

Supporting Information

Living cationic ring-opening polymerization of 2-oxazolines initiated by rare-earth metal triflates

Fangyu Hu, Shoulei Xie, Liming Jiang,* and Zhiquan Shen

MOE Key Laboratory of Macromolecular Synthesis and Functionalization,
Department of Polymer Science and Engineering, Zhejiang University, Hangzhou
310027, China

Correspondence to: L. Jiang (E-mail: cejlm@zju.edu.cn)

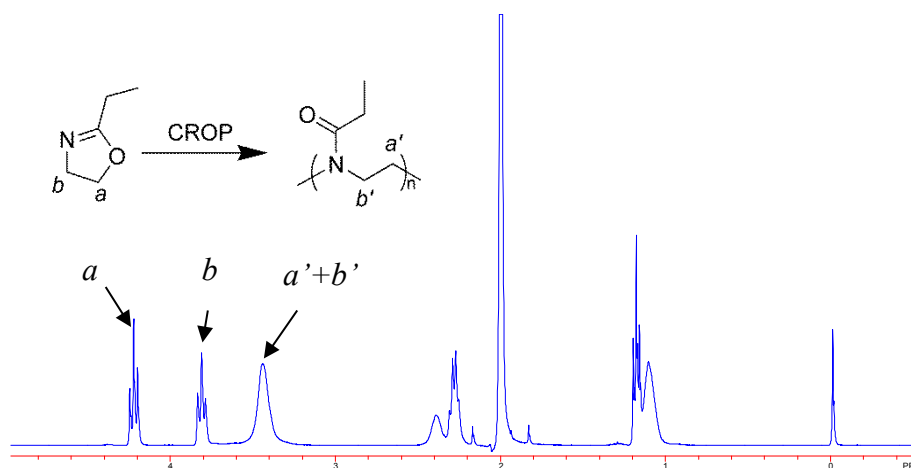


Figure S1. A typical ^1H NMR spectrum in CD_3Cl of samples collected from the EtOx polymerization mixture. The monomer conversion was determined by comparing the signal intensity from the released CH_2 ($a' + b'$) of polymer at 3.6–3.3 ppm with that from the remaining CH_2 ($a + b$) of unreacted monomer at 4.3 and 3.8 ppm.

