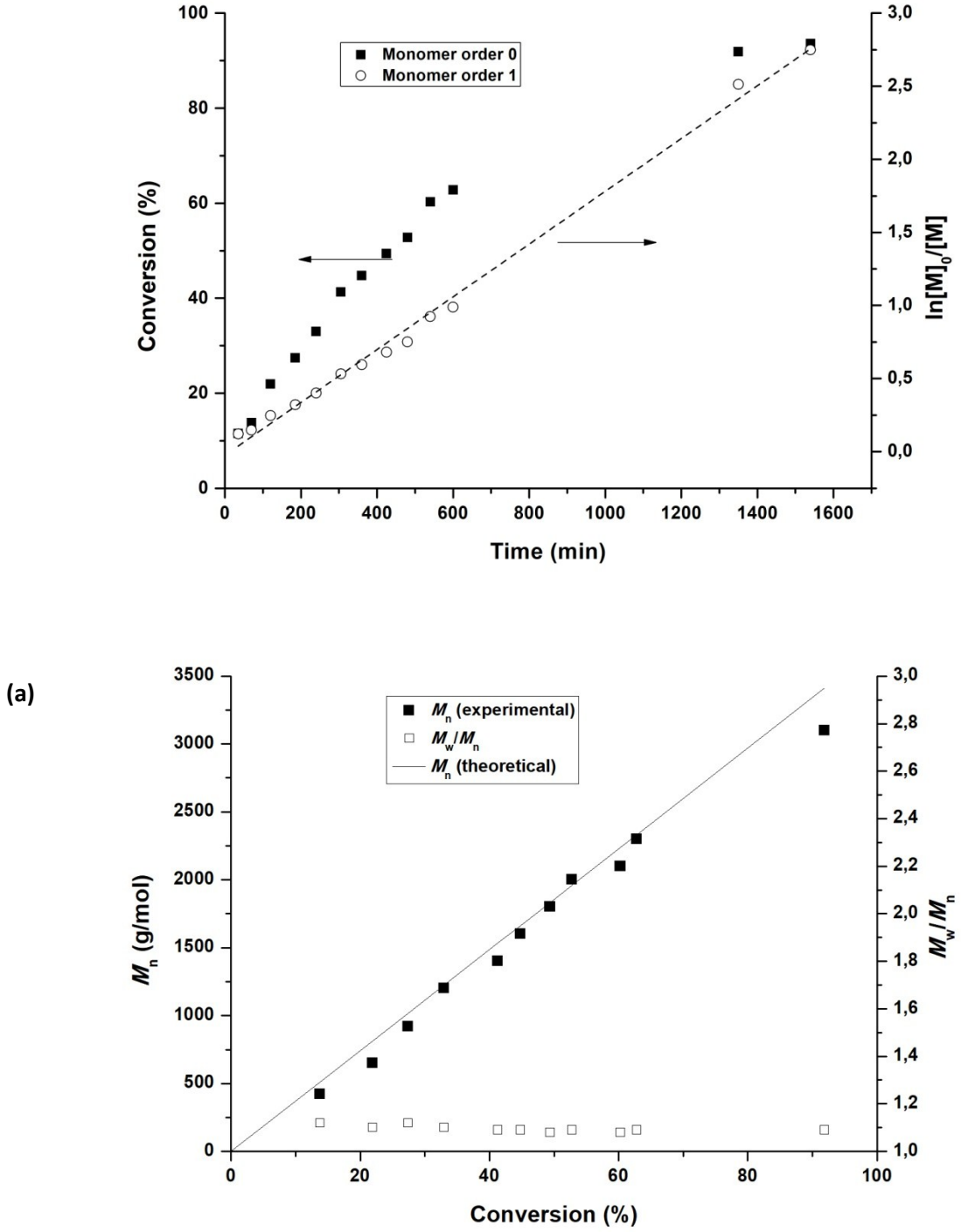
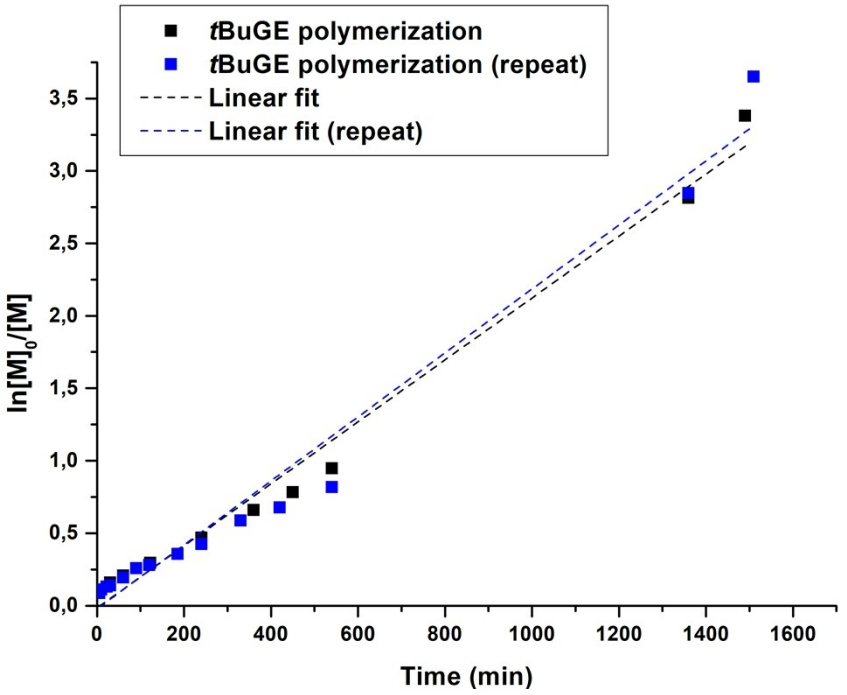


Figure S13. AROP of BO initiated by benzyl alcohol-*t*BuP$_4$ in THF at 25°C ([M]$_0$ = 2 M; [I]$_0$ = 4 x 10^{-2} mol.L^{-1}): (a) First order plot (slope of the linear regression = 0.0018 min^{-1}, R² = 0.994; $k_{p,\ app}$ = 4.51 x 10^{-2} L.mol^{-1}.min^{-1}); relationship observed between number-average molar mass (full squares; linear trend curve is indicated by the dashed line) or dispersity (empty squares) and monomer conversion.

