

Supplementary Information

Cationic Ring-Opening Polymerization of 2-Oxazolines  
in  $\gamma$ -Butyrolactones using Various Initiators

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**Experimental Section**

***Materials***

Toluene (Guangzhou Chemical Reagent, AR), tetrahydrofuran (THF; Guangzhou Chemical Reagent, AR) and acetic acid (AcOH; Energy, AR) were successively dried over molecular sieve (4 Å), calcium hydride (CaH<sub>2</sub>), and *n*-butyllithium (<sup>n</sup>BuLi) capped with 1,1-diphenylethylene before vacuum-distilled. Dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>; Guangzhou Chemical Reagent, AR), 2-methyltetrahydrofuran (2-MeTHF; Guangzhou Chemical Reagent, AR), and diethyl ether (Guangzhou Chemical Reagent, AR) were used as received. 2-Ethyl-2-oxazoline (EtOx; Energy, 98%) and acetonitrile (AN; Energy, 99.9%) were dried by CaH<sub>2</sub> and distilled. 2-Phenyl-2-oxazoline (PhOx; Energy, 98%), methyl *p*-toluenesulfonate (MeOTs; Energy, 98%),  $\gamma$ -

butyrolactone (BL),  $\gamma$ -valerolactone (GVL; Energy, 98%),  $\gamma$ -octalactone (GOL; Energy, 98%), and  $\gamma$ -undecalactone (GUL; Energy, 98%) were dried over  $\text{CaH}_2$  and distilled under vacuum. 1,1'-Binaphthyl-2,2'-diyl hydrogenphosphate (BNP; Energy, 98%), dibutyl phosphate (DBP; Energy, 97%), dibenzyl phosphate (DBnP; Energy, 98%), diphenylphosphinic acid (DPPA; Energy, 98%), diphenyl phosphate (DPP; Energy, 97%), benzoic acid (BA; Energy, 98%), salicylic acid (SCA; Energy, 98%), 4-cyanobenzoic acid (4-CBA; Energy, 98%), 2,6-dihydroxybenzoic acid (2,6-DHBA; Energy, 98%), 6-methoxysalicylic acid (6-OSCA; Energy, 98%), 2,4-dihydroxybenzoic acid (2,4-DHBA; Energy, 98%), 4-nitrosalicylic acid (4-NSCA; Energy, 98%), and 2,6-dihydroxybenzoic acid methyl ester (2,6-DHBM; Energy, 98%) were dried by azeotropic distillation of toluene, vacuum-dried, and used directly or in  $0.2 \text{ mol L}^{-1}$  toluene solutions.

### ***Instrumentation***

NMR spectra were recorded at  $25 \text{ }^\circ\text{C}$  on Bruker AV400 NMR spectrometer using deuterated chloroform ( $\text{CDCl}_3$ ) as the solvent and tetramethylsilane as the internal standard. Monomer conversion was calculated from  $^1\text{H}$  NMR spectrum of the crude product by comparison of the integrals of a characteristic signal from the remaining monomer and the corresponding signal from the polymer.  $^1\text{H}$  NMR spectra were used to calculate number-average molar mass ( $M_{n,\text{NMR}}$ ) by comparing the integrals of signals from end groups and polymer main bodies.

Size exclusion chromatography (SEC) coupled with refractive index (RI) detector was conducted in *N,N*-dimethylformamide (DMF) with LiBr (0.05 M) at  $50 \text{ }^\circ\text{C}$  and a flow rate of  $1.0 \text{ ml min}^{-1}$  using three successively connected Styragel columns (HR2, HR4, HR6). A series of narrowly distributed poly(methyl methacrylate) (PMMA) standards were used for calibration to obtain

apparent number-average molar mass ( $M_{n,SEC}$ ) and molar mass distribution ( $D_M$ ) of the (co)polymers.

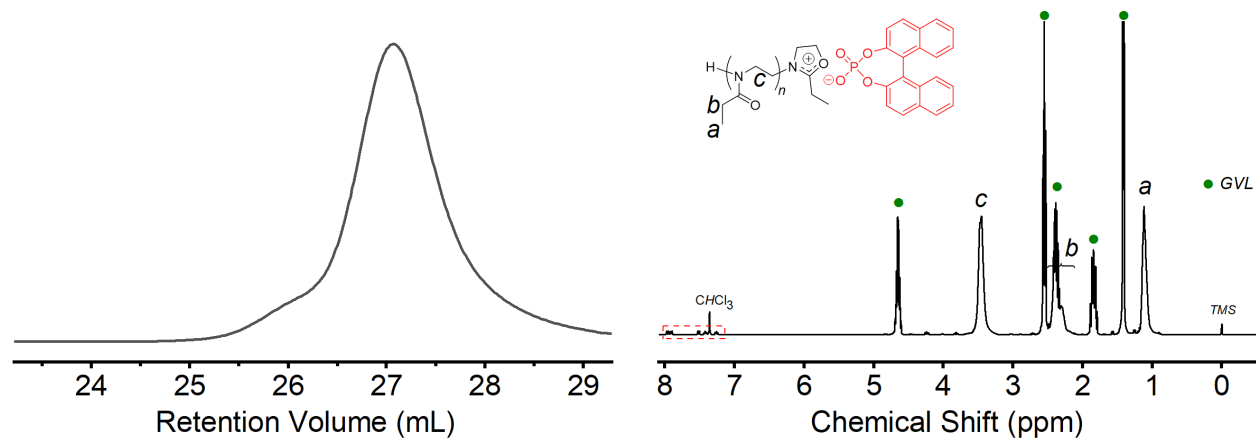
Matrix assisted laser desorption/ionization time of flight mass spectrometry (MALDI-TOF MS) measurement was performed on a Bruker Autoflex III Smartbeam MALDI-TOF mass spectrometer (Bruker, Germany). Samples were dissolved in THF (10.0 mg mL<sup>-1</sup>) and mixed with a solution of sodium acetate in THF (10.0 mg mL<sup>-1</sup>) in a volume ratio of 5:1. This solution was then mixed with a solution of matrix, *trans*-2-[3-(*tert*-butylphenyl)-2-methyl-2-propenylidene] malononitrile in THF (20.0 mg mL<sup>-1</sup>), in a volume ratio of 1:20. Then, 0.4  $\mu$ L of the final solution was spotted on the target plate (dried-droplet method). The reflective positive ion mode was used to acquire the mass spectra of the samples. Calibration was done externally with PMMA standards using the nearest neighbor positions.

### ***Polymer Synthesis***

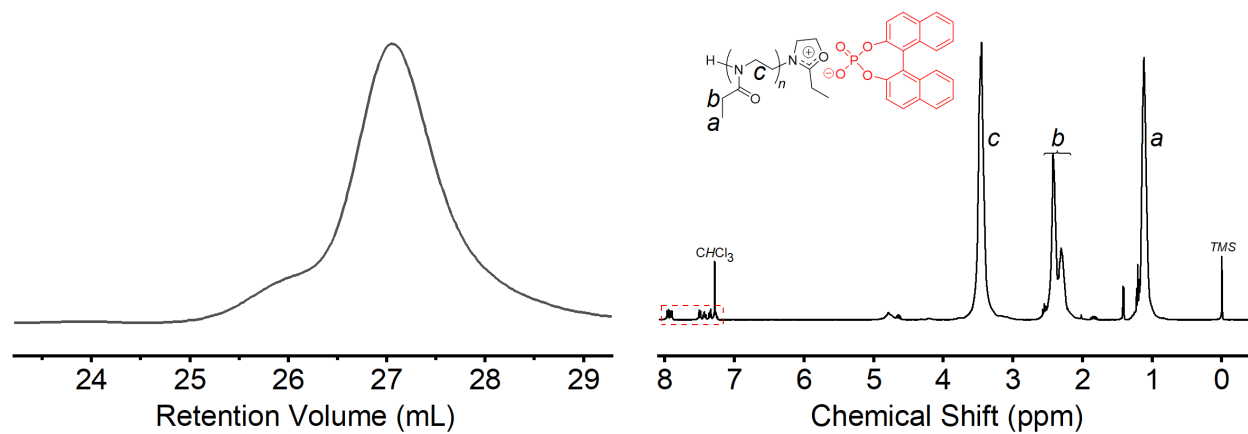
*Poly(2-ethyl-2-oxazoline) (PEtOx)* by cationic ring-opening polymerization (CROP) of EtOx. A typical procedure of entry 1 in Table 1 is as follows. BNP (29.5 mg, 84.8  $\mu$ mol) was loaded in a pre-dried Schlenk flask docked on the vacuum line and dried by azeotropic distillation of toluene at 50 °C, then vacuum-dried at room temperature (RT, 23~26 °C) for 1 h. The reaction flask with BNP was transferred in a glovebox where purified EtOx (0.40 mL, 4.24 mmol) and GVL (0.66 mL) were successively loaded ( $[EtOx]_0 = 4.0 \text{ mol L}^{-1}$ ). The mixture was removed from the glovebox and stirred at 140 °C for 30 min in an oil bath. A small aliquot (*ca.* 0.05 mL) was then withdrawn, injected into CDCl<sub>3</sub> (0.60 mL), and used for <sup>1</sup>H NMR analysis to determine the conversion of EtOx. The CDCl<sub>3</sub> solution was further diluted with DMF for SEC analysis to

determine  $M_{n,SEC}$  and  $D_M$  of the polymer.  $Conv.(EtOx) = 98.9\%$ , theoretical number-average molar mass ( $M_{n,th}$ ) = 5.2 kg mol<sup>-1</sup>. The product was precipitated in cold diethyl ether, or diluted with CH<sub>2</sub>Cl<sub>2</sub> (or 2-MeTHF) and then precipitated in cold diethyl ether, collected, and dried in vacuum to afford a white solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 7.99-7.19 (–OC<sub>20</sub>H<sub>12</sub>O–, from BNP), 3.54-3.38 (–NCH<sub>2</sub>CH<sub>2</sub>–), 2.49-2.19 (–COCH<sub>2</sub>CH<sub>3</sub>), 1.19-0.98 (–COCH<sub>2</sub>CH<sub>3</sub>).  $M_{n,SEC}(DMF) = 11.1$  kg mol<sup>-1</sup>,  $D_M = 1.19$ .  $M_{n,NMR}(PEtOx) = 5.7$  kg mol<sup>-1</sup>. Polymerization of EtOx in the other entries of Table 1 and Table 2 was performed in similar procedures with slight variations.