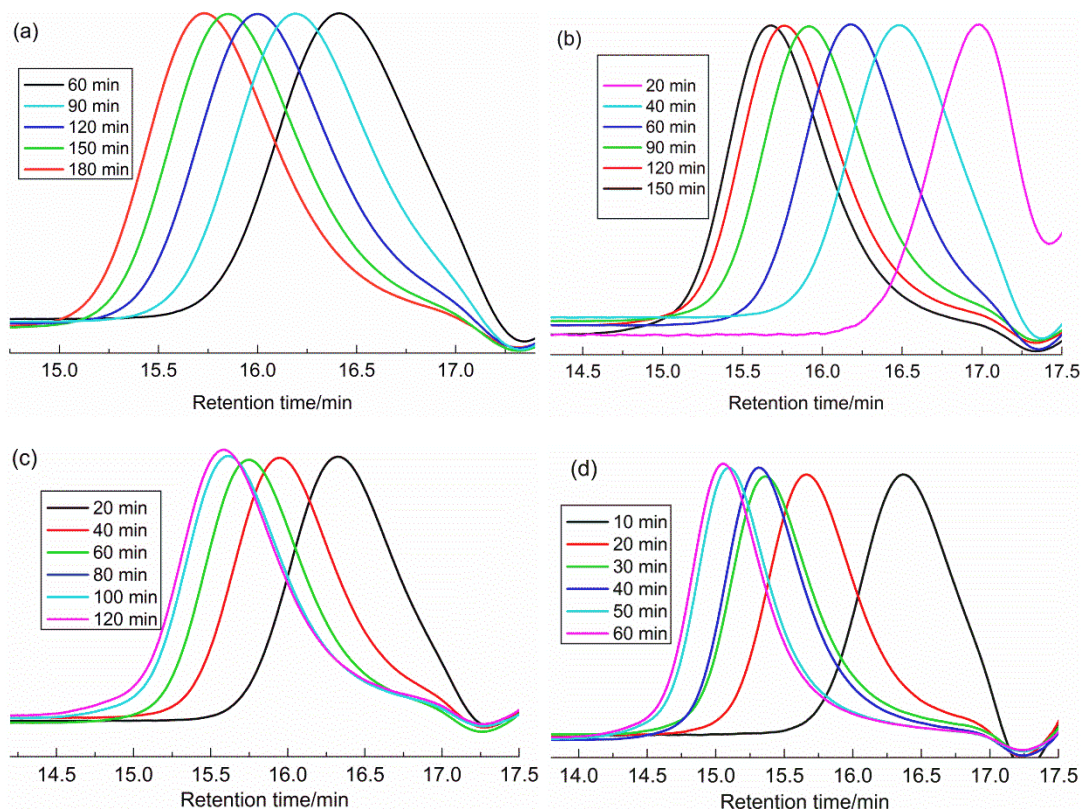


Figure S2. SEC traces of PEtOx samples collected periodically from the polymerization kinetic experiments, PMMA standard, DMF with 50 mM LiBr as the eluent. Polymerization conditions: $[\text{M}]_0 = 4.5 \text{ M}$, $[\text{M}]_0/[\text{I}]_0 = 100$, acetonitrile, using $\text{Sc}(\text{OTf})_3$ as the initiator; reaction temperature: (a) 70, (b) 80, (c) 90, and (d) 100°C.

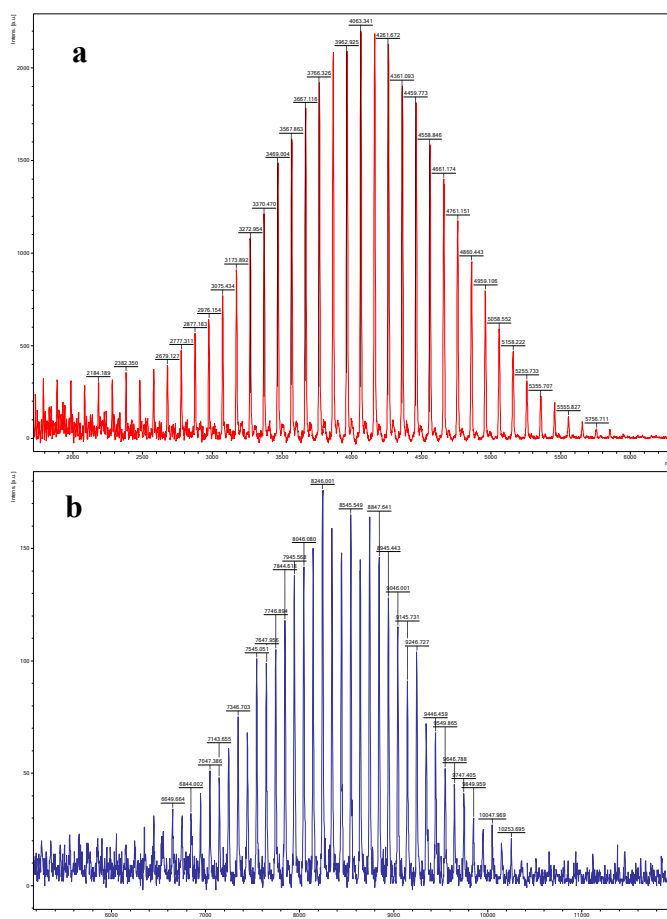


Figure S3. MALDI-TOF mass spectra of PEtOx with piperidine terminals. (a) $M_{n,SEC} = 5130$, PDI = 1.11; polymerization conditions: $[M]_0 = 4.5$ M, $[M]_0/[I]_0 = 100$, Sc(OTf)₃, CH₃CN, 80°C, 90 min. (b) $M_{n,SEC} = 9810$, PDI = 1.15; polymerization conditions: $[M]_0 = 4.5$ M, $[M]_0/[I]_0 = 200$, Sc(OTf)₃, CH₃CN, 80°C, 120 min. SEC: PMMA standard, using DMF containing 50 mM LiBr as the eluent.