(a)



(b)

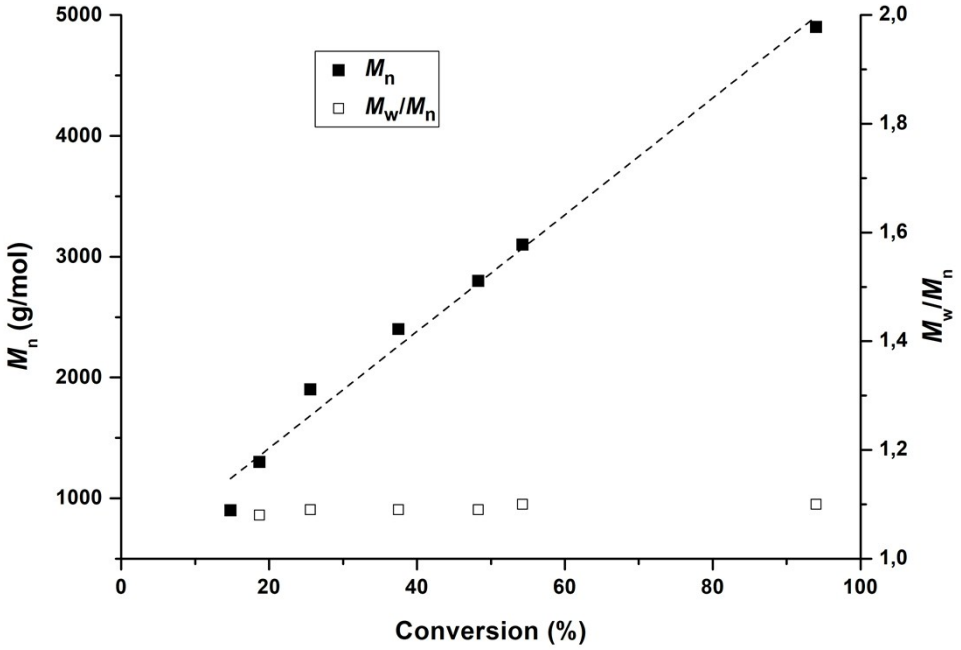
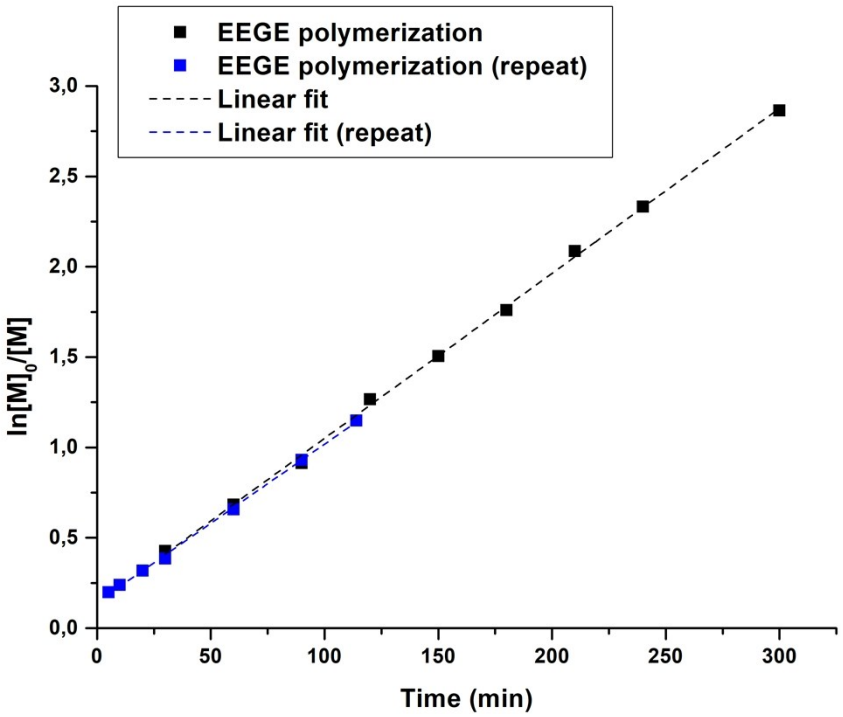


Figure S14. AROP of *t*BuGE initiated by benzyl alcohol-*t*BuP$_4$ in THF at 25°C ([M]$_0$ = 2 mol.L^{-1}; [I]$_0$ = 4 x 10^{-2} mol.L^{-1}): (a) First order plot ($k_{p,\,app}$(black) = 5.35 x 10^{-2} L.mol^{-1}.min^{-1}; $k_{p,\,app}$(blue) = 5.52 x 10^{-2} L.mol^{-1}.min^{-1}; average value $k_{p,\,app}$ = 5.43 x 10^{-2} L.mol^{-1}.min^{-1}); relationship observed between number-average molar mass (full squares; linear trend curve is indicated by the dashed line) or dispersity (empty squares) and monomer conversion.

(a)



(b)

