Protecting group free synthesis of nitroxide-functionalized poly(2-oxazoline)s: direct access to electroactive polynitroxide

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Materials

1-oxyl-2,2,6,6-tetramethylpiperidine-4-one was synthesised according to published literature[1], 1-oxyl-2,2,6,6-tetramethylpiperidine-4-carbonitrile was synthesised according to published literature[2], poly (2,2,6,6,tetramethyl-1-piperidinyloxy methacrylate) (PTMA) was synthesised according to published literature.[3] Anhydrous 1,2-dimethoxyethane 99.5%, Anhydrous Acetonitrile 99.8%, 2,2,6,6-tetramethyl-4-piperidone 95%, Potassium tert-butoxide 98%, Tert-butanol 99%, Ethanolamine 99% and Methyl p-toluenesulfonate 98% were purchased from Sigma-Aldrich and used as received. Methyl p-toluenesulfonate was distilled and stored under argon atmosphere prior to use. Hydrogen peroxide 30%, sodium tungstate 99%, lead dioxide 95% and butan-1-ol 99.5% were purchased from Ajax Finechem and used as received. Toluenesufonylmethyl isocyanide 98% was purchased from Combi-Blocks and used as received. Zinc acetate 99% was purchased from May & Baker LTD Dagenham England and used as received.

Characterization

Nuclear Magnetic Resonance: ^{1}H, ^{13}C-NMR were recorded on a *Bruker* System 600 Ascend LH, equipped with a BBO-Probe (5 mm) with z-gradient (^{1}H: 600.13 MHz, ^{13}C 150.90 MHz). Resonances are reported in parts per million (ppm) relative to tetramethylsilane (TMS). The δ-scale was calibrated to the respective solvent signal of $CHCl_3$ (δ = 7.26 ppm) and DMSO-D_6 (δ = 2.50 ppm) for ^{1}H spectra and for ^{13}C spectra on the middle signal of the $CDCl_3$ (δ = 77.2 ppm) triplet. Integration analysis was performed in MestReNova

Electrospray Ionization-Mass Spectrometry: The ESI-MS Spectra were recorded on a Q Exactive Plus (Orbitrap) mass spectrometer (*Thermo Fisher Scientific,* San Jose, CA, USA) equipped with a HESI II probe. The instrument was calibrated in the m/z range 74-1822 using premixed calibration solutions (*Thermo Scientific*) and for the high mass mode in the m/z range of 600-8000. Spectra of all small molecules were run in positive mode, the polymer was run in negative mode doped with a sodium iodide solution to support ionization. Analysis of the ESI-MS spectra was performed in Thermo Xcalibur, isotope simulations were performed using the built-in program (under info bar in Thermo Xcalibur) by inputting the chemical formula of a specific polymer chain length which would calculate the simulated isotope pattern for that chain length.

Size Exclusion Chromatography: SEC measurements were conducted on a *PSS* SECurity2 system consisting of a *PSS* SECurity Degasser, *PSS* SECurity TCC6000 Column Oven (60 °C), *PSS* GRAM Column Set (8x150 mm 10 µm Precolumn, 8x300 mm 10 µm Analytical Columns, 1000 Å, 1000 Å and 30 Å) and an *Agilent* 1260 Infinity Isocratic Pump, *Agilent* 1260 Infinity Standard Autosampler, *Agilent* 1260 Infinity Diode Array and Multiple Wavelength Detector (A: 254 nm, B: 360 nm), *Agilent* 1260 Infinity Refractive Index Detector (35 °C). HPLC grade DMAc, 0.01 M LiBr, is used as eluent at a flow rate of 1 mL·min-1. Narrow disperse linear poly(styrene) (Mn: 266 g·mol-1 to 2.52x106 g·mol-1) and poly(methyl methacrylate) (Mn: 202 g·mol-1 to 2.2x106 g·mol-1) standards (*PSS* ReadyCal) were used as calibrants. All samples were passed over 0.22 µm PTFE membrane filters. Molecular weight and dispersity analysis was performed in *PSS* WinGPC UniChrom software (version 8.2).

Cyclic Voltammetry: All electrochemistry experiments were controlled by a BioLogic SP-150 potentiostat and EC-Lab software. The reference electrode employed was a leakless Ag/AgCl electrode (ET069-1, eDAQ) which was calibrated to the external standard of ferrocene (−0.42 V vs. Fc/Fc^{+}). The working electrode was a 1 mm diameter glassy carbon electrode, a length of platinum wire served as the counter electrode. The active materials were diluted to 0.01 M in dry acetonitrile with NBu_4PF_6 ($TBAPF_6$) 0.1 M as supporting salt. Each experiment was performed at a scan rate of 100 mV/s.

Electron Paramagnetic Resonance: Continuous-wave (CW) X-band (ca. 9.46 GHz) electron paramagnetic resonance (EPR) were recorded on a Bruker Magnettech ESR5000 spectrometer. Measurements were carried out at 300 K using a modulation amplitude of 0.01 mT, a modulation frequency of 100 kHz and a microwave power of 3.98 mW. Spin quantification was performed using the SpinCount software module of the spectrometer, utilising the absolute factory calibration of the resonator. As SpinCount quantification is sensitive to sample geometry and positioning, the sample was positioned in the centre of the resonator and the mass and depth of sample (typically ca. 1-3 mg, ca. 1-2 mm) and sample tube inner diameter (3 mm) were accurately measured for entry into the SpinCount module. The integration and baseline regions of the spectra were adjusted to ensure accuracy of the double integral calculation. Further details into the process can be found in the Bruker Magnetech ESR5000 spectrometer manual (section 9.2.1 SpinCount - Reference-Free Spin Concentration Measurements).

Infrared spectroscopy:

Infrared spectroscopy measurements were performed on a Thermo Fisher Scientific Nicolet FTIR Spectrometer equipped with a DTGS ATR detector and KBr beamsplitter. Measurements were taken from 4000 – 500 cm^{-1}.

Monomer synthesis

4-(4,5-dihydrooxazol-2-yl)-2,2,6,6-tetramethylpiperidin-1-ol ***(2)***: 1-oxyl-2,2,6,6-tetramethylpiperidine-4-carbonitrile (5g, 27 mmol, 1 equiv) and $Zn(OAc)_2$ (0.2g, 1 mmol, 0.04 equiv) were placed into a two-necked round bottom flask, the flask was purged with argon. 1-butanol (25 mL) and ethanolamine (5 mL, 83 mmol, 3 equiv) were added through the second neck of the round bottom flask, the round bottom was then seal. The solution was stirred and heated to 130°C for 24 hrs with an argon flow. After cooling to room temperature, DCM (300 mL) was added to the solution. The organic phase was then washed with brine and dionised water. The organic layer was dried over Na_2SO_4 and filtered. The solution was then concentrated via rotary evaporation to yield crude orange/white solid. The hydroxylamine is then purified by washing the orange/white solid with cold DCM to yield a white powder (2.3g, 37%) (M.P: 161.4 -163.6 °C).

^{1}H NMR of **hydroxylamine** (600 MHz, $CDCl_3$): δ = 1.14 (s, 6H), 1.19 (s, 6H), 1.61 – 1.65 (t, *J* = 12 Hz, 2H), 1.80 – 1.84 (ddt, *J* = 6, 12 Hz, 2H,), 2.65 – 2.71 (ttd, *J* = 6, 12 Hz, 1H), 3.80 – 3.83 (td, *J* = 6, 12 Hz, 3H), 4.20 – 4.23 (t, *J* = 0.12 Hz, 3H)

^{13}C NMR DEPTQ (MHz 600, $CDCl_3$): δ = 18.9 (CH_3-C), 28.2 (CH), 31.8 (CH_3-C), 42.0 (CH_2), 53.8 (N-CH_2), 58.0 (CR_4), 66.8 (O-CH_2), 170.4 (O-C=N)

ESI-MS of **hydroxylamine** m/z: $[M]^+$ calcd. For $[C_{12}H_{22}N_2O_2]$, 226.1681; found, 226.1681, $[M+H]^+$ calcd. For $[C_{12}H_{23}N_2O_2 + H]^+$, 227.1755; found, 227.1754, $[M+H]^+$ isotope calcd. For $[C_{12}H_{23}N_2O_2 + H]^+$, 228.1788; found, 228.1787.

*4-(4,5-dihydrooxazol-2-yl)-2,2,6,6-tetramethylpiperidin-1-oxyl (**TOx**)*: 4-(4,5-dihydrooxazol-2-yl)-2,2,6,6-tetramethylpiperidin-1-ol (80 mg, 0.35 mmol, 1 equiv) is treated with lead dioxide (160 mg, 0.7 mmol, 2 equiv) and stirred in DCM (100 ml) for 24 hours. After 24 hrs lead dioxide was filtered off and the solution was concentrated via rotary evaporation to give an orange powder (which was used for polymerisations without further purification) (73 mg, 91%).

^{1}H NMR of **TOx** (600 MHz, $CDCl_3$): δ = 3.83 – 3.86 (broad t, 2H), 4.35 – 4.38 (broad t, 2H).

ESI-MS of **TOx** m/z: $[M]^+$ calcd. For $[C_{12}H_{21}N_2O_2]^+$, 225.1603; found, 225.1599, $[M+H]^+$ calcd. For $[C_{12}H_{22}N_2O_2 + H]^+$, 226.1637; found, 226.1672, $[M+H]^+$ isotope calcd. For $[C_{12}H_{22}N_2O_2 + 2H]^+$, 227.1715; found, 227.1714, $[MH-Me]^+$ calcd. For $[C_{11}H_{19}N_2O_2]^+$, 211.1442; found, 211.1438.

*4-(4,5-dihydrooxazol-2-yl)-2,2,6,6-tetramethylpiperidin-1-oxyl (**TOx**) (*0ne-pot). 1-oxyl-2,2,6,6-tetramethylpiperidine-4-carbonitrile (5g, 27 mmol, 1 equiv) and $Zn(OAc)_2$ (0.2g, 1 mmol, 0.04 equiv) were placed into a two-necked round bottom flask, the flask was purged with argon. 1-butanol (25 mL) and ethanolamine (5 mL, 83 mmol, 3 equiv) were added through the second neck of the round bottom flask, the round bottom was then seal. The solution was stirred and heated to 130°C for 24 hrs with an argon flow. After cooling to room temperature, DCM (250 mL) was added to the solution. The organic phase was then washed with brine and dionised water. The organic layer was dried over Na_2SO_4 and filtered. The solution was then concentrated via rotary evaporation to yield crude orange/white solid. the crude material (3.4g) is then treated with lead dioxide (3.5 g, 15.6 mmol) and stirred in DCM (300 ml) for 24 hours. After 24 hrs lead dioxide was filtered off and the solution was concentrated via rotary evaporation to give an orange powder. The crude material was purified via recrystallisation in diethyl ether to give orange crystals (3.1g, 50%, M.P: 112.5 – 113.2 °C).

Polymer synthesis

*Poly[1-oxyl-2,2,6,6-tetramethylpiperidin-4-(2-oxazoline)] (PTOx) (**P1**).*

TOx (400 mg, 1.77 mmol, 14 equiv) was dried overnight under high vacuum in the glove box chamber in a crimp neck vial. The vial was then moved into the glove box and a solution of acetonitrile (1100 µL, monomer concentration 1.6M) and methyl tosylate (20 µL, 0.130 mmol, 1 equiv) were Added to the vial and sealed. The polymerization proceeded at 80 °C for 7 hours. The polymerization was terminated by the addition of H_2O (10 µL) and left overnight. The residue was taken up in minimal amount of DCM and precipitated from room temperature in cyclohexane and dried under high vaccum to yield **P1** as an orange powder solid (370 mg, 93%).

*Poly[1-oxyl-2,2,6,6-tetramethylpiperidin-4-(2-oxazoline)] (PTOx) (**P2**).*

TOx (650 mg, 2.88 mmol, 90 equiv) was dried overnight under high vacuum in the glove box chamber in a crimp neck vial. The vial was then moved into the glove box and a solution of acetonitrile (1100 µL, monomer concentration 1.6M) and methyl tosylate (5 µL, 0.03 mmol, 1 equiv) were Added to the vial and sealed. The polymerization proceeded at 80 °C for 48 hours. The polymerization was terminated by the addition of H_2O (10 µL) and left overnight. The residue was taken up in minimal amount of DCM and precipitated from room temperature in cyclohexane and dried under high vaccum to yield **P2** as an orange powder solid (310 mg, 47%).

*Poly[1-oxyl-2,2,6,6-tetramethylpiperidin-4-(2-oxazoline)] (PTOx) (**P3**).*

TOx (400 mg, 1.77 mmol, 180 equiv) was dried overnight under high vacuum in the glove box chamber in a crimp neck vial. The vial was then moved into the glove box and a solution of acetonitrile (1100 µL, monomer concentration 1.6M) and methyl tosylate (3.2 µL, 0.01 mmol, 1 equiv) were Added to the vial and sealed. The polymerization proceeded at 80 °C for 48 hours. The polymerization was terminated by the addition of H_2O (10 µL) and left overnight. The residue was taken up in minimal amount of DCM and precipitated from room temperature in cyclohexane and dried under high vaccum to yield **P3** as an orange powder solid (70 mg, 18%).

