

Supporting Information

Protected amine-functional initiators for the synthesis of α -amine homo- and heterotelechelic poly(2-ethyl-2-oxazoline)s

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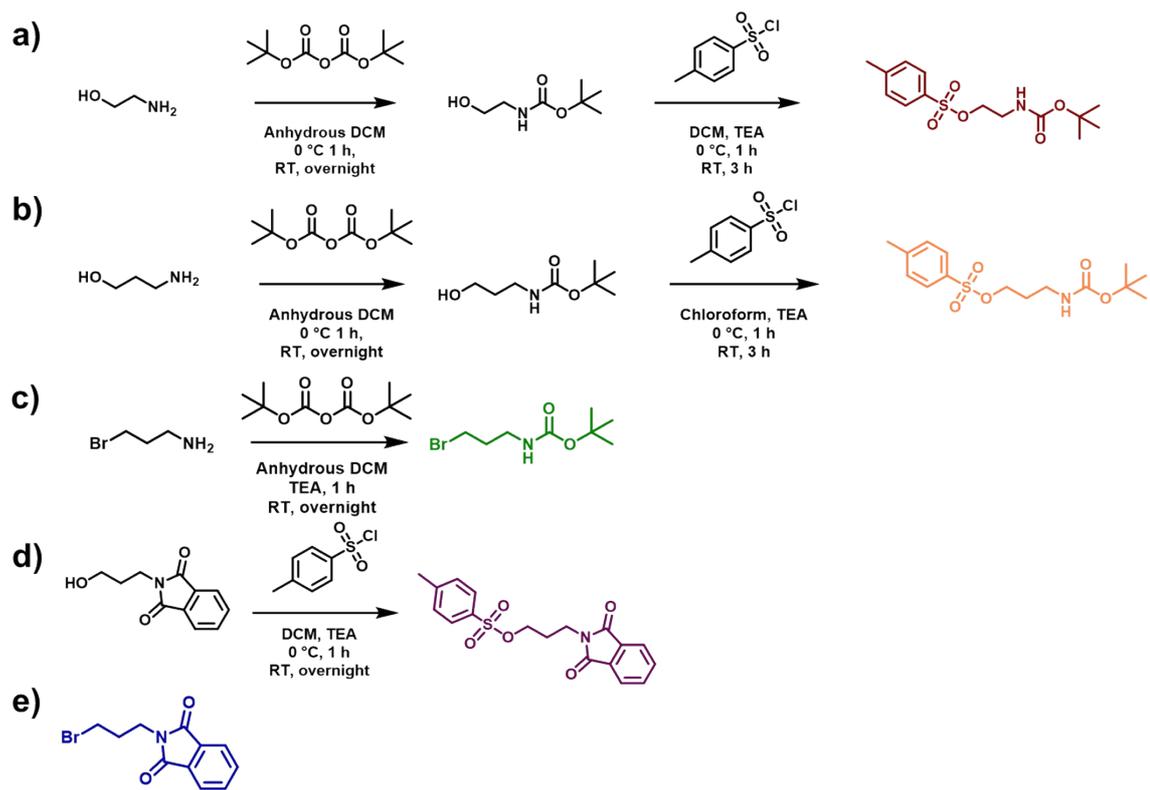


Figure S1. Schematic representation of the initiator synthesis. (a) BOC-NH₂-C2-Tos, (b) BOC-NH₂-C3-Tos, (c) BOC-NH₂-C3-Br, (d) phthalimide-NH₂-C3-Tos, and (e) commercially available phthalimide-NH₂-C3-Br.

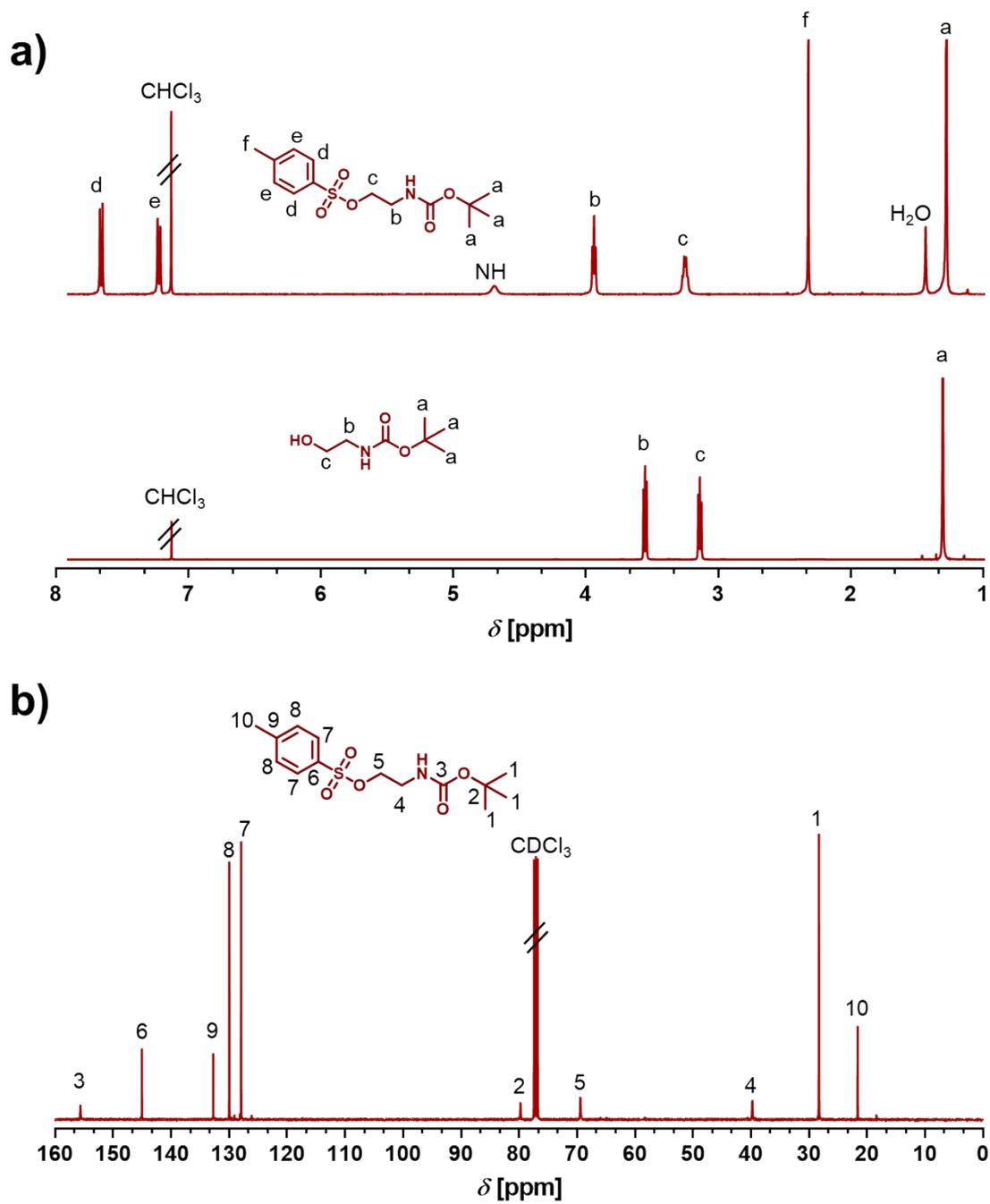
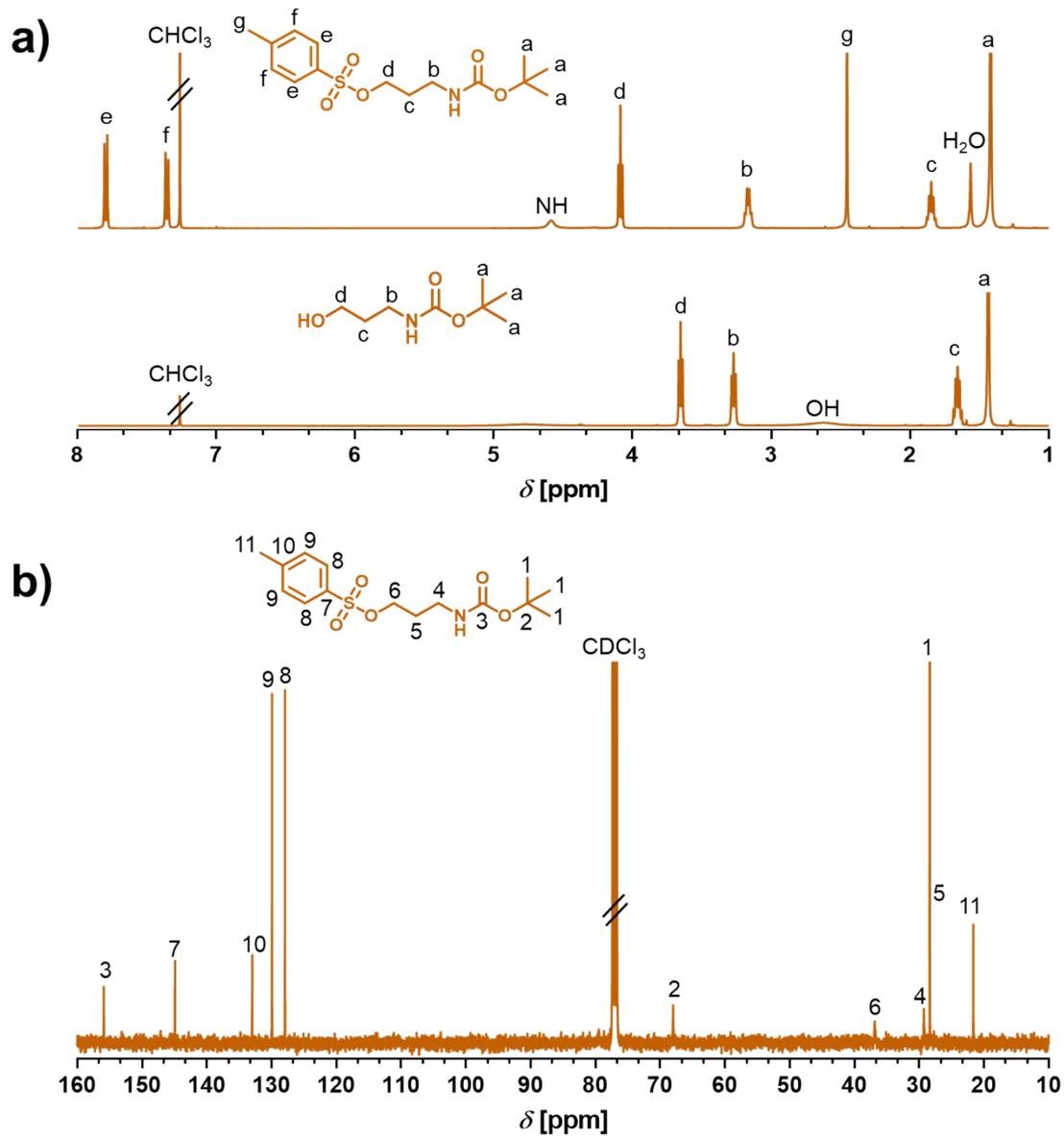


