Electronic Supplementary Material (ESI) for RSC Advances.

Supporting information for

Maleimide End-Functionalized Poly(2-oxazoline)s by the Functional Initiator Route: Synthesis and (Bio)conjugation

*Gabriela Gil Alvaradejo,[a,b] Mathias Glassner,[c] Richard Hoogenboom,[c] Guillaume Delaittre[a,b]**

Characterization Data for the New Initiators

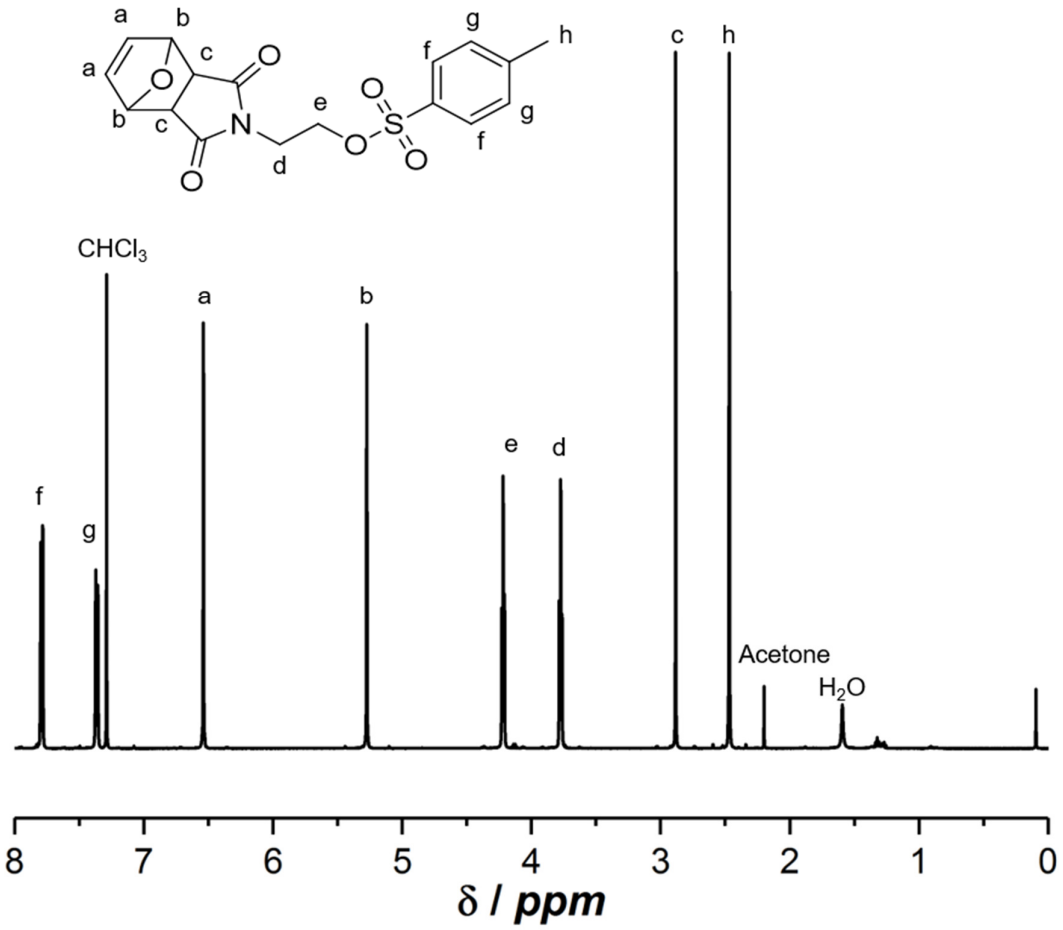

Figure S1. ^{1}H NMR spectrum of **FurMalTos** 3 in $CDCl_3$.

