



## Supporting Information

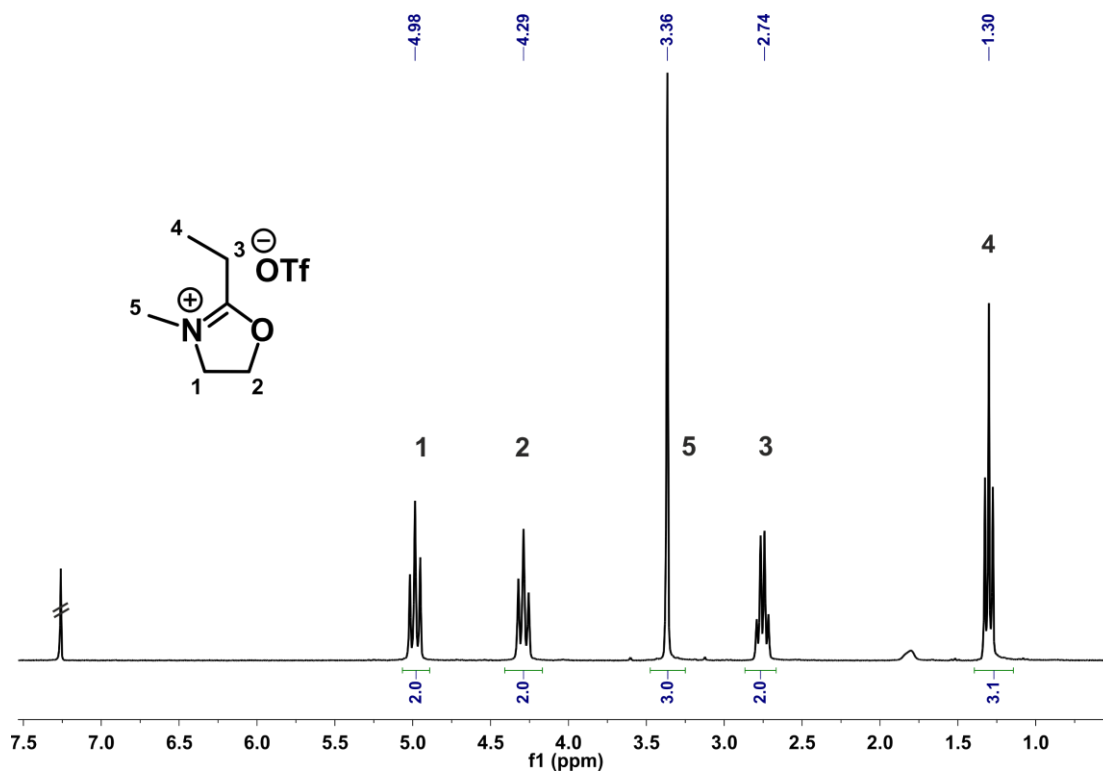
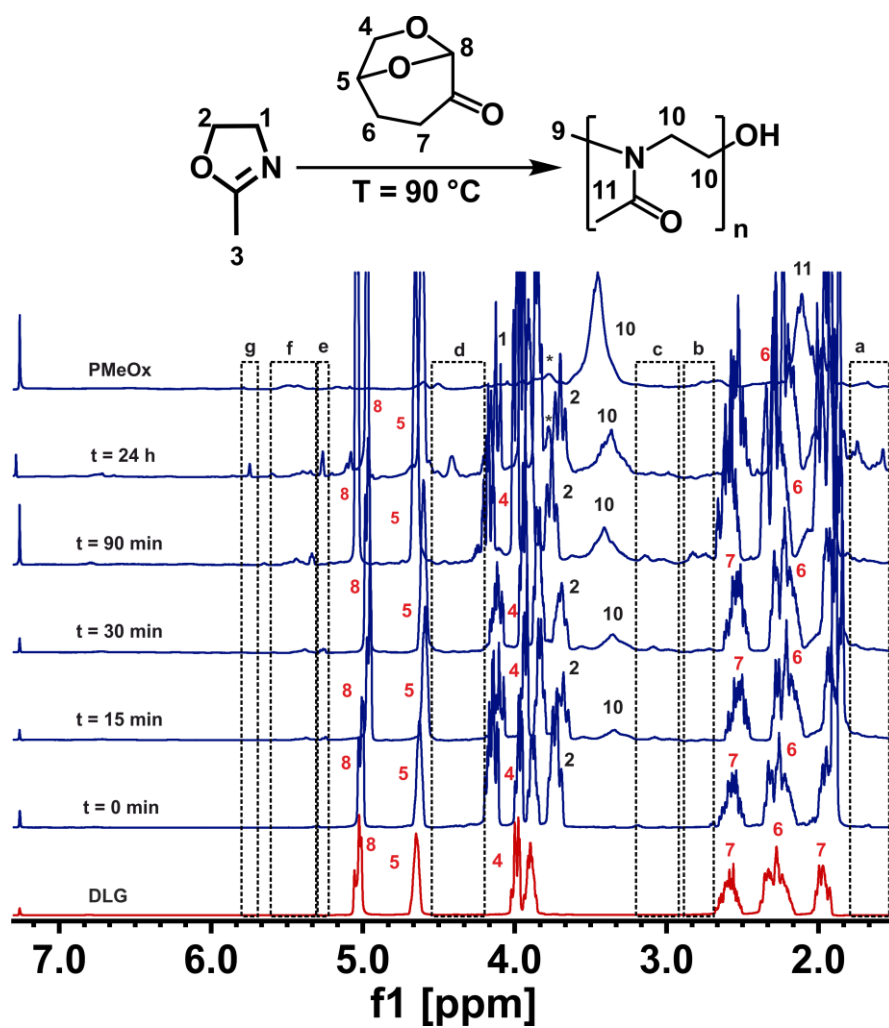
for