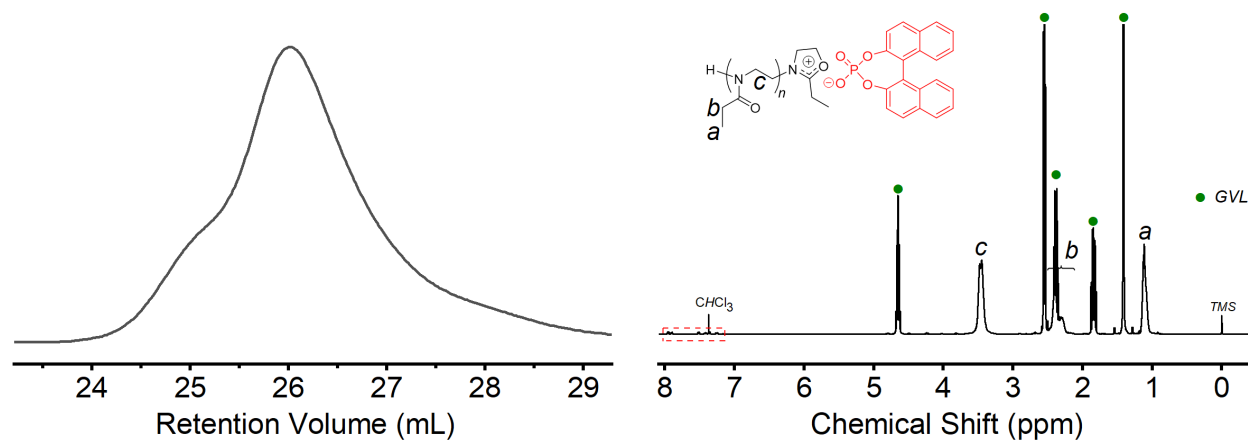
*Block copolymerization of EtOx and PhOx.* A typical procedure for entry 1 in Table 3 is given as follows. BNP (29.5 mg, 0.0848 mmol), EtOx (0.40 mL, 4.24 mmol), and GOL (0.66 mL) were loaded in a pre-dried flask, then stirred at 140 °C for 30 min in an oil bath. A small aliquot was quickly withdrawn for <sup>1</sup>H NMR and SEC analysis.  $Conv.(EtOx) = 93.3\%$ .  $M_{n,SEC}(DMF) = 9.4$  kg mol<sup>-1</sup>,  $D_M = 1.12$ . After that, PhOx (0.56 mL, 4.24 mmol) was added, and the new reaction mixture was stirred at 140 °C for another 3 h with a small aliquot withdrawn afterwards. The product was diluted with CH<sub>2</sub>Cl<sub>2</sub> (or 2-MeTHF) and precipitated in cold diethyl ether. A slightly orange solid was collected and dried in vacuum.  $Conv.(PhOx) = 64.4\%$ .  $M_{n,SEC}(DMF) = 22.1$  kg mol<sup>-1</sup>,  $D_M = 1.26$ . <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 3.84-2.71 (–NCH<sub>2</sub>CH<sub>2</sub>–), 2.49-2.19 (–COCH<sub>2</sub>CH<sub>3</sub>), 1.19-0.98 (–COCH<sub>2</sub>CH<sub>3</sub>), 7.44-6.69 (–COC<sub>6</sub>H<sub>5</sub>).



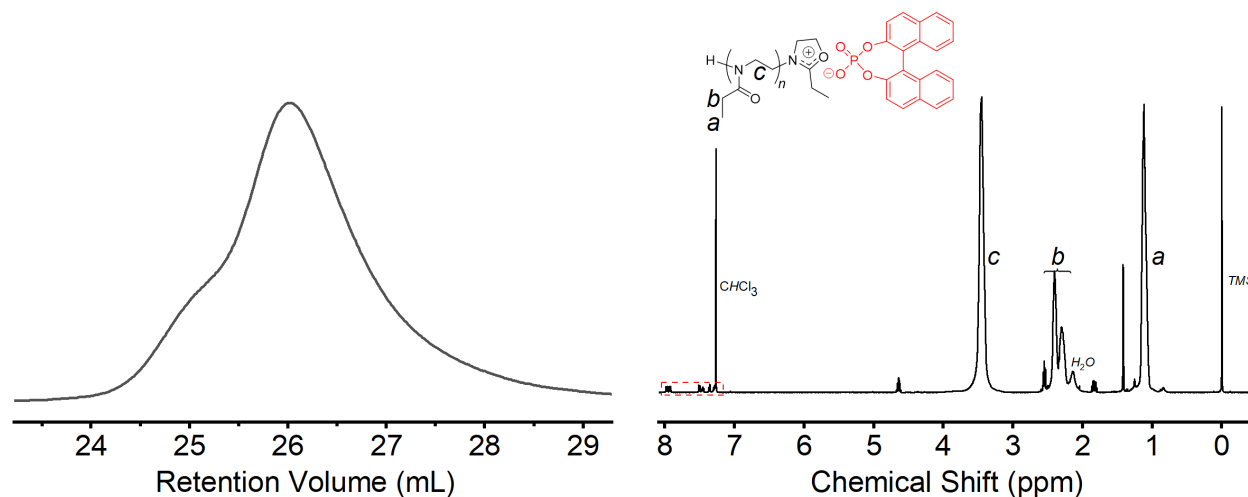
**Figure S1.** Left: SEC trace (DMF, 50 °C, RI signal) of the PEtOx (crude product, DP = 50) synthesized at 140 °C with BNP as the initiator and GVL as the solvent (entry 1 in Table 1). Right:  $^1\text{H}$  NMR spectrum (in  $\text{CDCl}_3$ ) of the crude product with green circles above the solvent signals.



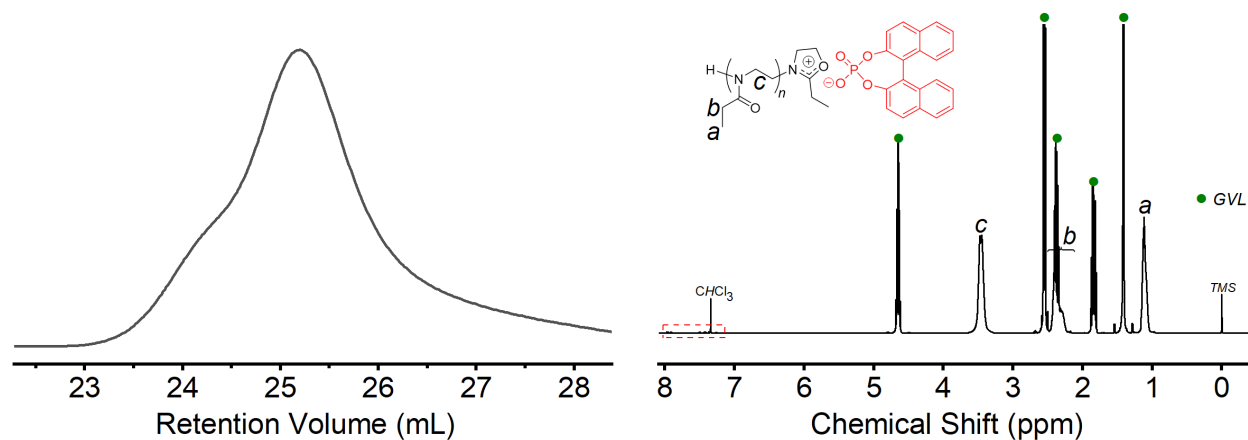
**Figure S2.** SEC trace (DMF, 50 °C, RI signal) and  $^1\text{H}$  NMR spectrum (in  $\text{CDCl}_3$ ) of the isolated product of entry 1 in Table 1.



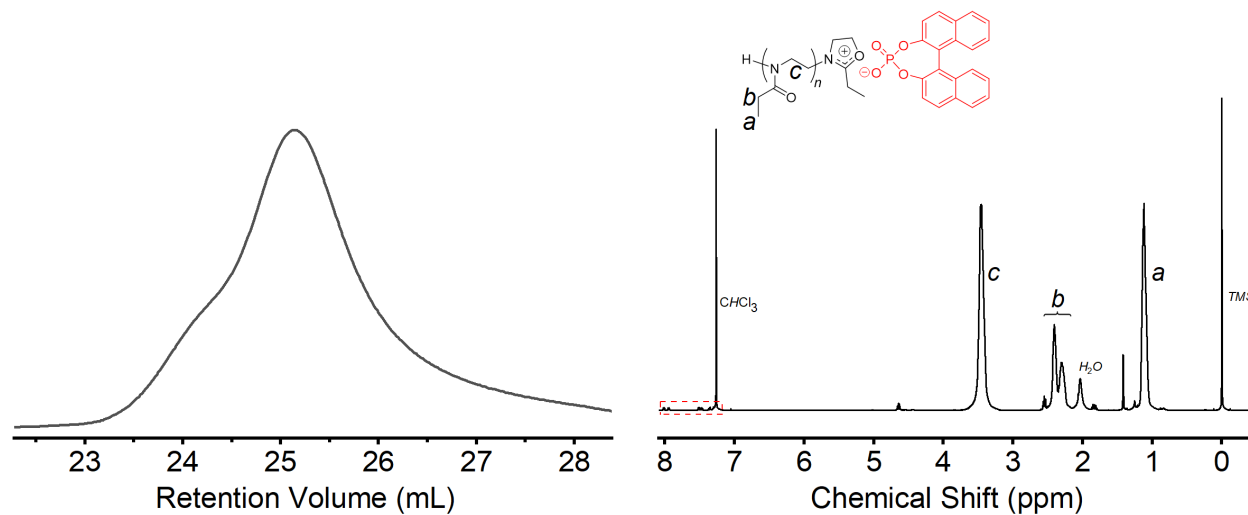
**Figure S3.** Left: SEC trace (DMF, 50 °C, RI signal) of the PEtOx (crude product, DP = 100) synthesized at 140 °C with BNP as the initiator and GVL as the solvent (entry 2 in Table 1). Right: <sup>1</sup>H NMR spectrum (in CDCl<sub>3</sub>) of the crude product with green circles above the solvent signals.