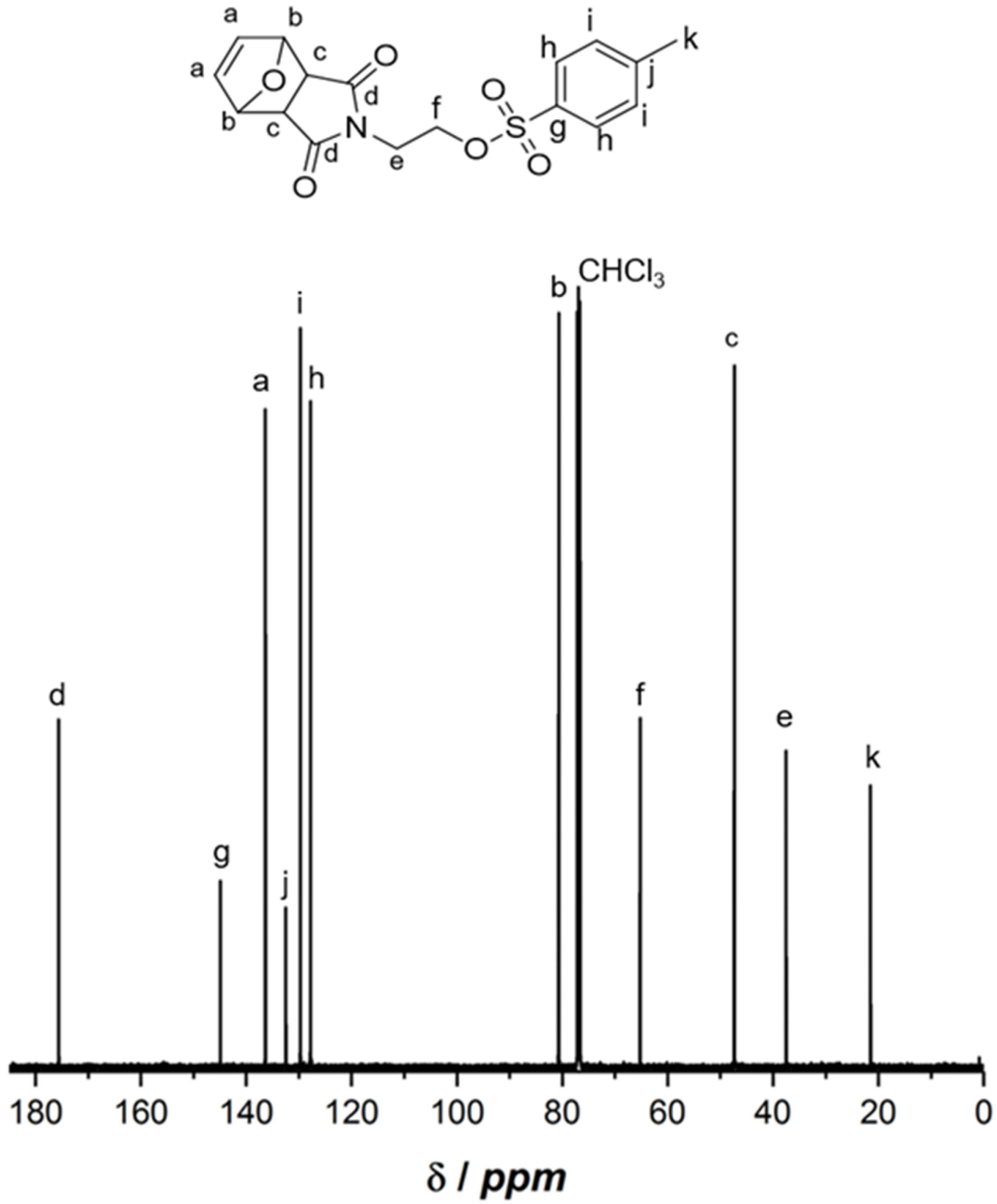

Figure S2. ^{13}C NMR spectrum of **FurMalTos 3** in $CDCl_3$.

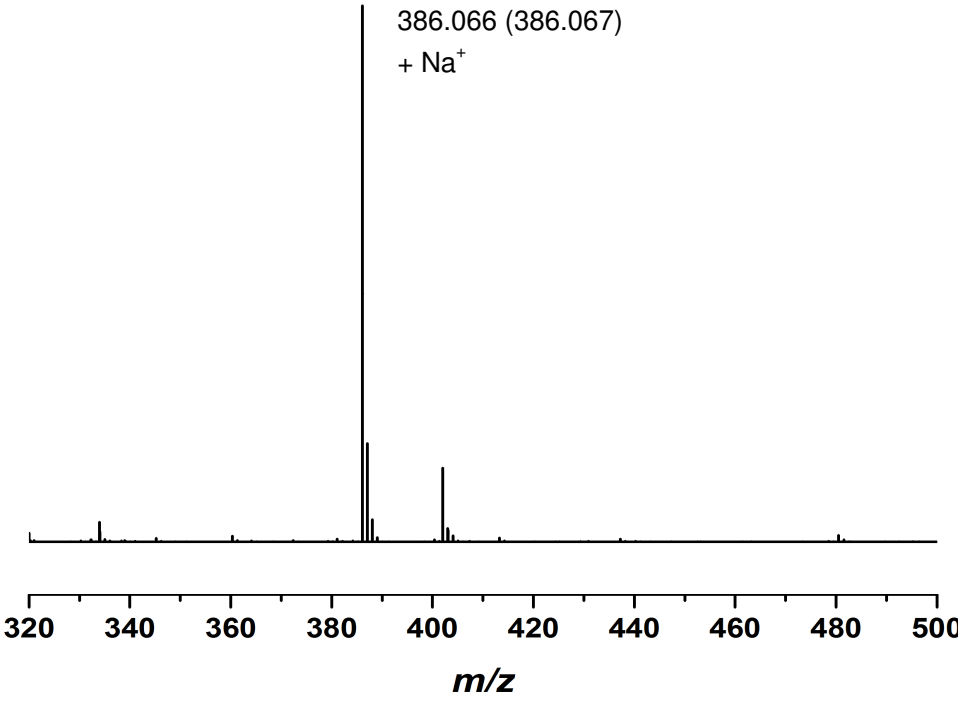

Figure S3. ESI mass spectrum of **FurMalTos 3**.