Figures and tables

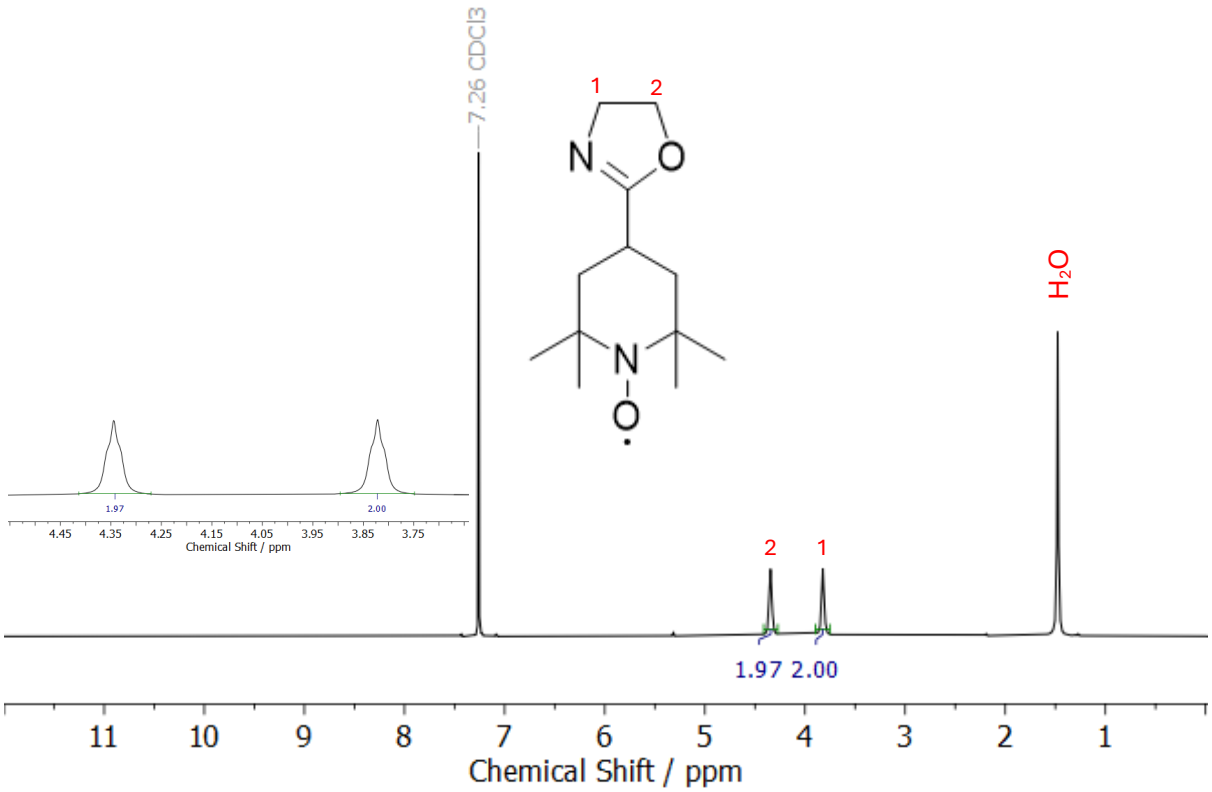

Figure S1. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **TOx** and assignment of signals to the corresponding chemical structure, also including an expansion of the broadening effect the nitroxide induces on the protons associated with the oxazoline ring.

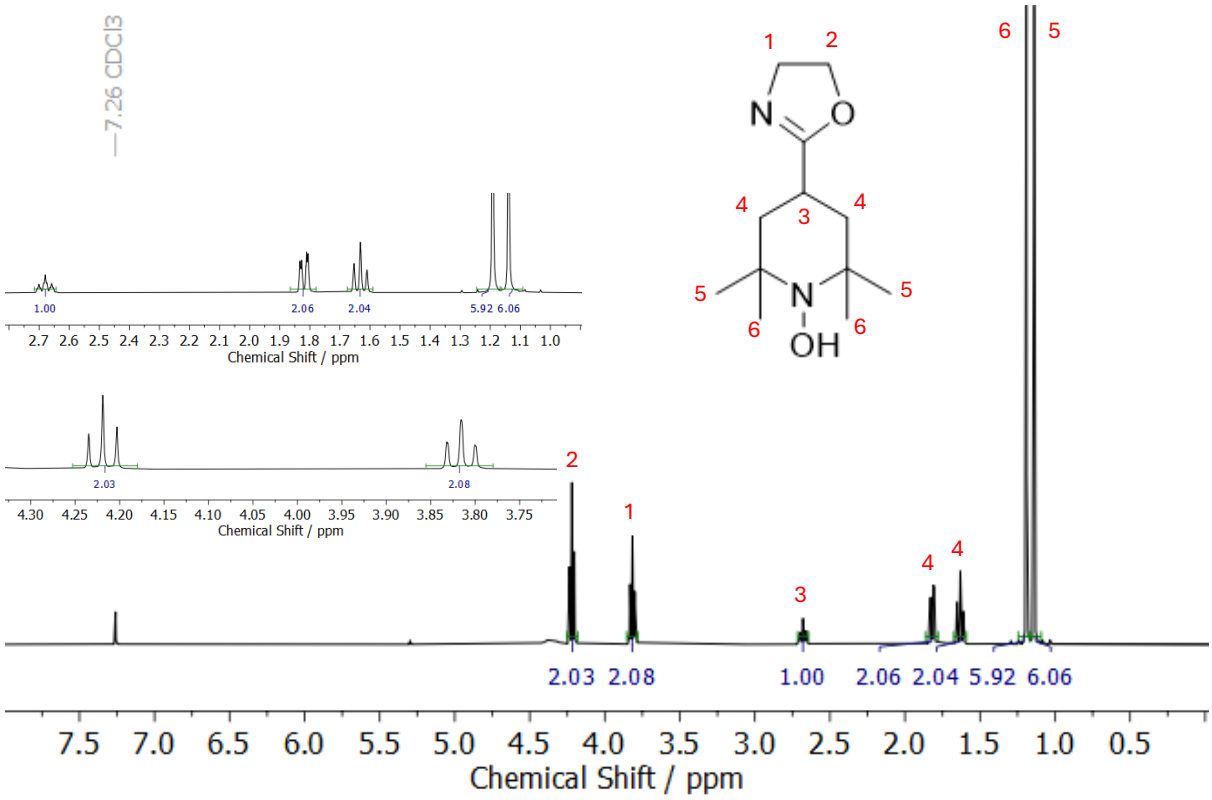

Figure S2. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **hydroxylamine** (2) and assignment of signals to the corresponding chemical structure, also an expansion to show the coupling of the tetramethylpiperidine ring (top) and oxazoline ring (bottom) protons.

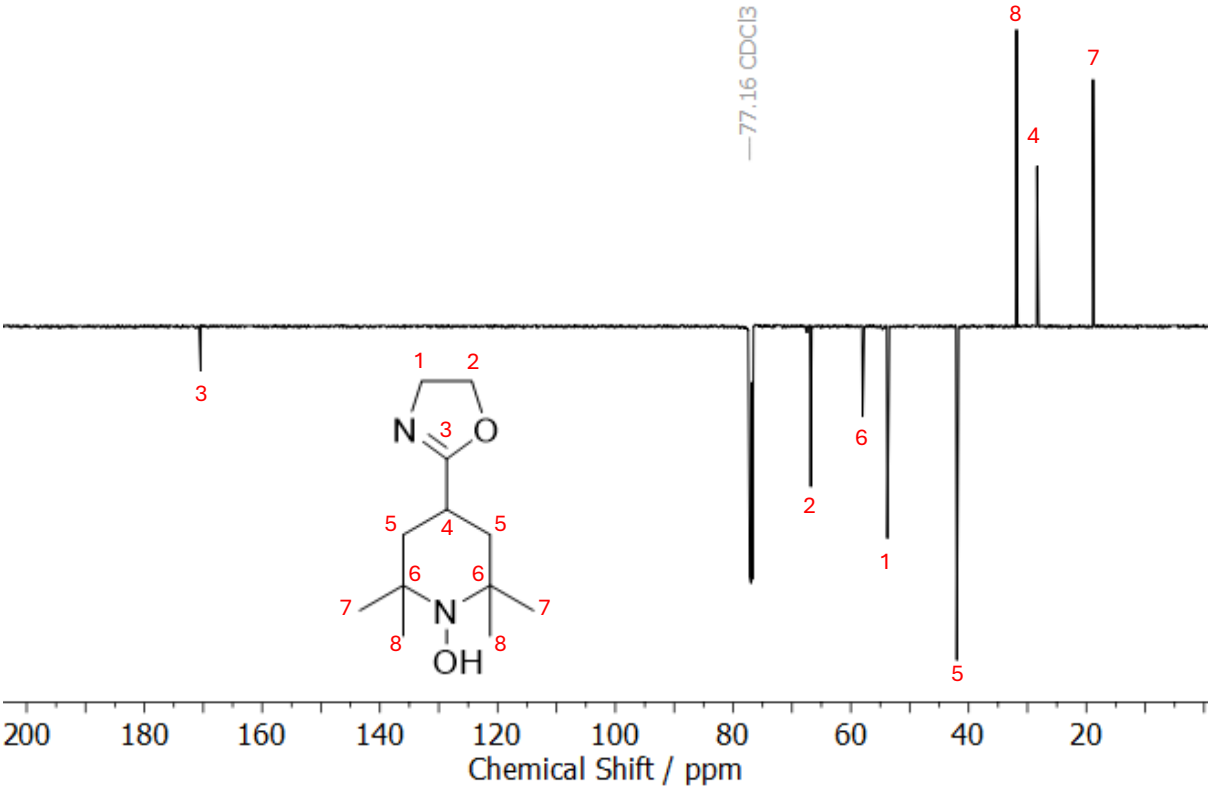

Figure S1. ^{13}C NMR spectrum (DEPTQ) (600 MHz, $CDCl_3$) of **hydroxylamine** (2) and assignment of signals to the corresponding chemical structure.

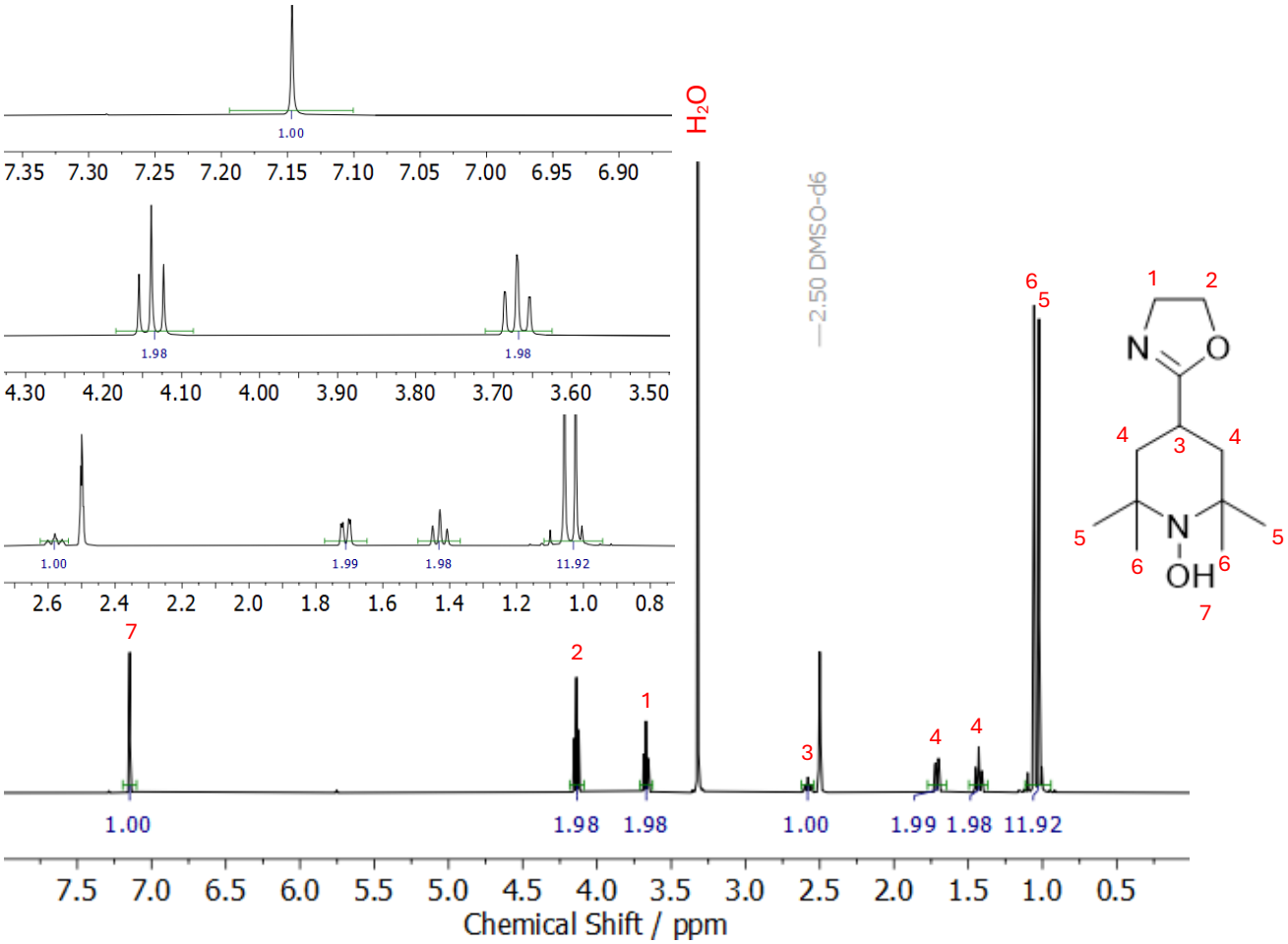

Figure S4. [1]H NMR spectrum (600 MHz, DMSO-d6) of **hydroxylamine** (2) and assignment of signals to the corresponding chemical structure, also an expansion to show the coupling of the tetramethylpiperidine ring (bottom) and oxazoline ring (middle) protons, also the additional proton of the hydroxylamine (top) when preformed in deuterated DMSO.