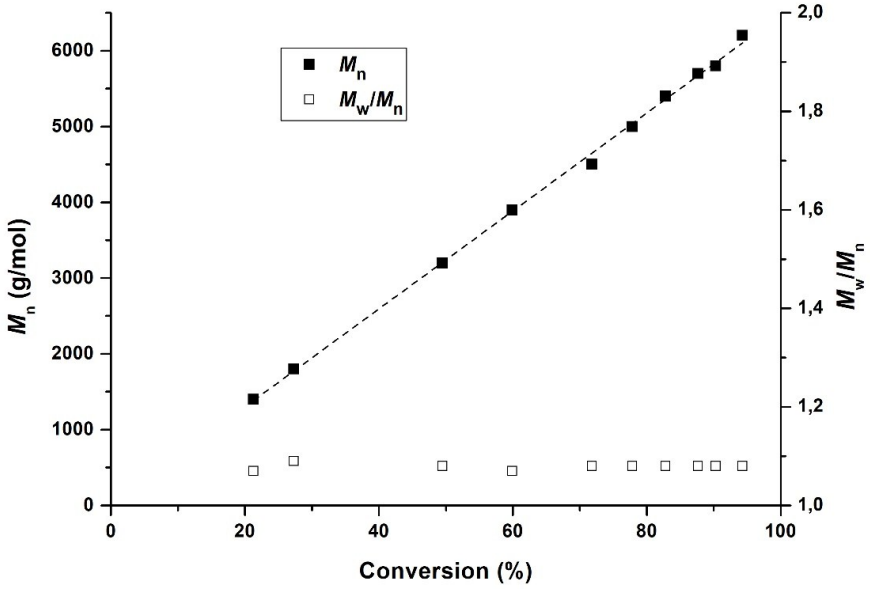
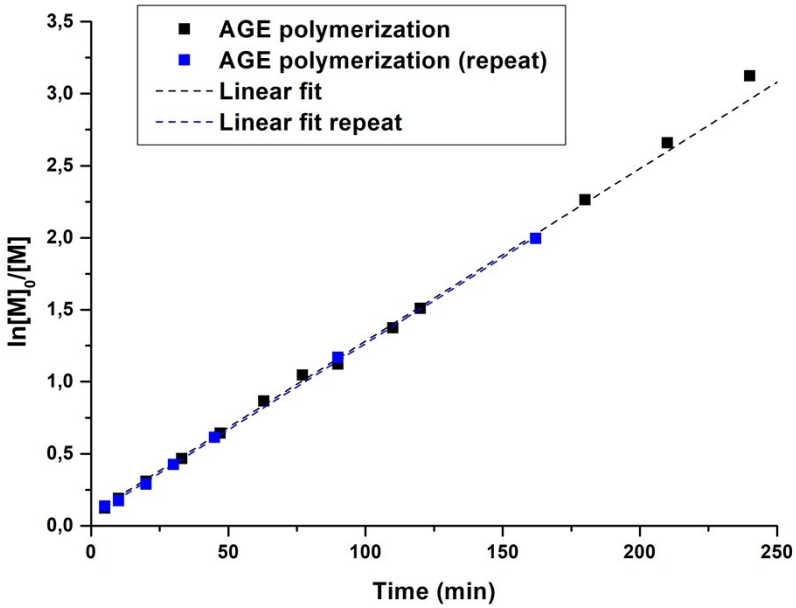


Figure S15. AROP of EEGE initiated by benzyl alcohol-*t*BuP$_4$ in THF at 25°C ([M]$_0$ = 2 mol.L^{-1}; [I]$_0$ = 4 x 10^{-2} mol.L^{-1}): (a) First order plot ($k_{p,\ app}$(black) = 2.28 x 10^{-1} L.mol^{-1}.min^{-1}; $k_{p,\ app}$(blue) = 2.19 x 10^{-1} L.mol^{-1}.min^{-1}; average value $k_{p,\ app}$ = 2.23 x 10^{-1} L.mol^{-1}.min^{-1}); relationship observed between number-average molar mass (full squares; linear trend curve is indicated by the dashed line) or dispersity (empty squares) and monomer conversion.

(a)



(b)

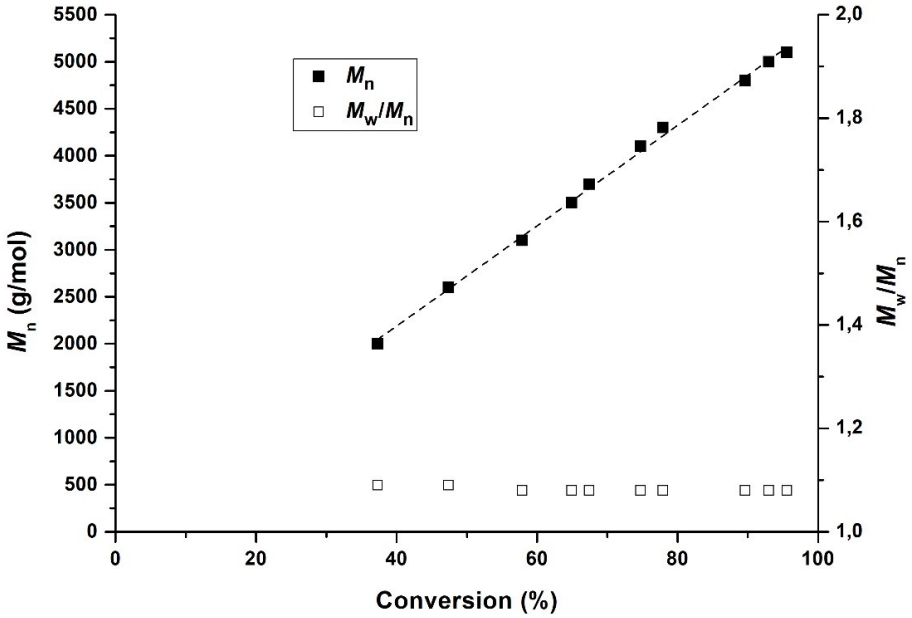
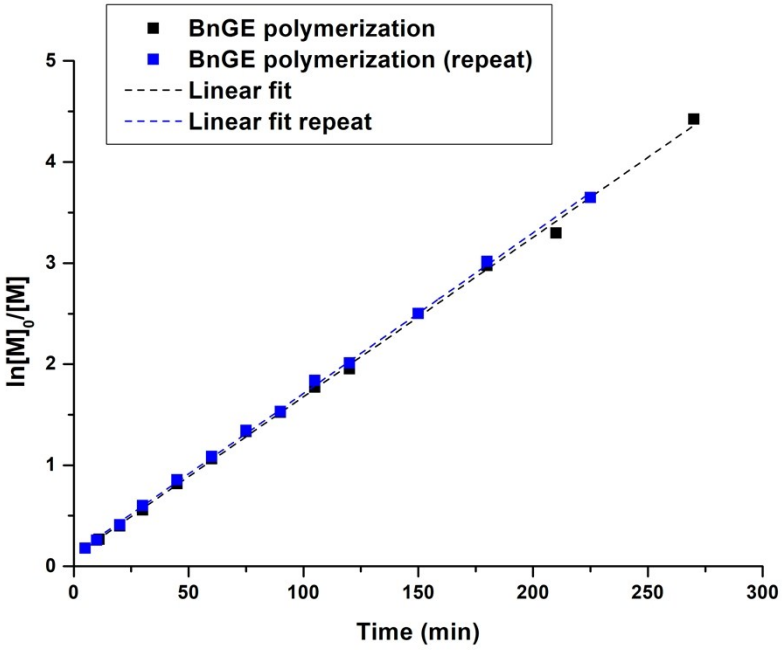


Figure S16. AROP of AGE initiated by benzyl alcohol-*t*BuP$_4$ in THF at 25°C ([M]$_0$ = 2 mol.L^{-1}; [I]$_0$ = 4 x 10^{-2} mol.L^{-1}): (a) First order plot ($k_{p,\,app}$(black) = 3.00 x 10^{-1} L.mol^{-1}.min^{-1}; $k_{p,\,app}$(blue) = 3.00 x 10^{-1} L.mol^{-1}.min^{-1}; average value $k_{p,\,app}$ = 3.00 x 10^{-1} L.mol^{-1}.min^{-1}); relationship observed between number-average molar mass (full squares; linear trend curve is indicated by the dashed line) or dispersity (empty squares) and monomer conversion.