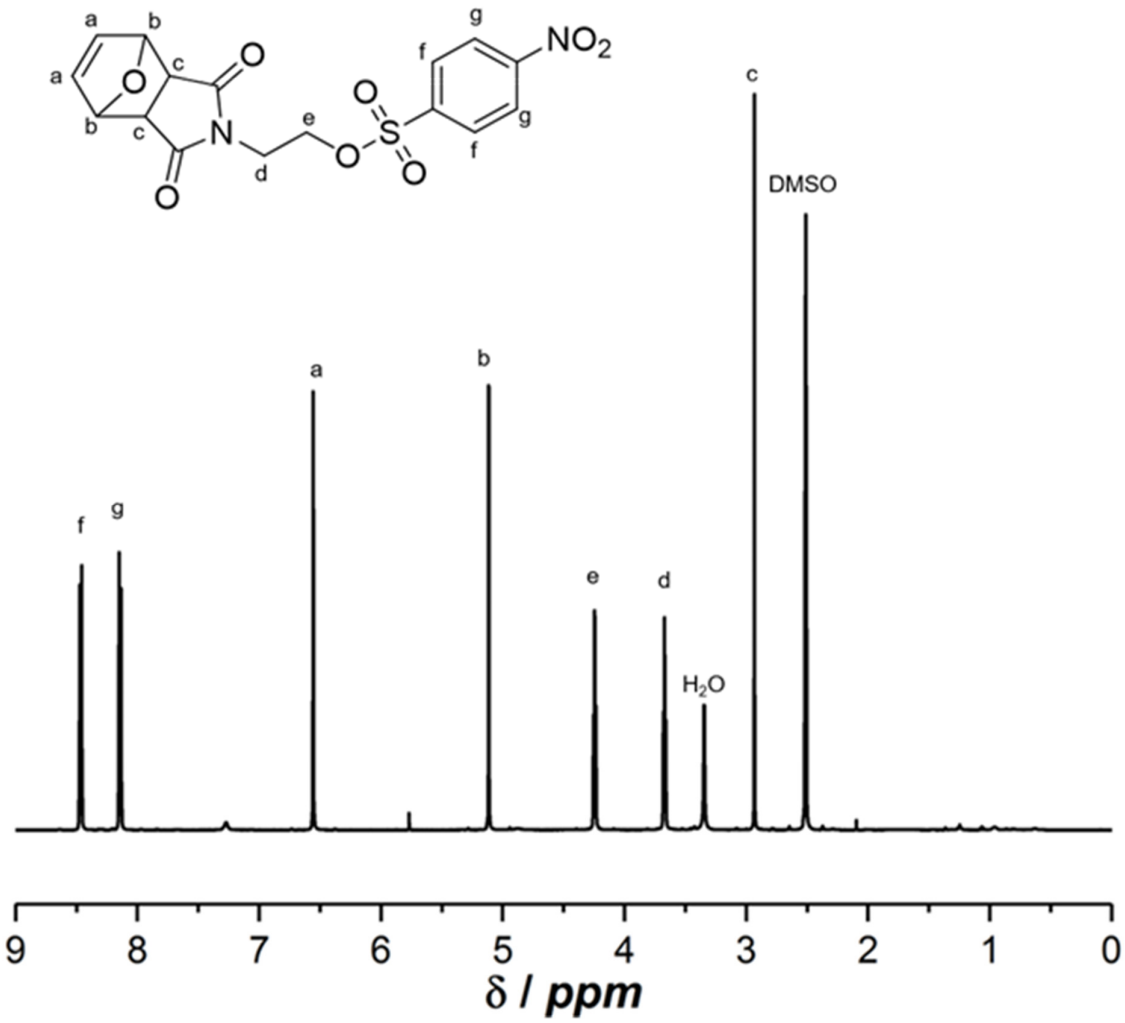

Figure S4. ^{1}H NMR spectrum of **FurMalNos 4** in DMSO-*d6*.