Figure S2. Characterization of BOC-NH₂-C₂-Tos. (a) ¹H NMR (400 MHz, CDCl₃) and (b) ¹³C NMR (400 MHz, CDCl₃).



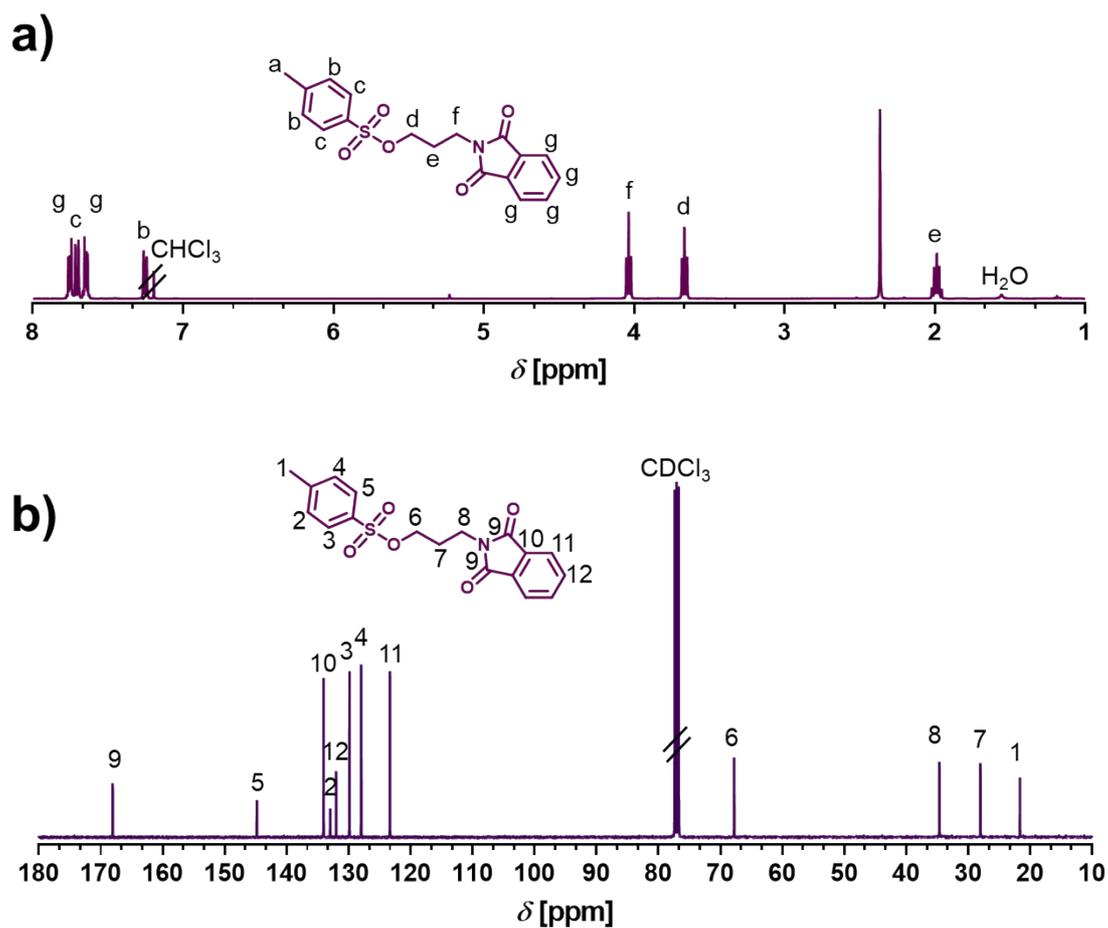


Figure S4. Characterization of phthalimide-NH₂-C₃-Tos. (a) ¹H NMR (400 MHz, CDCl₃) and (b) ¹³C NMR (400 MHz, CDCl₃).

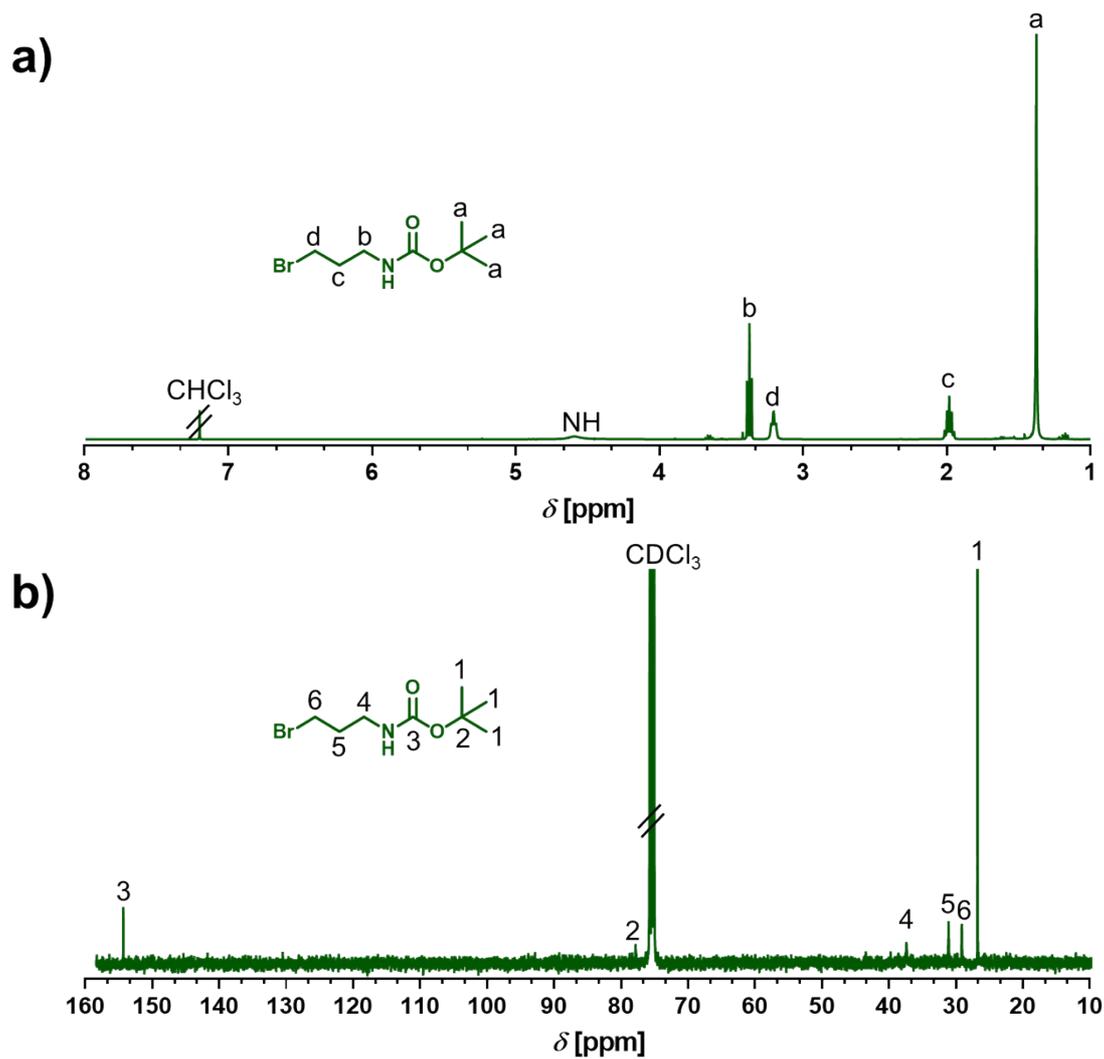


Figure S5. Characterization of BOC-NH₂-C₃-Br. (a) ¹H NMR (400 MHz, CDCl₃) and (b) ¹³C NMR (400 MHz, CDCl₃).