(a)



(b)

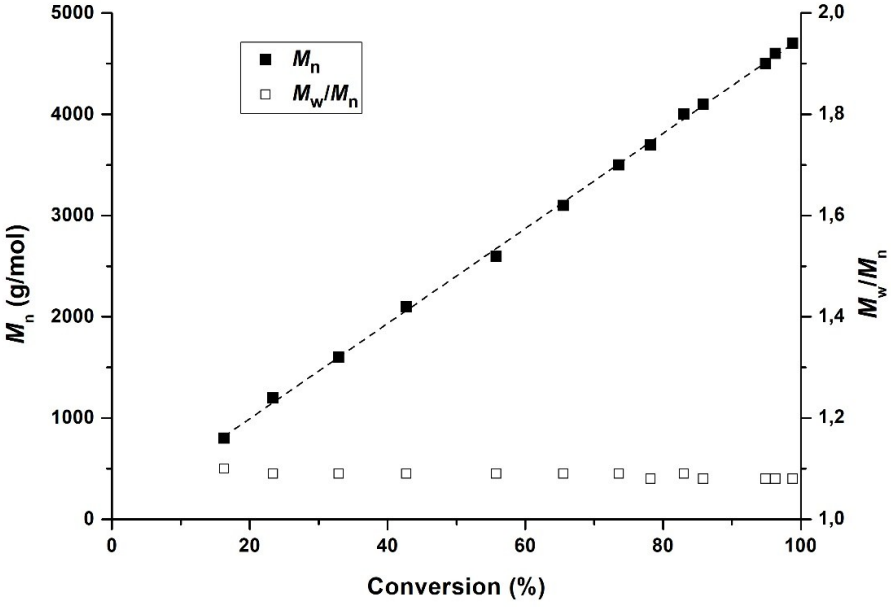


Figure S17. AROP of BnGE initiated by benzyl alcohol-*t*BuP$_4$ in THF at 25°C ([M]$_0$ = 2 mol.L^{-1}; [I]$_0$ = 4 x 10^{-2} mol.L^{-1}): (a) First order plot ($k_{p,\ app}$(black) = 3.95 x 10^{-1} L.mol^{-1}.min^{-1}; $k_{p,\ app}$(blue) = 4.30 x 10^{-1} L.mol^{-1}.min^{-1}; average value $k_{p,\ app}$ = 4.12 x 10^{-1} L.mol^{-1}.min^{-1}); relationship observed between number-average molar mass (full squares; linear trend curve is indicated by the dashed line) or dispersity (empty squares) and monomer conversion.

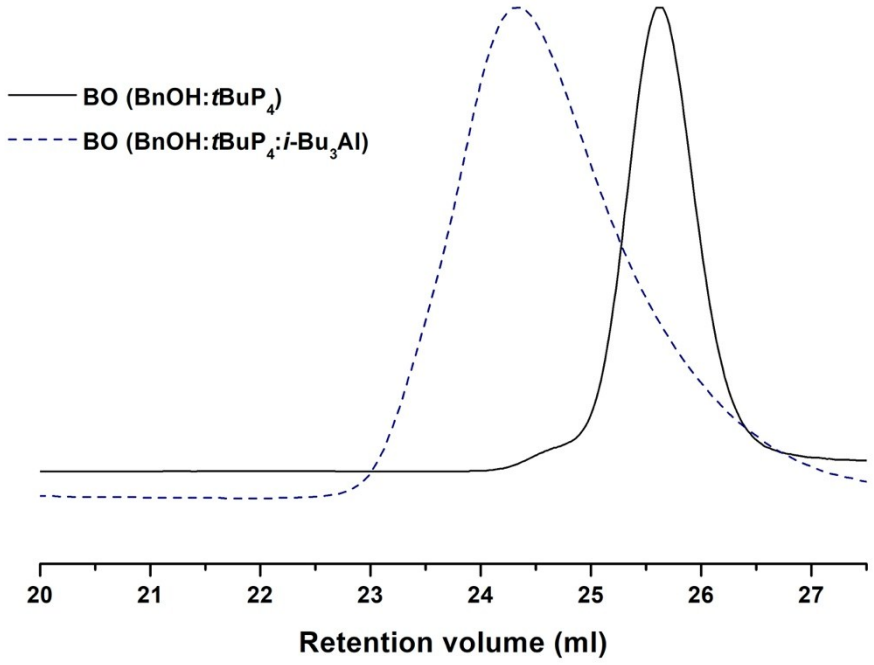


Figure S18. SEC traces of the poly(BO) classical AROP without *i*-Bu_3Al (solid line), monomer-activated AROP with *i*-Bu_3Al (dashed line), detected by RI detector (eluent: THF; 40°C; flow rate: 1 $ml.min^{-1}$)