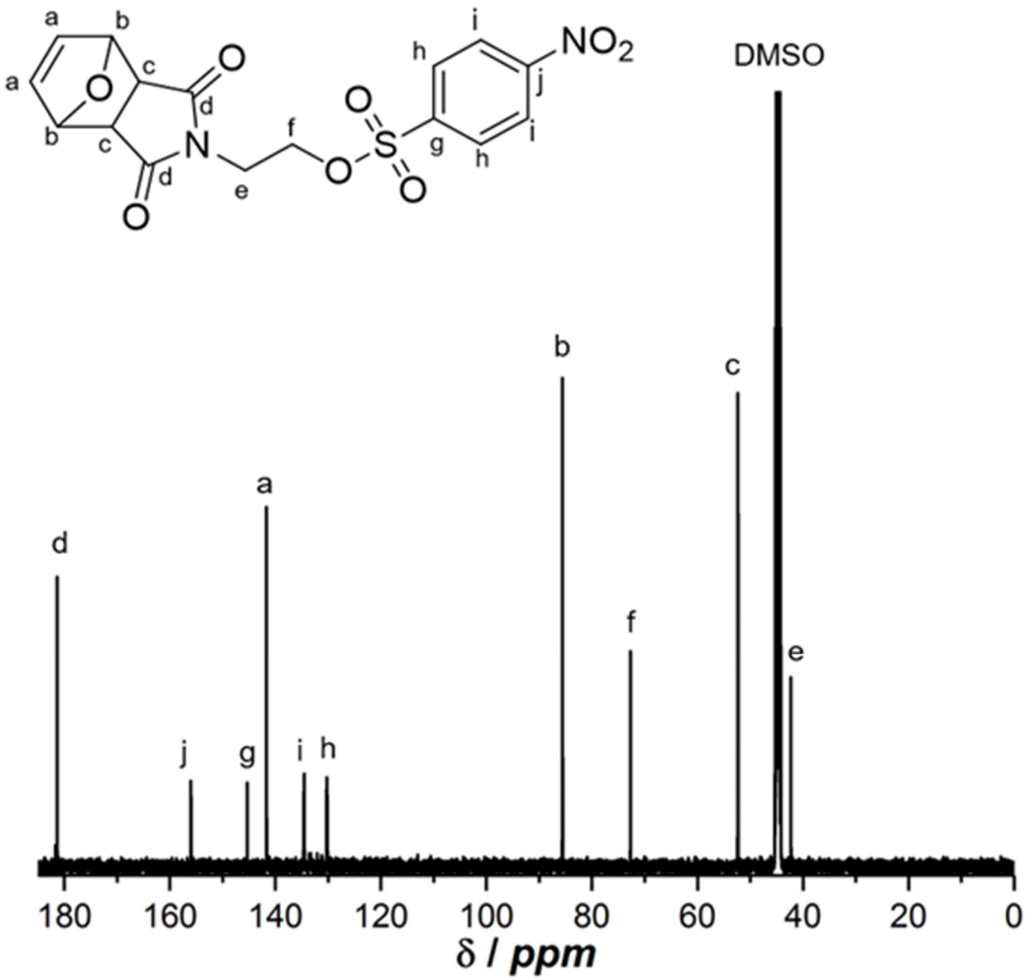

Figure S5. ^{13}C NMR spectrum of **FurMalNos 4** in DMSO-*d6*.

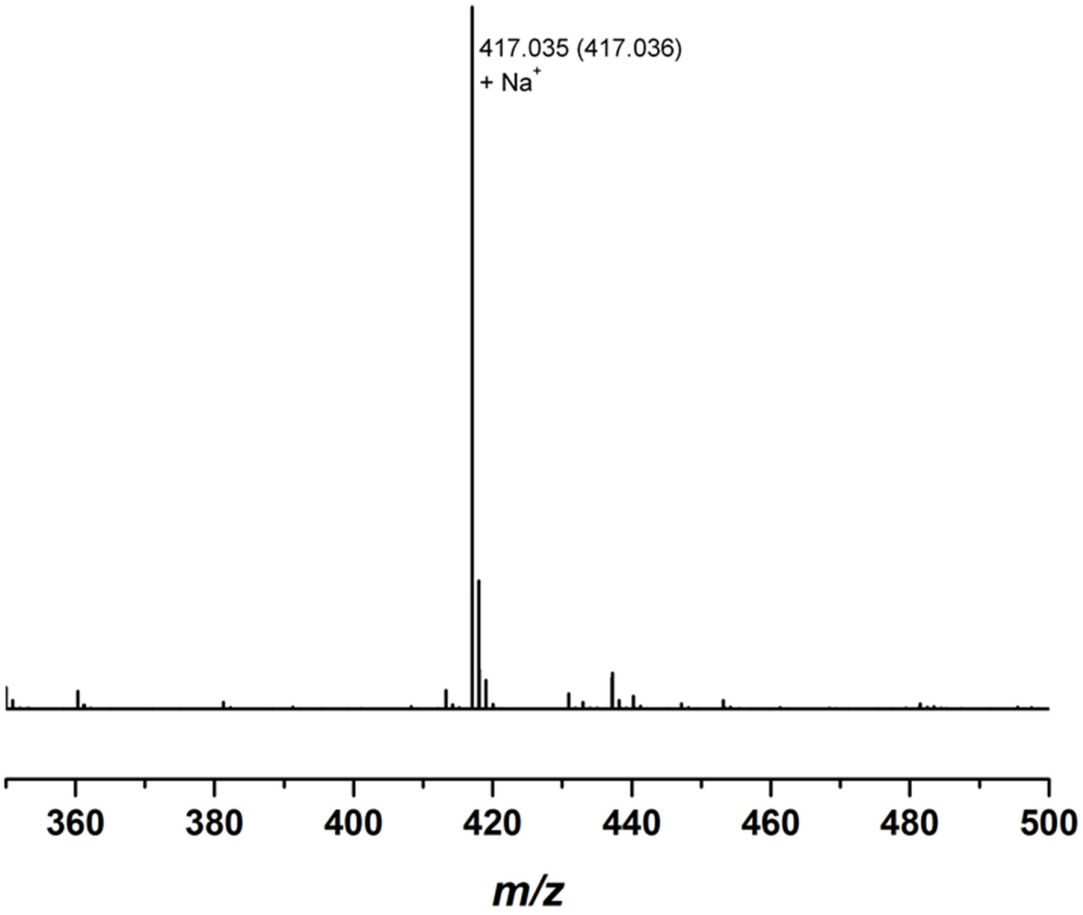

Figure S6. ESI mass spectrum of **FurMalNos 4**.