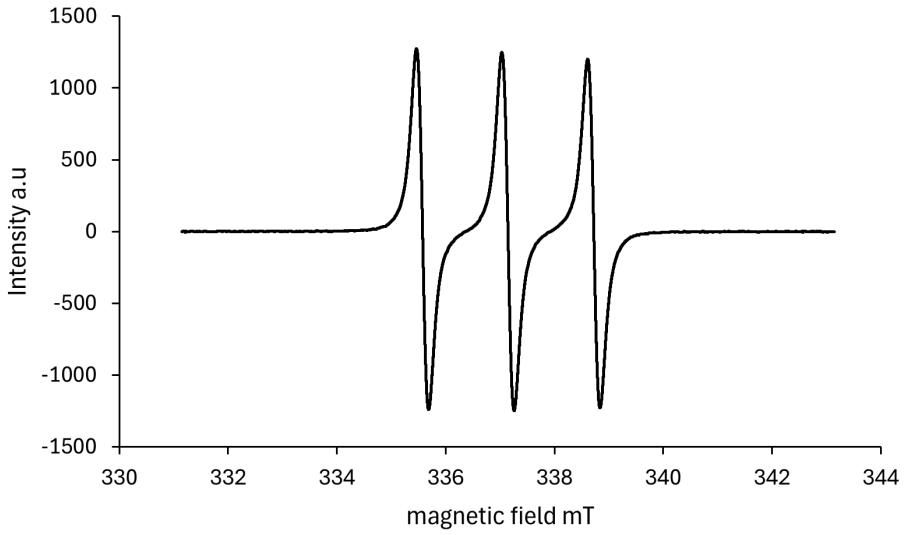

Figure S5. EPR spectra of **TOx** in DCM. Microwave frequency = 9.46906 GHz, temperature = 300K, g value = 2.0066.

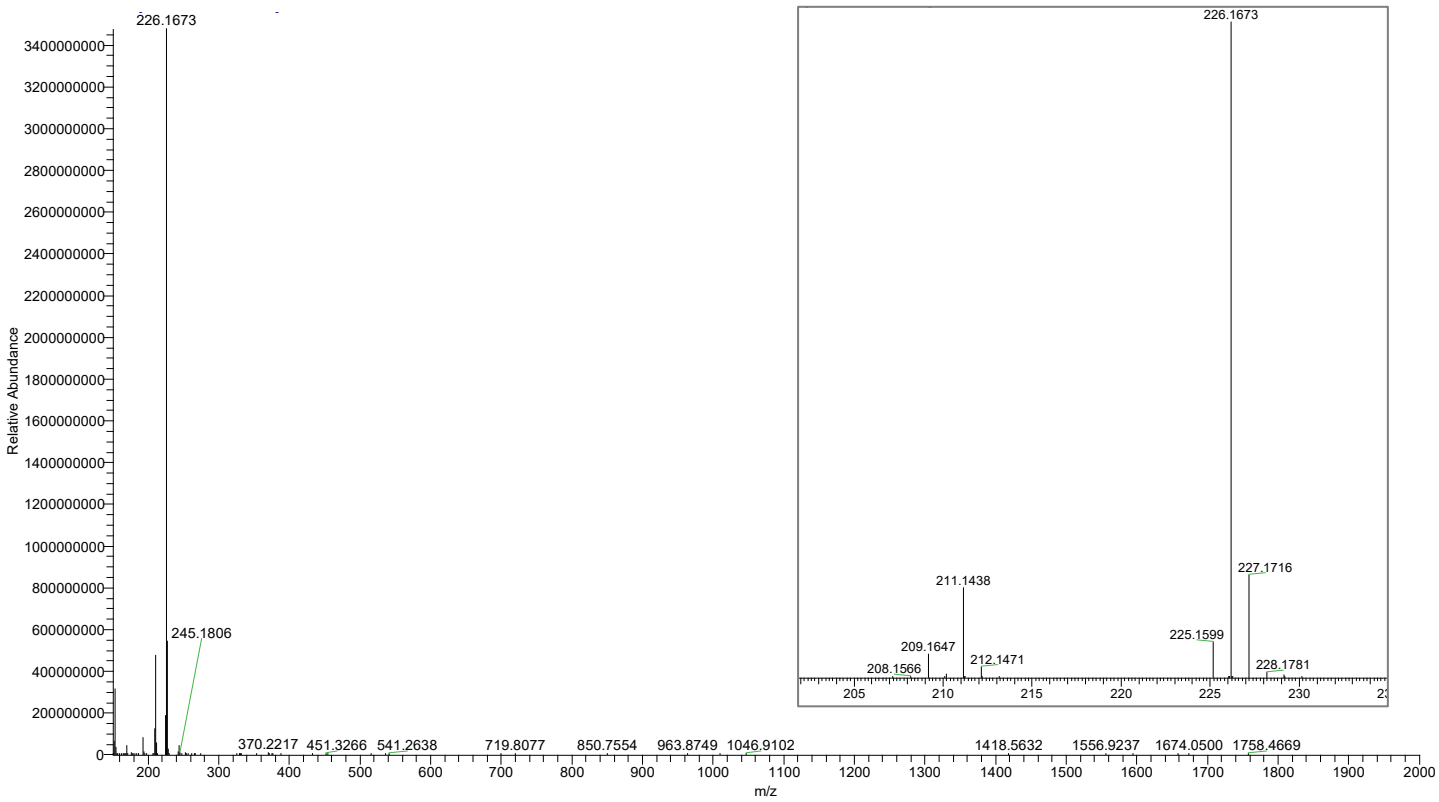

Figure S6. electron spray ionisation-Mass spectrometry (ESI-MS) of **TOx**. a) full sweep of the ESI-MS (150 – 2000 *m/z)*. b) isotopic pattern of [M], $[M + H]^+$, $[M + H]^+$ isotope, $[M – Me]^+$

Table S1. theoretical and experimentally observed m/z values of relevant species as shown in figure 6.

m/z_{exp}	Ion assignment	formula	m/z_{theor}	Δm/z
225.1599	$[M]^+$	$C_{12}H_{21}N_2O_2$	225.1598	0.0001
226.1673	$[M+H]^+$	$C_{12}H_{22}N_2O_2$	226.1676	0.0003
227.1716	$[M+H]^+$ isotope	$C_{12}H_{22}N_2O_2$	227.1710	0.0006
211.1438	$[MH-Me]^+$	$C_{11}H_{19}N_2O_2$	211.1442	0.0004

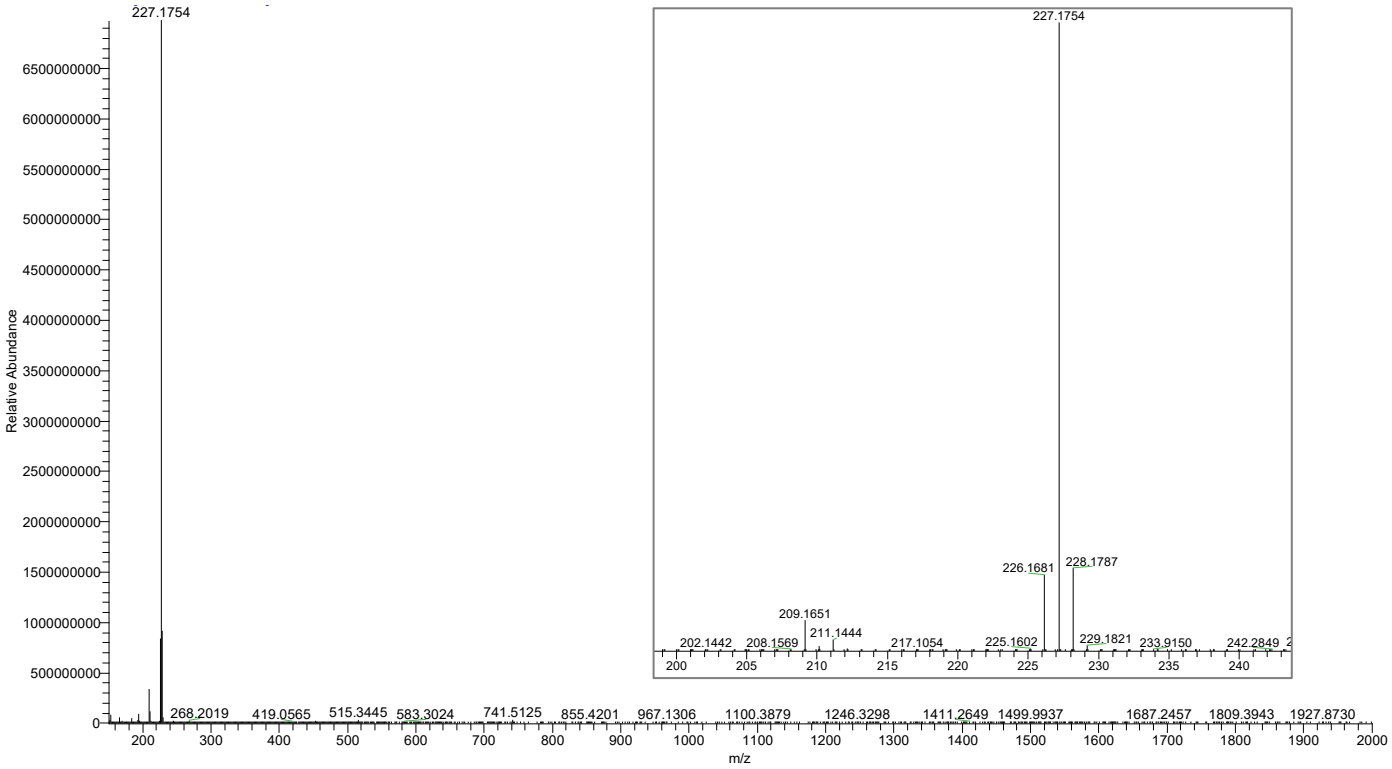

Figure S7. electron spray ionisation-Mass spectrometry (ESI-MS) of **hydroxylamine** (2)**.** a) full sweep of the ESI-MS (150 – 2000 *m/z)*. b) zoom in on isotopic pattern of [M], $[M + H]^+$, $[M + H]^+$ isotope.