### Investigation of cationic ring-opening polymerization of 2-oxazolines in the “green” solvent dihydrolevoglucosenone

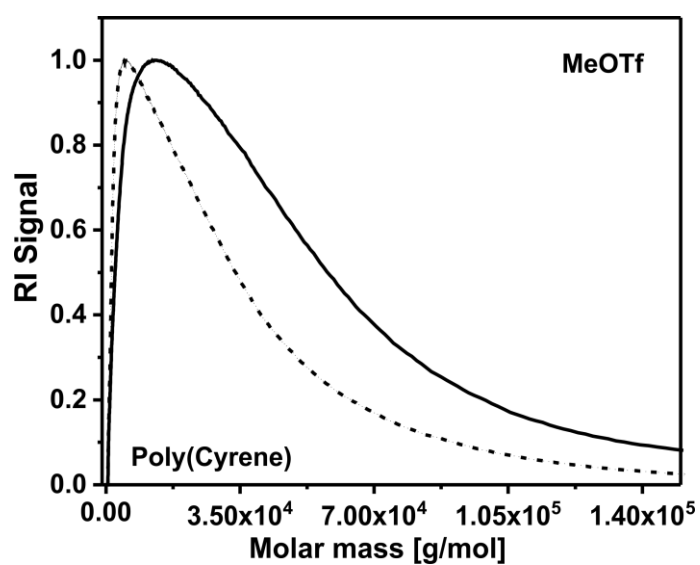
Solomiia Borova and Robert Luxenhofer

*Beilstein J. Org. Chem.* **2023**, *19*, 217–230. doi:10.3762/bjoc.19.21

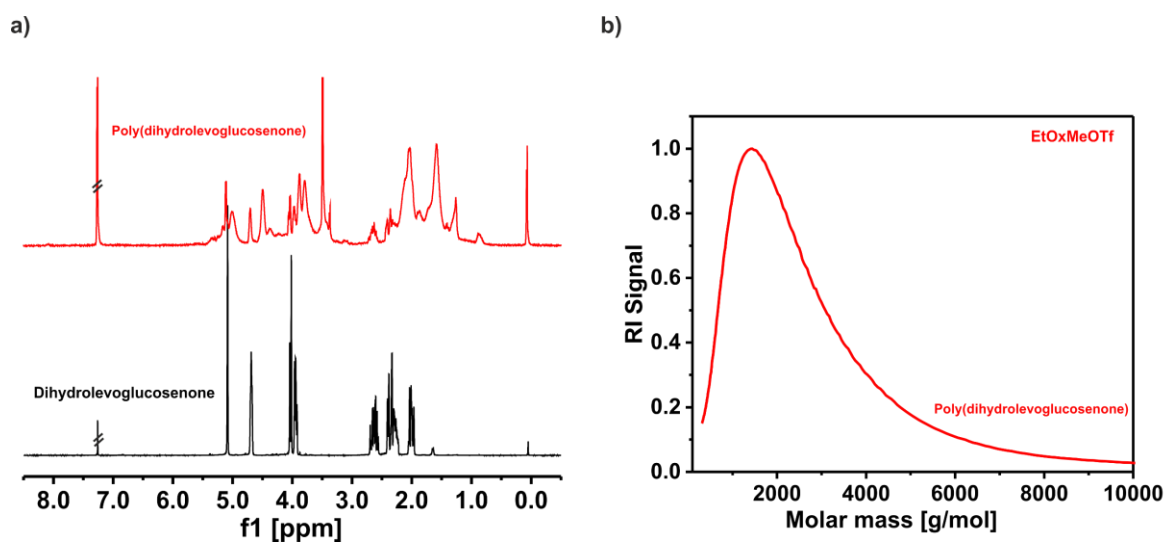