Initial Polymerization Trials

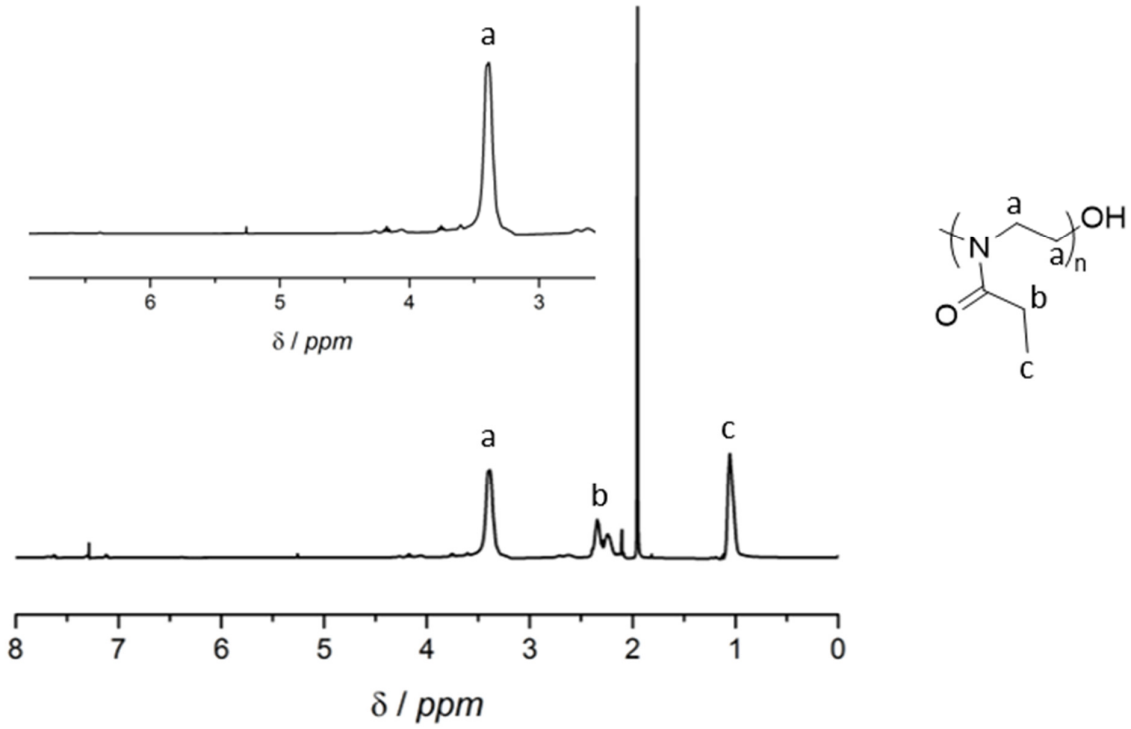

Figure S7. ^{1}H NMR spectrum of crude polymer mixture after microwave-assisted polymerization of 2-ethyl-2-oxazoline using [EtOx]/[**FurMalTos 3**] = 40 at 80 °C for 50 minutes in acetonitrile. No end group signals remain.

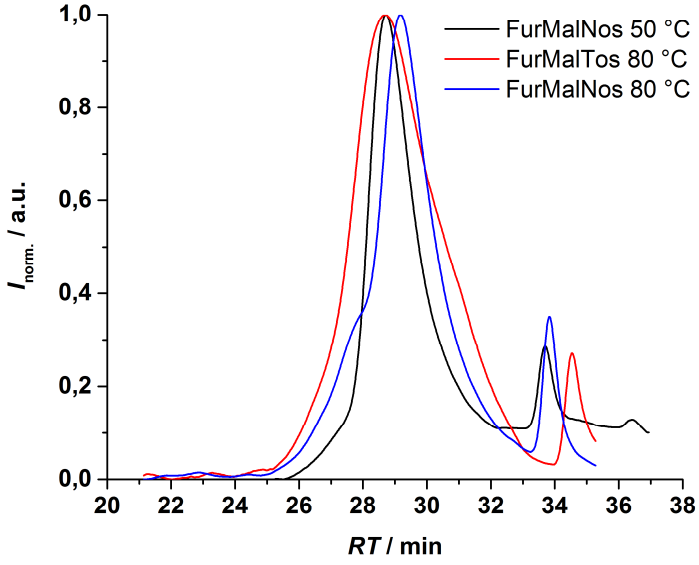

Figure S8. SEC traces of PEtOx obtained with either **FurMalNos 4** or **FurMalTos 3** as initiator and at either 50°C for 75 h or 80°C for 3 hours. Polymers made at 80 °C show a broader distribution, indicating the loss of control over the polymerization at such temperature.