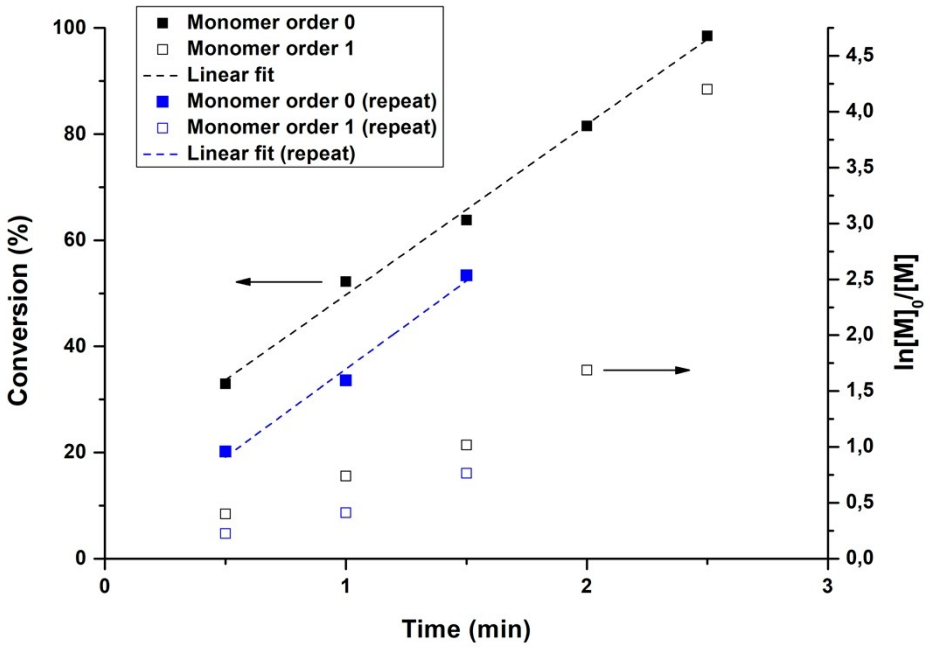


Figure S19. Monomer conversion and $\ln([M]_0/[M])$ vs time for the AROP of PO initiated by benzyl alcohol-*t*BuP_4 in the presence of *i*Bu_3Al in MeTHF at 25°C ($[M]_0$ = 2 mol.L^{-1}; $[I]_0$ = 3.7 x 10^{-2} mol.L^{-1}, Benzyl Alcohol:*t*-BuP_4:*i*-Bu_3Al (1:1:2)).

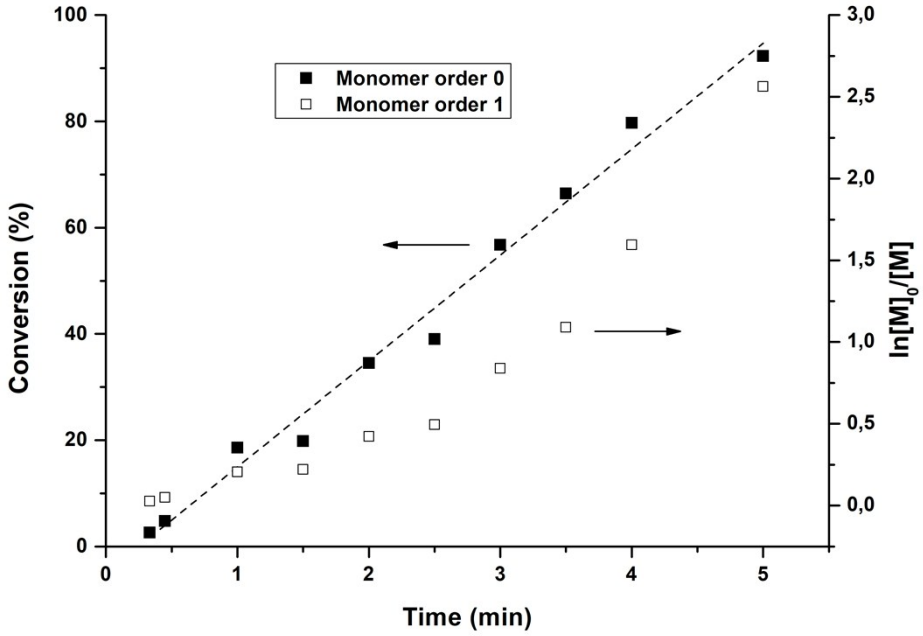


Figure S20. Monomer conversion and ln($[M]_0$/[M]) vs time for the AROP of BO initiated by benzyl alcohol-*t*BuP_4 in the presence of *i*Bu_3Al in MeTHF at 25°C ($[M]_0$ = 2 mol.L^{-1}; $[I]_0$ = 3.7 x 10^{-2} mol.L^{-1}, Benzyl Alcohol:*t*-BuP_4:*i*-Bu_3Al (1:1:2)).

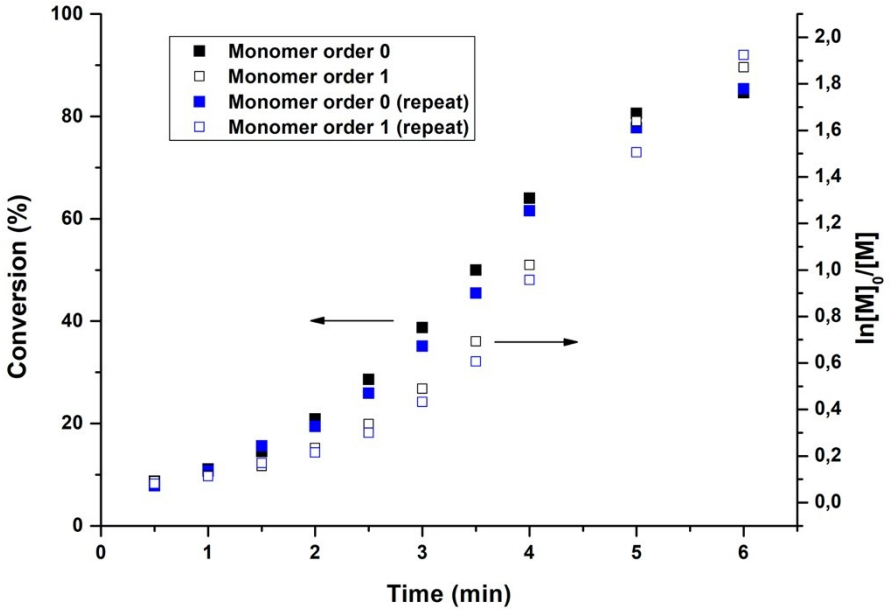


Figure S21. Monomer conversion and $\ln([M]_0/[M])$ vs time for the AROP of AGE initiated by benzyl alcohol-*t*BuP_4 in the presence of *i*Bu_3Al in MeTHF at 25°C ($[M]_0$ = 2 mol.L^{-1}; $[I]_0$ = 3.7 x 10^{-2} mol.L^{-1}, Benzyl Alcohol:*t*-BuP_4:*i*-Bu_3Al (1:1:2)).