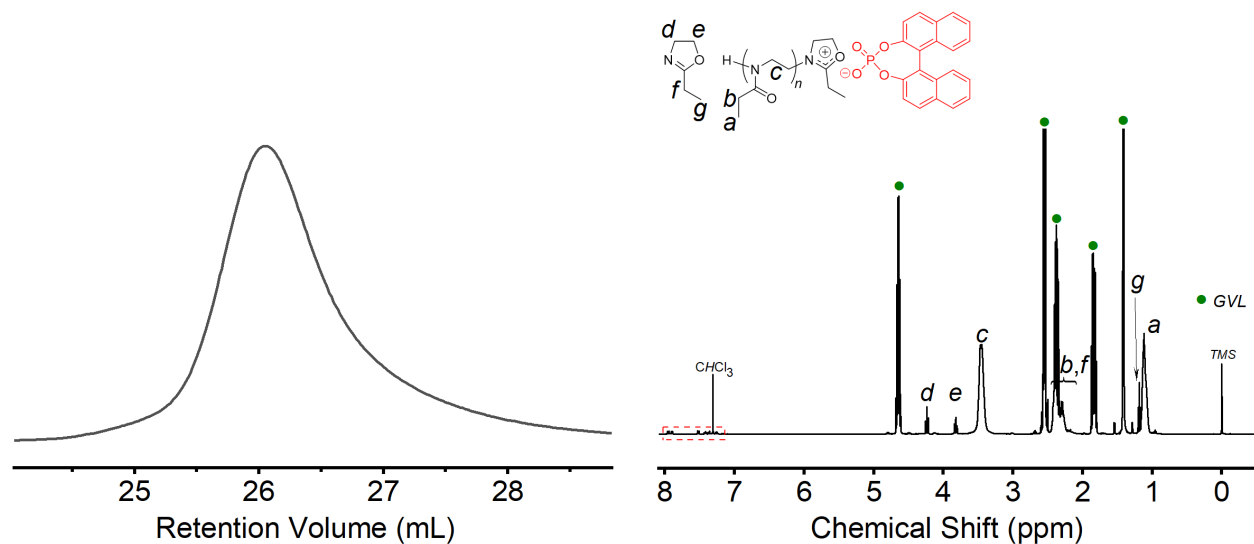
**Figure S4.** SEC trace (DMF, 50 °C, RI signal) and <sup>1</sup>H NMR spectrum (in CDCl<sub>3</sub>) of the isolated product of entry 2 in Table 1.



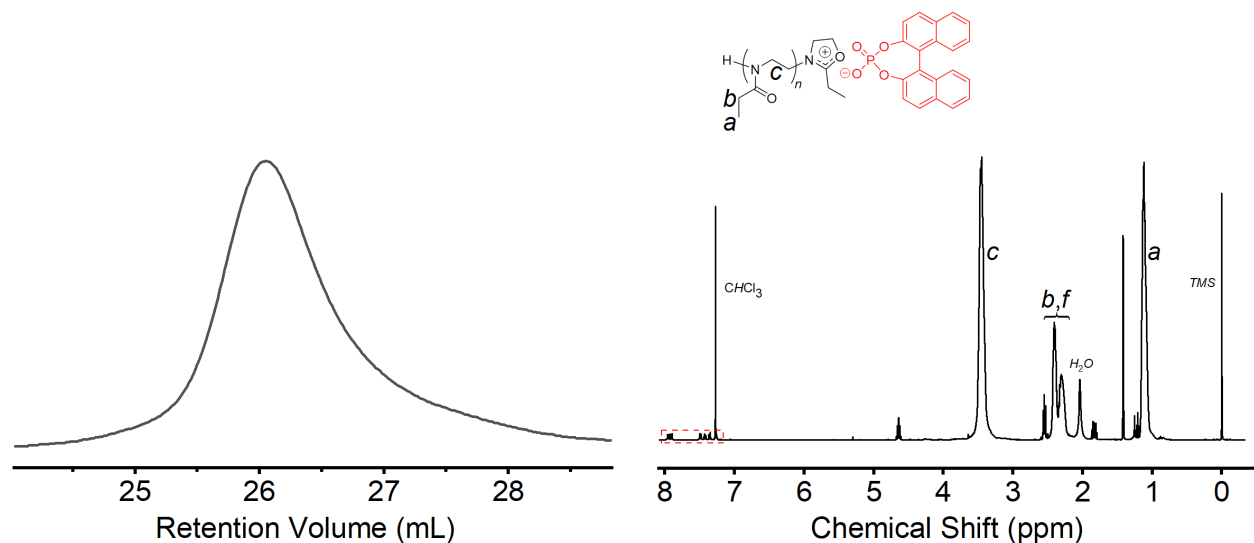
**Figure S5.** Left: SEC trace (DMF, 50 °C, RI signal) of the PEtOx (crude product, DP = 220) synthesized at 140 °C with BNP as the initiator and GVL as the solvent (entry 3 in Table 1). Right: <sup>1</sup>H NMR spectrum (in CDCl<sub>3</sub>) of the crude product with green circles above the solvent signals.



**Figure S6.** SEC trace (DMF, 50 °C, RI signal) and <sup>1</sup>H NMR spectrum (in CDCl<sub>3</sub>) of the isolated product of entry 3 in Table 1.

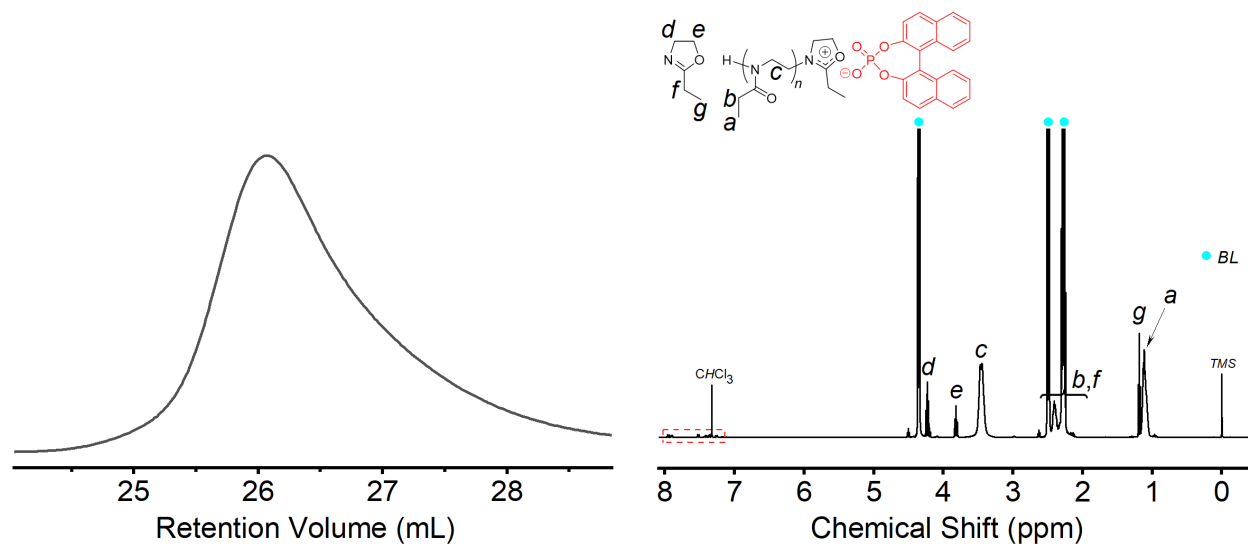


**Figure S7.** Left: SEC trace (DMF, 50 °C, RI signal) of the PEtOx (crude product, DP = 110) synthesized at 80 °C with BNP as the initiator and GVL as the solvent (entry 4 in Table 1). Right: <sup>1</sup>H NMR spectrum (in CDCl<sub>3</sub>) of the crude product with green circles above the solvent signals.

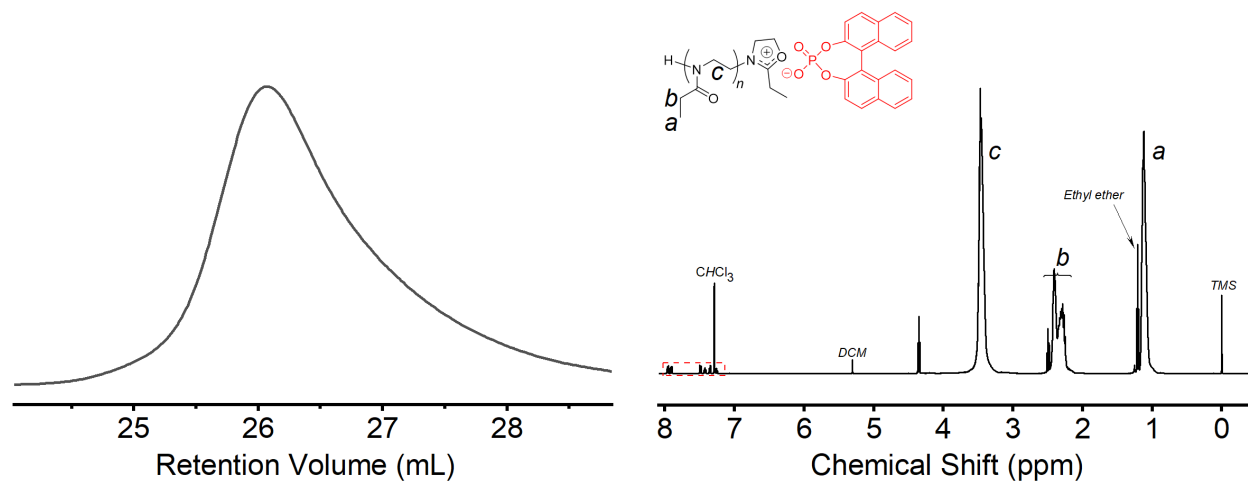


**Figure S8.** SEC trace (DMF, 50 °C, RI signal) and <sup>1</sup>H NMR spectrum (in CDCl<sub>3</sub>) of the isolated product of entry 4 in Table 1.