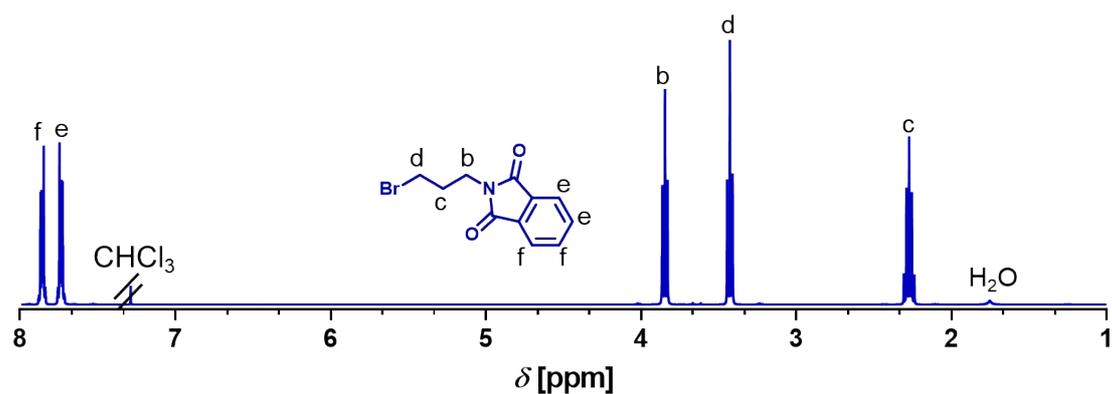


Figure S6. ¹H NMR (400 MHz, CDCl₃) of phthalimide-NH₂-C₃-Br.

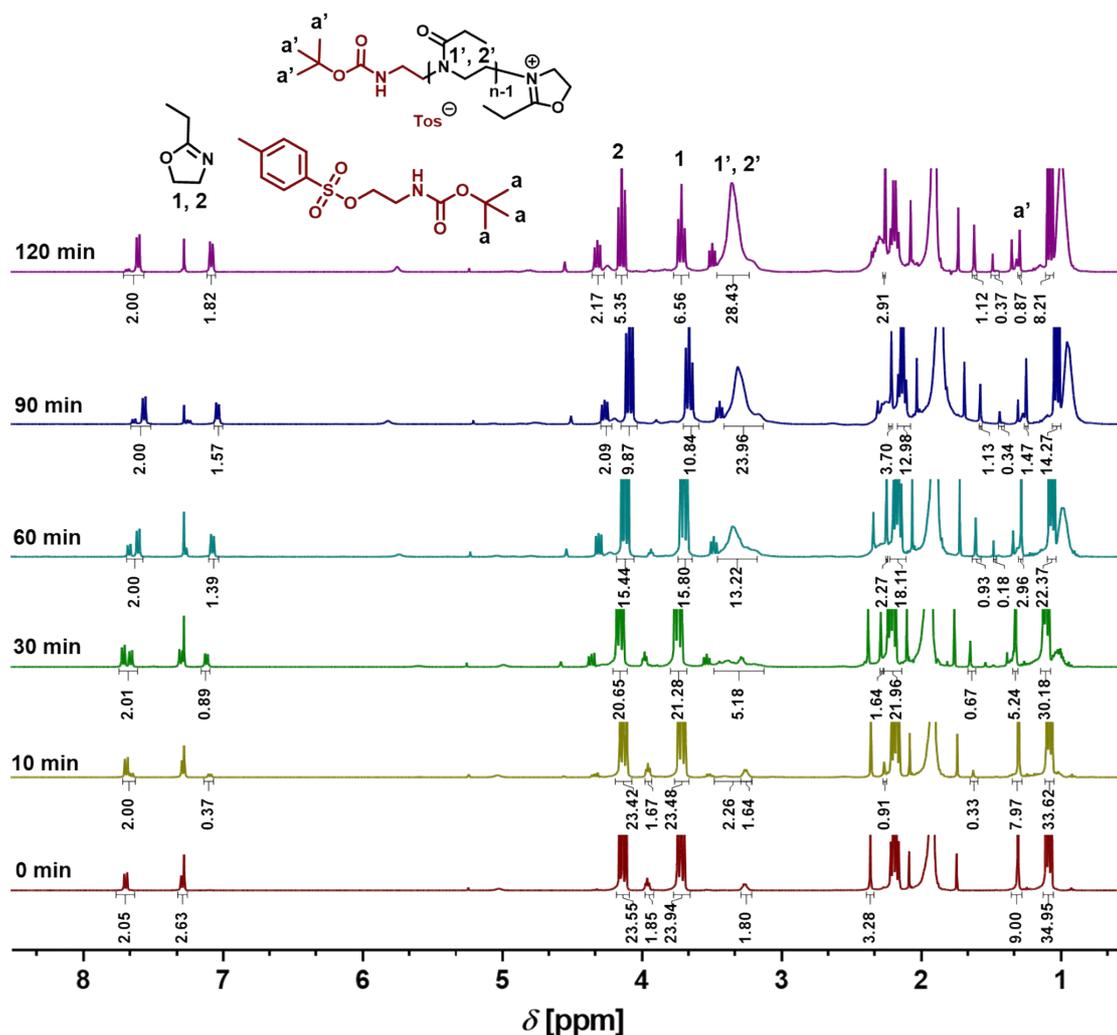


Figure S7. Kinetic studies of the CROP of EtOx initiated by BOC-NH₂-C2-Tos ([M]/[I] = 15) in MeCN at 80 °C. ^1H NMR spectra (400 MHz, CDCl_3) of reaction mixtures at indicated reaction times showing the reduction of the 2-oxazoline monomer peaks (H1 and H2) and the increase of the resulting backbone signals (H1' and H2') over time. The signals with an apostrophe (Ha') represent the deprotected *tert*-butyl protons (Ha) from the initiator and polymer. The CHCl_3 (7.26 ppm) signals were used as a standard for chemical shift of overlaid spectra.

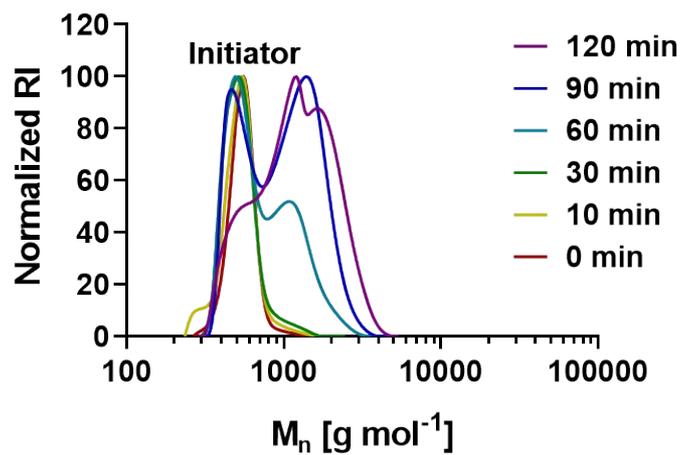


Figure S8. Evolution of the molar mass determined by SEC (DMAc, PS-calibration) at indicated polymerization times of EtOx initiated by BOC-NH₂-C2-Tos ([M]/[I] = 15) in MeCN at 80 °C.