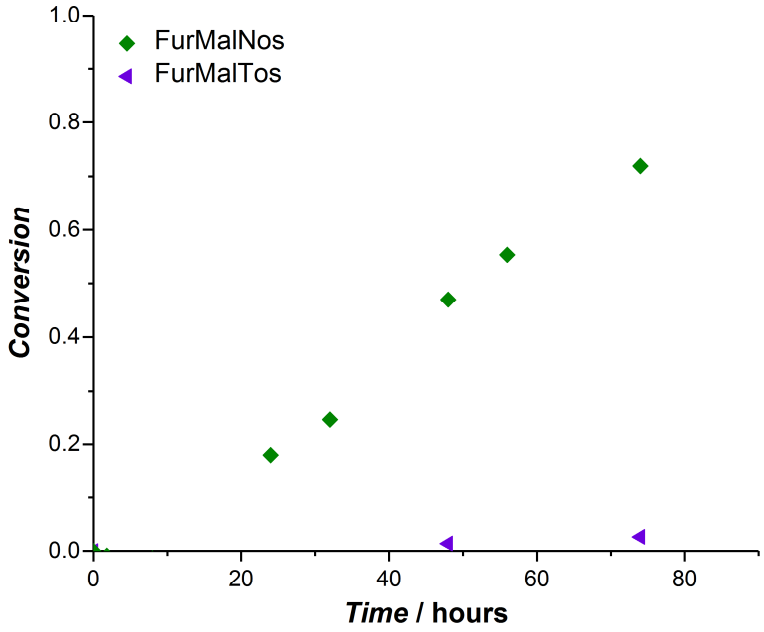

Figure S9. Monomer conversion as a function of time for the CROP of 2-ethyl-2-oxazoline at 50 °C in acetonitrile using **FurMalTos** and **FurMalNos** as initiators. [EtOx] = 1.5 M; [EtOx]/[Initiator] = 50.

Kinetic Data Corresponding to the Polymerizations Described in Full in the Main Text (i.e., at 50 °C, [EtOx] = 1 M, using FurMalNos 4)

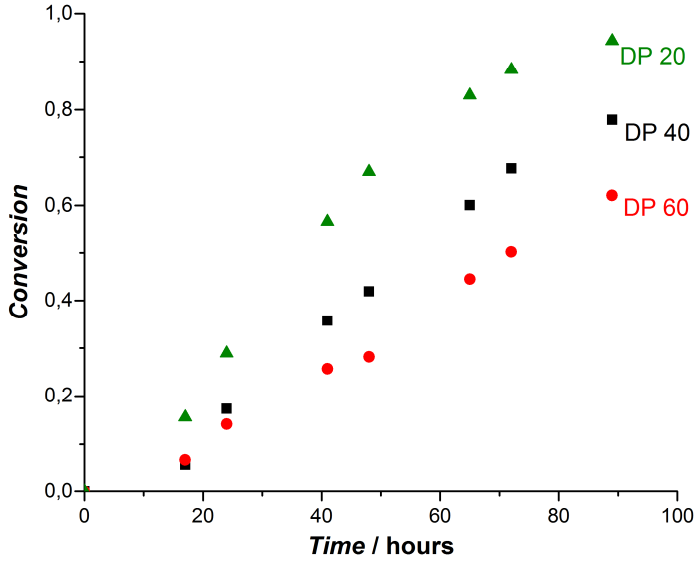

Figure S10. Monomer conversion as a function of time for the CROP of 2-ethyl-2-oxazoline at 50 °C in acetonitrile using **FurMalNos 4** as initiator at three distinct targeted degrees of polymerization (DP = [EtOx]/[**FurMalNos**]. [EtOx] = 1.5 M.

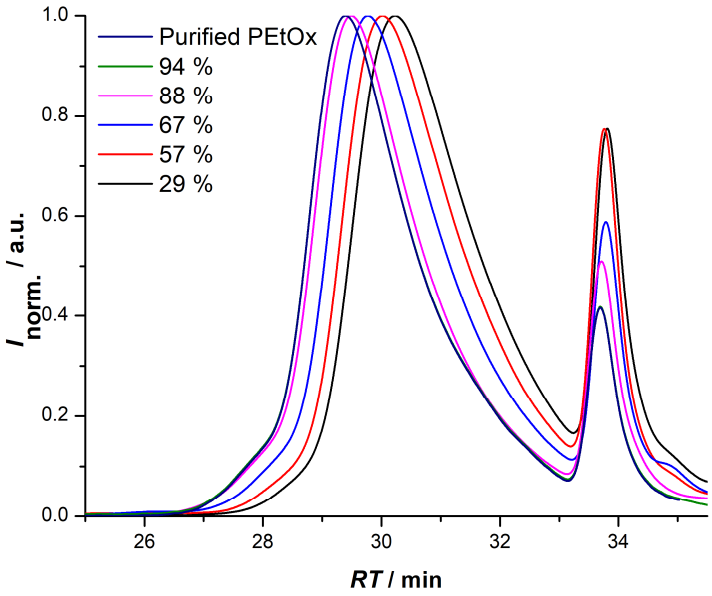

Figure S11. Overlay of SEC traces for the CROP of 2-ethyl-2-oxazoline at 50 °C in acetonitrile using **FurMalNos 4** as initiator. [EtOx] = 1.5 M. [EtOx]/[**FurMalNos**] = 20.