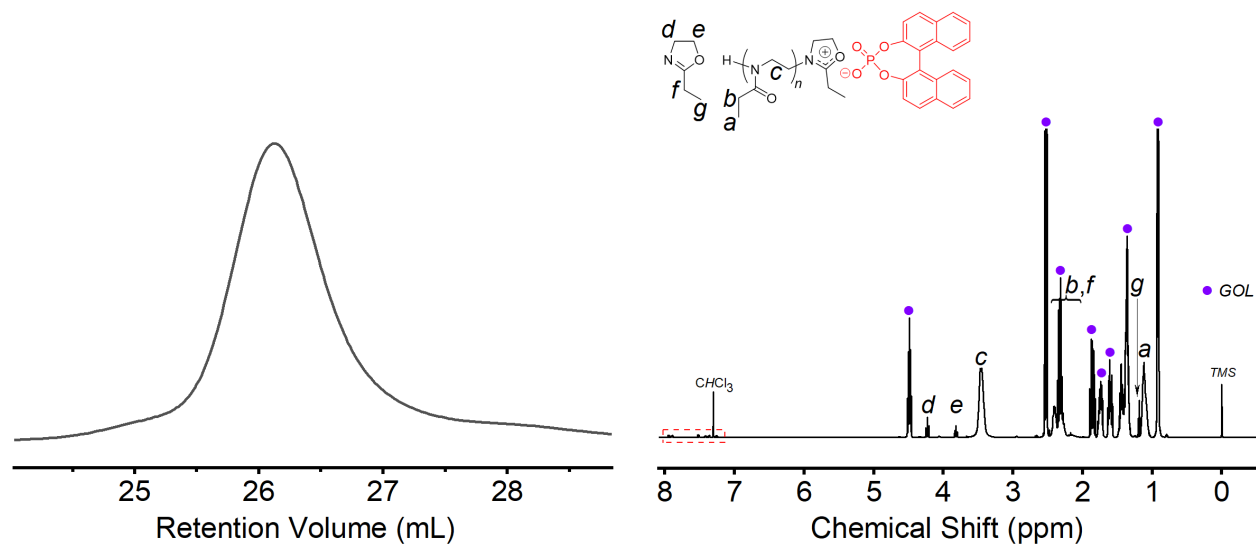




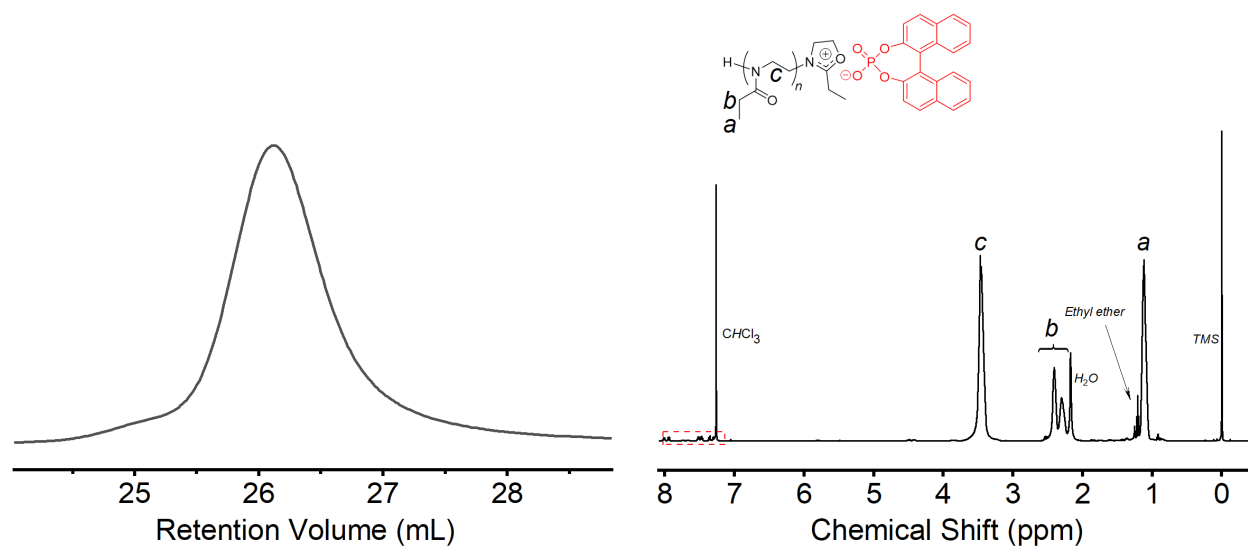
**Figure S9.** Left: SEC trace (DMF, 50 °C, RI signal) of the PEtOx (crude product, DP = 110) synthesized at 80 °C with BNP as the initiator and BL as the solvent (entry 5 in Table 1). Right: <sup>1</sup>H NMR spectrum (in CDCl<sub>3</sub>) of the crude product with blue circles above the solvent signals.



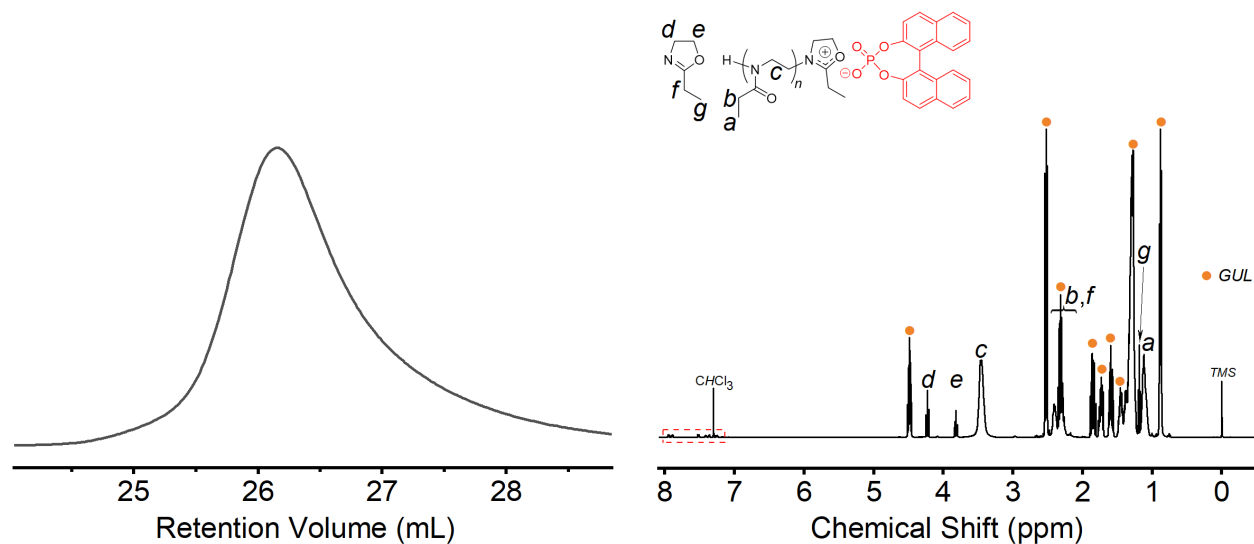
**Figure S10.** SEC trace (DMF, 50 °C, RI signal) and <sup>1</sup>H NMR spectrum (in CDCl<sub>3</sub>) of the isolated product of entry 5 in Table 1.



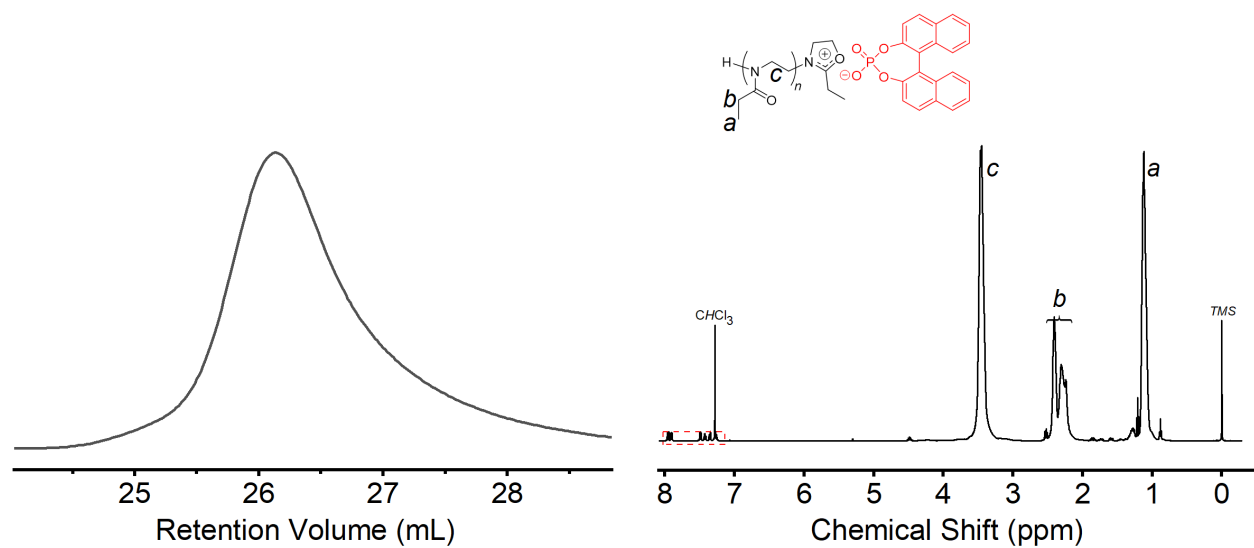
**Figure S11.** Left: SEC trace (DMF, 50 °C, RI signal) of the PEtOx (crude product, DP = 110) synthesized at 80 °C with BNP as the initiator and GOL as the solvent (entry 6 in Table 1). Right:  $^1\text{H}$  NMR spectrum (in  $\text{CDCl}_3$ ) of the crude product with purple circles above the solvent signals.



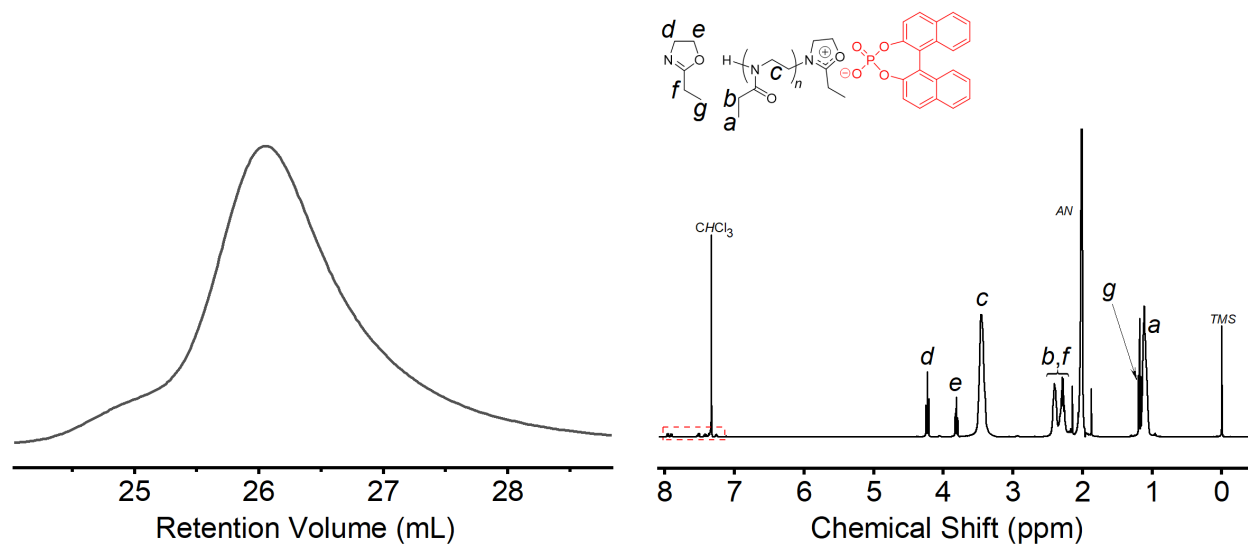
**Figure S12.** SEC trace (DMF, 50 °C, RI signal) and  $^1\text{H}$  NMR spectrum (in  $\text{CDCl}_3$ ) of the isolated product of entry 6 in Table 1.