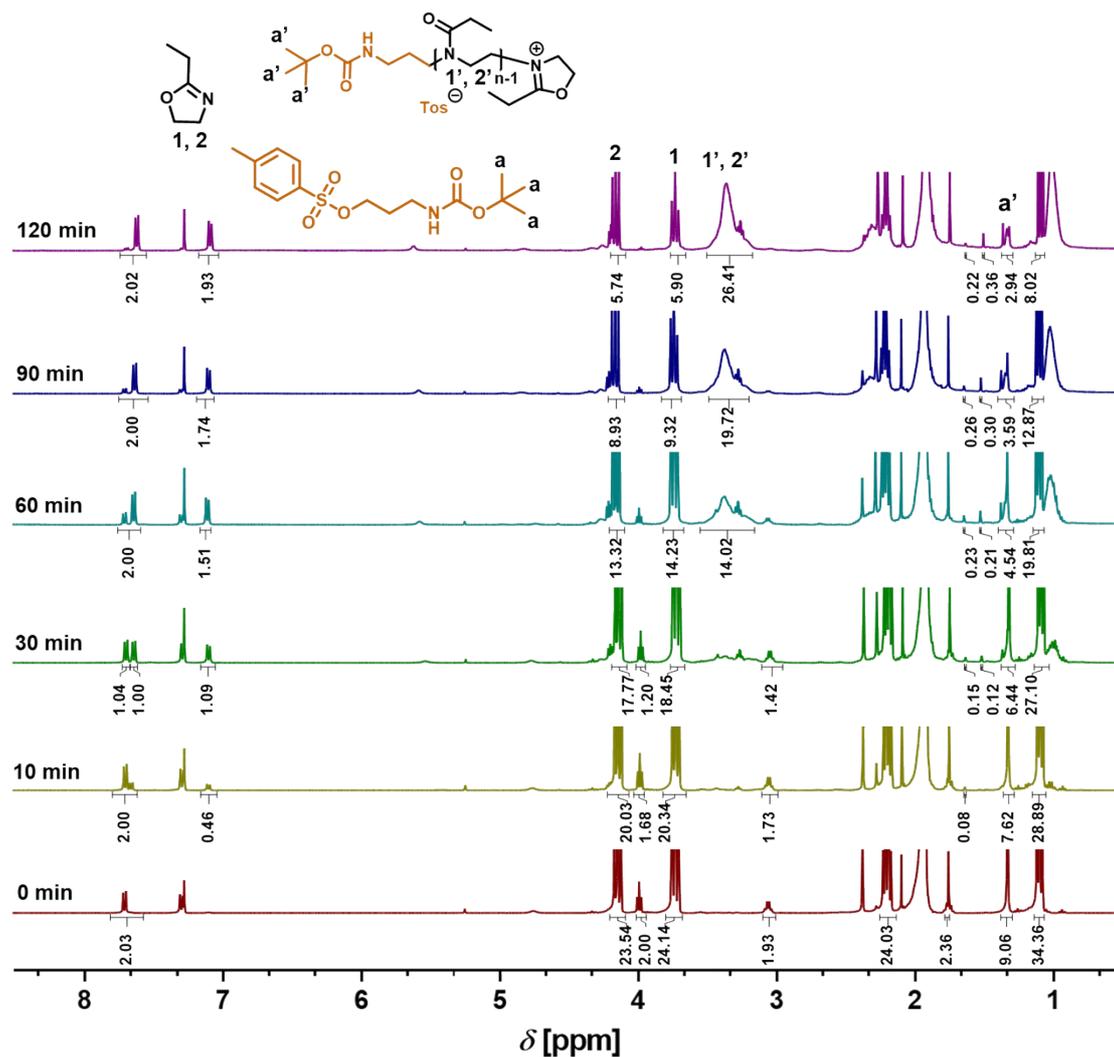


Figure S9. Kinetic studies of the CROP of EtOx initiated by BOC-NH₂-C3-Tos ([M]/[I] = 15) in MeCN at 80 °C. ^1H NMR spectra (400 MHz, CDCl_3) of reaction mixtures at indicated reaction times showing the reduction of the 2-oxazoline monomer peaks (H1 and H2) and the increase of the resulting backbone signals (H1' and H2') over time. The signals with an apostrophe (Ha') represent the deprotected *tert*-butyl protons (Ha) from the initiator and polymer. The CHCl_3 (7.26 ppm) signals were used as a standard for chemical shift of overlaid spectra.

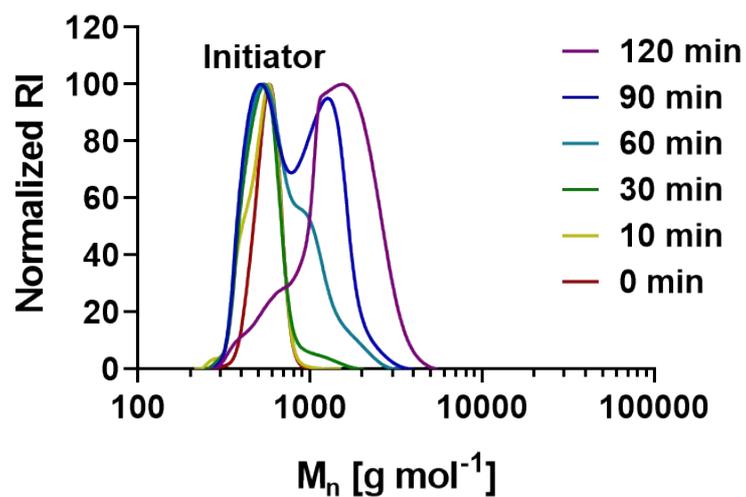


Figure S10. Evolution of the molar mass determined by SEC (DMAc, PS-calibration) at indicated polymerization times of EtOx initiated by BOC-NH₂-C3-Tos ([M]/[I] = 15) in MeCN at 80 °C.

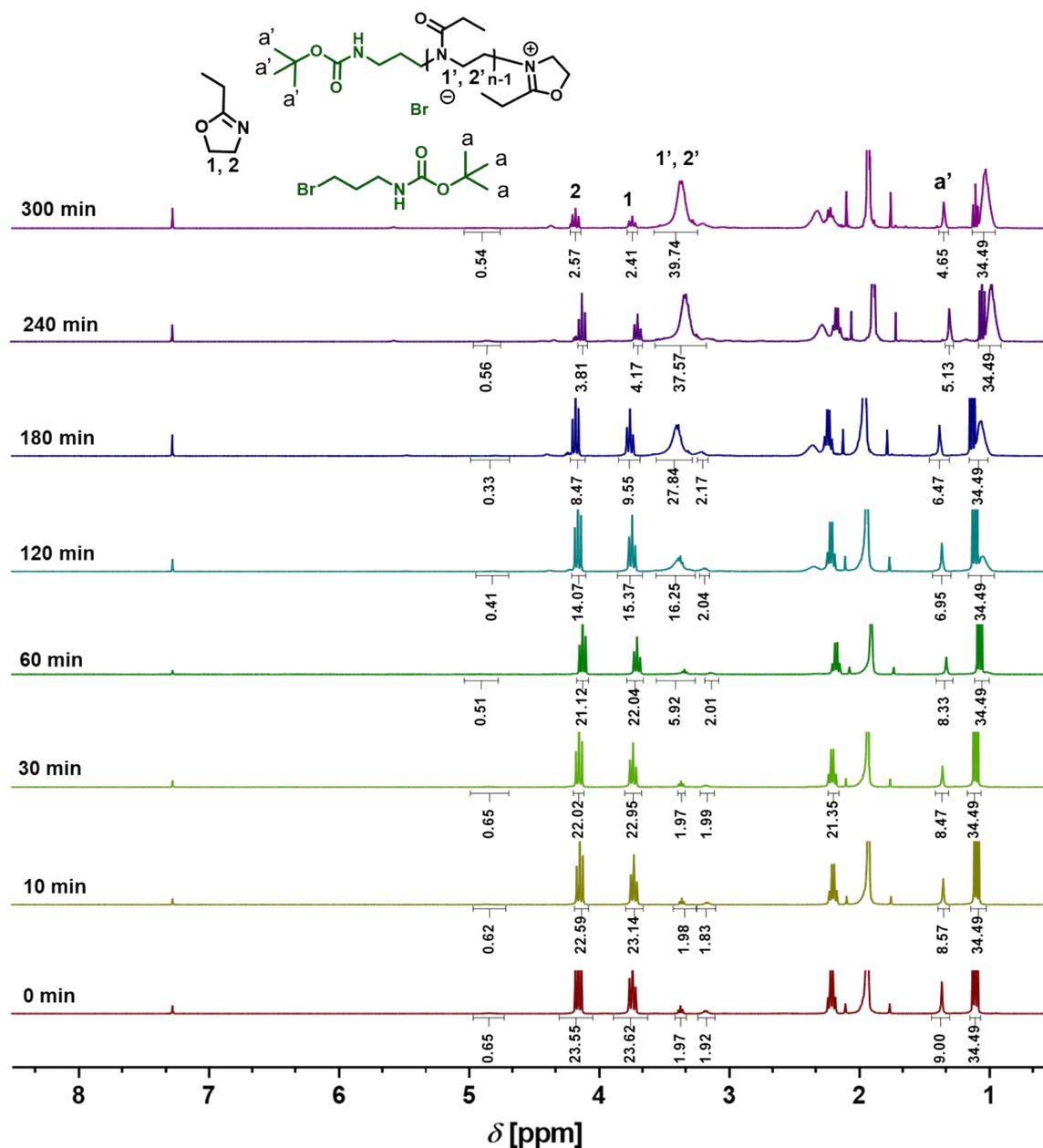


Figure S11. Kinetic studies of the CROP of EtOx initiated by BOC-NH₂-C₃-Br ([M]/[I] = 15) in MeCN at 80 °C. ¹H NMR spectra (400 MHz, CDCl₃) of reaction mixtures at indicated reaction times showing the reduction of the 2-oxazoline monomer peaks (H1 and H2) and the increase of the resulting backbone signals (H1' and H2') over time.

The signals with an apostrophe (Ha') represent the deprotected *tert*-butyl protons (Ha) from the initiator and polymer. The CHCl₃ (7.26 ppm) signals were used as a standard for chemical shift of overlaid spectra.