Table S2. theoretical and experimentally observed m/z values of relevant species as shown in figure 7.

m/z_{exp}	Ion assignment	formula	m/z_{theor}	Δm/z
226.1681	$[M]^+$	$C_{12}H_{22}N_2O_2$	226.1681	0.0000
227.1754	$[M+H]^+$	$C_{12}H_{23}N_2O_2$	227.1755	0.0001
228.1787	$[M+H]^+$ isotope	$C_{12}H_{23}N_2O_2$	228.1788	0.0001

Table S3. CROP polymerization results

	Time (hours)	Target MW (g/mol)	M_n (g/mol)	M_p (g/mol)	Đ
P1	7	3 000	5300	5400	1.3
P2	48	20 000	10 700	13 700	1.4
P3	48	40 000	10 100	11 900	1.4

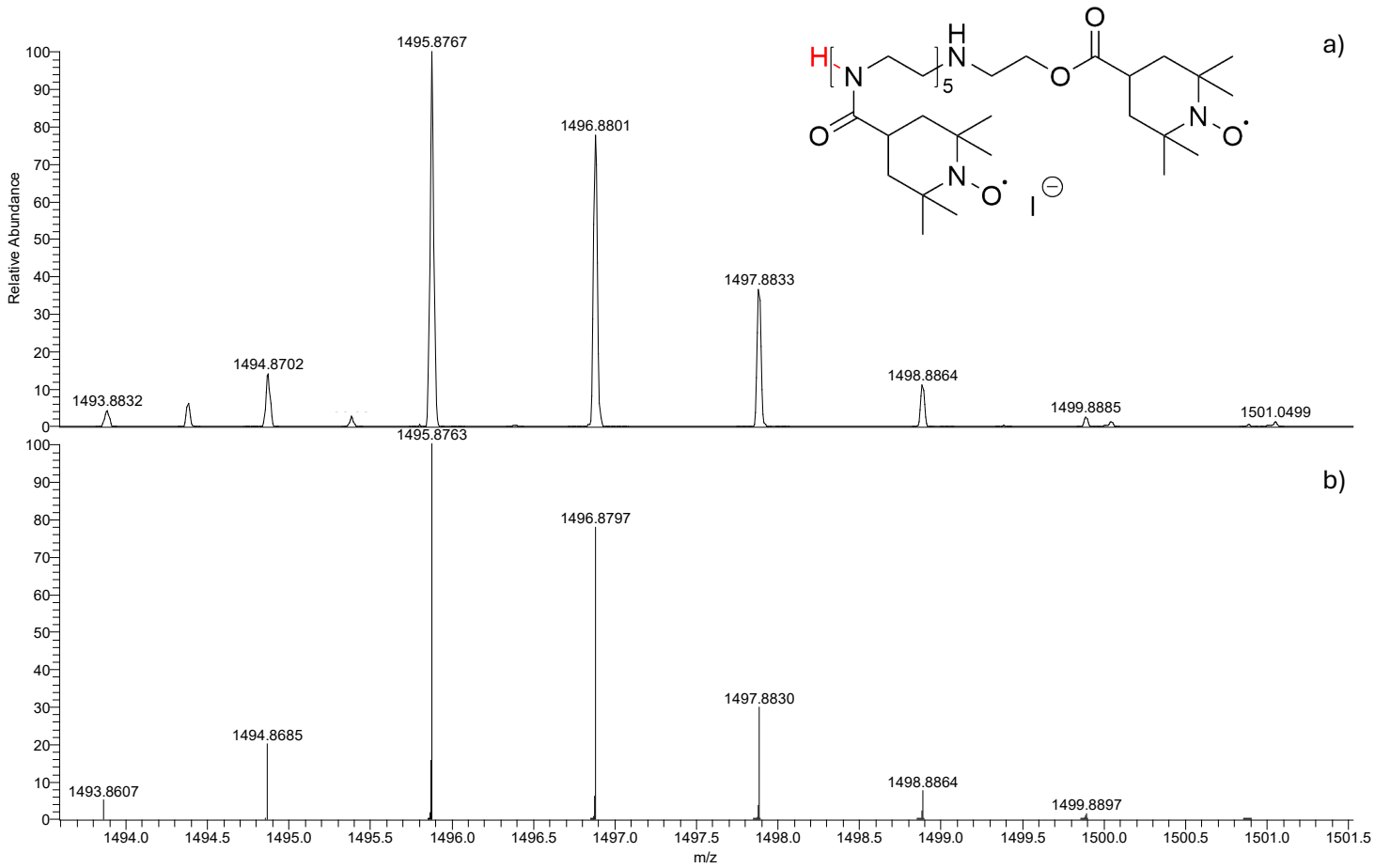

Figure S8. a) ESI-MS experimental of hydrogen initiated **PTOx** chain length 5 . b) calculated isotopic pattern of a simulation mixture ($[MI]^-$:$[MI-H]^-$:$[MI-2H]^-$) (75:20:5) ratio for chain length 5 hydrogen initiated PTOx.

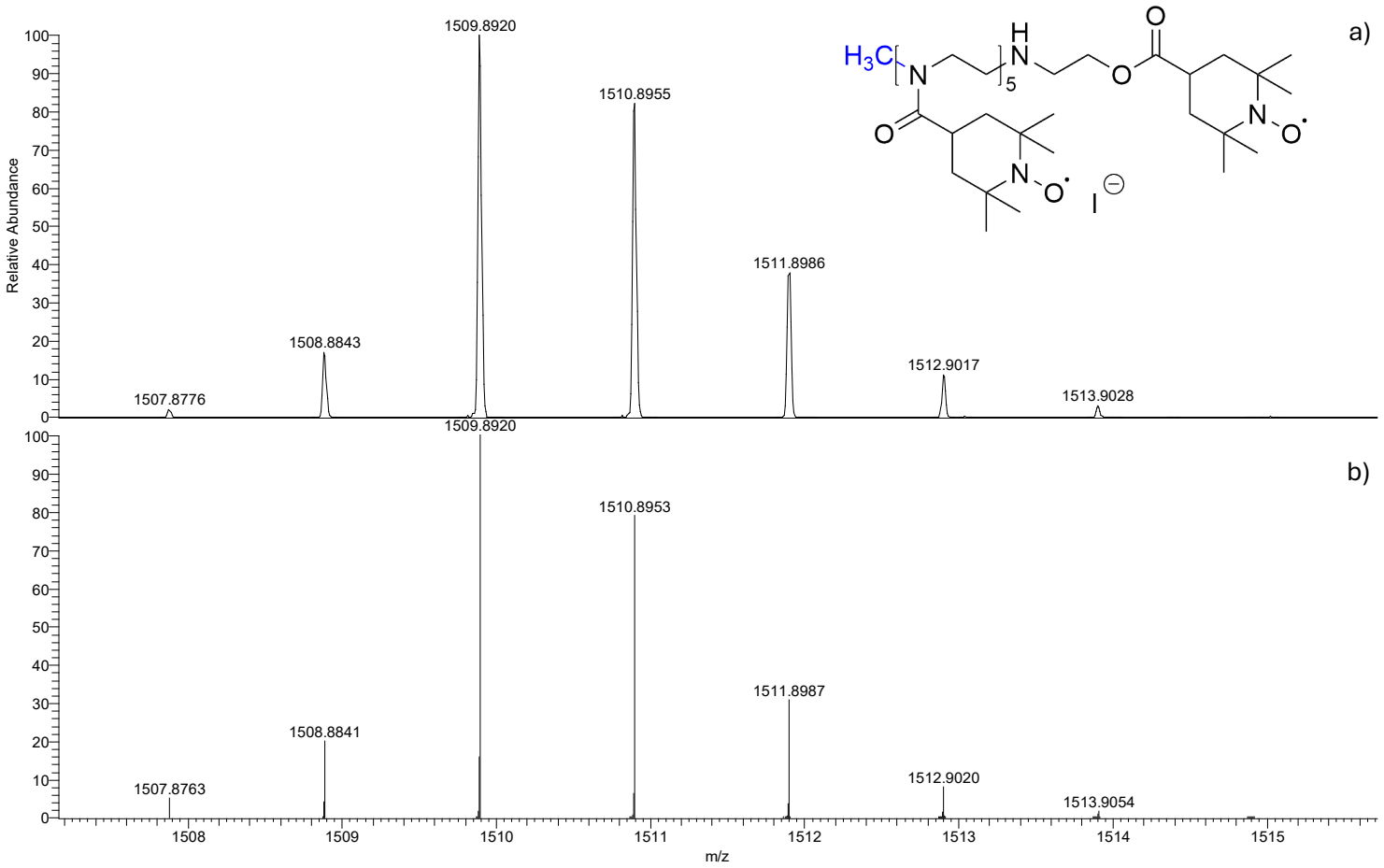

Figure S9. a) ESI-MS experimental of methyl initiated **PTOx** chain length 5 . b) calculated isotopic pattern of a simulation mixture ($[MI]^{-}$:$[MI-H]^{-}$:$[MI-2H]^{-}$) (75:20:5) ratio for chain length 5 methyl initiated PTOx.

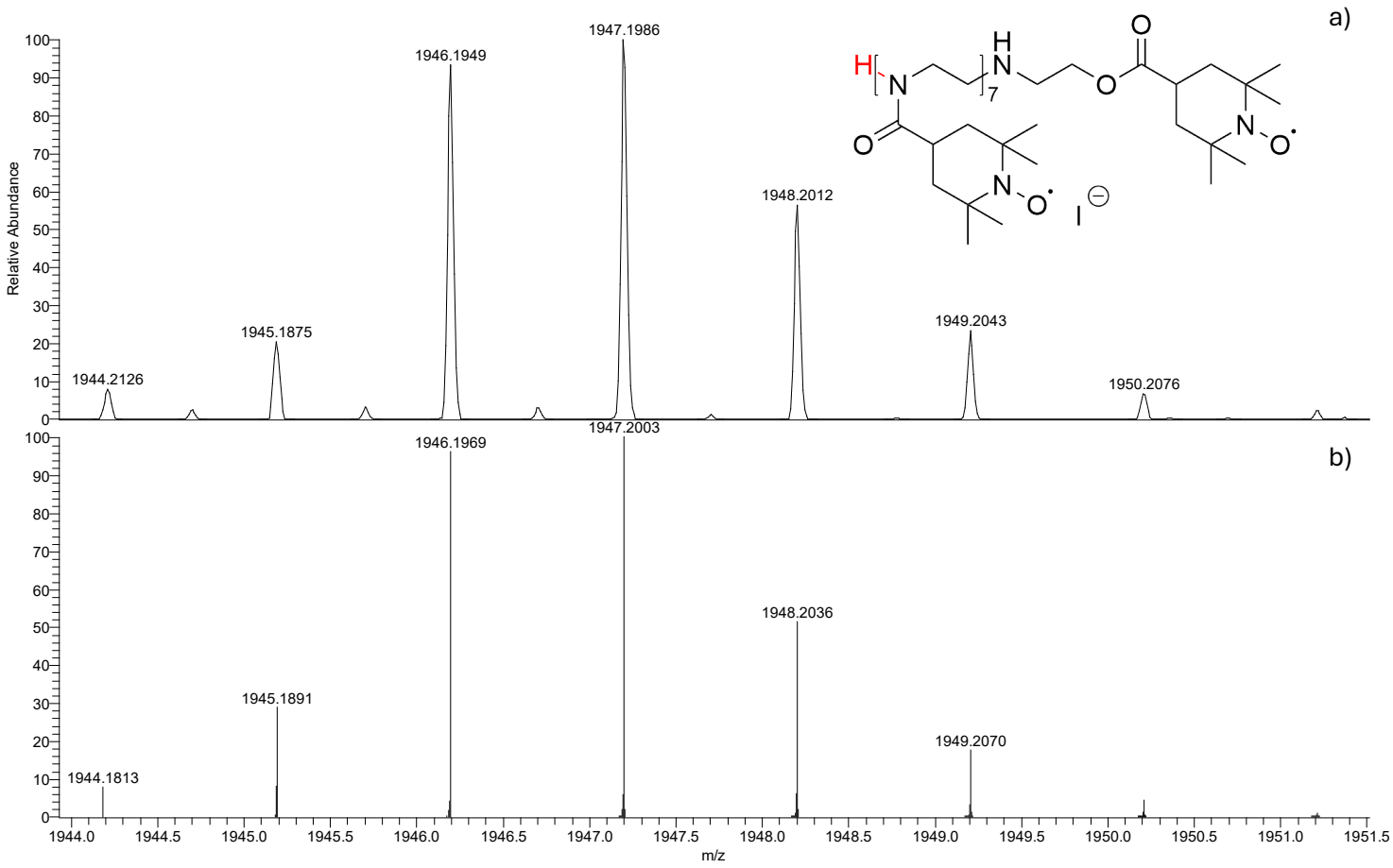

Figure S10. a) ESI-MS experimental of hydrogen initiated **PTOx** chain length 7 . b) calculated isotopic pattern of a simulation mixture ($[MI]^-$:$[MI-H]^-$:$[MI-2H]^-$) (62:30:8) ratio for chain length 7 hydrogen initiated PTOx.