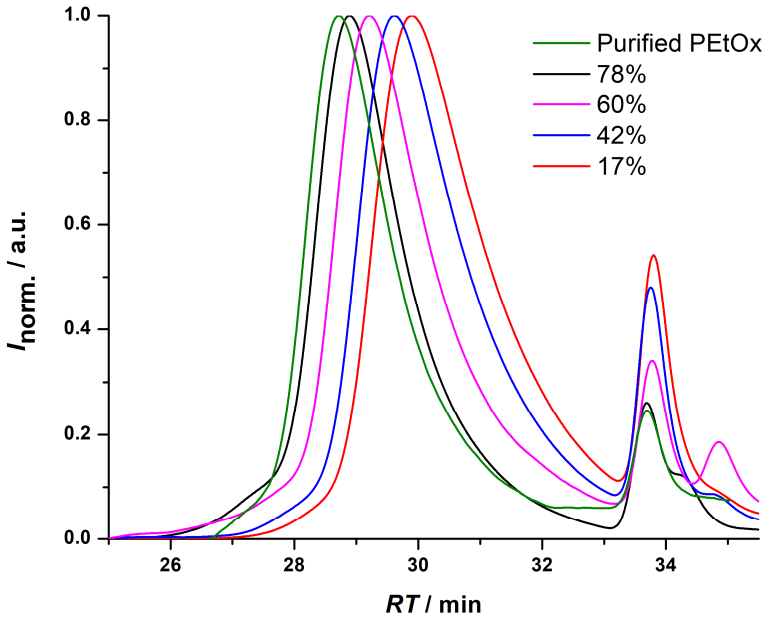

Figure S12. Overlay of SEC traces for the CROP of 2-ethyl-2-oxazoline at 50 °C in acetonitrile using **FurMalNos 4** as initiator. [EtOx] = 1.5 M. [EtOx]/[**FurMalNos**] = 40.

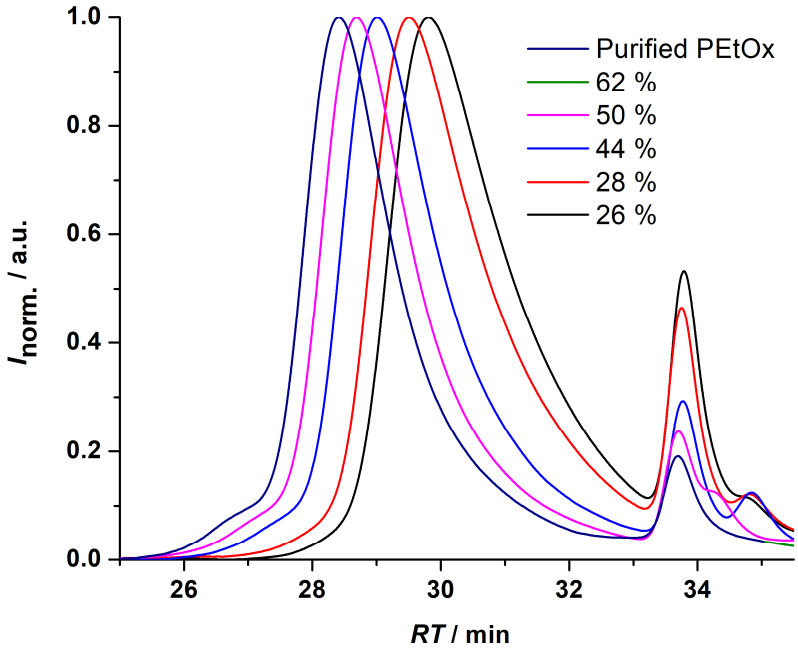

Figure S13. Overlay of SEC traces for the CROP of 2-ethyl-2-oxazoline at 50 °C in acetonitrile using **FurMalNos 4** as initiator. [EtOx] = 1.5 M. [EtOx]/[**FurMalNos**] = 60.

The apparent propagation rate constant for each kinetic run (Figure 1) was calculated according to the following expression for the rate of polymerization:

$$-\frac{d[M]}{dt} = k_p \cdot [P^*] \cdot [M]$$

where [M] and [P*] are the concentration in monomer and propagating species, respectively. Assuming that all initiators simultaneously react upon heating and therefore that $[P^*] = [I]_0$ (the initial initiator concentration), integration of the previous equation leads to:

$$ln\frac{[M]_0}{[M]} = k_p \cdot [I]_0 \cdot t$$

Table S1. Estimated polymerization rate k_p of the polymerization of PEtOx with **FurMalNos 4** using three different monomer to initiator ratios.

[EtOx]/[FurMalNos]	k_p **(10^{-6} L mol^{-1} s^{-1})**
20:1	158
40:1	166
60:1	160

Table S2. Summary of the characterization of the final purified products used for this study. Polymerization of EtOx with **FurMalNos** as the initiator.