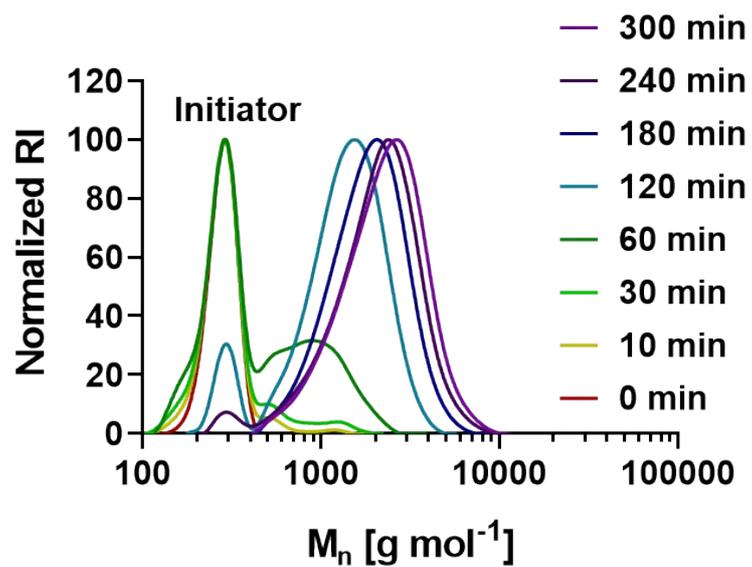


Figure S12. Evolution of the molar mass determined by SEC (DMAc, PS-calibration) at indicated polymerization times of EtOx initiated by BOC-NH₂-C3-Br ([M]/[I] = 15) in MeCN at 80 °C.

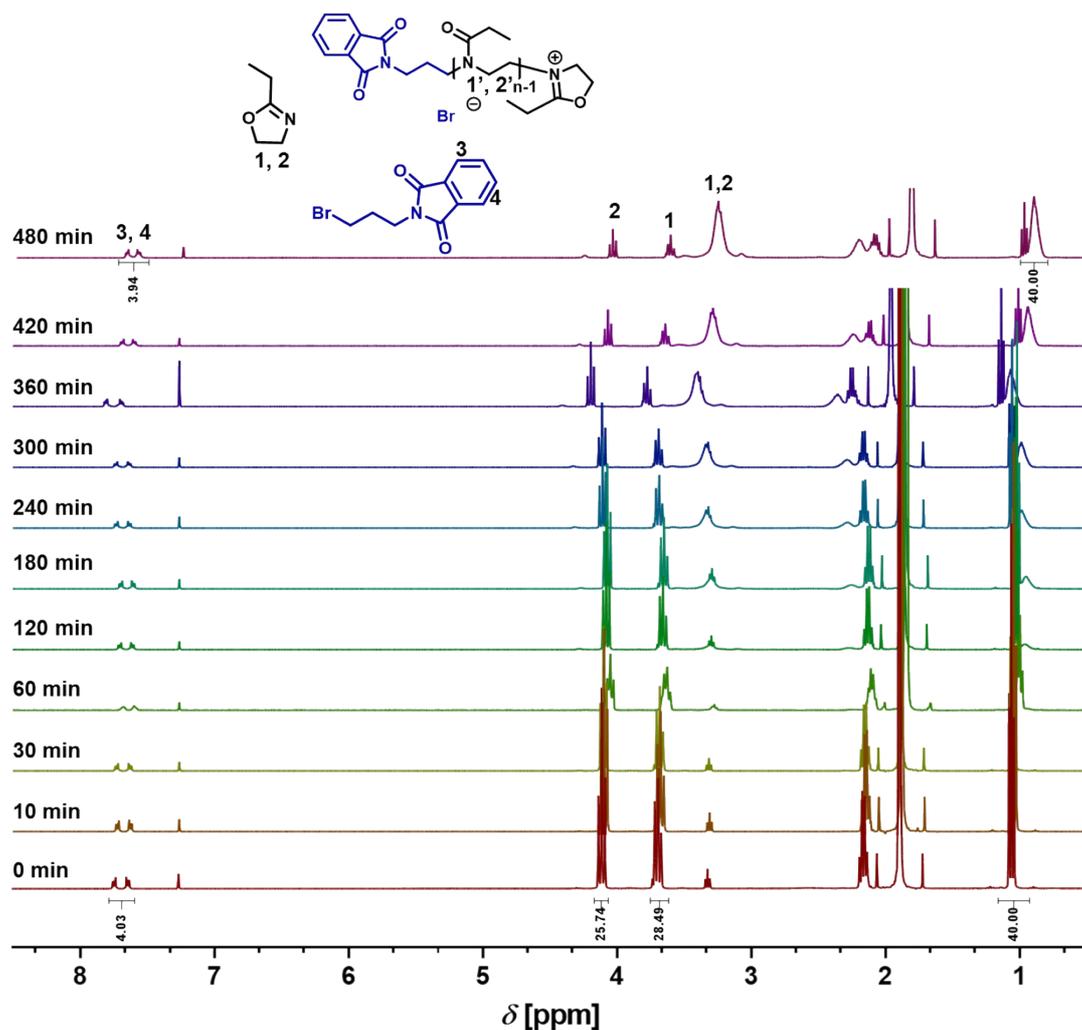


Figure S13. Kinetic studies of the CROP of EtOx initiated by phthalimide-NH₂-C₃-Br ([M]/[I] = 15) in MeCN at 80 °C. ¹H NMR spectra (400 MHz, CDCl₃) of reaction mixtures at indicated reaction times showing the reduction of the 2-oxazoline monomer peaks (H1 and H2) and the increase of the resulting backbone signals (H1' and H2') over time. The CHCl₃ (7.26 ppm) signals were used as a standard for chemical shift of overlaid spectra

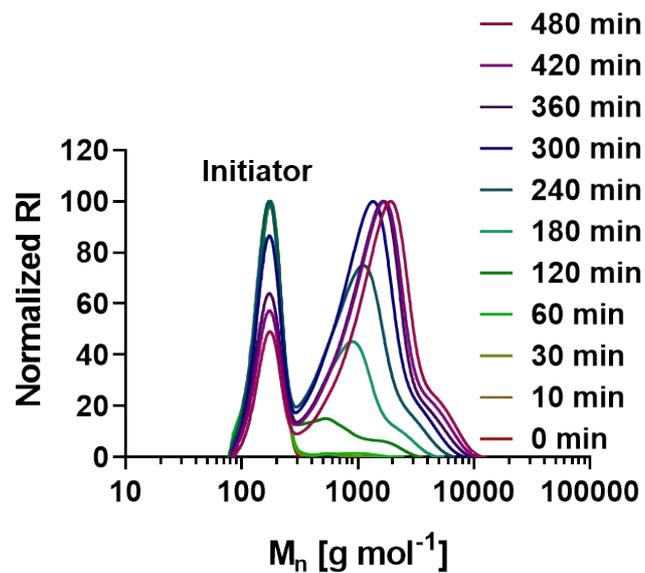


Figure S14. Evolution of the molar mass determined by SEC (DMAc, PS-calibration) at indicated polymerization times of EtOx initiated by phthalimide-NH₂-C3-Br ($[M]/[I] = 15$) in MeCN at 80 °C.