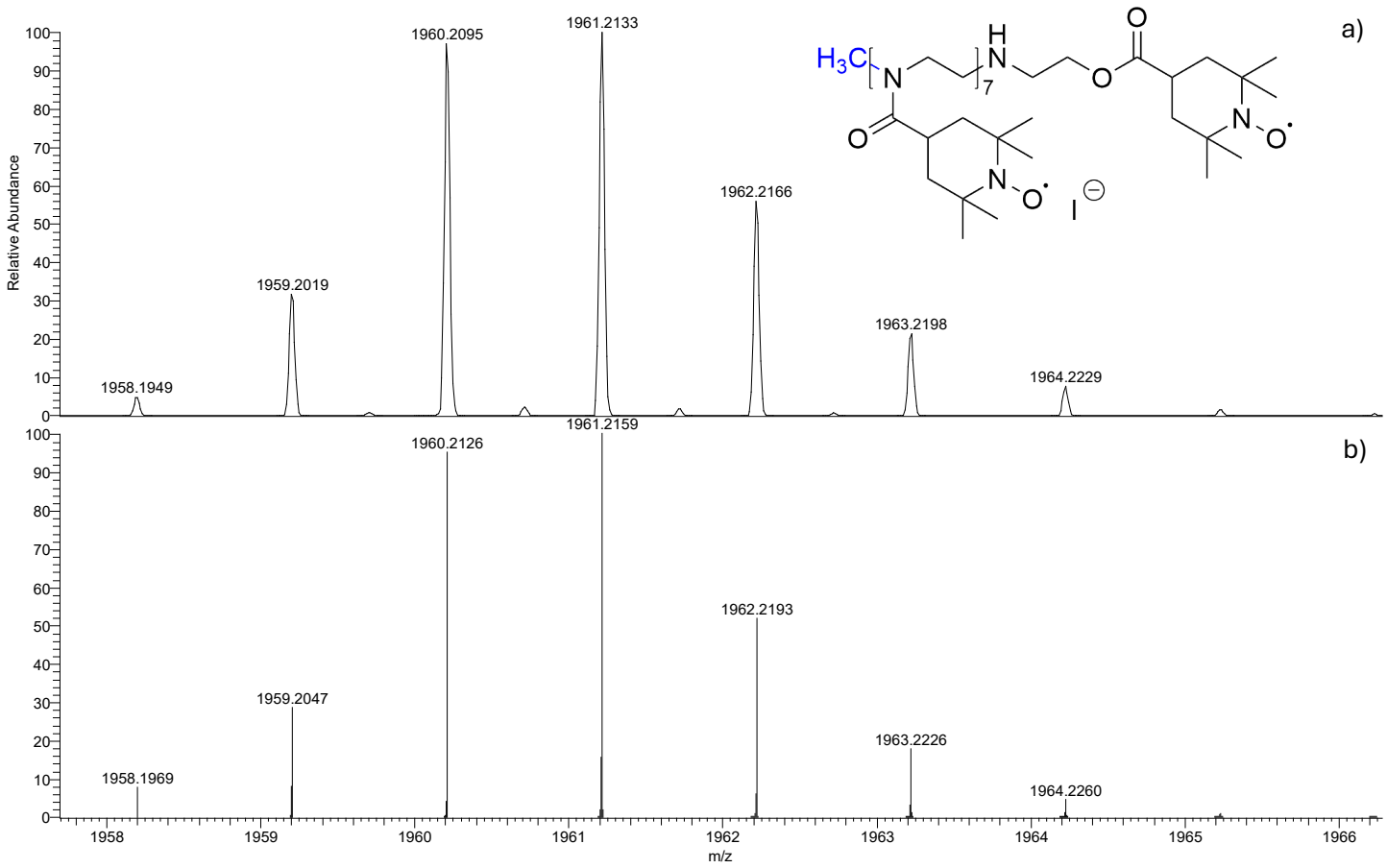

Figure S11. a) ESI-MS experimental of Methyl initiated **PTOx** chain length 7 . b) calculated isotopic pattern of a simulation mixture ($[MI]^-$:$[MI-H]^-$:$[MI-2H]^-$) (62:30:8) ratio for chain length 7 methyl initiated PTOx.

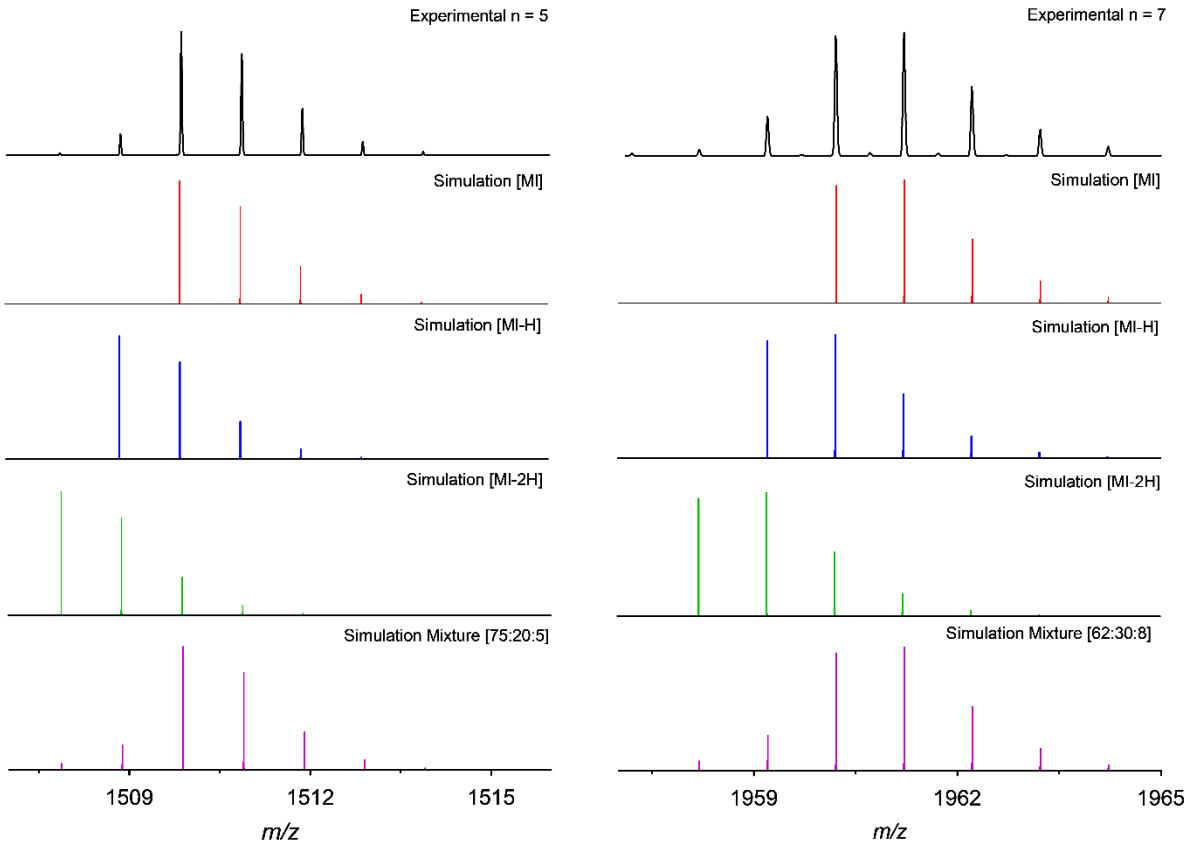

Figure S12. ESI-MS overlay of methyl initiated **PTOx** (P1). Experimental (black), simulation of mass + iodine ion $[MI]^-$ (red), simulation of mass + iodine ion - hydrogen $[MI\text{-}H]^-$ (blue), simulation of mass + iodine ion - 2 hydrogen $[MI\text{-}2H]^-$ (green) and calculated isotopic pattern of a simulation mixture ($[MI]^-$:$[MI\text{-}H]^-$:$[MI\text{-}2H]^-$) ratio (purple).

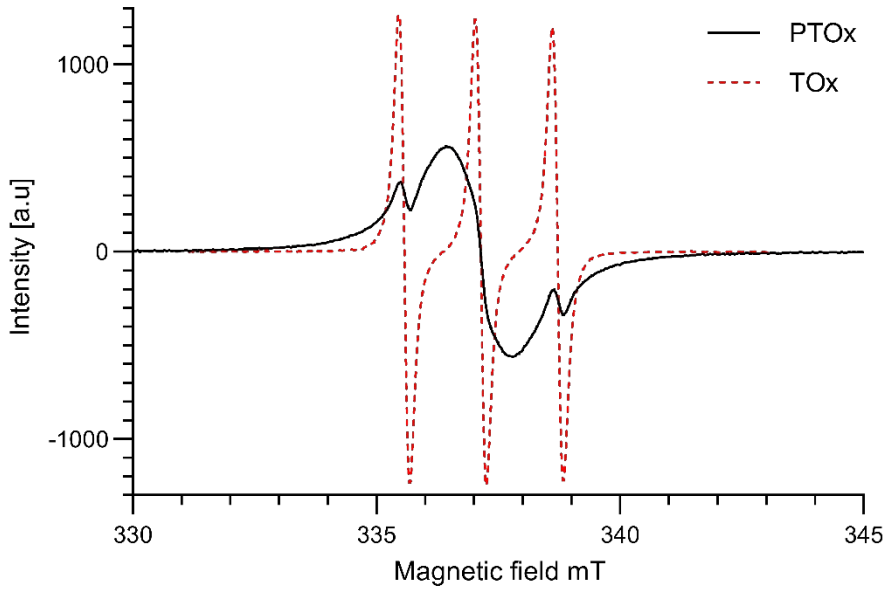

Figure S13. EPR spectra of **PTOx** (P3) in DCM. Microwave frequency = 9.46913 GHz, temperature = 300K, g value = 2.0066. Also overlayed with the EPR spectra of the TOx monomer

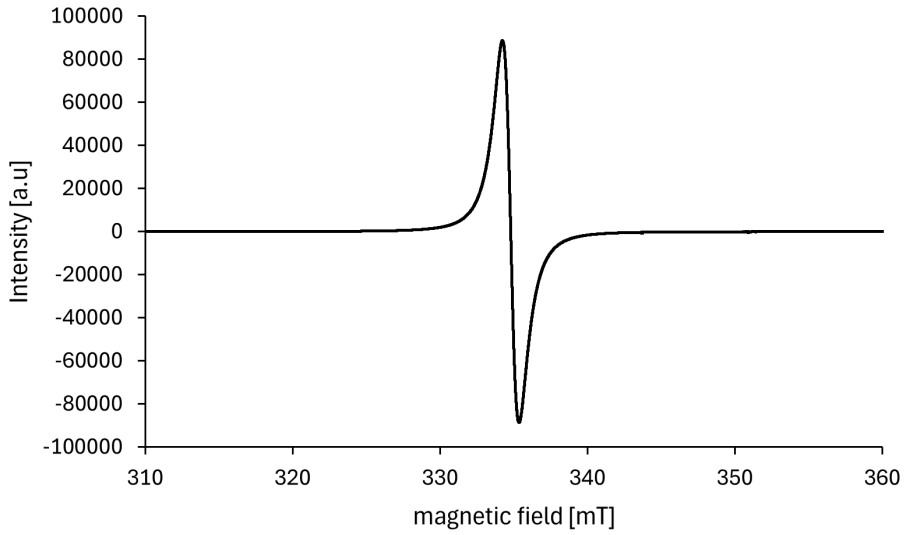

Figure S14. solid state EPR spectra of **P1**, sample weight = 1.9 mg, total spins = 4.91e^{18}, radical percentage = 97%. Microwave frequency = 9.40439 GHz, temperature = 300K, g value = 2.0069.

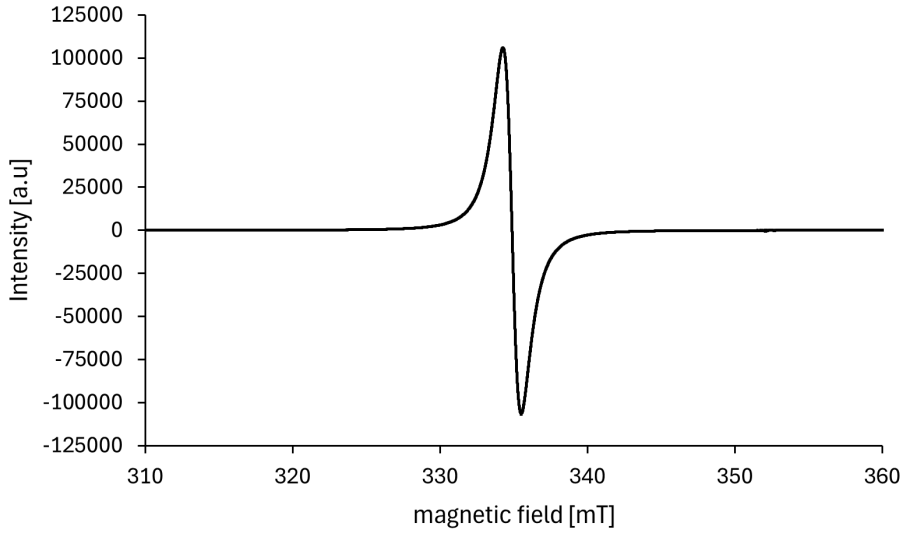

Figure S15. solid state EPR spectra of **P2**, sample weight = 2.8 mg, total spins = 7.29e^{18}, radical percentage = 98%. Microwave frequency = 9. 40810 GHz, temperature = 300K, g value = 2.0072.