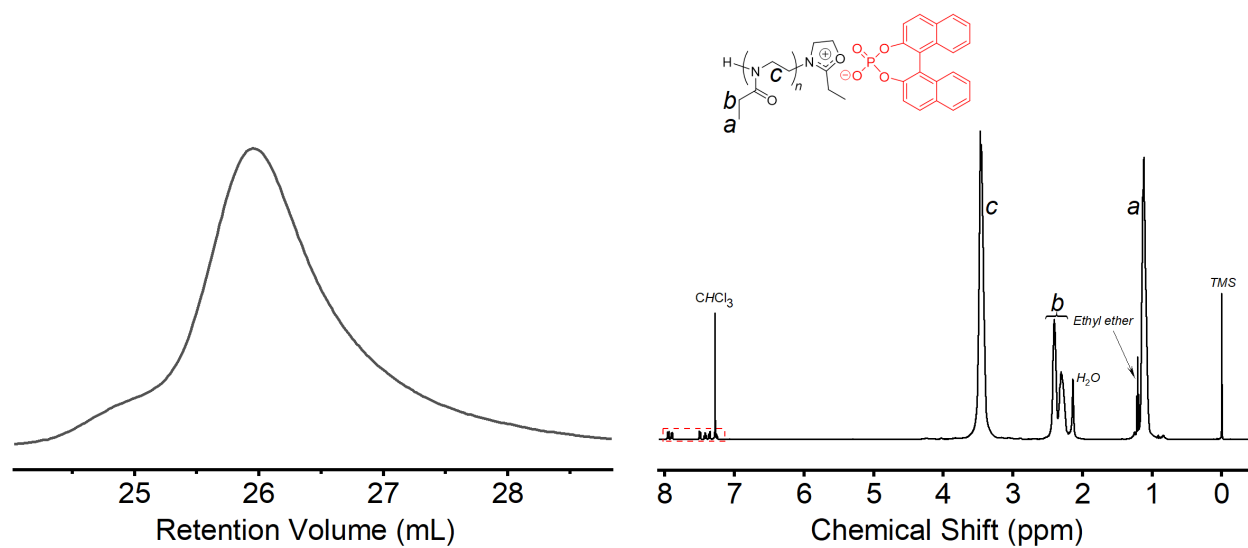
**Figure S13.** Left: SEC trace (DMF, 50 °C, RI signal) of the PEtOx (crude product, DP = 110) synthesized at 80 °C with BNP as the initiator and GUL as the solvent (entry 7 in Table 1). Right:  $^1\text{H}$  NMR spectrum (in  $\text{CDCl}_3$ ) of the crude product with orange circles above the solvent signals.



**Figure S14.** SEC trace (DMF, 50 °C, RI signal) and  $^1\text{H}$  NMR spectrum (in  $\text{CDCl}_3$ ) of the isolated product of entry 7 in Table 1.

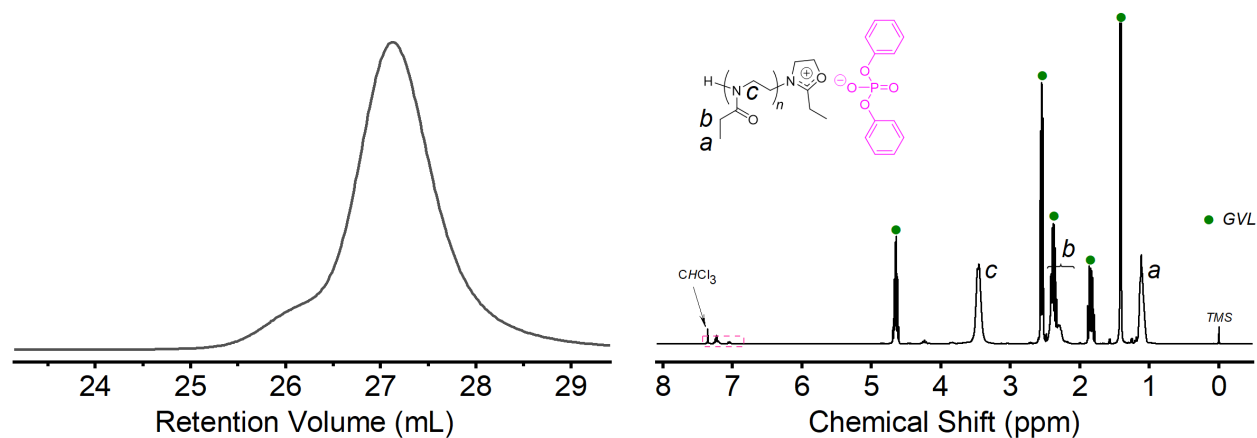


**Figure S15.** Left: SEC trace (DMF, 50 °C, RI signal) of the PEtOx (crude product, DP = 110) synthesized at 80 °C with BNP as the initiator and AN as the solvent (entry 8 in Table 1). Right: <sup>1</sup>H NMR spectrum (in CDCl<sub>3</sub>) of the crude product.

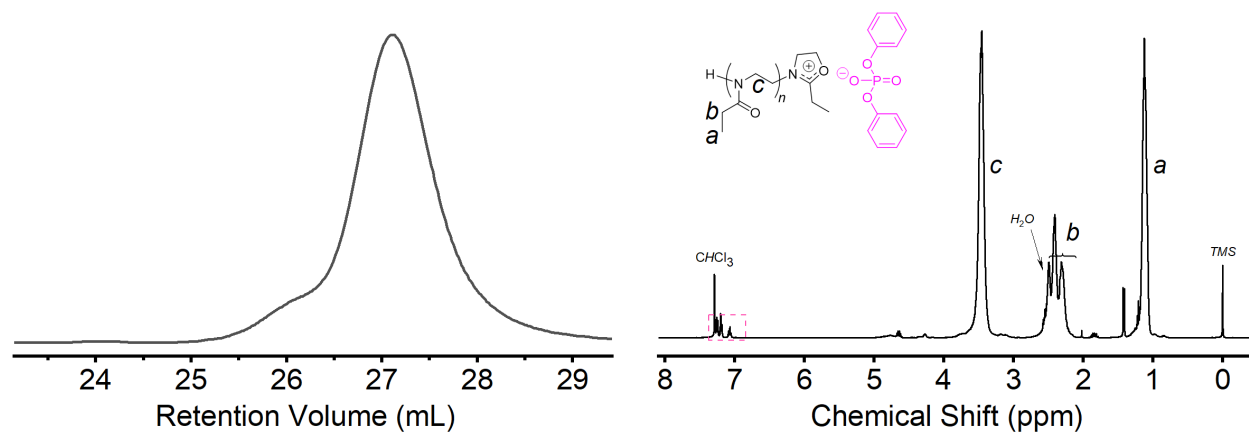


**Figure S16.** SEC trace (DMF, 50 °C, RI signal) and <sup>1</sup>H NMR spectrum (in CDCl<sub>3</sub>) of the isolated product of entry 8 in Table 1.

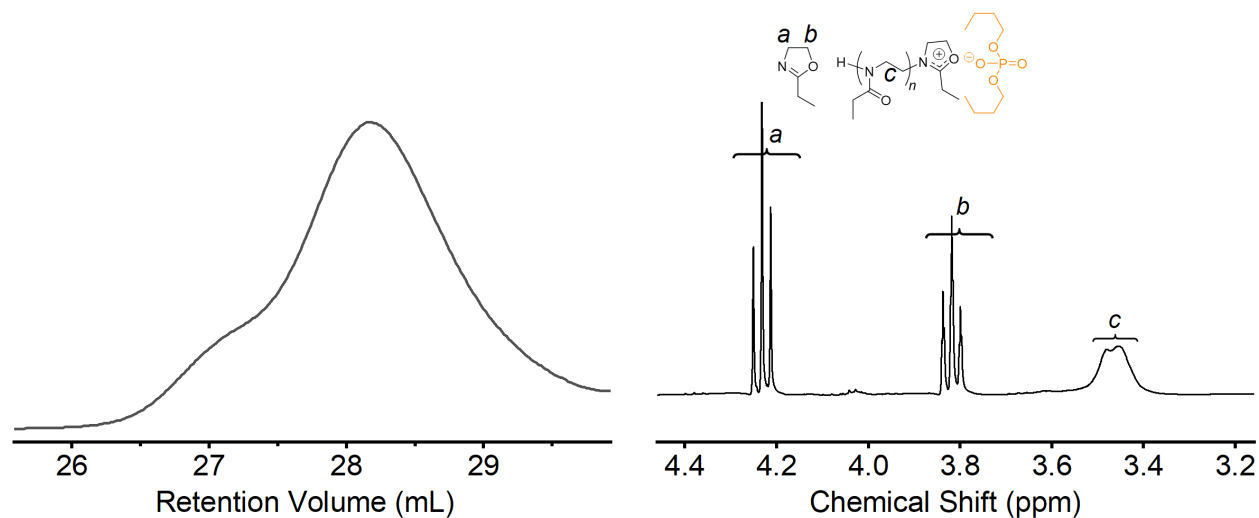




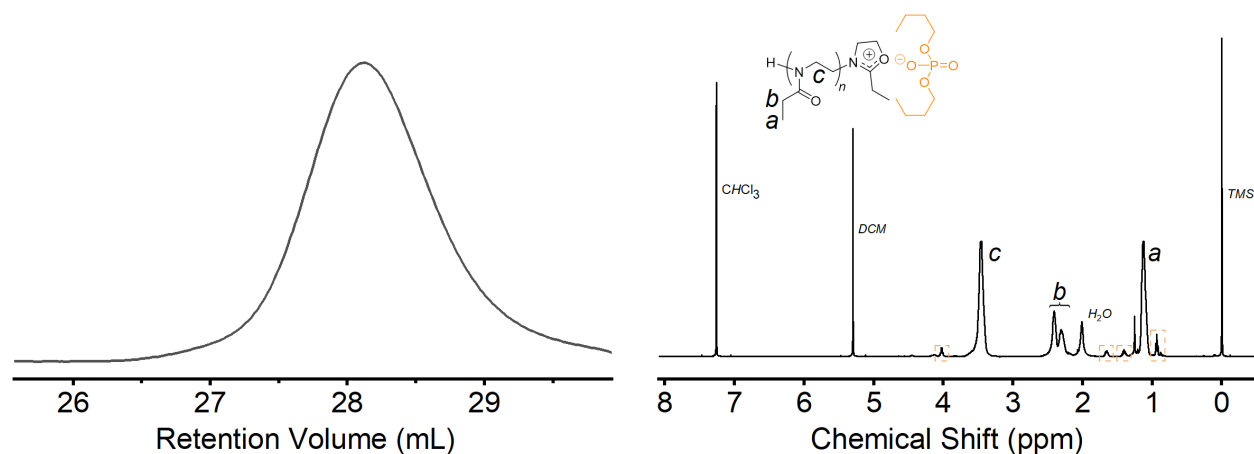
**Figure S18.** Left: SEC trace (DMF, 50 °C, RI signal) of the PEtOx (crude product, DP = 50) synthesized at 140 °C with DPP as the initiator and GVL as the solvent (entry 1 in Table 2). Right: <sup>1</sup>H NMR spectrum (in CDCl<sub>3</sub>) of the crude product with green circles above the solvent signals.