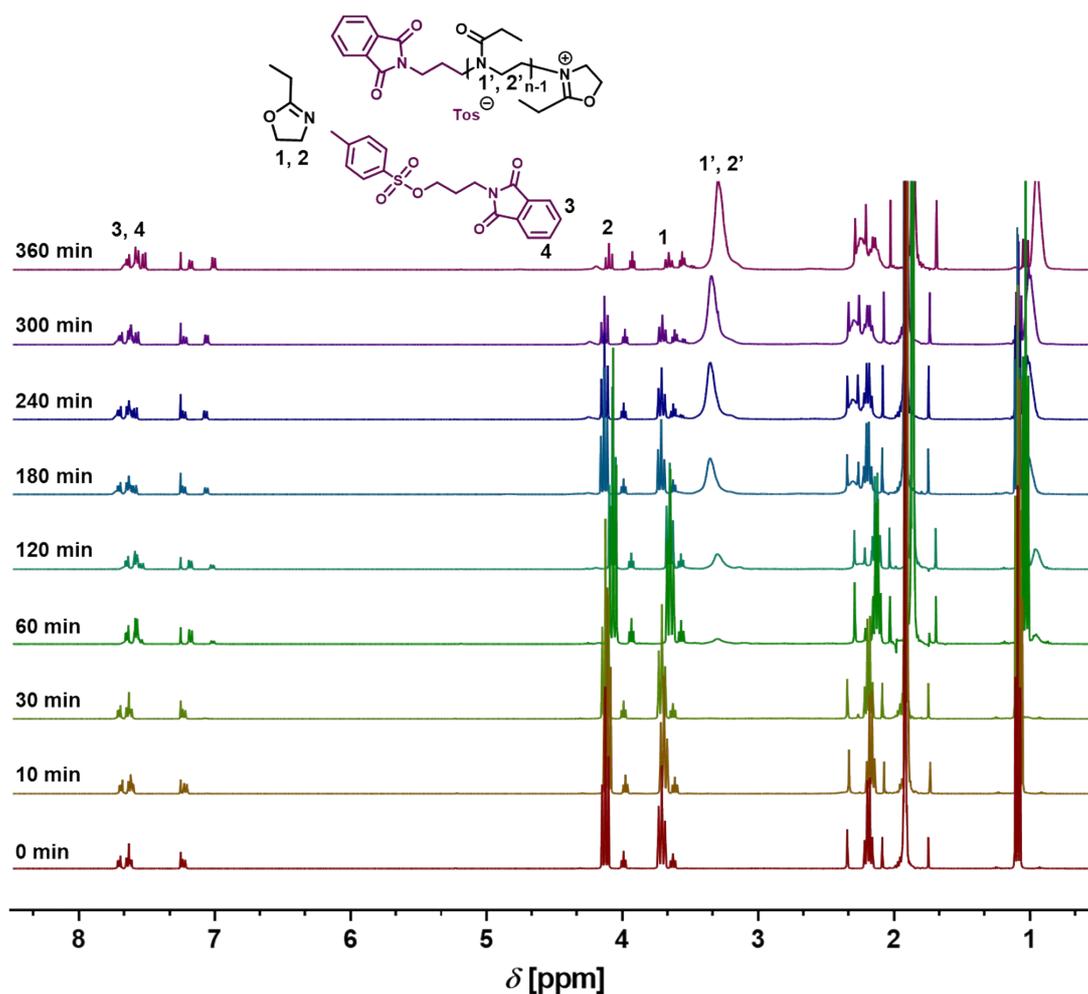


Figure S15. Kinetic studies of the CRCP of EtOx initiated by phthalimide- NH_2 -C3-Tos ($[\text{M}]/[\text{I}] = 15$) in MeCN at 80°C . ^1H NMR spectra (400 MHz, CDCl_3) of reaction mixtures at indicated reaction times showing the reduction of the 2-oxazoline monomer peaks (H1 and H2) and the increase of the resulting backbone signals (H1' and H2') over time. The CHCl_3 (7.26 ppm) signals were used as a standard for chemical shift of overlaid spectra.

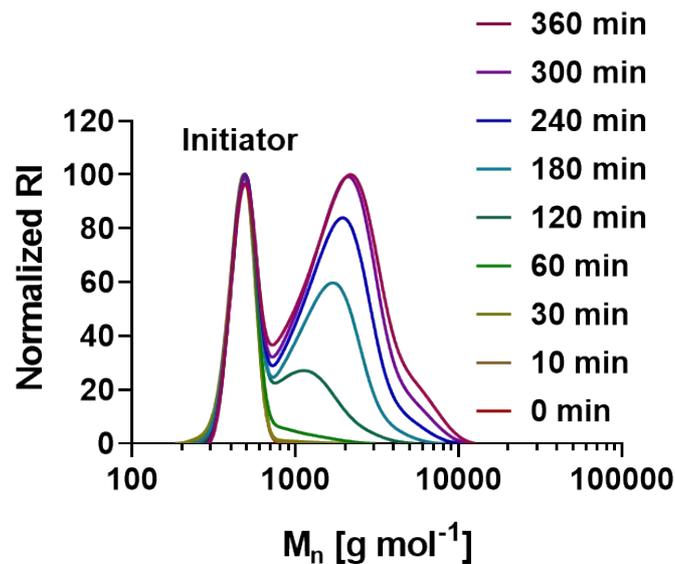


Figure S16. Evolution of the molar mass determined by SEC (DMAc, PS-calibration) at indicated polymerization times of EtOx initiated by phthalimide-NH₂-C3-Tos ([M]/[I] = 15) in MeCN at 80 °C.

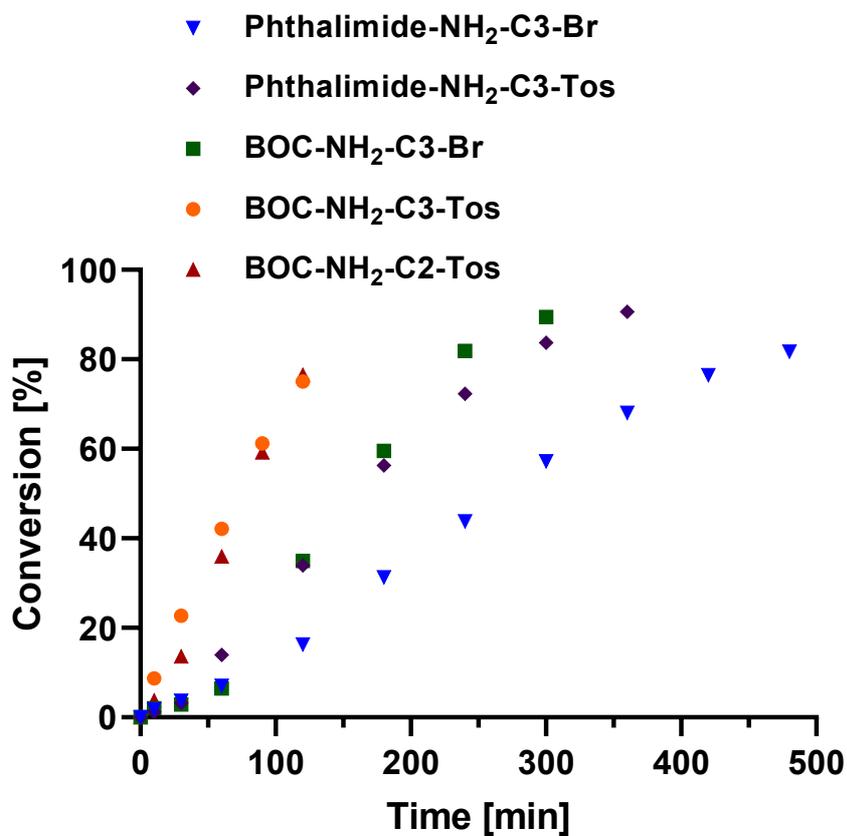


Figure S17. Monomer conversion versus polymerization time for different initiators concentrations of the CROP of EtOx ([M]/[I] = 15) in MeCN at 80 °C.

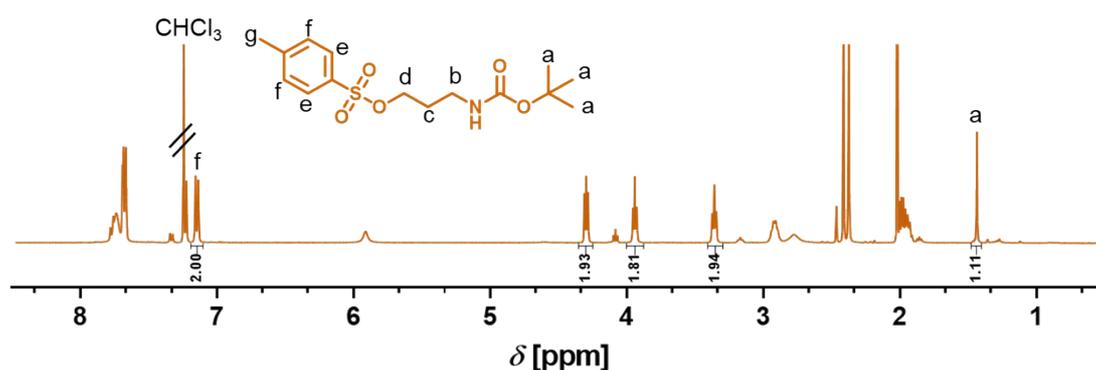


Figure S18. ^1H NMR spectrum of BOC-NH₂-C3-Tos after 2 h of incubation at 80 °C in MeCN (400 MHz, CDCl₃).