## Additional figures and spectra



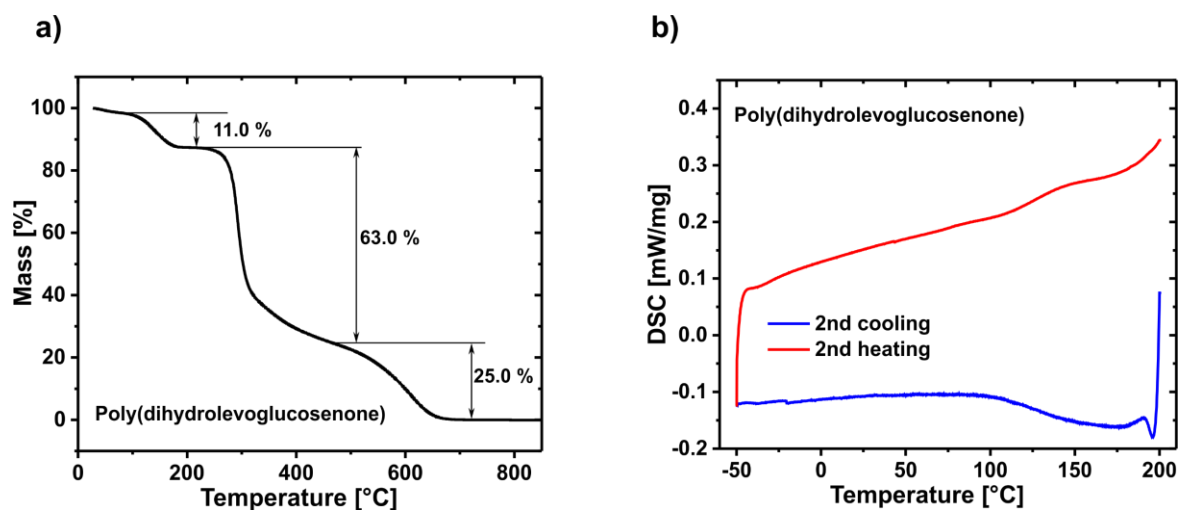
**Figure S2.**  $^1\text{H-NMR}$  spectrum (300MHz,  $\text{CDCl}_3$ ) of 2-ethyl-3-methyloxazoliniumtriflate after purification.



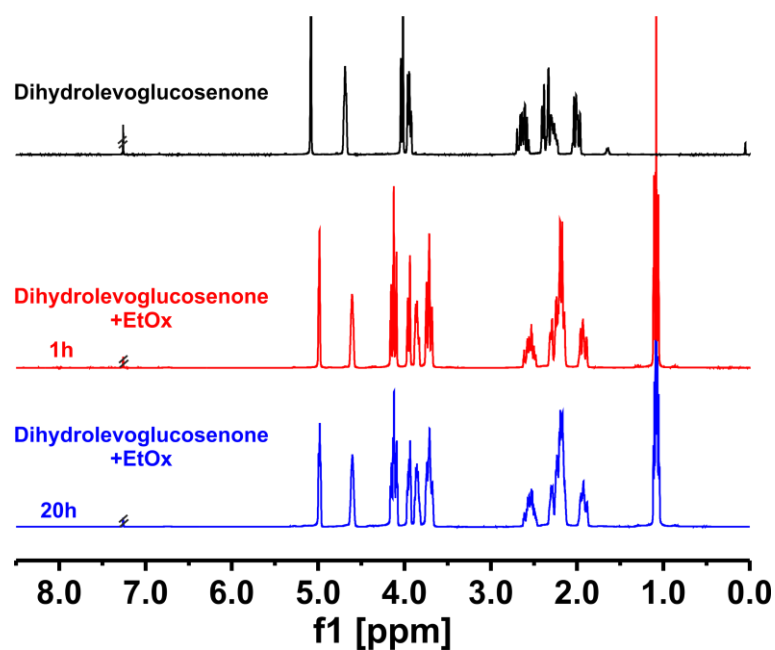
**Figure S3.** HFIP SEC traces of the product obtained after incubation of dihydrolevoglucosenone with MeOTf at 90 °C.