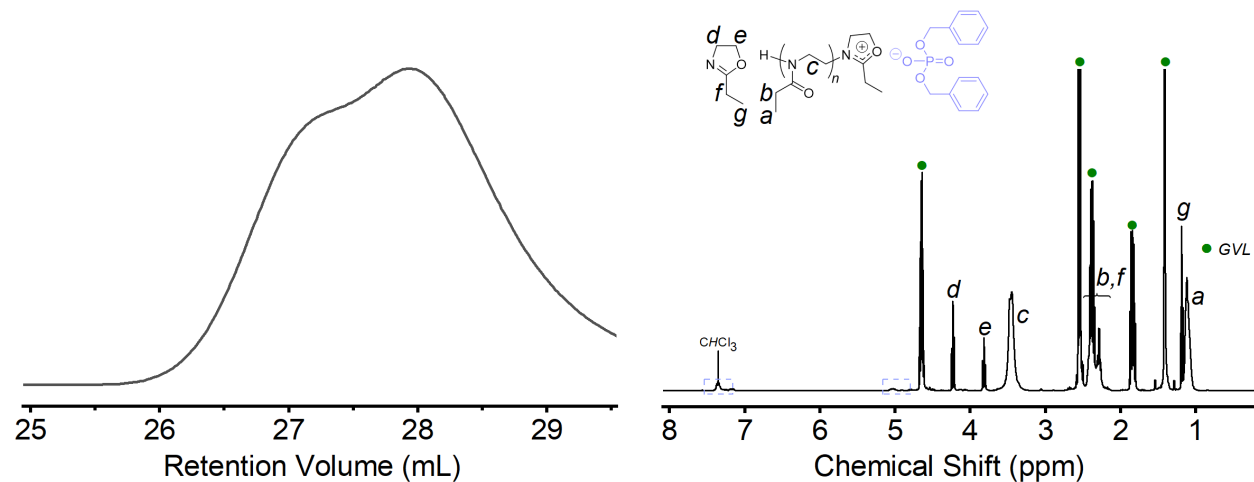
**Figure S19.** SEC trace (DMF, 50 °C, RI signal) and <sup>1</sup>H NMR spectrum (in CDCl<sub>3</sub>) of the isolated product of entry 1 in Table 2.



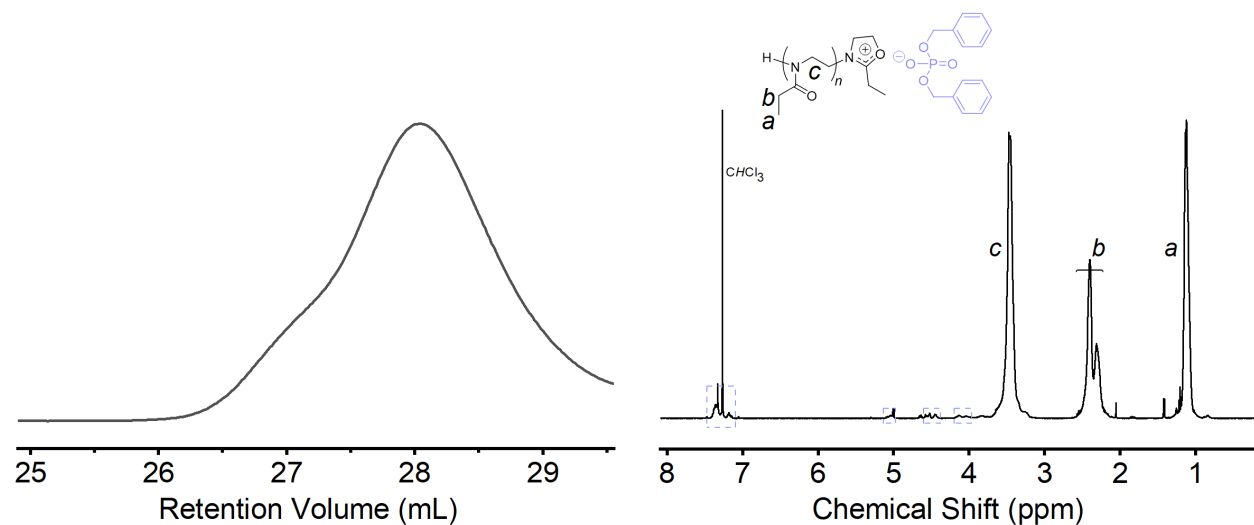
**Figure S20.** Left: SEC trace (DMF, 50 °C, RI signal) of the PEtOx (crude product, DP = 50) synthesized at 140 °C with DBP as the initiator and GVL as the solvent (entry 2 in Table 2). Right: <sup>1</sup>H NMR spectrum (in CDCl<sub>3</sub>) of the crude product with green circles above the solvent signals.



**Figure S21.** SEC trace (DMF, 50 °C, RI signal) and <sup>1</sup>H NMR spectrum (in CDCl<sub>3</sub>) of the isolated product of entry 2 in Table 2.

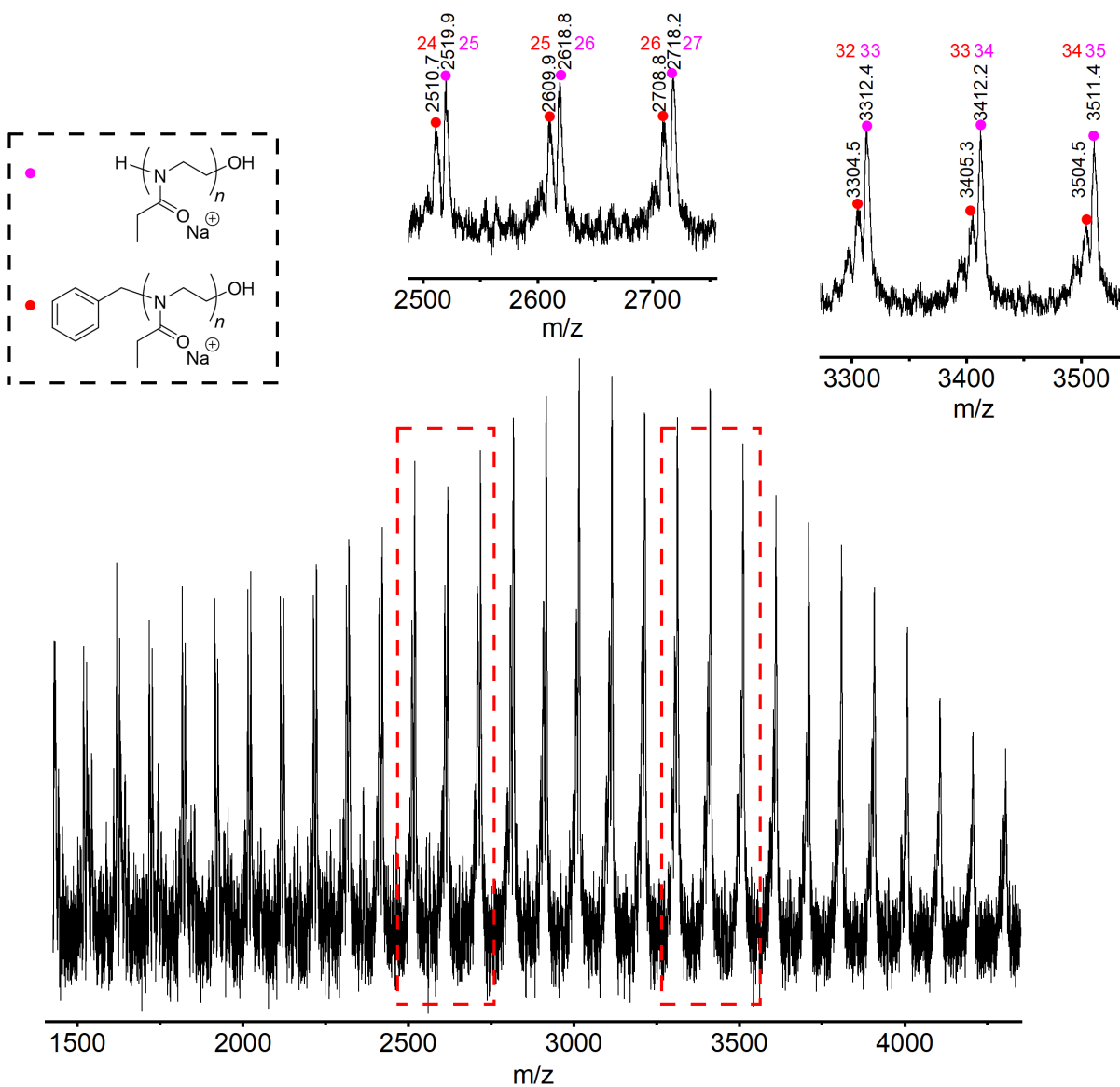


**Figure S22.** Left: SEC trace (DMF, 50 °C, RI signal) of the PEtOx (crude product, DP = 50) synthesized at 140 °C with DBnP as the initiator and GVL as the solvent (entry 3 in Table 2). Right: <sup>1</sup>H NMR spectrum (in CDCl<sub>3</sub>) of the crude product with green circles above the solvent signals.

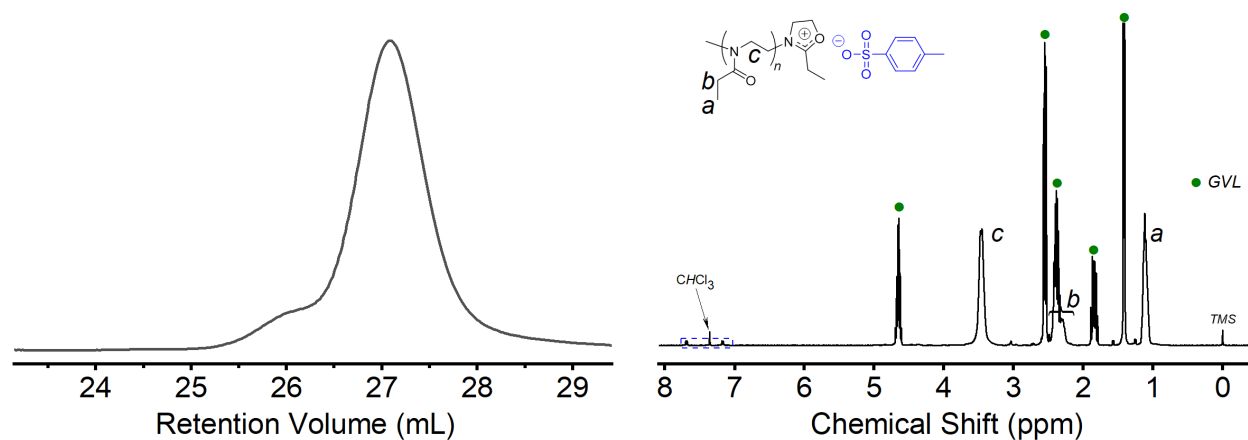


**Figure S23.** SEC trace (DMF, 50 °C, RI signal) and <sup>1</sup>H NMR spectrum (in CDCl<sub>3</sub>) of the isolated product of entry 3 in Table 2.