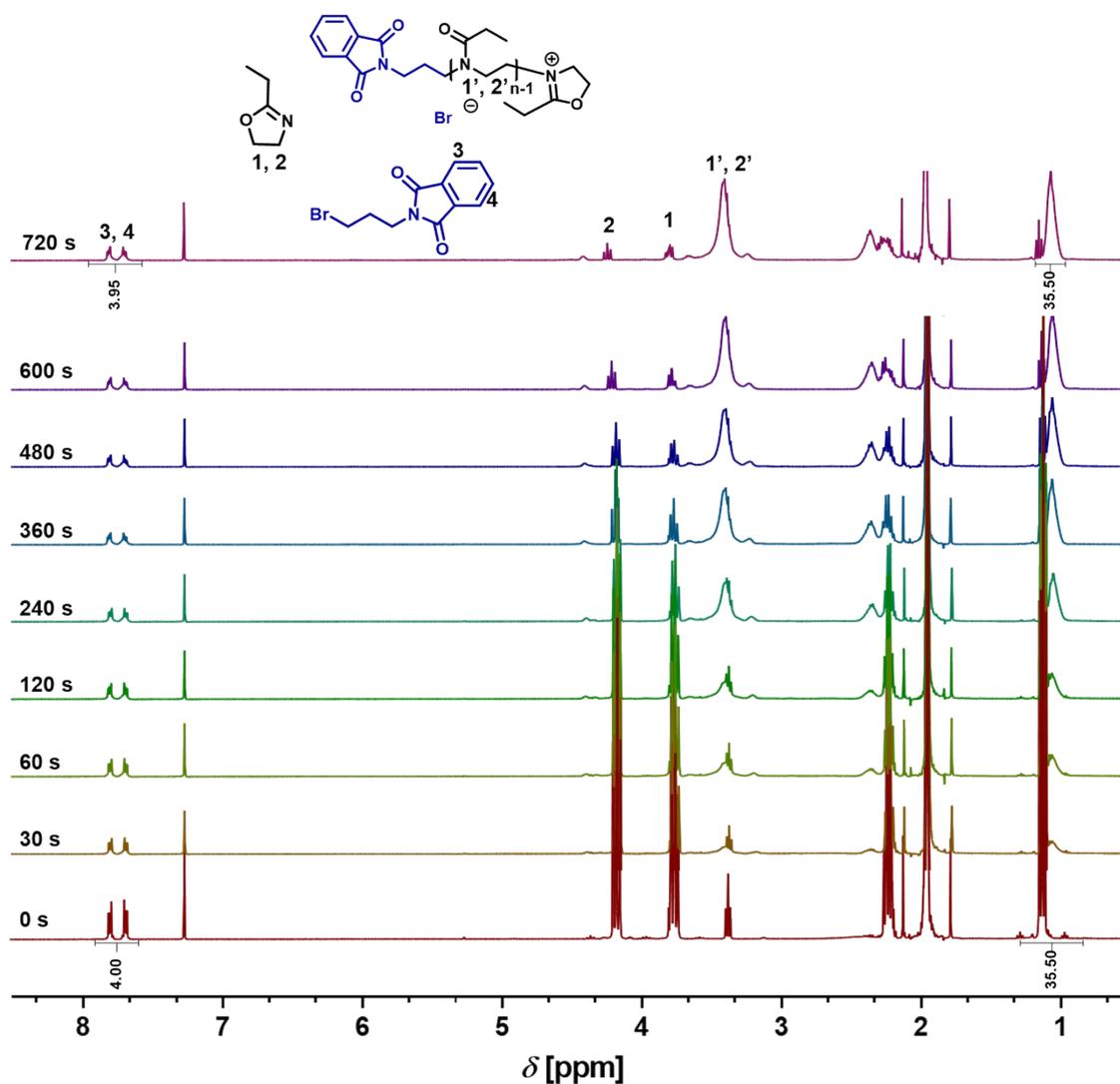


Figure S19. Kinetic studies of EtOx initiated with phthalimide-NH₂-C3-Br ([M]/[I] = 15) in MeCN at 140 °C. ^1H NMR spectra (400 MHz, CDCl₃) of reaction mixtures at indicated reaction times showing the reduction of the 2-oxazoline monomer peaks (H1

and H2) and the increase of the resulting backbone signals (H1' and H2') over time. The CHCl_3 (7.26 ppm) signals were used as a standard for chemical shift of overlaid spectra.

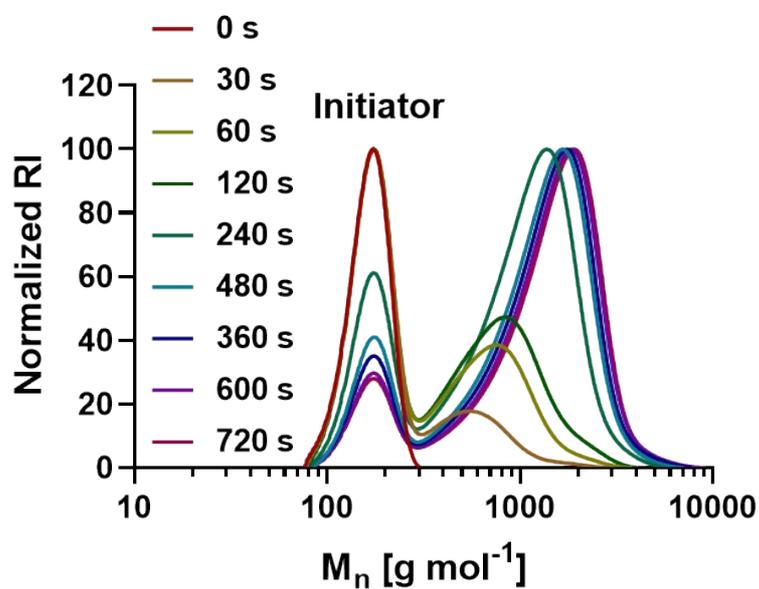


Figure S20. Evolution of the molar mass determined by SEC (DMAc, PS-calibration) at indicated polymerization times of EtOx initiated by phthalimide- $\text{NH}_2\text{-C}_3\text{-Br}$ ($[\text{M}]/[\text{I}] = 15$) in MeCN at 140 °C.

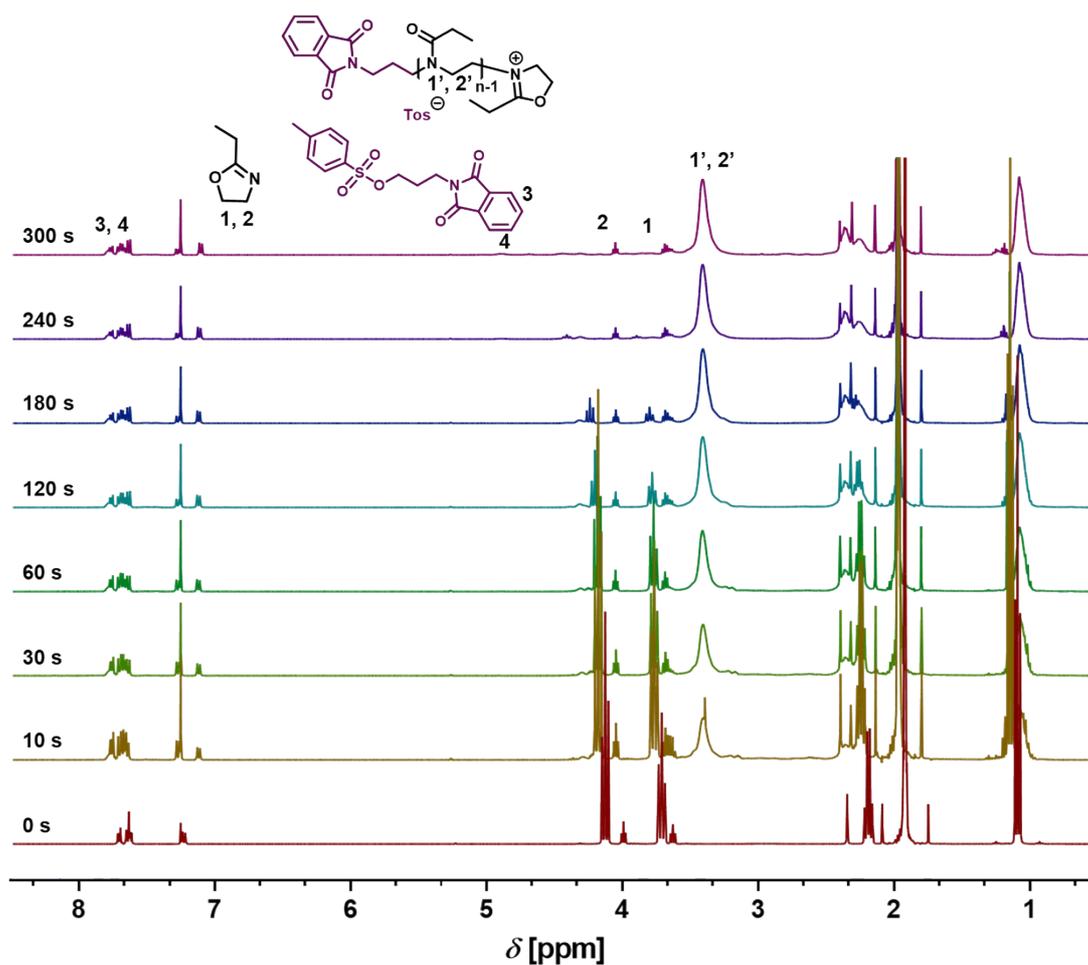


Figure 21. Kinetic studies of EtOx initiated phthalimide- NH_2 -C3-Tos ($[\text{M}]/[\text{I}] = 15$) in MeCN at 140 °C. ^1H NMR spectra (400 MHz, CDCl_3) of reaction mixtures at indicated reaction times showing the reduction of the 2-oxazoline monomer peaks (H1 and H2) and the increase of the resulting backbone signals (H1' and H2') over time. CHCl_3 (7.26 ppm) signals were used as a standard for chemical shift of overlaid spectra.

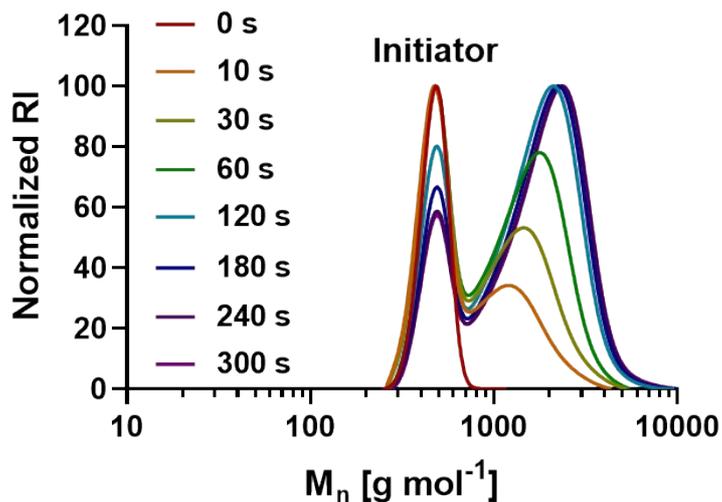


Figure S22. Evolution of the molar mass determined by SEC (DMAc, PS-calibration) at indicated polymerization times of EtOx initiated by phthalimide-NH₂-C3-Tos ([M]/[I] = 15) in MeCN at 140 °C.