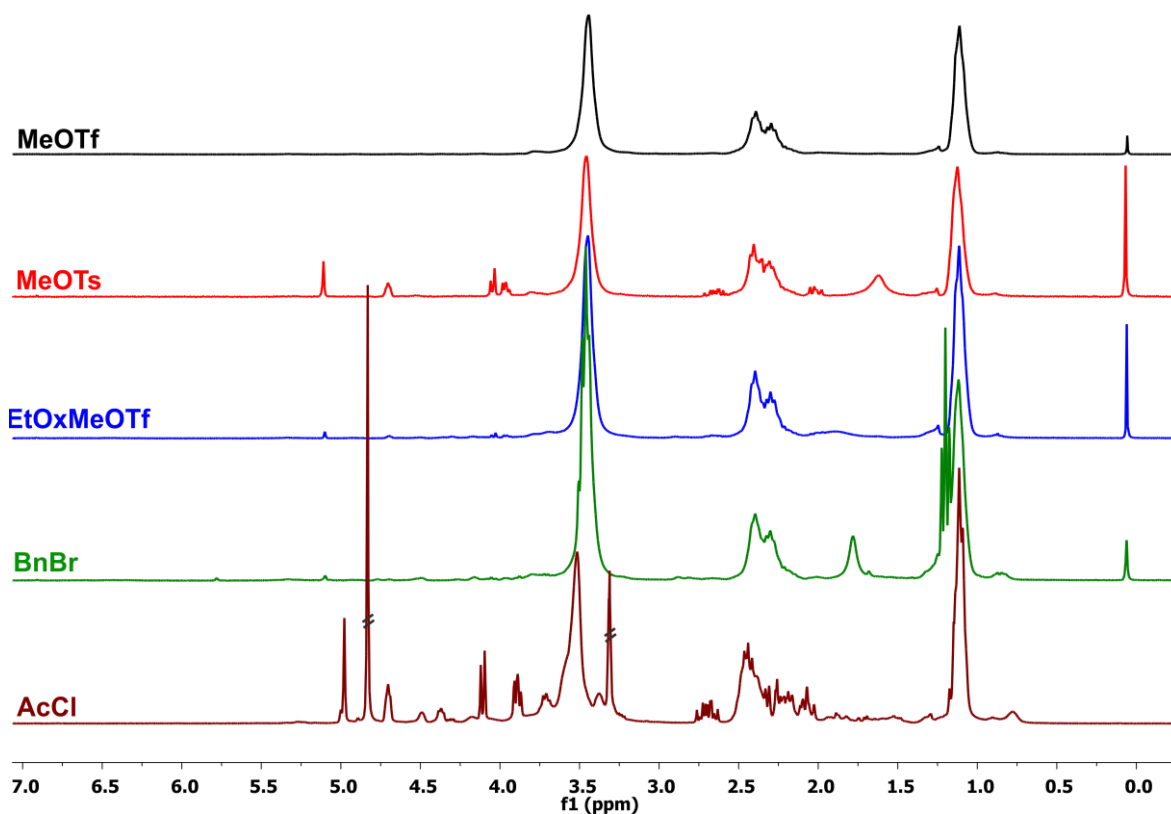
**Figure S4.**  $^1\text{H}$  NMR spectra ( $\text{CDCl}_3$ , 300 MHz) obtained after incubation of dihydrolevoglucosenone with EtOxMeOTf at 0°C with warming up to room temperature for 24 h (red). b) SEC trace of the resulting polymer after incubation of dihydrolevoglucosenone with EtOxMeOTf.



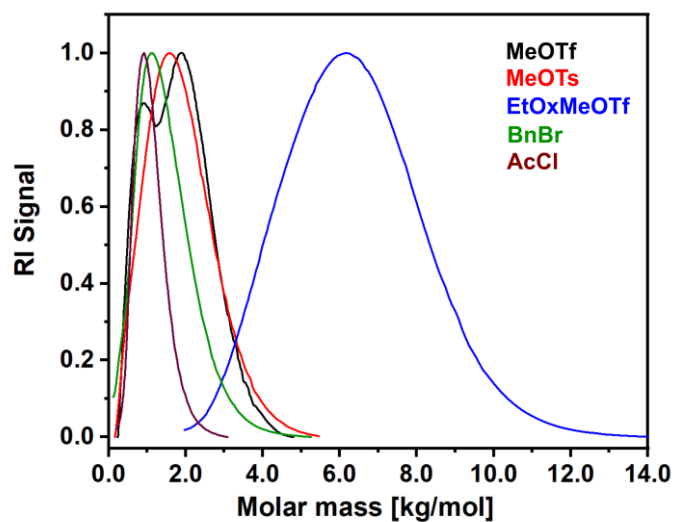
**Figure S5.** a) Thermogravimetric analysis (TGA) and b) differential scanning calorimetry (DSC) second heating curve (heating rate:  $10\text{ K min}^{-1}$ ) of the poly(dihydrolevoglucosenone) obtained after incubation of dihydrolevoglucosenone with MeOTf at  $90\text{ }^{\circ}\text{C}$  for 5 minutes.