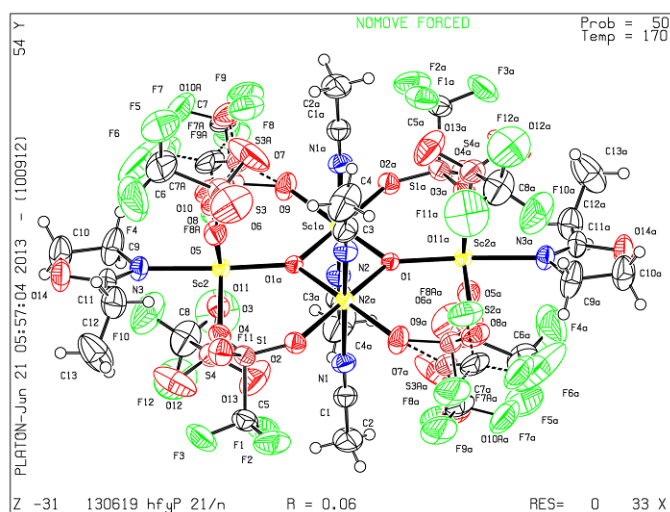


Figure S4. The single crystal X-ray diffraction of Sc(OTf)₃-EtOx complex formed in CH₃CN.

Crystal data. $C_{26}H_{30}F_{24}N_6O_{28}S_8Sc_4$, $M = 1766.88$, monoclinic, $a = 15.0544(11)$, $b = 12.7946(7)$, $c = 17.315(1) \text{ \AA}$, $U = 3214.4(3) \text{ \AA}^3$, $\alpha = 90$, $\beta = 105.464(7)$, $\gamma = 90$, $T = 170 \text{ K}$, space group $P 21/n$, $Z = 2$, 5867 reflections measured.

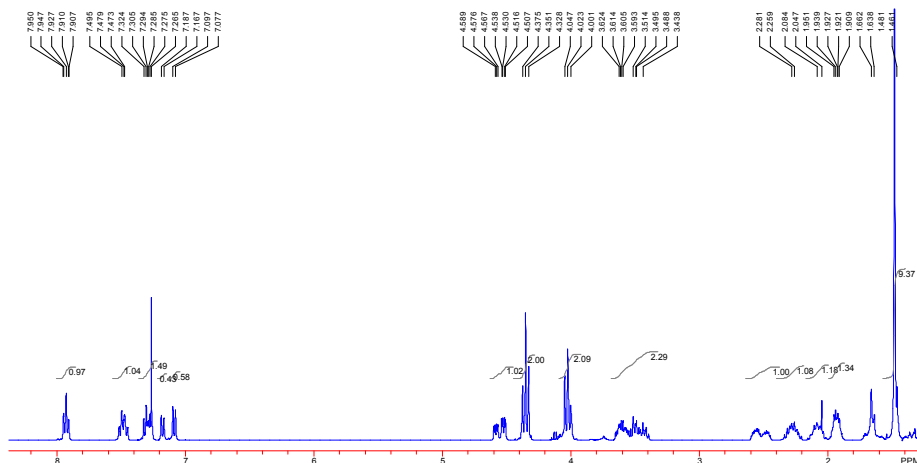


Figure S5. 1H NMR spectrum of **ProPhOx-1**.