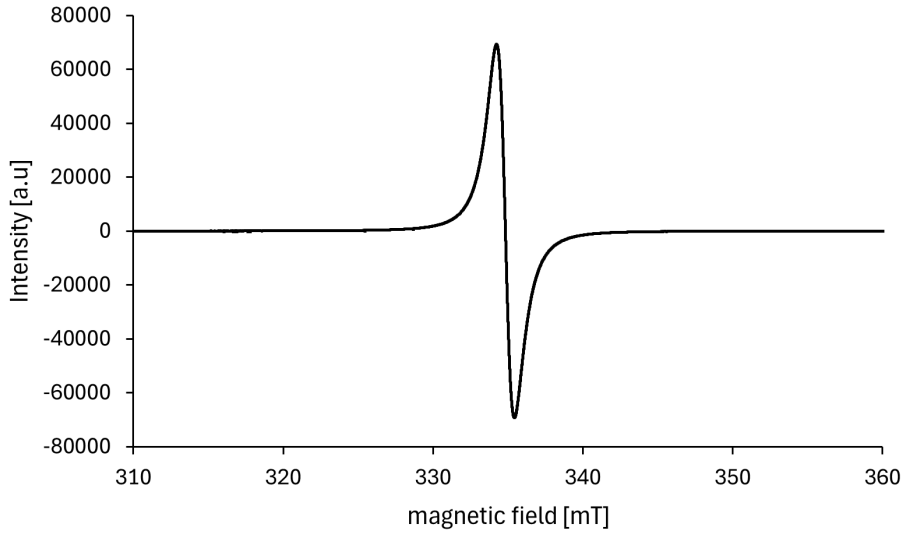

Figure S16. solid state EPR spectra of **P3**, sample weight = 1.6 mg, total spins = $4.28e^{18}$, radical percentage = 100%. Microwave frequency = 9.40547 GHz, temperature = 300K, g value = 2.0068.

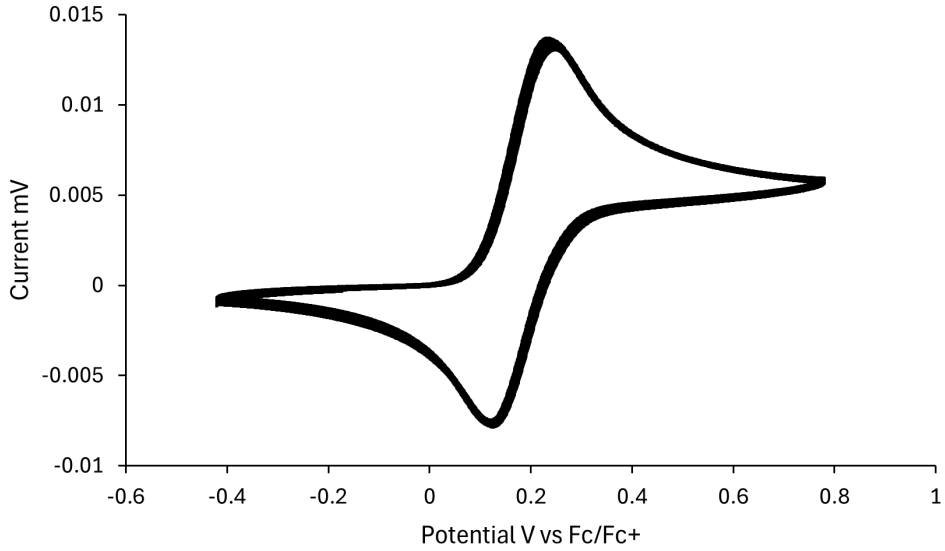

Figure S17. Cyclic voltammogram of **PTOx.** 100 mV s^{-1} scan rate, 10 scans (0.01M) /TBAPF6 (0.1M)/ ACN. Ag/AgCl (RE), glassy carbon (WE), platinum wire (CE).

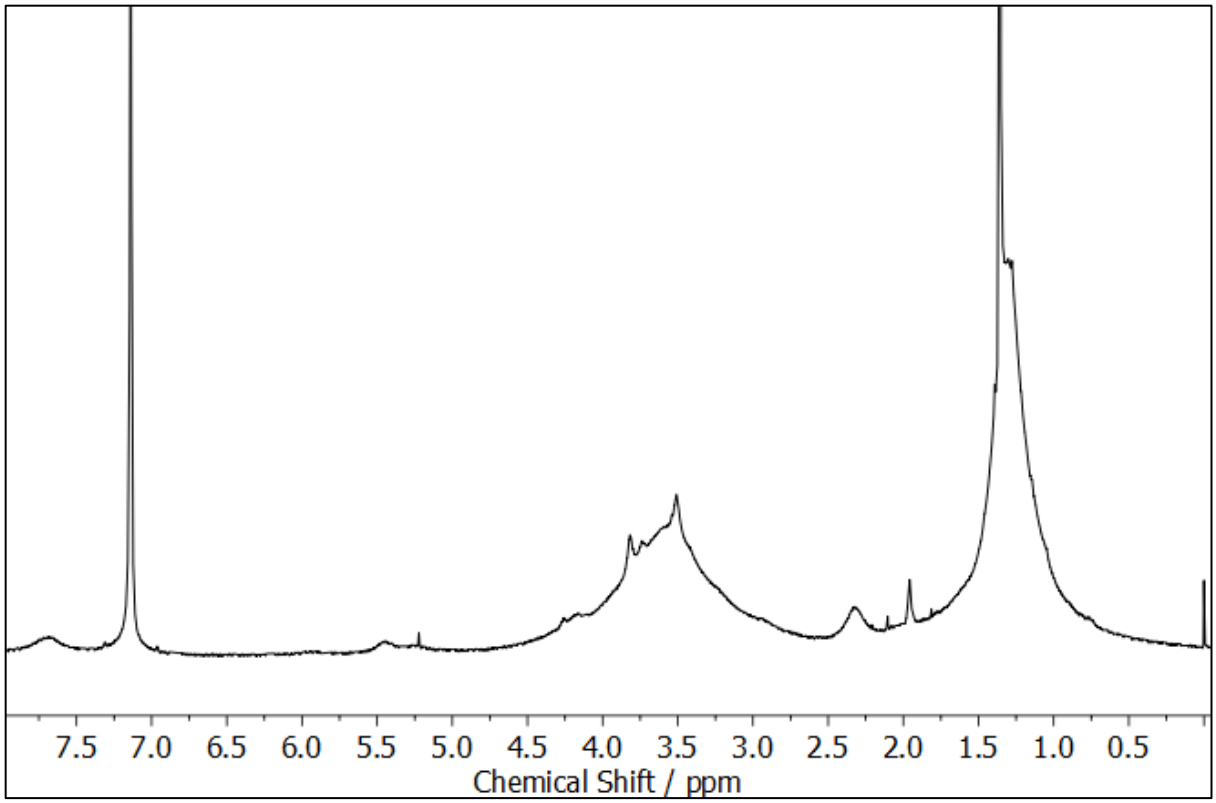

Figure S18. ^{1}H NMR spectrum (600 MHz,$CDCl_3$) of PTOx (**P1**).

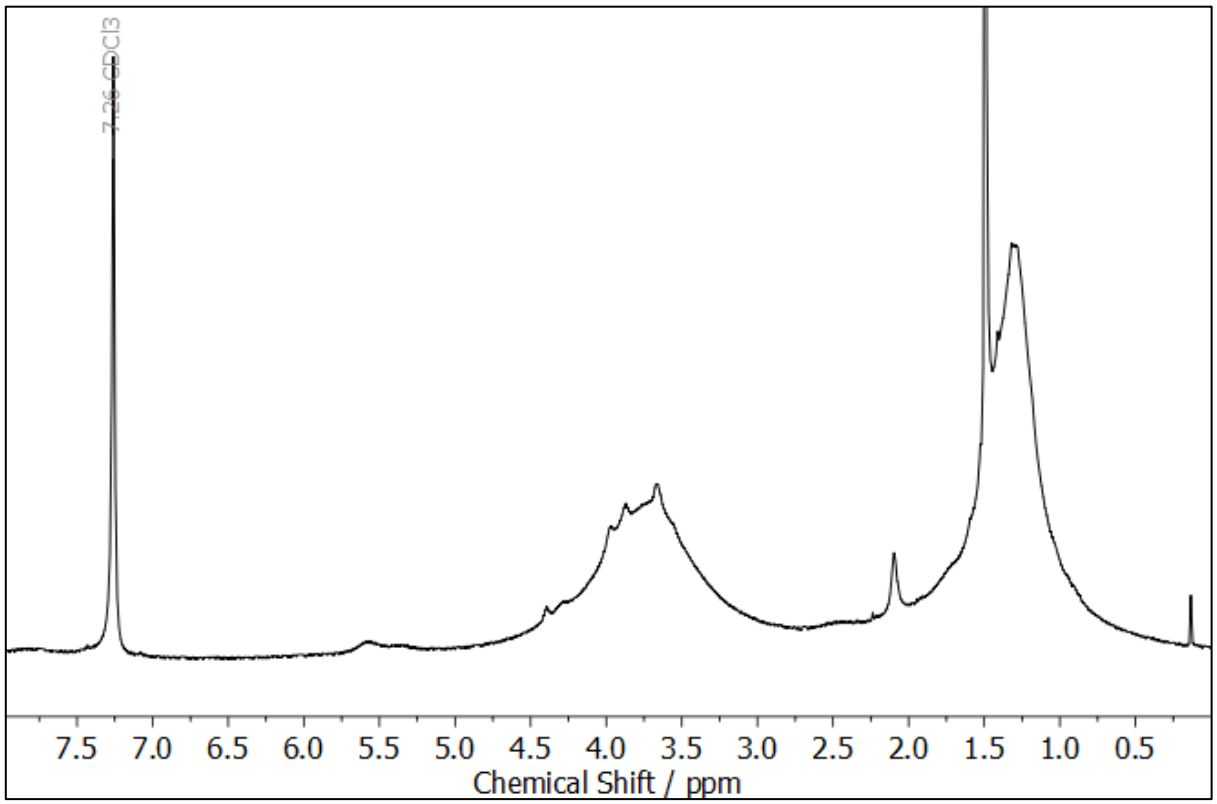

Figure S19. ^{1}H NMR spectrum (600 MHz,CDCl3) of PTOx (**P2**).

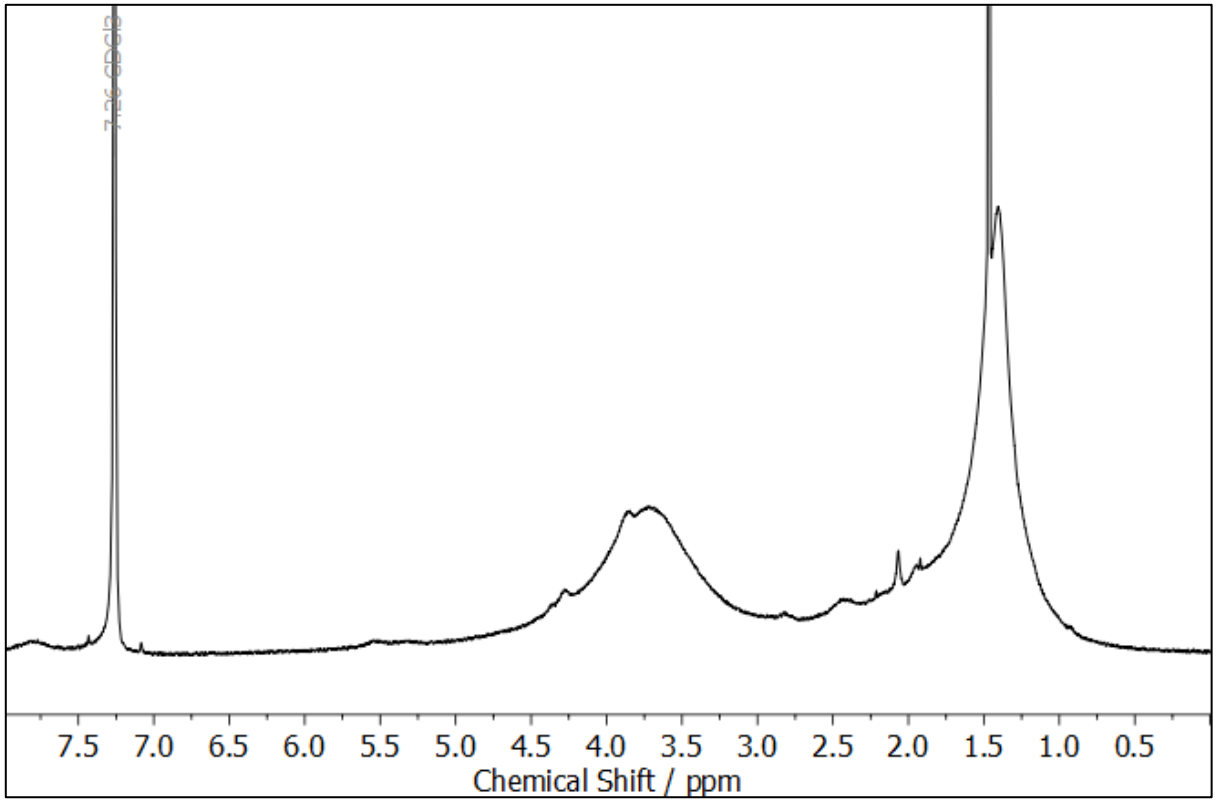

Figure S20. ^{1}H NMR spectrum (600 MHz,CDCl3) of PTOx (**P3**).