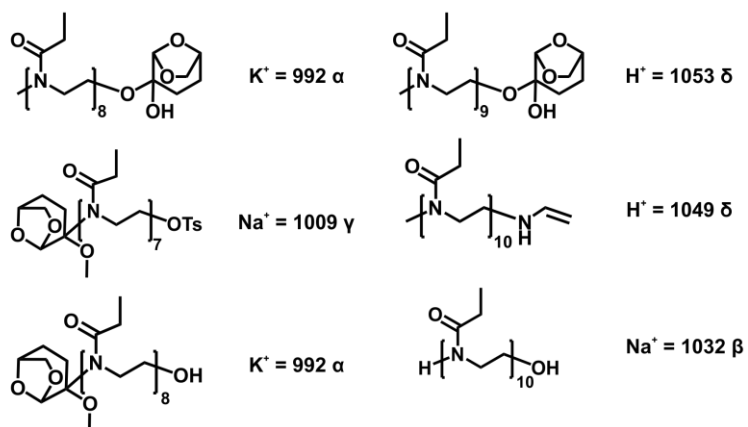
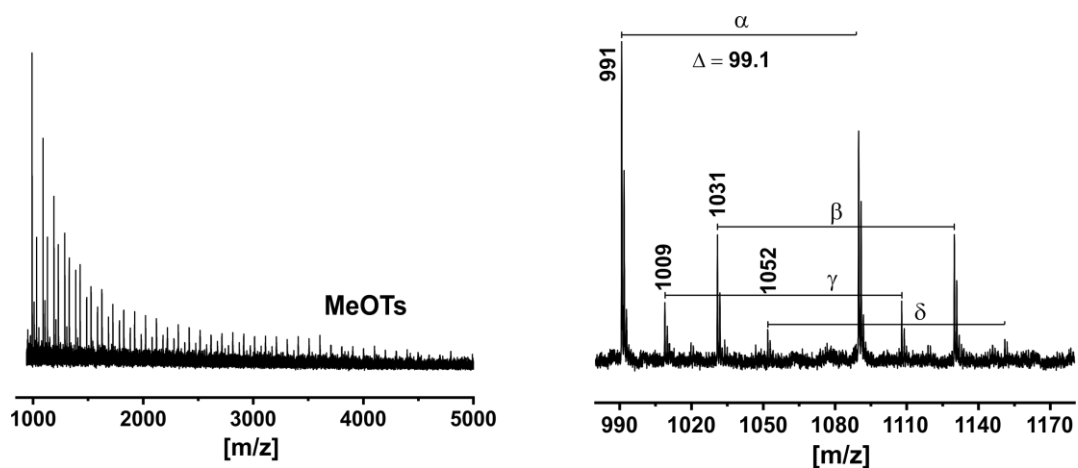
**Figure S6.**  $^1\text{H}$  NMR (CDCl<sub>3</sub>, 300 MHz) spectra obtained during the incubation of dihydrolevoglucosenone with 2-ethyl-2-oxazoline at  $90\text{ }^{\circ}\text{C}$  up to 20 h.



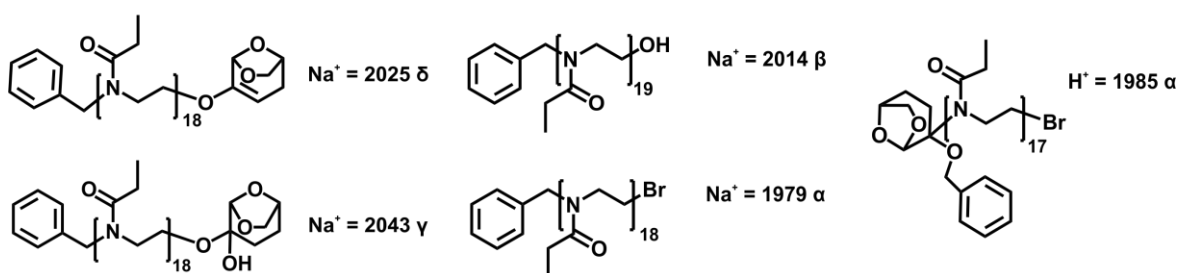
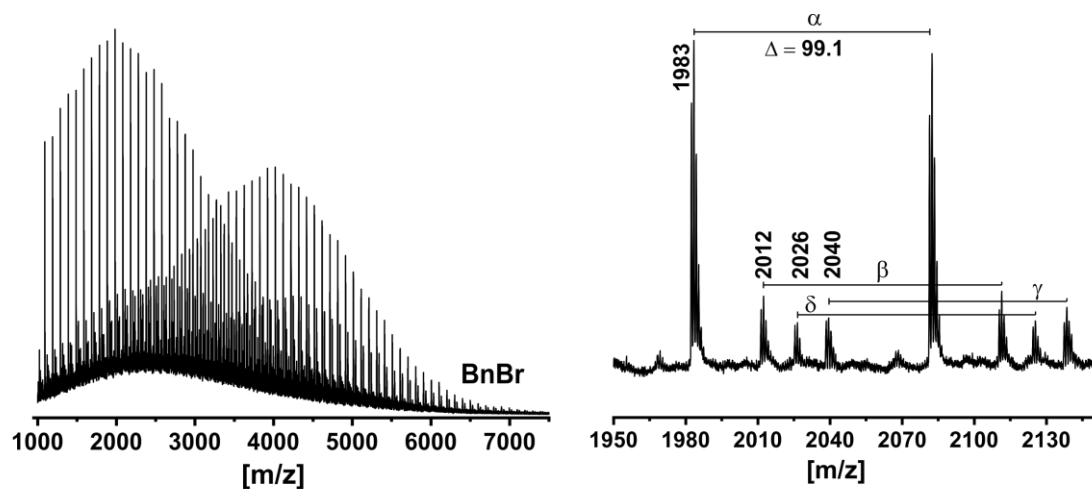
**Figure S7.**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz) spectra of poly(2-ethyl-2-oxazoline) after precipitation using methyl triflate (black), methyl tosylate (red), 2-ethyl-3-methyl-2-oxazoline triflate (blue), benzyl bromide (green) and acyl chloride (dark red) as initiator in dihydrolevoglucosenone.