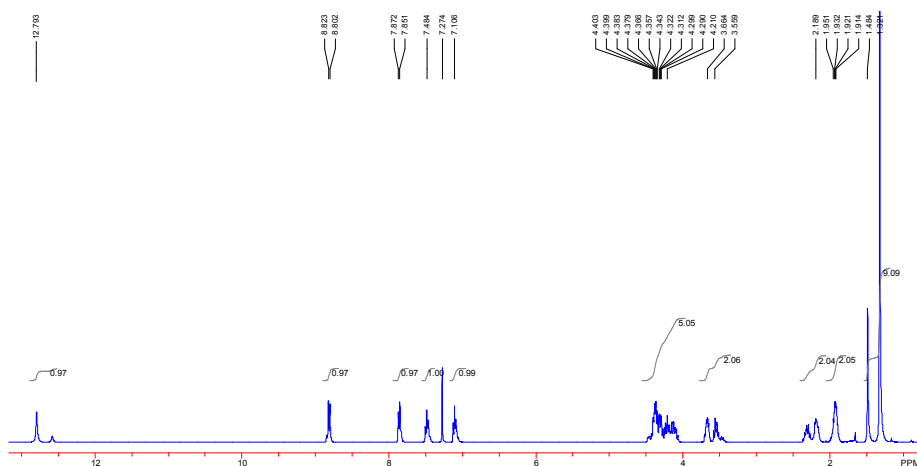


Figure S6. 1H NMR spectrum of **ProPhOx-2**.

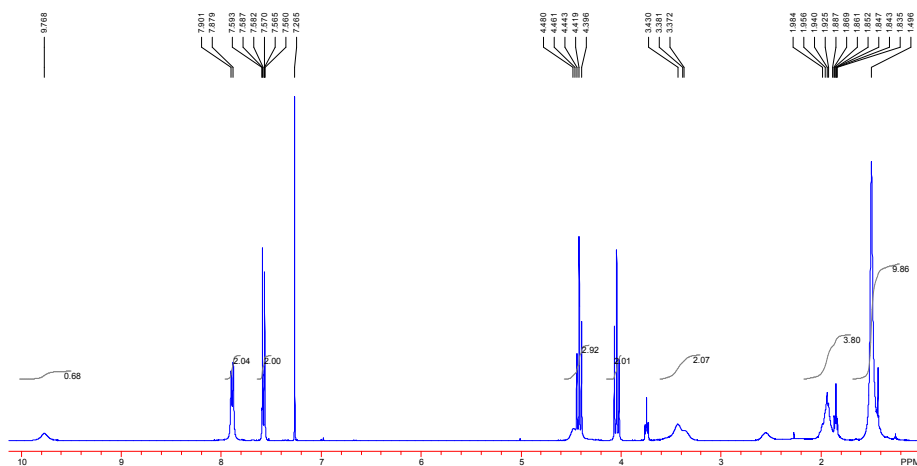


Figure S7. 1H NMR spectrum of **ProPhOx-3**.

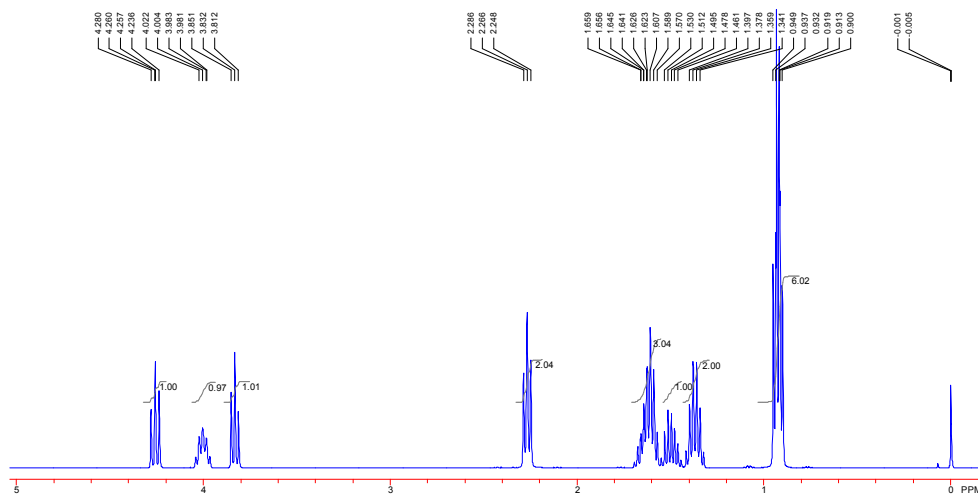


Figure S8. ¹H NMR spectrum of **4-EtBuOx**.