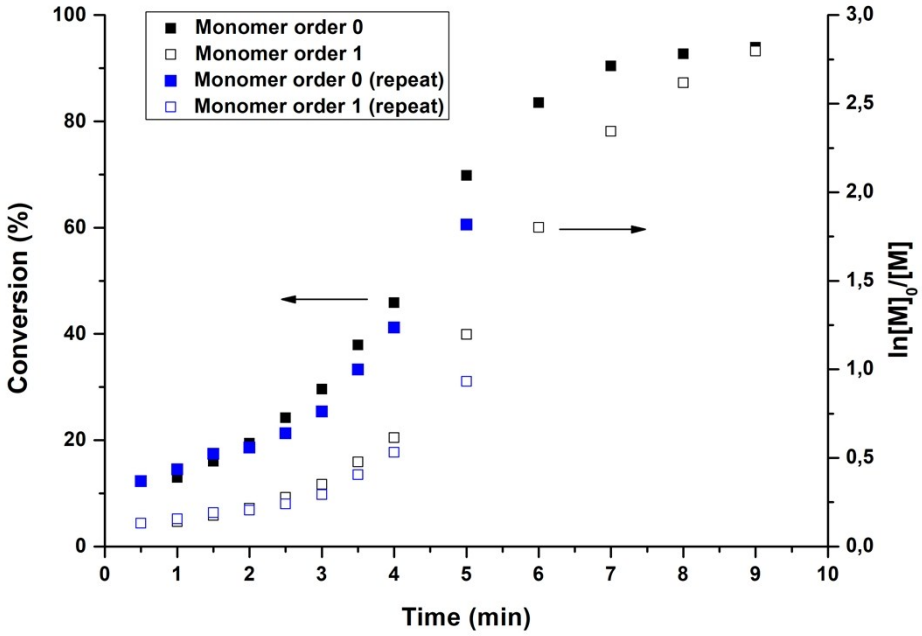


Figure S22. Monomer conversion and ln($[M]_0$/[M]) vs time for the AROP of EEGE initiated by benzyl alcohol-*t*BuP_4 in the presence of *i*Bu_3Al in MeTHF at 25°C ($[M]_0$ = 2 mol.L^{-1}; $[I]_0$ = 3.7 x 10^{-2} mol.L^{-1}, Benzyl Alcohol:*t*-BuP_4:*i*-Bu_3Al (1:1:2)).

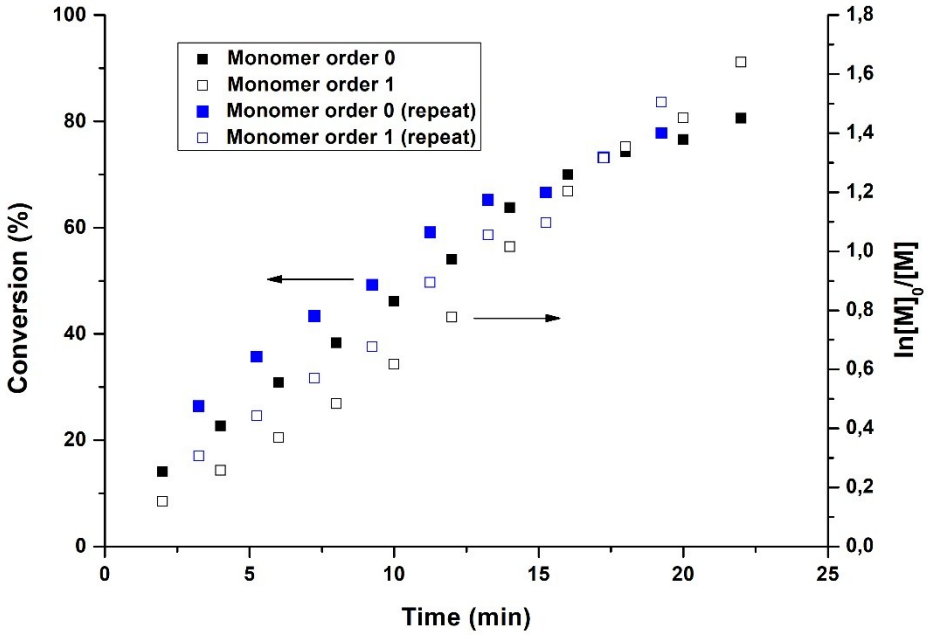


Figure S23. Monomer conversion and $\ln([M]_0/[M])$ vs time for the AROP of *t*BuGE initiated by benzyl alcohol-*t*BuP_4 in the presence of *i*Bu_3Al in MeTHF at 25°C ($[M]_0$ = 2 mol.L^{-1}; $[I]_0$ = 3.7 x 10^{-2} mol.L^{-1}, Benzyl Alcohol:*t*-BuP_4:*i*-Bu_3Al (1:1:2)).

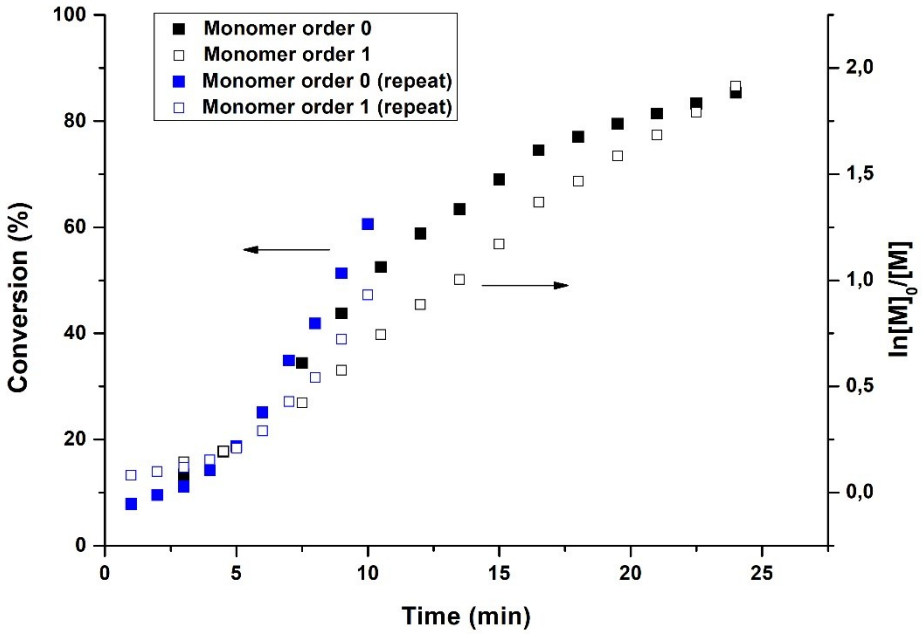


Figure S24. Monomer conversion and $\ln([M]_0/[M])$ vs time for the AROP of BnGE initiated by benzyl alcohol-*t*BuP_4 in the presence of *i*Bu_3Al in MeTHF at 25°C ($[M]_0$ = 2 mol.L^{-1}; $[I]_0$ = 3.7 x 10^{-2} mol.L^{-1}, Benzyl Alcohol:*t*-BuP_4:*i*-Bu_3Al (1:1:2)).