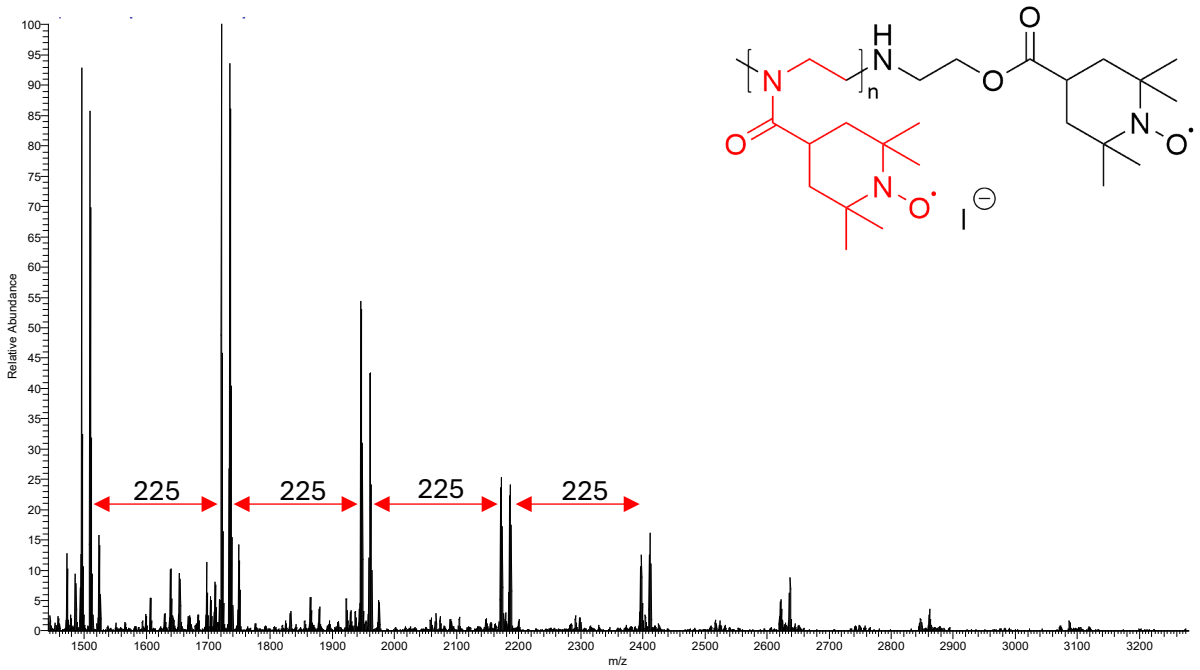

Figure S21. ESI mass spectrum of polymer **PTOx** (P1) displaying single repeating distribution (Δm/z = 225.15) as depicted in red.

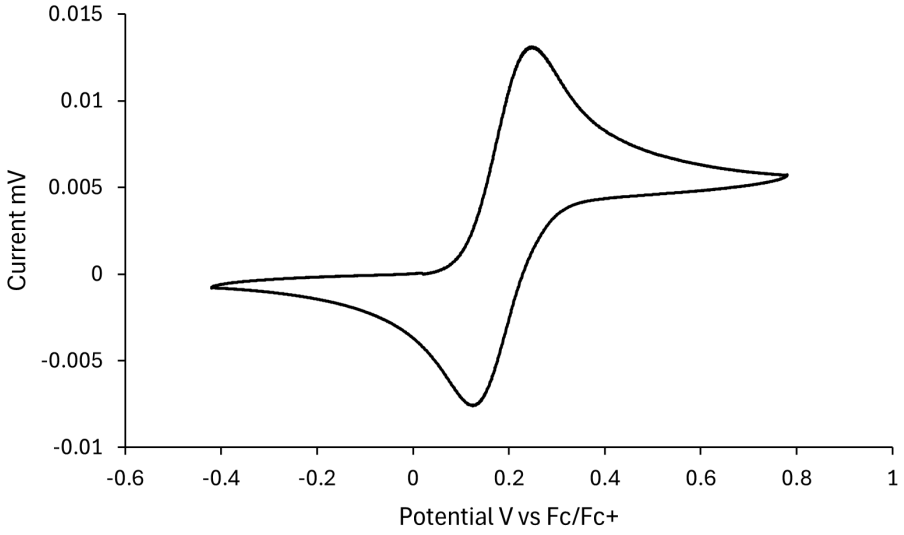

Figure S22. Cyclic voltammogram of **PTOx**. 100 mV s^{-1} scan rate, 1 scan (0.01M) /TBAPF6 (0.1M)/ ACN, $E^{1/2}$ = 0.19V. Ag/AgCl (RE), glassy carbon (WE), platinum wire (CE).

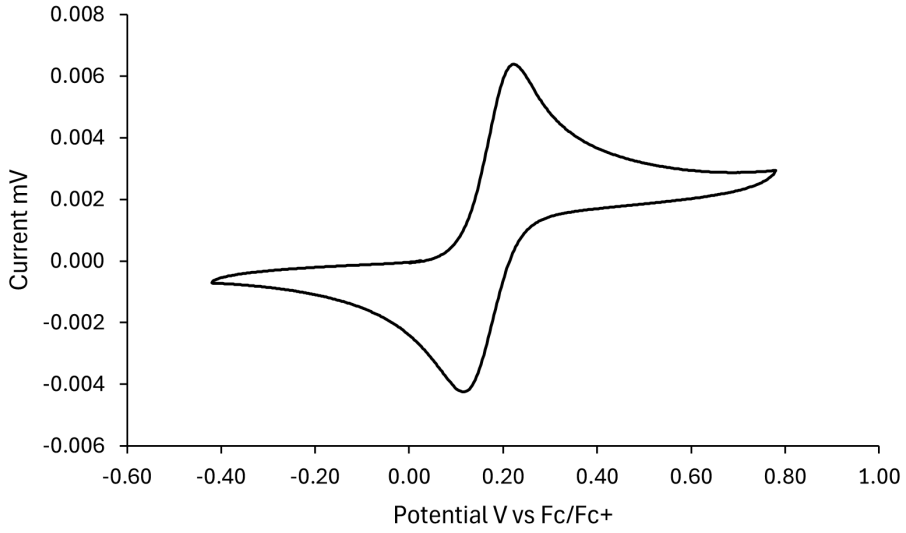

Figure S23. Cyclic voltammogram of **PTMA.** 100 mV s^{-1} scan rate, 1 scan (0.01M) /TBAPF6 (0.1M)/ ACN, $E^{1/2}$ = 0.17V. Ag/AgCl (RE), glassy carbon (WE), platinum wire (CE).

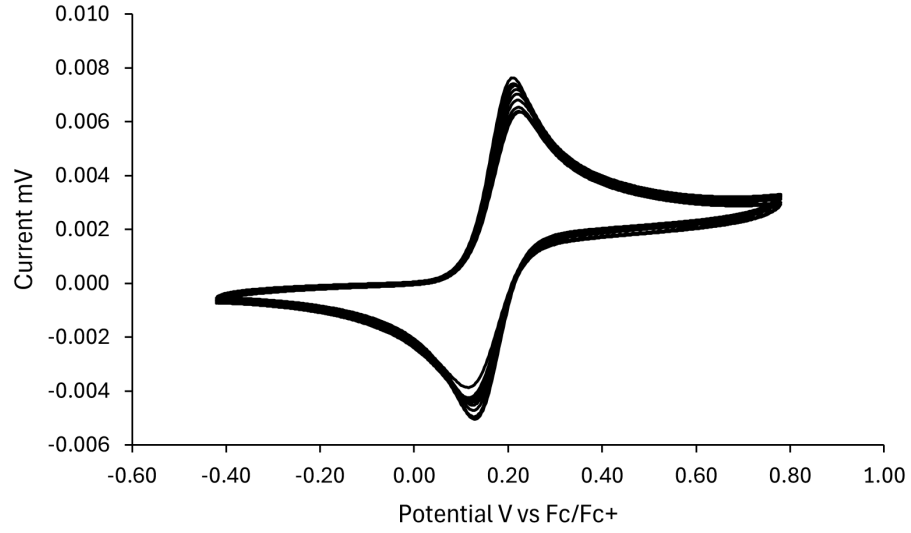

Figure S24. Cyclic voltammogram of **PTMA**. 100 mV s^{-1} scan rate, 10 scans (0.01M) /TBAPF6 (0.1M)/ ACN. Ag/AgCl (RE), glassy carbon (WE), platinum wire (CE).

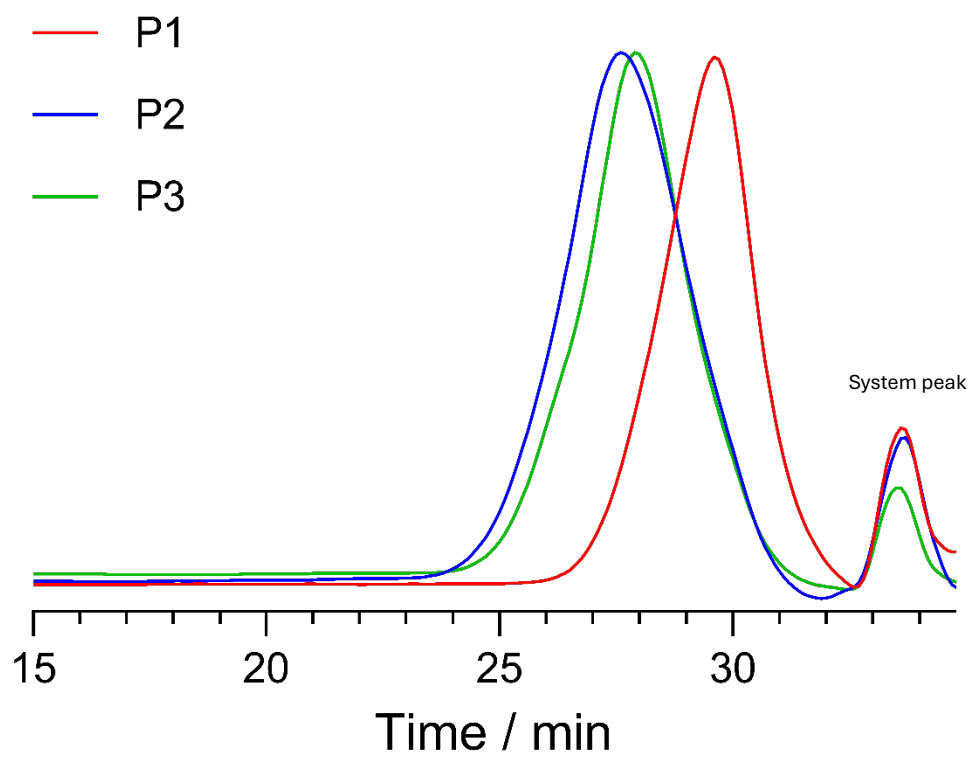

Figure S25. Full GPC elugrams of CROP polymers **P1** – **P3**. (DMAc, 0.08 % LiBr, RI detection).

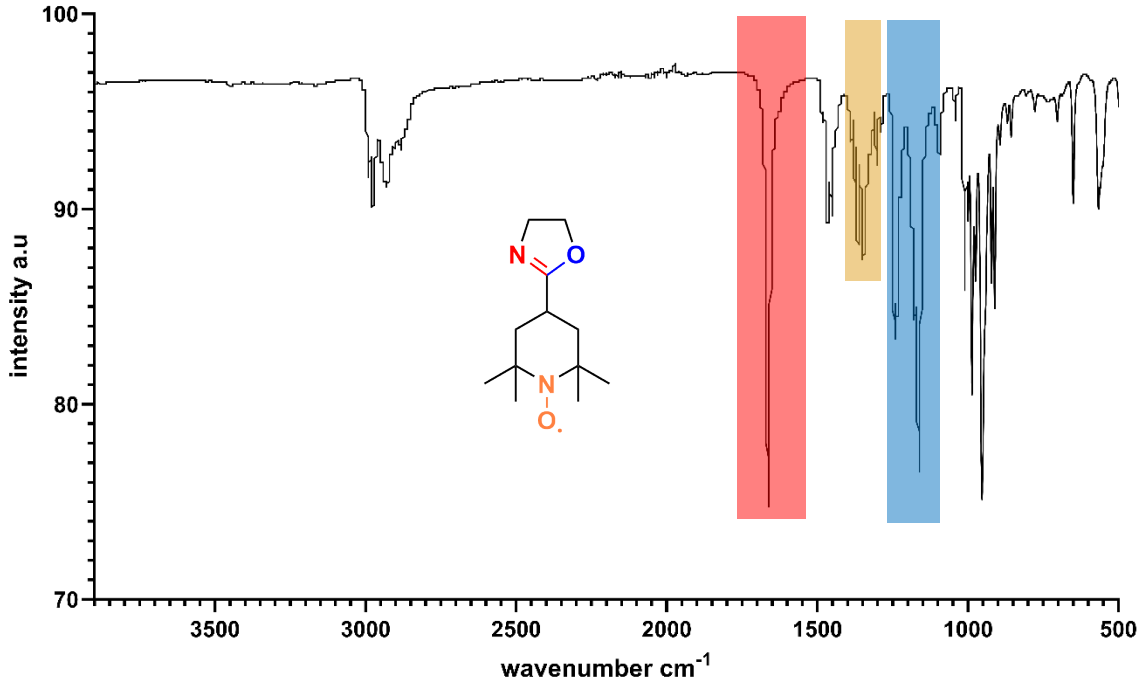

Figure S26. Infrared spectra of TOx, red; 1662 cm^{-1}, C=O stretch. orange; 1348 cm^{-1}, N-O˙ stretch (TEMPO-based systems 1340 – 1380 cm^{-1})[4], blue; 1161 & 1243 cm^{-1}, C-O stretch.