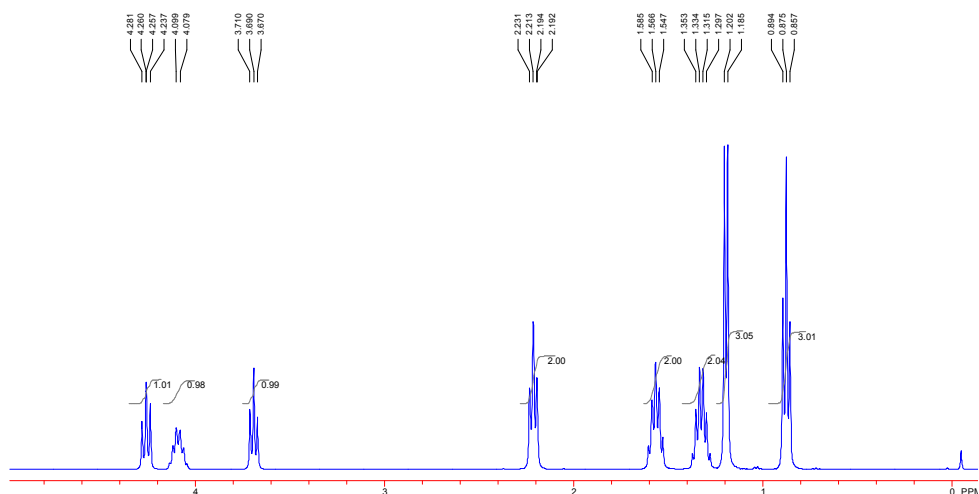


Figure S9. ¹H NMR spectrum of **4-MeBuOx**.

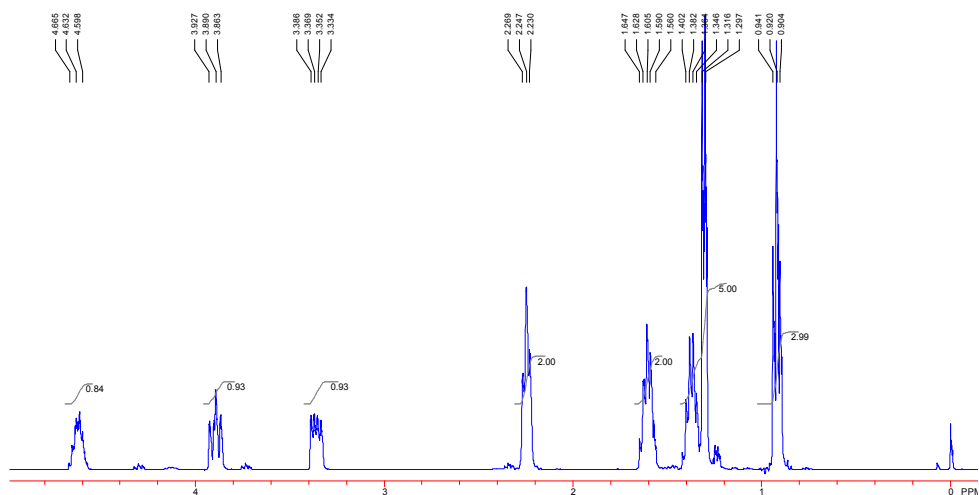


Figure S10. ¹H NMR spectrum of **5-MeBuOx**.