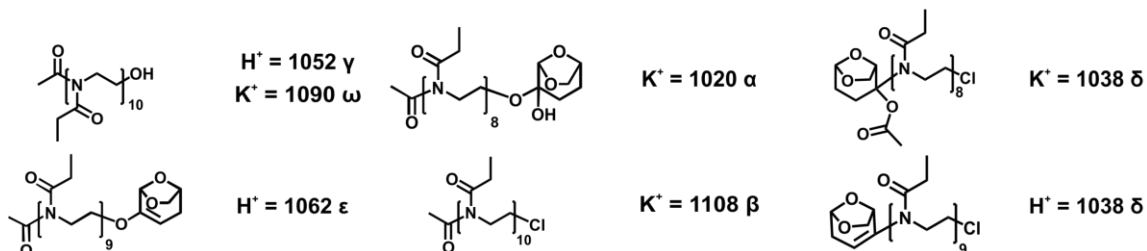
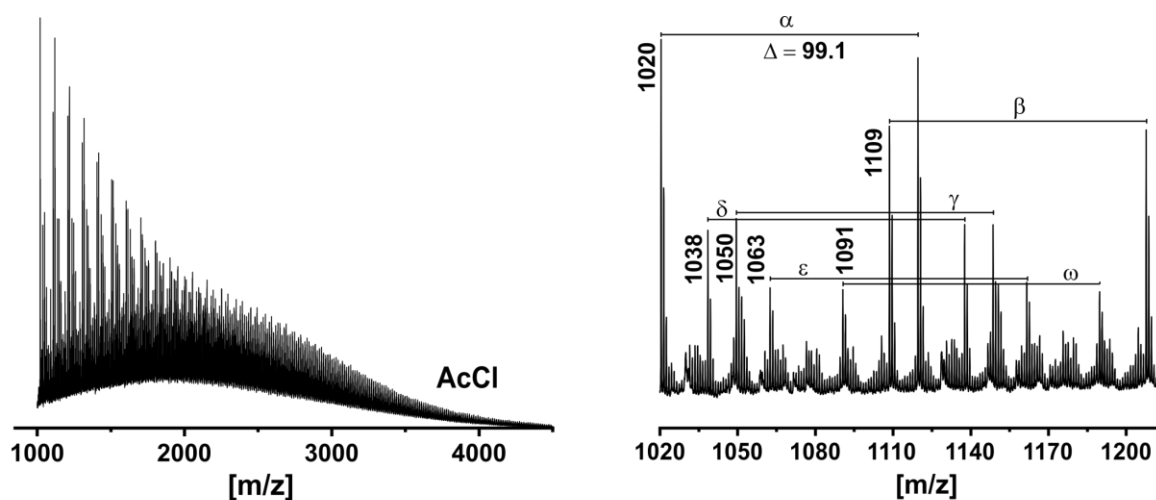
**Figure S8.** HFIP SEC traces of the precipitated poly(2-ethyl-2-oxazoline)s obtained in dihydrolevoglucosenone using methyl triflate (black), methyl tosylate (red), 2-ethyl-3-methyl-2-oxazoline triflate (blue), benzyl bromide (green) and acyl chloride (dark red) as initiator.