[EtOx]/ [FurMalNos]	**Conv.**	**Yield** (%)	$M_{n,theo}$ (g mol^{-1})	$M_{n,NMR}$ (g mol^{-1})	$M_{n,SEC}$[a] (g mol^{-1})	$Đ$
20	94	88	2190	4400	6500	1.20
40	78	71	4172	6100	10600	1.13
60	62	56	6153	6700	11900	1.16

[a]Relative to poly(methyl methacrylate) standards.

Additional Data for End-Group Transformations

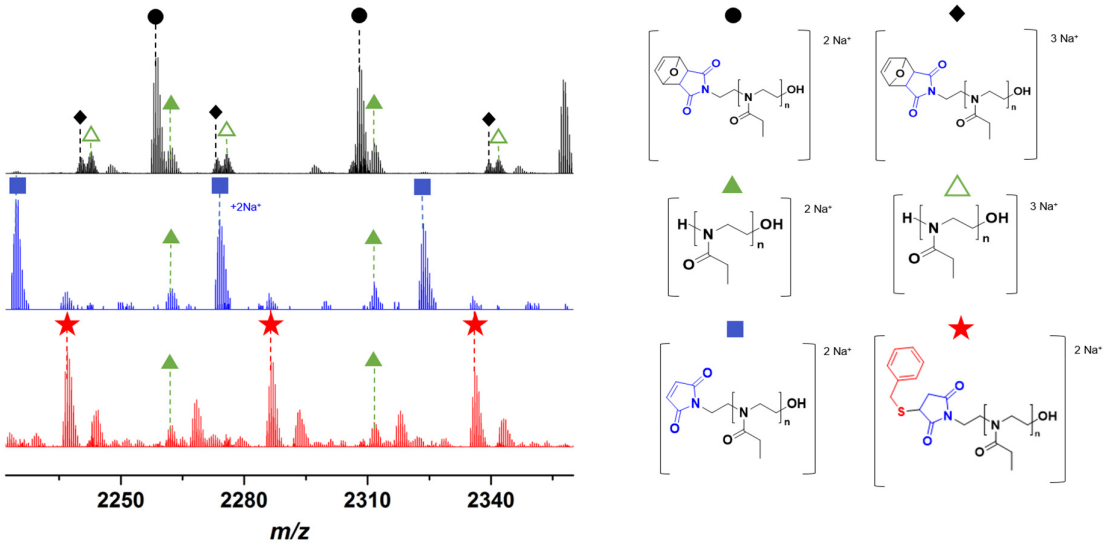

Figure S14. Detailed ESI-MS spectra with assignments of (A) **FurMal-PEtOx** as obtained after CROP of EtOx initiated by **FurMalNos**, (B) **Mal-PEtOx** obtained after thermal treatment of **FurMal-PEtOx**, and (C) the Michael addition product of **Mal-PEtOx** with benzyl (**BzMal-PEtOx**).

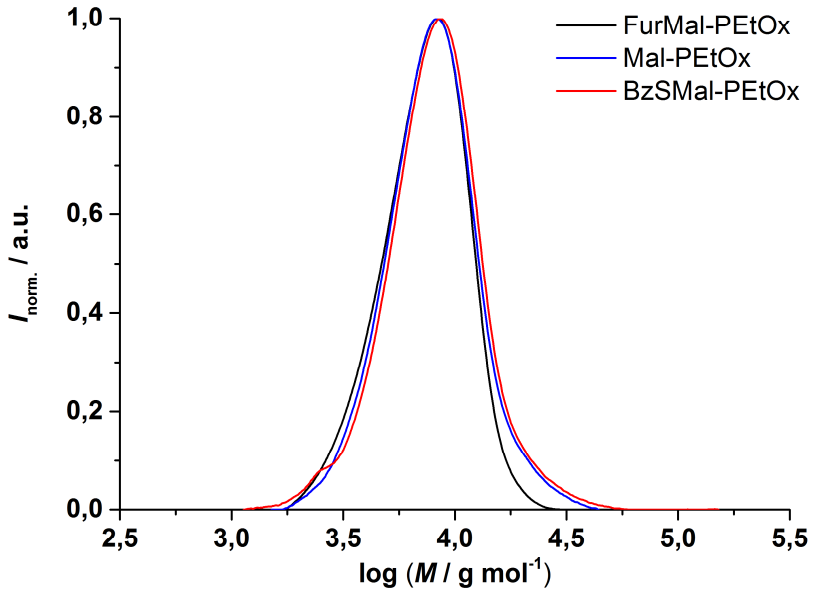

Figure S15. Overlay of SEC traces of **FurMal-PEtOx** ($M_{n,SEC}$ = 6500 g mol^{-1}, $Đ$ = 1.20), its deprotection **Mal-PEtOx** ($M_{n,SEC}$ = 6900 g mol^{-1}, $Đ$ = 1.24), and **BzSMal-PEtOx** ($M_{n,SEC}$ = 7000 g mol^{-1}, $Đ$ = 1.27) obtained by Michael addition with benzyl mercaptan.