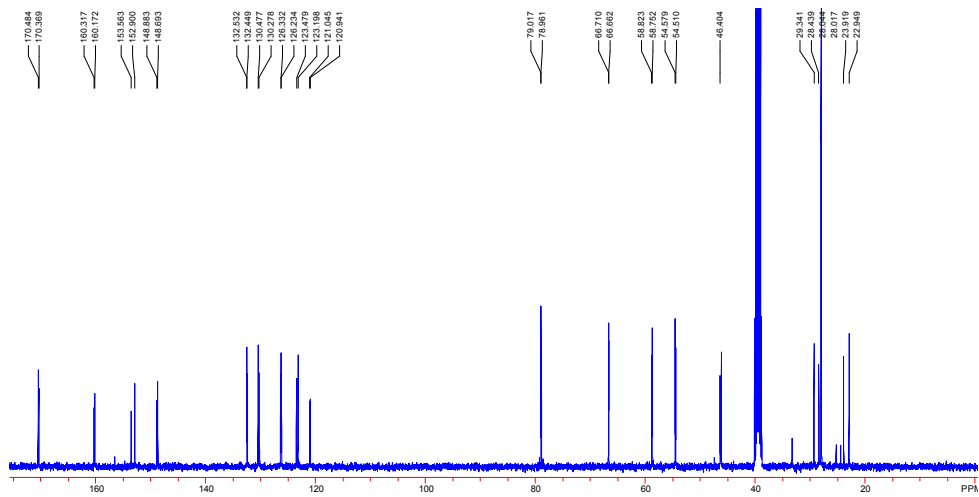


Figure S11. ^{13}C NMR spectrum of **ProPhOx-1**.

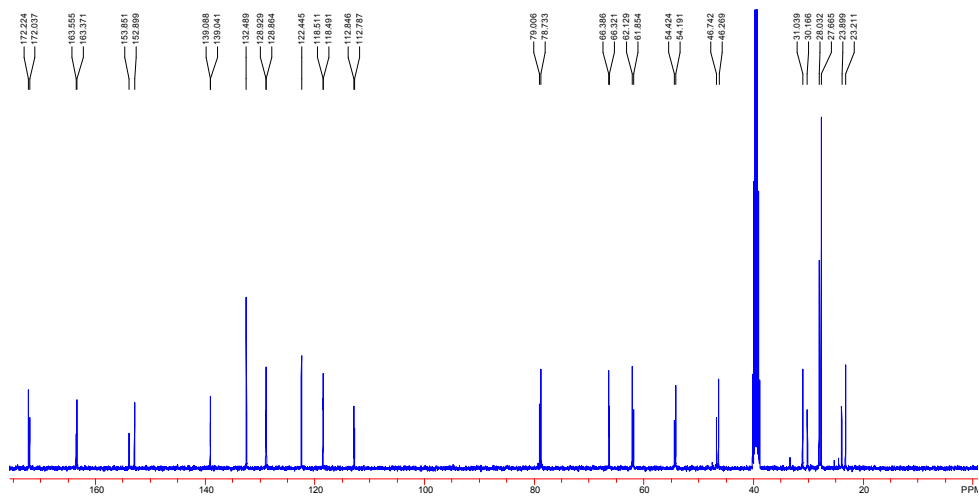


Figure S12. ^{13}C NMR spectrum of **ProPhOx-2**.

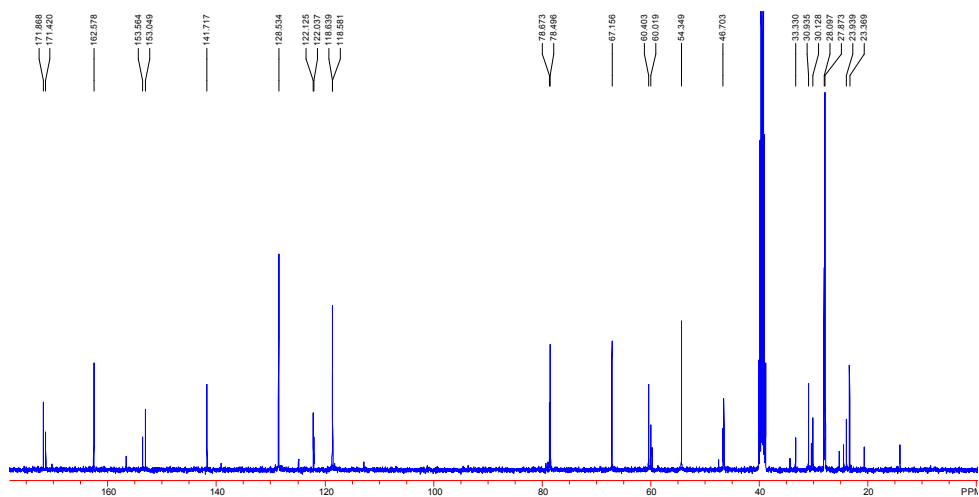


Figure S13. ^{13}C NMR spectrum of **ProPhOx-3**.