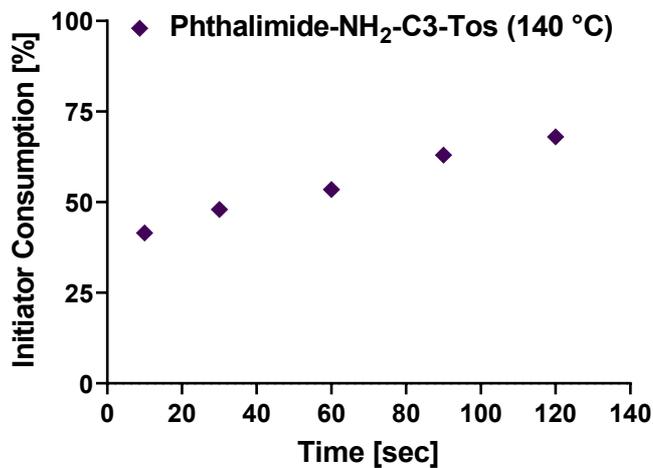


Figure S23. Evolution of the initiator consumption with polymerization time of the kinetic studies for cationic ring-opening polymerization of EtOx in MeCN using phthalimide-NH₂-C3-Tos at ([M]/[I] = 15; T = 140 °C, [M] = 2 M) evaluated by ¹H NMR measurements.

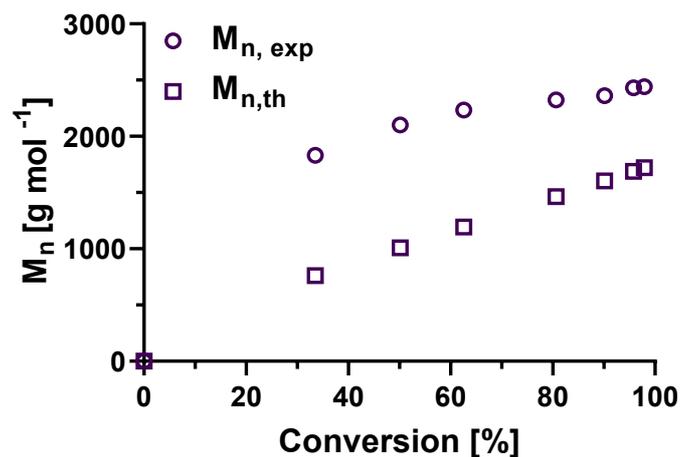


Figure S24. Summary of the theoretical molar mass ($M_{n,th}$) determined by conversion and the initial $[M]/[I] = 15$ in MeCN at 80 °C using ^1H NMR and the molar mass ($M_{n,exp}$) determined by the theoretical molar mass and initiator consumption originating from ^1H NMR of PEtOx initiated by phthalimide- NH_2 -C3-Tos.

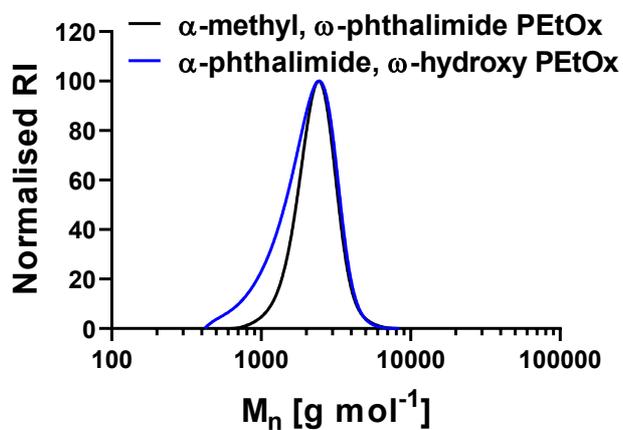


Figure S25. Molar mass distribution traces obtained from SEC measurements (DMAc, PS-cal.) of α-phthalimide, ω-hydroxy PEtOx and α-methyl, ω-phthalimide PEtOx.

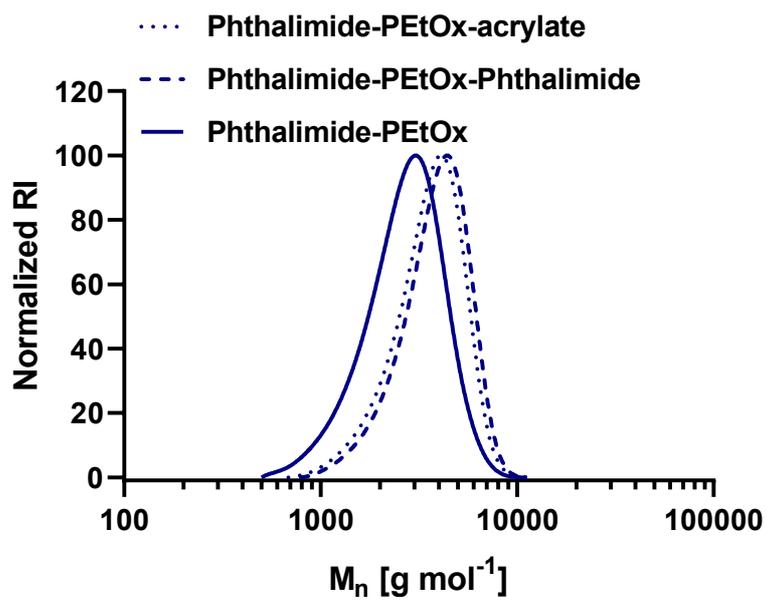


Figure S26. Molar mass distribution traces obtained from SEC measurements (DMAc, PS-cal.) of the telechelic PEtOx polymers.

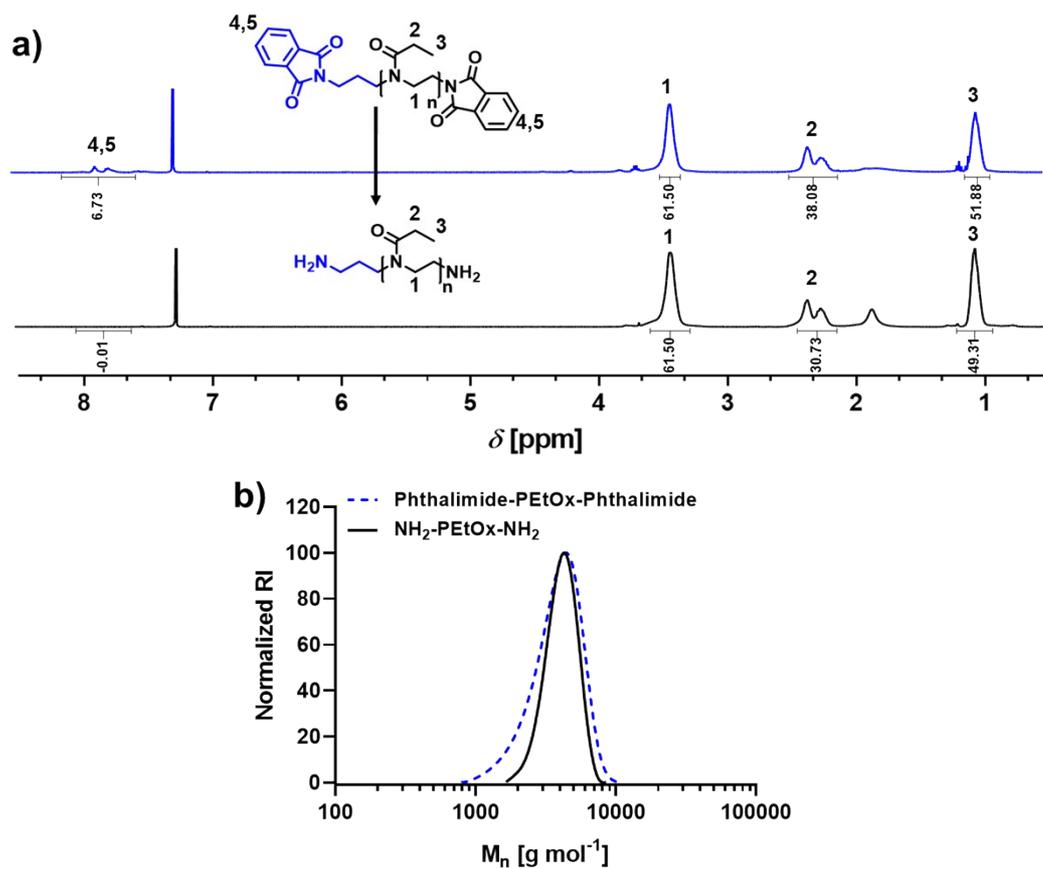


Figure S27. (a) ^1H NMR spectra of phthalimide α and ω functionalized PEtOx (400 MHz, CDCl_3), before (top - blue) and after deprotection (bottom - black). (b) Molar mass distribution traces obtained from SEC measurements (DMAc, PS-cal.) before (dashed blue line) and after deprotection (solid black line) of the phthalimide.