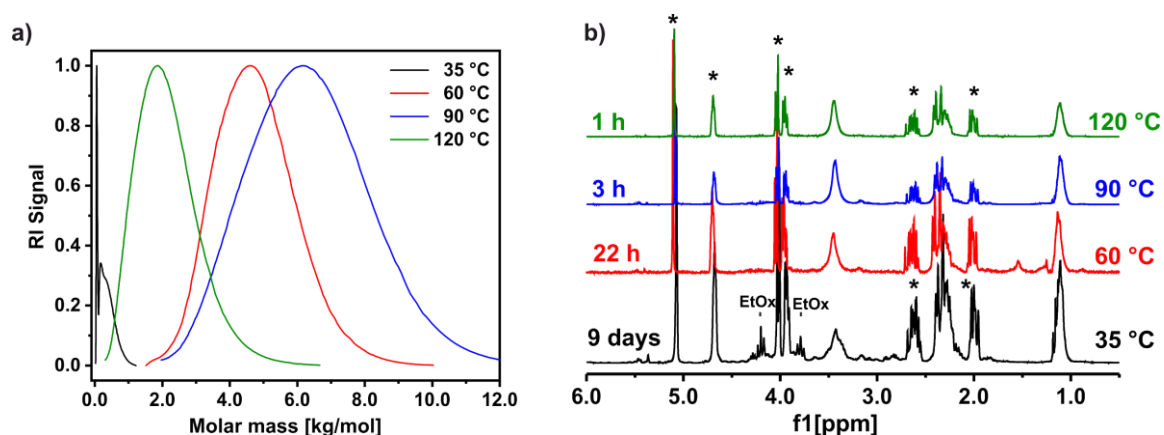
**FigureS9.** Maldi-ToF mass spectrometry analysis of the poly(2-ethyl-2-oxazoline) initiated with methyltosylate in dihydrolevoglucosenone at 90 °C.



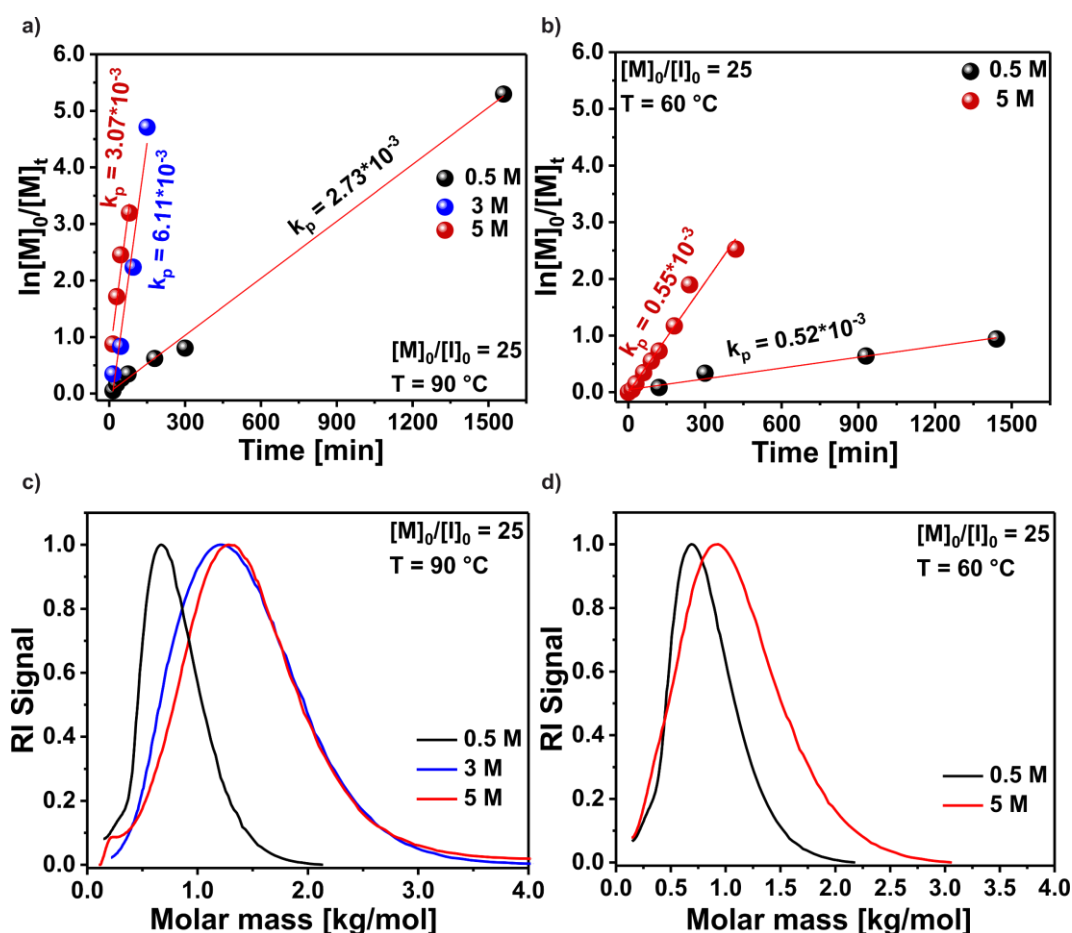
**Figure S10.** Maldi-ToF mass spectrometry analysis of the poly(2-ethyl-2-oxazoline) initiated with benzyl bromide in dihydrolevoglucosenone at 90 °C.