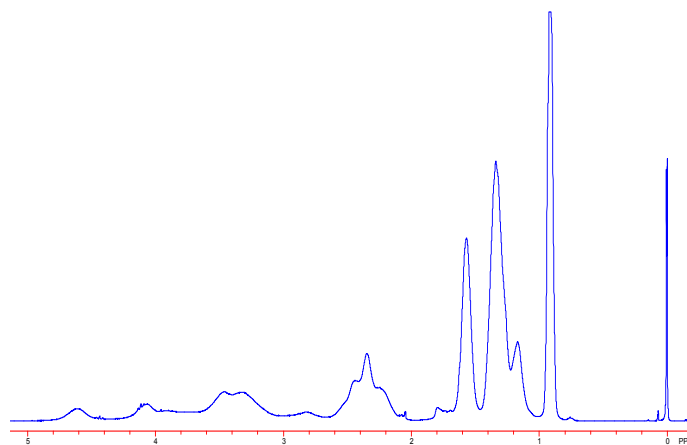


Figure S14. ^1H NMR spectrum of poly(4-MeBuOx).

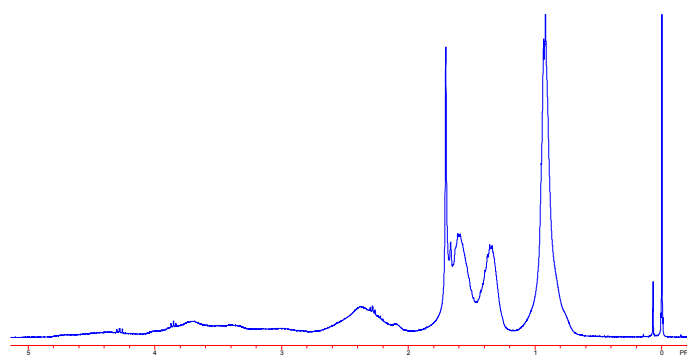


Figure S15. ^1H NMR spectrum of poly(4-EtBuOx).

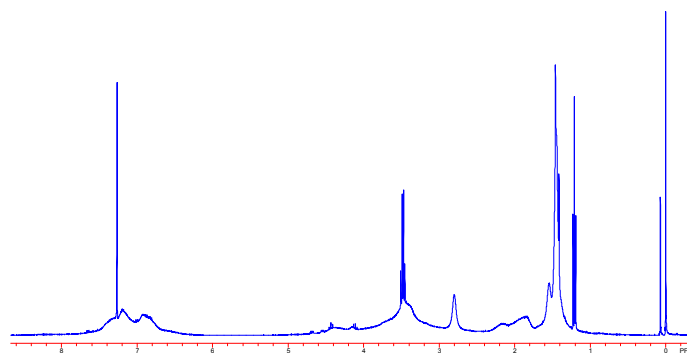


Figure S16. ^1H NMR spectrum of poly(ProPhOx-1).

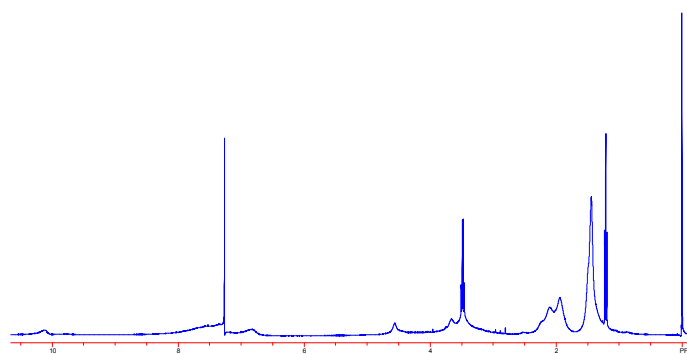


Figure S17. ^1H NMR spectrum of P(ProPhOx-3).