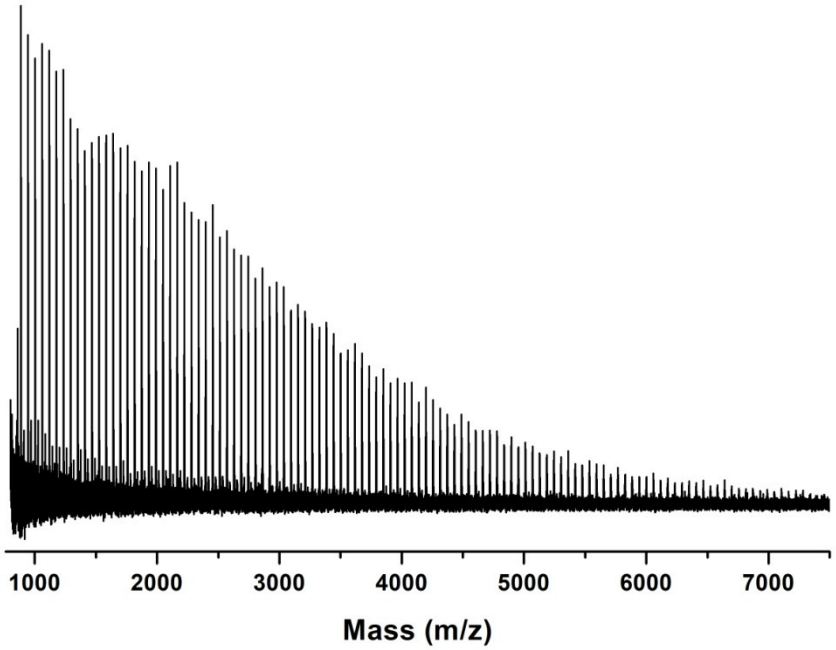


Figure S25. MALDI-TOF spectrum of poly(PO) (MeTHF, 25°C, $[M]_0$ = 2 mol.L^{-1}, [benzyl alcohol] = 3,7 x 10^{-2} mol.L^{-1}, Benzyl Alcohol:*t*-BuP_4:*i*-Bu_3Al (1:1:2)).

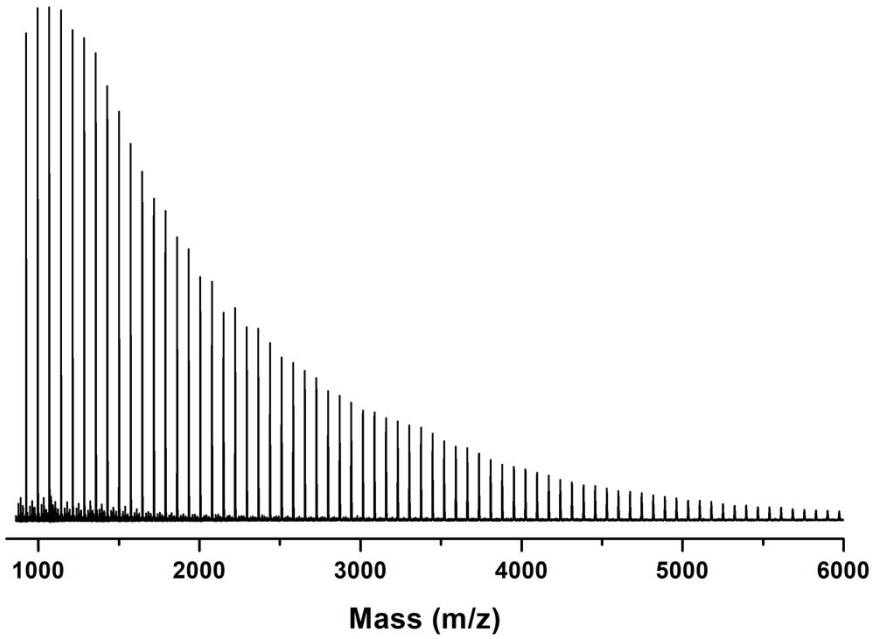


Figure S26. MALDI-TOF spectrum of poly(BO) (MeTHF, 25°C, $[M]_0$ = 2 mol.L^{-1}, [benzyl alcohol] = 3,7 x 10^{-2} mol.L^{-1}, Benzyl Alcohol:*t*-BuP_4:*i*-Bu_3Al (1:1:2)).

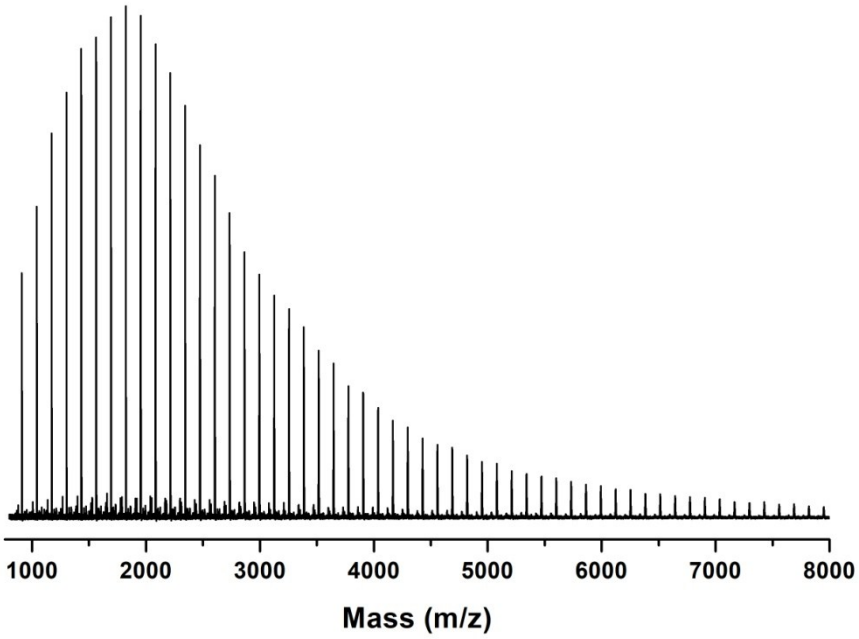


Figure S27. MALDI-TOF spectrum of poly(tBuGE) (MeTHF, 25°C, $[M]_0$ = 2 mol.L^{-1}, [benzyl alcohol] = 3,7 x 10^{-2} mol.L^{-1}, Benzyl Alcohol:*t*-BuP_4:*i*-Bu_3Al (1:1:2)).