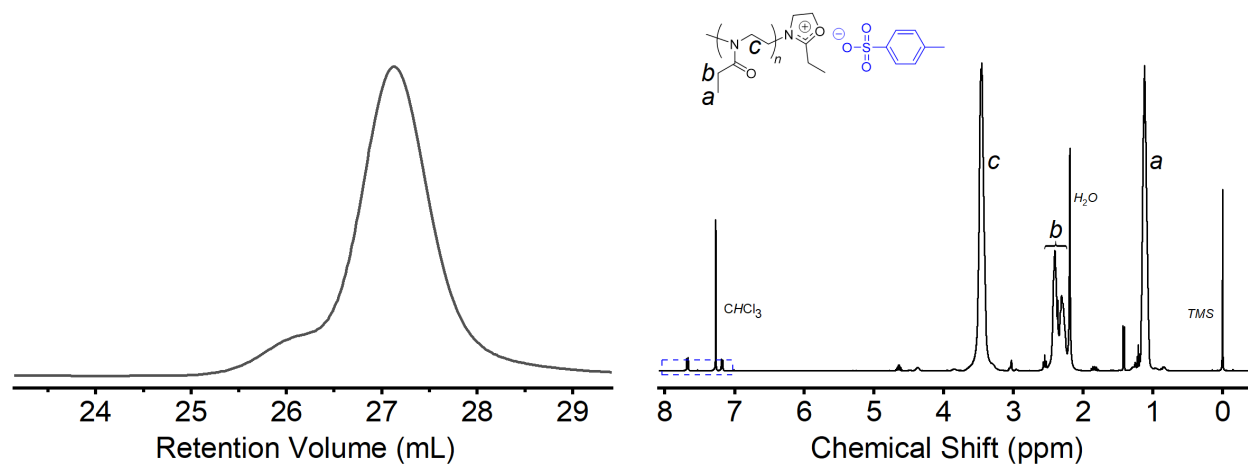




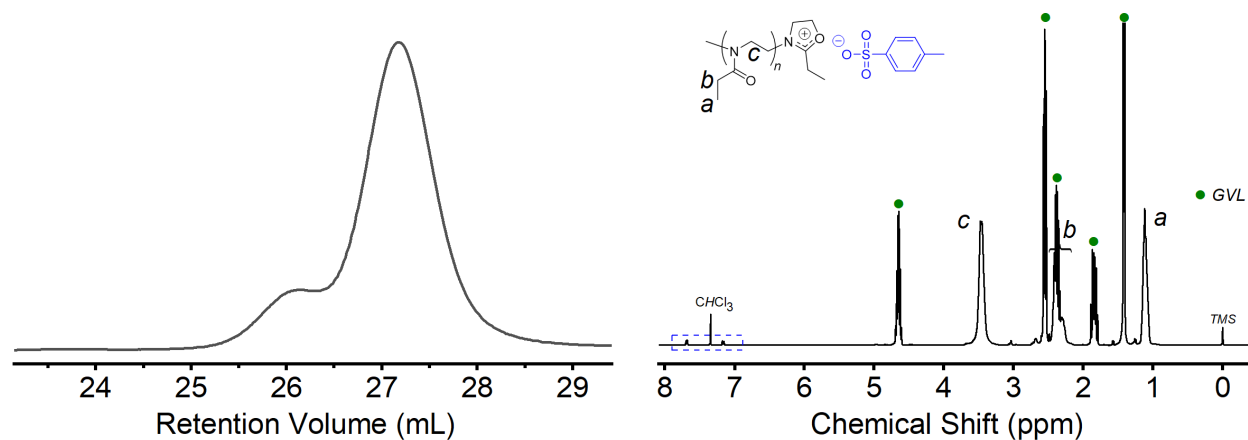
**Figure S24.** MALDI-TOF MS spectrum of a low-molar-mass PEtOx synthesized at 140 °C with DBnP as the initiator and GVL as the solvent (isolated product entry 3 in Table 2). Calculated mass for  $n = 25$ , red circle, is 2607.8; calculated mass for  $n = 26$ , pink circle, is 2616.8.



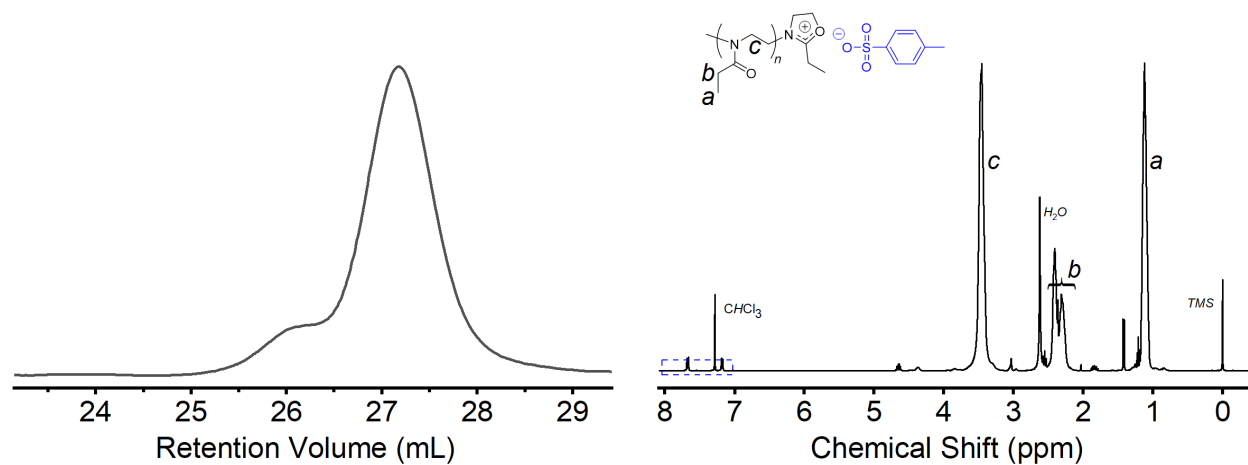
**Figure S25.** Left: SEC trace (DMF, 50 °C, RI signal) of the PEtOx (crude product, DP = 50) synthesized at 140 °C for 30 min with MeOTs as the initiator and GVL as the solvent (entry 5 in Table 2). Right: <sup>1</sup>H NMR spectrum (in CDCl<sub>3</sub>) of the crude product with green circles above the solvent signals.



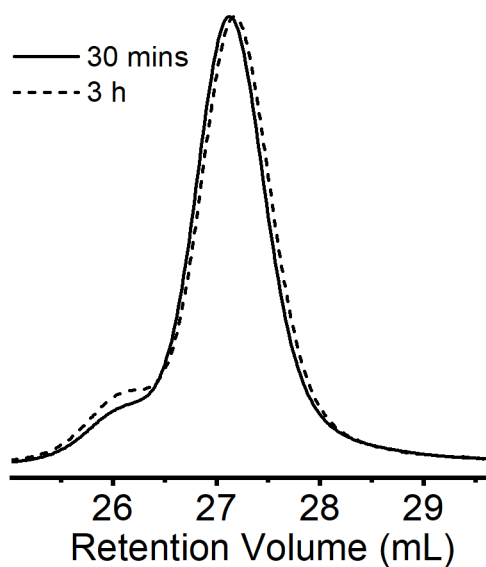
**Figure S26.** SEC trace (DMF, 50 °C, RI signal) and <sup>1</sup>H NMR spectrum (in CDCl<sub>3</sub>) of the isolated product, entry 5 in Table 2.



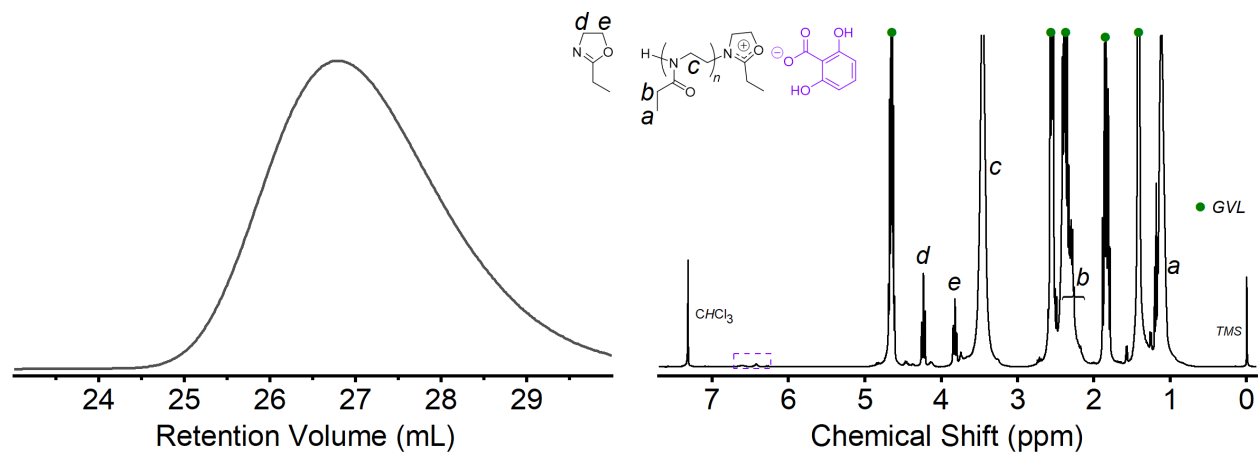
**Figure S27.** Left: SEC trace (DMF, 50 °C, RI signal) of the PEtOx (crude product, DP = 50) synthesized at 140 °C for 3 h with MeOTs as the initiator and GVL as the solvent (entry 6 in Table 2). Right: <sup>1</sup>H NMR spectrum (in CDCl<sub>3</sub>) of the crude product with green circles above the solvent signals.