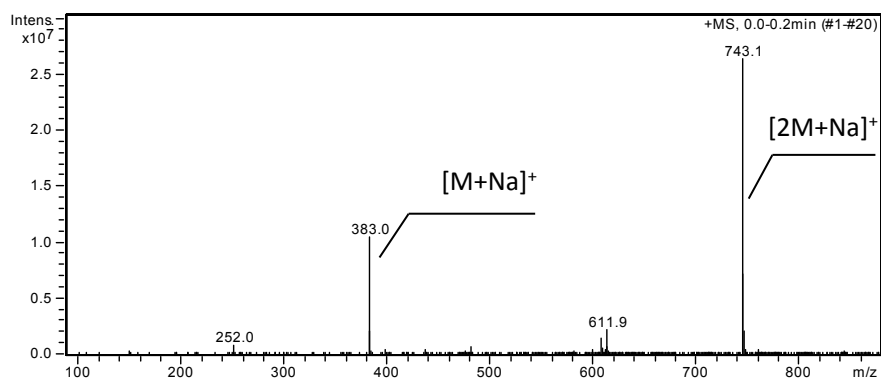


Figure S18. ESI-MS spectrum of **ProPhOx-1**.

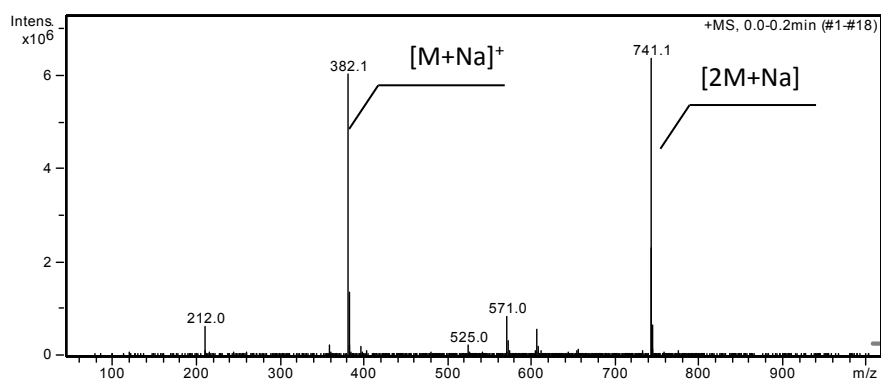


Figure S19. ESI-MS spectrum of **ProPhOx-2**.

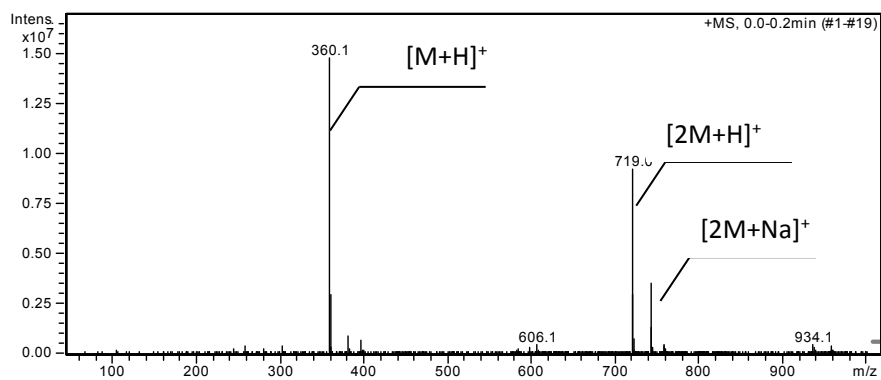


Figure S20. ESI-MS spectrum of **ProPhOx-3**.