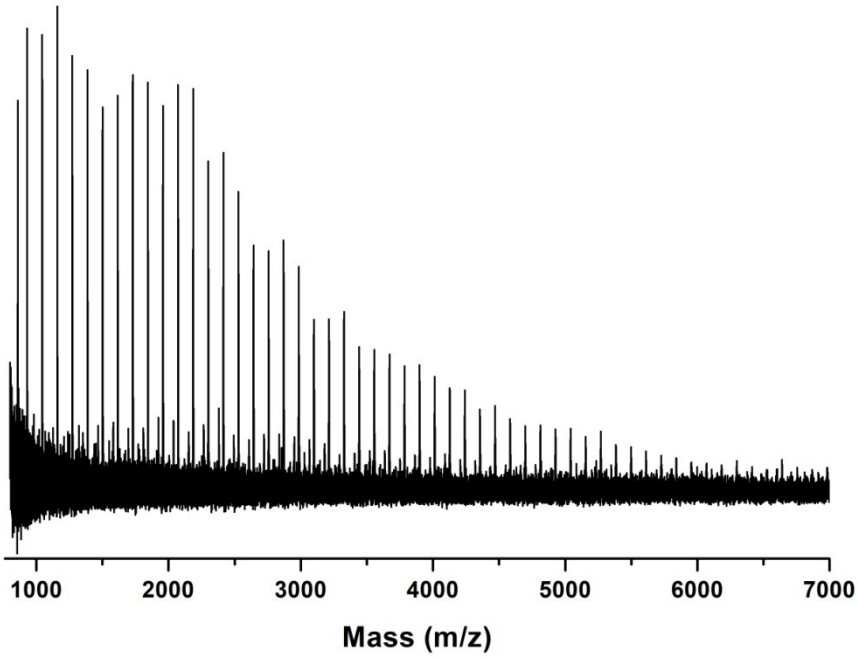


Figure S28. MALDI-TOF spectrum of poly(AGE) (MeTHF, 25°C, $[M]_0$ = 2 mol.L^{-1}, [benzyl alcohol] = 3,7 x 10^{-2} mol.L^{-1}, Benzyl Alcohol:*t*-BuP_4:*i*-Bu_3Al (1:1:2)).

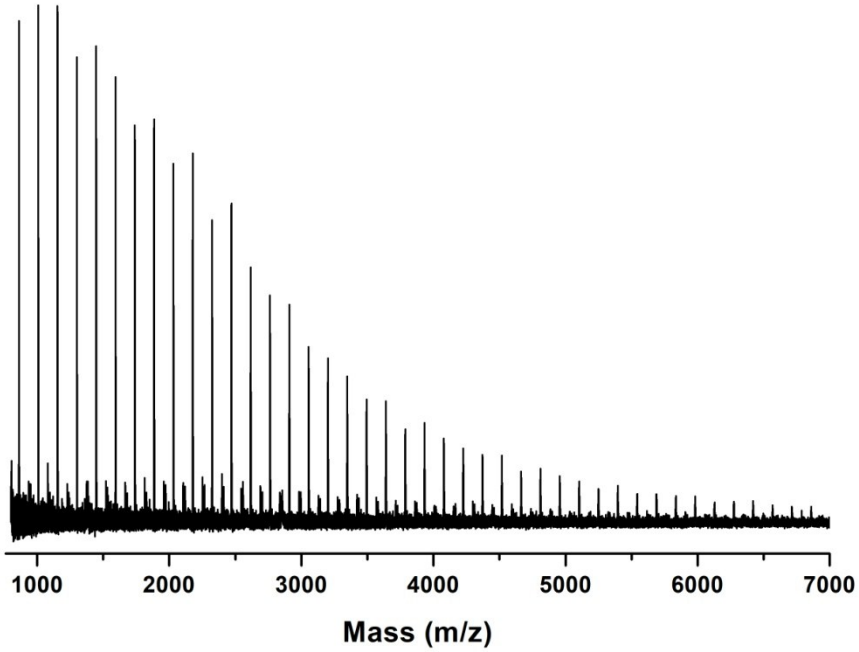


Figure S29. MALDI-TOF spectrum of poly(EEGE) (MeTHF, 25°C, $[M]_0$ = 2 mol.L^{-1}, [benzyl alcohol] = 3,7 x 10^{-2} mol.L^{-1}, Benzyl Alcohol:*t*-BuP_4:*i*-Bu_3Al (1:1:2)).

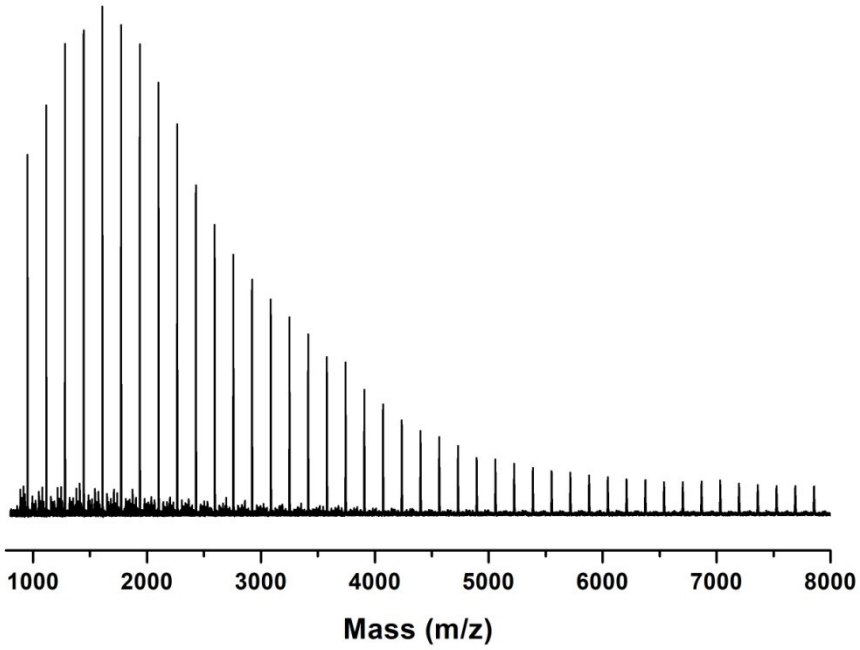


Figure S30. MALDI-TOF spectrum of poly(BnGE) (MeTHF, 25°C, $[M]_0$ = 2 mol.L^{-1}, [benzyl alcohol] = 3,7 x 10^{-2} mol.L^{-1}, Benzyl Alcohol:*t*-BuP_4:*i*-Bu_3Al (1:1:2)).