**Figure S11.** Maldi-ToF mass spectrometry analysis of the poly(2-ethyl-2-oxazoline) initiated with acetyl chloride in dihydrolevoglucosenone at 90 °C.

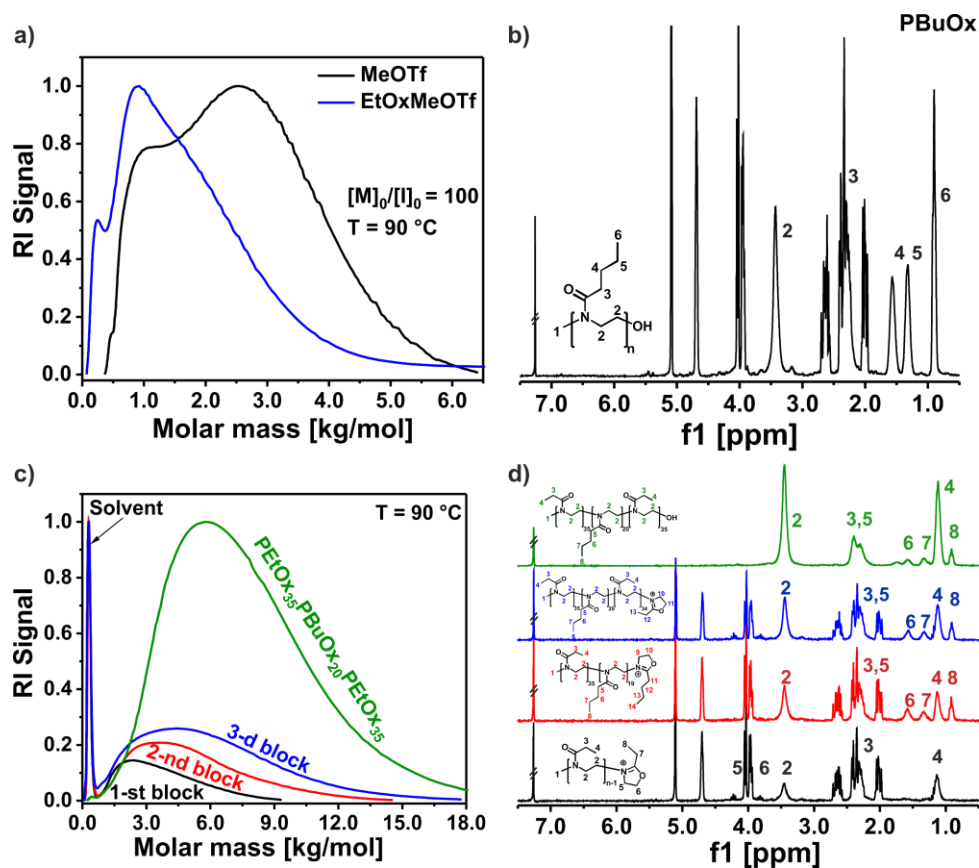


**Figure S12.** Investigation of the effect of incubation temperature on 2-ethyl-2-oxazoline polymerization. (a) HFIP SEC traces of the resulting polymers after precipitation and dialysis; (b) <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) analysis of the resulting poly(2-ethyl-2-oxazoline) polymer solution after complete monomer conversion at 35 °C (black), 60 °C (red), 90 °C (blue) and 120 °C (green). The peaks marked with asterisks are from the residual solvent signals.



**Figure S13.** Kinetic details obtained by NMR for the polymerization with different monomer concentration performed at 90 °C (a) and at 60 °C (b) and the SEC traces of the resulting polymers performed at 90 °C (c) and at 60 °C (d).





**Figure S14.** a) SEC traces of the resulting poly(2-butyl-2-oxatoline) obtained after initiation with MeOTf and EtOxMeOTf at  $90^\circ\text{C}$  in dihydrolevoglucosenone. b)  $^1\text{H}$  NMR spectra of the resulting polymerization mixture during the BuOx polymerization. c) GPC traces of the resulting block co-polymer of EtOx and BuOx obtained after initiation with EtOxMeOTf at  $90^\circ\text{C}$  in dihydrolevoglucosenone. d)  $^1\text{H}$  NMR traces of the resulting block co-polymer of EtOx and BuOx obtained after initiation with EtOxMeOTf at  $90^\circ\text{C}$  in dihydrolevoglucosenone.