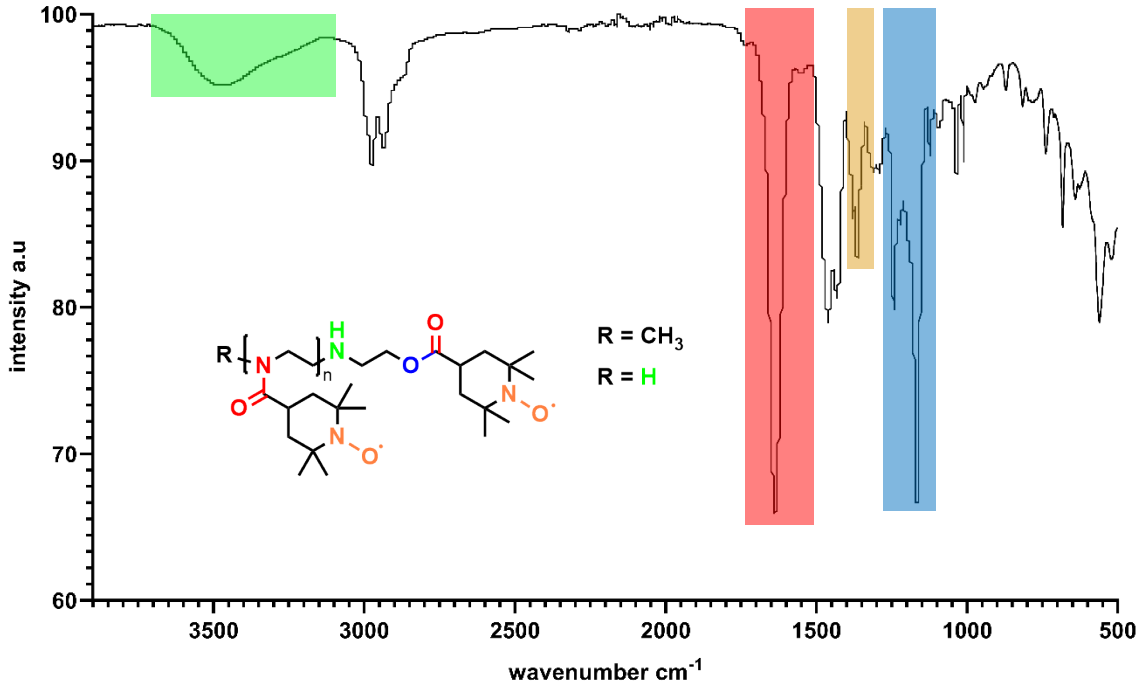

Figure S27. Infrared spectra of PTOx. green; 3473 cm^{-1}, N-H stretch. red; 1637 cm^{-1}, C=O stretch. orange; 1364 cm^{-1}, N-O˙ stretch (TEMPO-based systems 1340 – 1380 cm^{-1})[4]. blue; 1165 & 1243 cm^{-1}, C-O stretch.

EPR error measurements

The following outlines the process of how EPR error measurements for the spin counting of the polymers was determined; error associated with instrument parameters like sample centring, tube inner diameter and sample depth was determined by running replicates of the same sample (P1) after removing and re-placing in the Bruker Magnettech ESR5000 spectrometer to determine the deviation between number of spins and can be seen in figures S29 – S31 and Table S4. Error associated with weighing of the polymer was determined by weighing multiple runs (P1) and recording the spectra to determine the deviation between spins/mg of each sample. Which can be seen in figures S32 and Table S5. (EPR parameters can be seen on page 2 of the supporting information).

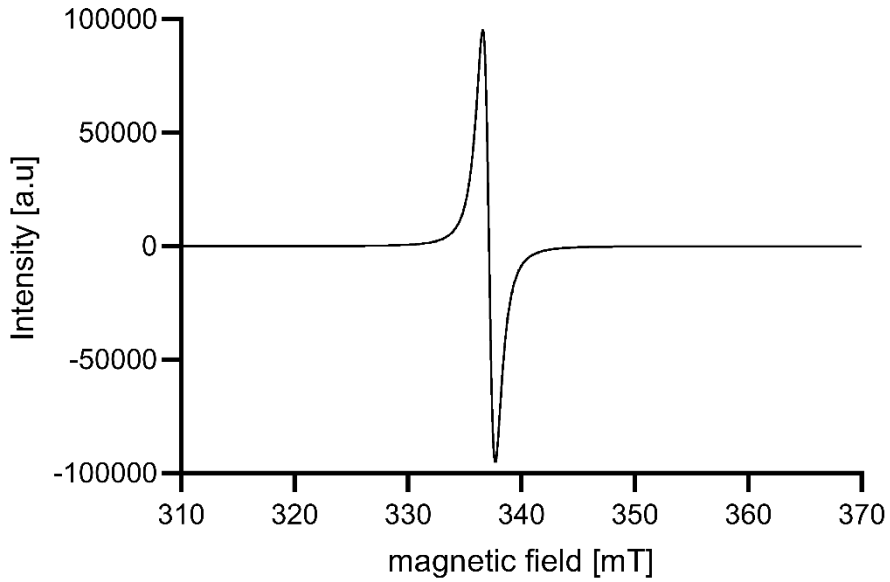

Figure S28. solid state EPR spectra of **P1** (replicate 1), sample parameters can be seen in **Table S4**.

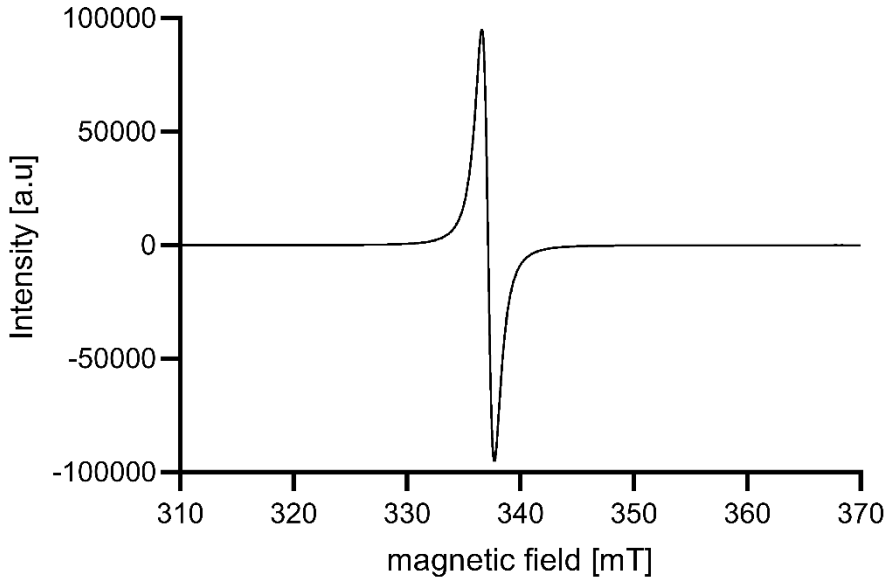

Figure S29. solid state EPR spectra of **P1** (replicate 2), sample parameters can be seen in **Table S4**.

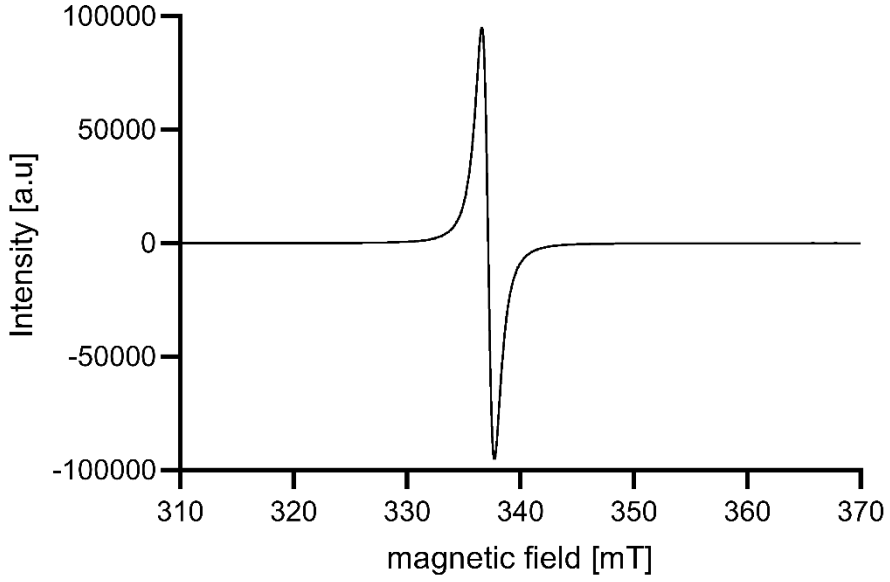

Figure S30. solid state EPR spectra of **P1** (replicate 3), sample parameters can be seen in **Table S4**.

Table S4. Error associated with instrument parameters determined by deviation of the number of spins between each replicate.

Run 1	Mass (mg)	Sample depth (mm)	Tube inner diameter (mm)	Number of spins
Replicate 1	1.9	3.5	2.04	$4.761e^{18}$
Replicate 2	1.9	3.5	2.04	$4.759e^{18}$
Replicate 3	1.9	3.5	2.04	$4.767e^{18}$
Standard deviation	-	-	-	$\pm 0.004e^{18}$

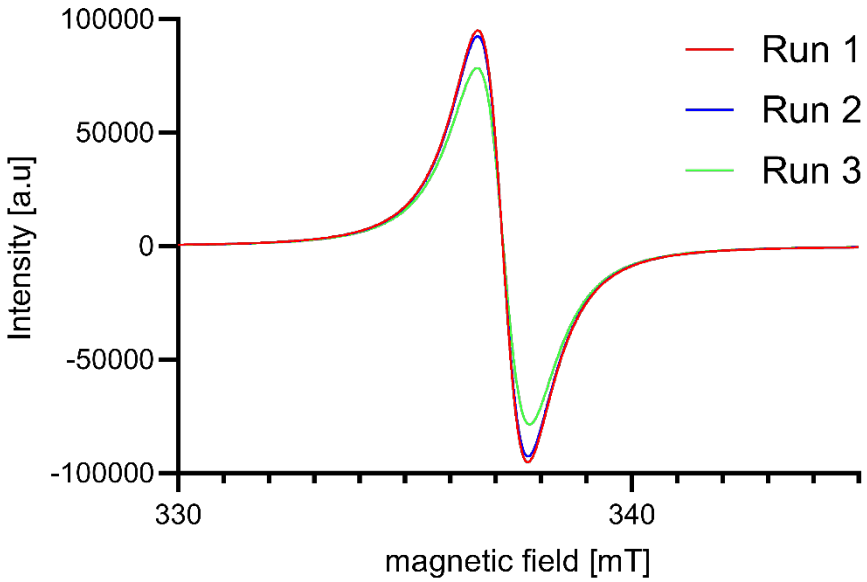

Figure S31. solid state EPR spectra of **P1** (run 1-3), sample parameters can be seen in **Table S5**.

Table S5. Error associated with weighing of samples determined by the deviation of spins/mg between each Run.

Runs	Mass (mg)	Sample depth (mm)	Number of spins	Spins/mg
Run 1	1.9	3.5	$4.761e^{18}$	$2.506e^{18}$
Run 2	2.3	4	$4.707e^{18}$	$2.046e^{18}$
Run 3	2.1	3.5	$4.272e^{18}$	$2.034e^{18}$
Standard deviation	-	-	-	$\pm 0.269e^{18}$

References

1. Yamada, K., Kinoshita, Y., Yamasaki, T., Sadasue, H., Mito, F., Nagai, M., Matsumoto, S., Aso, M., Suemune, H., Sakai, K., & Utsumi, H. *Arch. Pharm. (Weinheim)*, 2008, *341*(9), 548–553.
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4. Rintoul, L., Micallef, A. S., & Bottle, S. E. *Spectrochim Acta Part A*. 2008, *70*, 713–717.