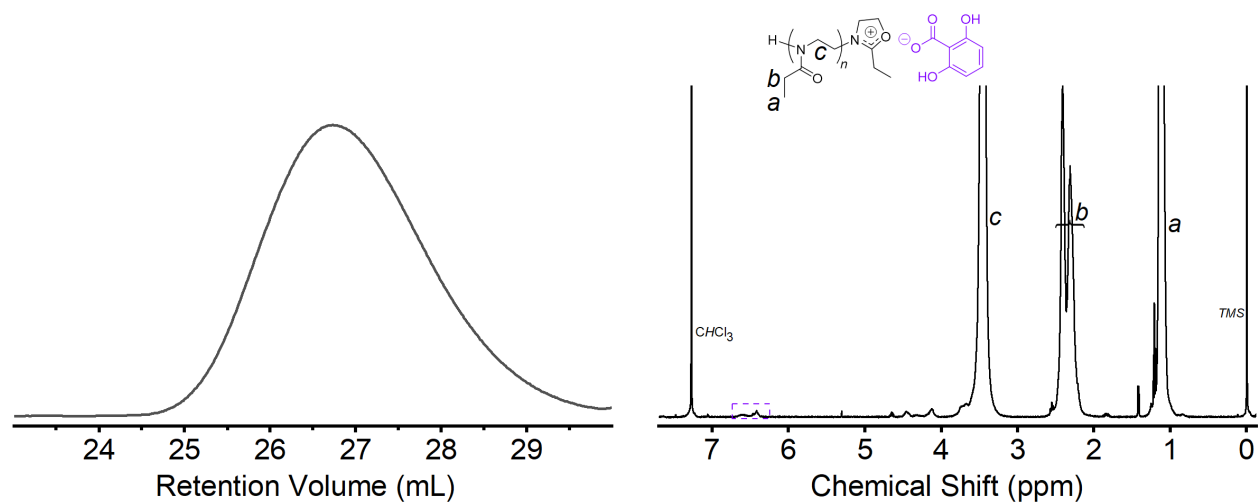
**Figure S28.** SEC trace (DMF, 50 °C, RI signal) and <sup>1</sup>H NMR spectrum (in CDCl<sub>3</sub>) of the isolated product of entry 6 in Table 2.



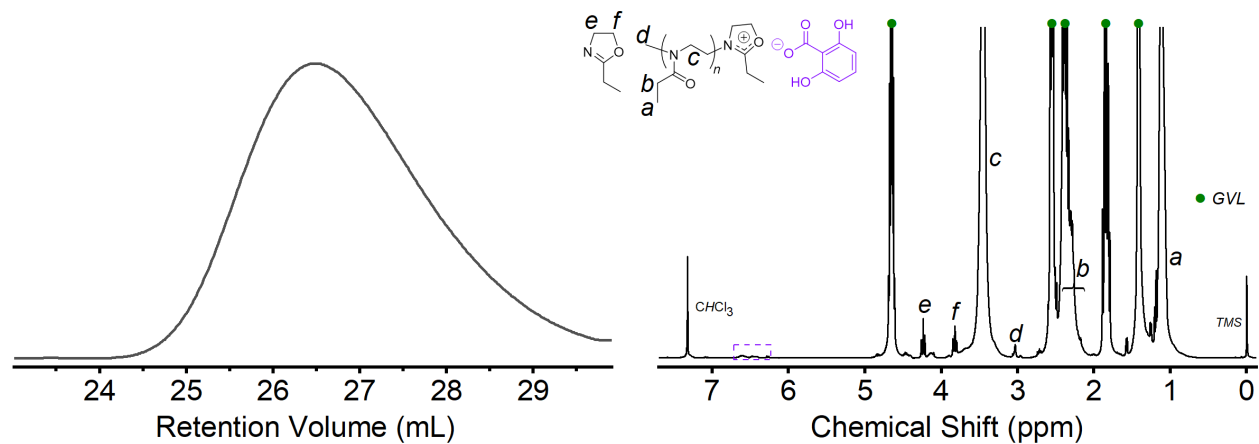
**Figure S29.** SEC traces (DMF, 50 °C, RI signals) of the PEtOx (isolated products) synthesized with the same initiator (MeOTs) at 140 °C for different reaction times (entry 5-6 in Table 2).



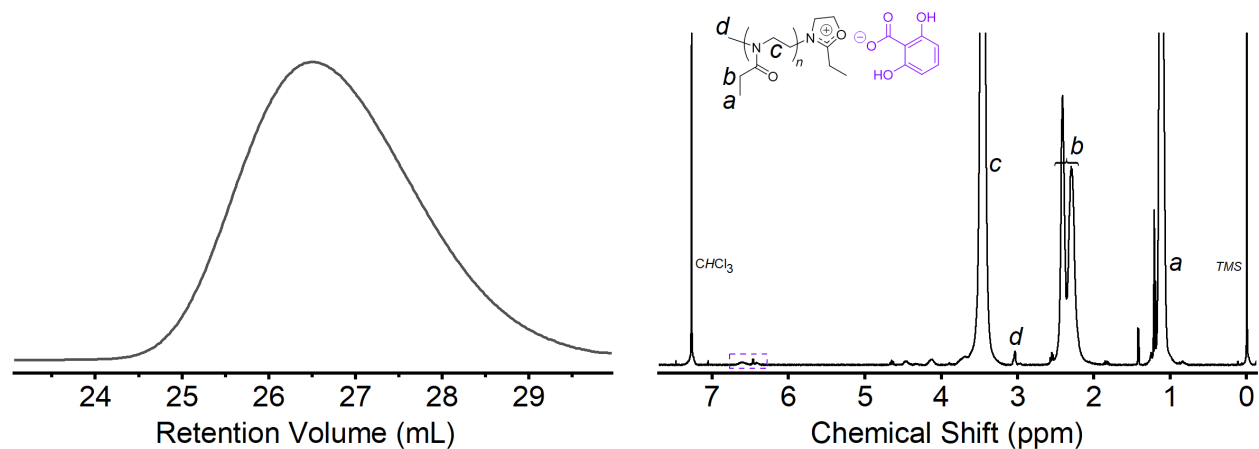
**Figure S30.** Left: SEC trace (DMF, 50 °C, RI signal) of the PEtOx (crude product, DP = 50) synthesized at 140 °C with 2,6-DHBA as the initiator and GVL as the solvent (entry 7 in Table 2). Right: <sup>1</sup>H NMR spectrum (in CDCl<sub>3</sub>) of the crude product with green circles above the solvent signals.



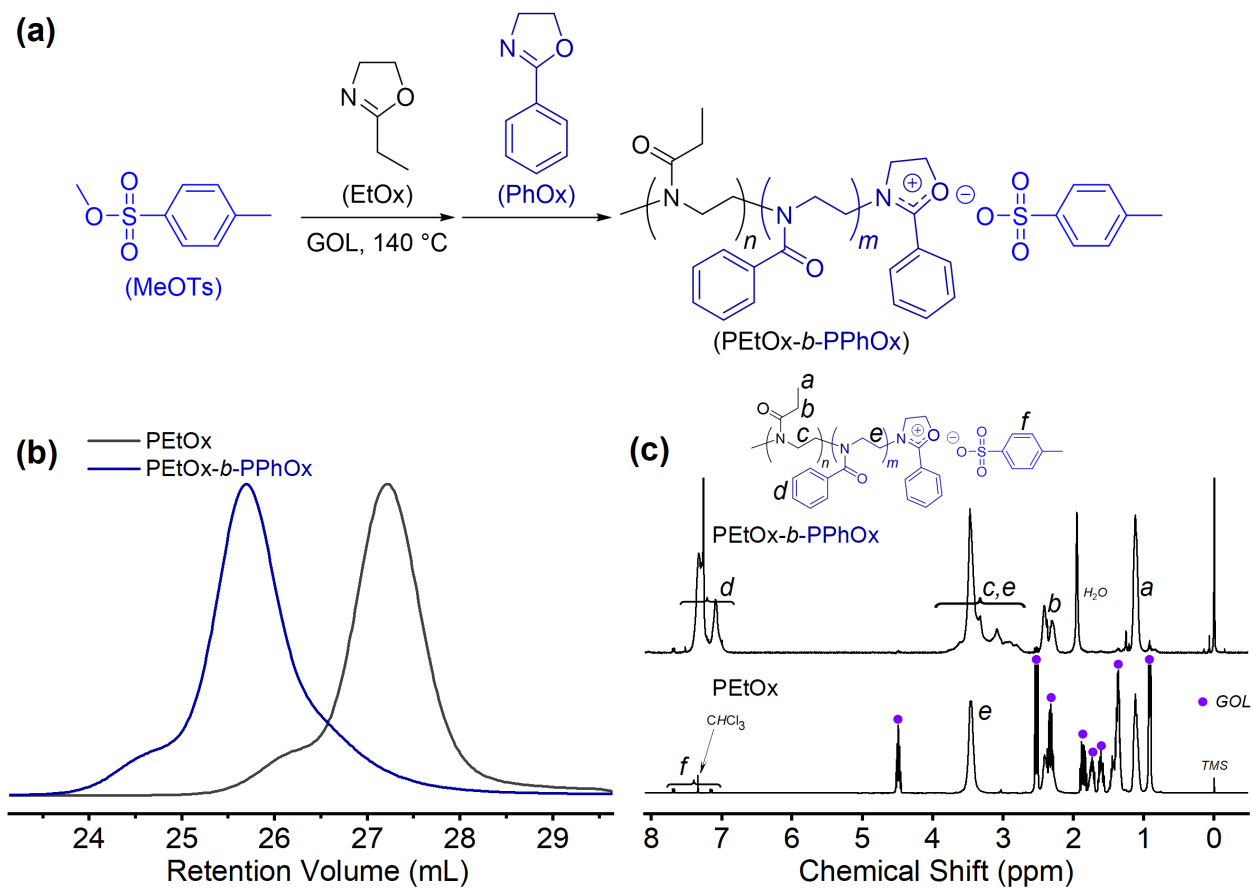
**Figure S31.** SEC trace (DMF, 50 °C, RI signal) and <sup>1</sup>H NMR spectrum (in CDCl<sub>3</sub>) of the isolated product, entry 7 in Table 2.



**Figure S32.** Left: SEC trace (DMF, 50 °C, RI signal) of the PEtOx (crude product, DP = 50) synthesized at 140 °C with 2,6-DHBM as the initiator and GVL as the solvent (entry 8 in Table 2). Right: <sup>1</sup>H NMR spectrum (in CDCl<sub>3</sub>) of the crude product with green circles above the solvent signals. Based on the change of chemical shift of signal *d* from 4.09-4.07 ppm (methyl ester) to 3.06-2.94 ppm (*N*-methyl amide), initiation efficiency of 2,6-DHBM can be calculated to be 93%.



**Figure S33.** SEC trace (DMF, 50 °C, RI signal) and <sup>1</sup>H NMR spectrum (in CDCl<sub>3</sub>) of the isolated product, entry 8 in Table 2.



**Figure S34.** (a) Schematic illustration of one-pot sequential block copolymerization of EtOx and PhOx with MeOTs as the initiator in GOL at 140 °C (entry 2 in Table 3). (b) SEC traces (RI signals, DMF, 50 °C) of the crude product of 1st step (black) and the isolated product of 2nd step (blue). (c)  $^1\text{H}$  NMR spectra of PEtOx (lower; crude product, the precursor of the block copolymer; with purple circles above the solvent signals) and PEtOx-*b*-PPhOx (upper; isolated product).