

- Supporting information -

Ferrocene Containing Redox-Responsive Poly(2-Oxazoline)s

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Experimental section

Materials and instrumentation:

Materials:

2-Ethyl-2-oxazoline (EtOx, TCI, 98%) and 2-methyl-2-oxazoline (MeOx, Acros Organics, 99%) were dried over BaO or CaH₂, respectively, and distilled under inert atmosphere. Acetonitrile and chlorobenzene were dried in a solvent purification system (SPS, Pure solv EN, InnovativeTechnology). Acetic acid (VWR, 100%) was used without further purification. Methyltosylate (MeTos, Sigma Aldrich 97%) was dried over CaH₂, distilled under reduced pressure and stored under inert atmosphere. NaOMe (0.5 M in MeOH), triethylamine (anhydrous, $\geq 99\%$), calcium hydride ($> 90\%$), ferrocenecarbaldehyde (98%) and tetrabutylammonium hexafluorophosphate ($\geq 99\%$) were bought from Sigma Aldrich and used as received. Aminoethanol (98%, Sigma Aldrich) was distilled under argon atmosphere prior to usage and stored with 3 Å molar sieves. Sodium acetate ($\geq 99\%$, Sigma Aldrich) and zinc acetate ($\geq 98\%$, Laborchemie Apolda) were dried at 110 °C in high vacuum for one day and kept in an argon atmosphere afterwards. Propylene carbonate ($>98\%$, TCI), sodium ascorbate (99%, Alfa Aesar) and silver triflate (98%, Alfa Aesar) were used as received.

Instrumentation:

The cationic ring-opening polymerizations were performed in a microwave synthesizer from Biotage (Initiator sixty) under temperature control.

The glovebox used for sample preparation was manufactured by MBRAUN and is equipped with an UNIlab inert gas purification system, a vacuum pump and high efficiency box filters HEPA H13.

Nuclear magnetic resonance (NMR) spectra were measured on a 300 MHz spectrometer from Bruker equipped with an Avance I console, a dual ^1H and ^{13}C sample head or on an Avance III 400 MHz device with a BBFO probe head by Bruker. All shifts are given in ppm using the residual non-deuterated solvent signal as a reference.

The UV-VIS spectra were recorded on a Specord 250 spectrometer from Analytik Jena.

Size exclusion chromatography (SEC) was measured on an Agilent 1200 series system, equipped with a PSS degasser, a G1310A pump, a G1362A refractive index (RI) detector and a Techlab oven at 40 °C. The eluent was a solution of 0.21 wt.% LiCl in *N,N*-dimethylacetamide (DMAc), and the flow rate was 1 mL min⁻¹. A PSS Gram 30 and a PSS Gram 1000 column placed in series served as a column set. The molar masses were estimated using poly(styrene) (PS) standards (Polymer Standard Services, ca. 400 to 1,000,000 g mol⁻¹).

Matrix-assisted laser desorption ionization mass spectrometry (MALDI MS) was measured using an Ultraflex III ToF/ToF instrument from Bruker Daltonics equipped with a Nd-YAG laser. All spectra were measured in the positive mode using dithranol as a matrix.

Electrospray ionization mass spectrometry (ESI MS) was performed with a micOTOF Q-II from Bruker Daltonics. The samples were injected with an automatic syringe pump from KD Scientific. Nitrogen was used as nebulizing and drying gas and the spectrometer was operating at 4.5 kV in positive ion mode. The fractions were injected at a constant flow rate of 3 $\mu\text{L min}^{-1}$ and desolvated at 180 °C. An ESI-L low concentration tuning mix from Agilent Technologies was used to calibrate the spectrometer to an *m/z* range from 50 to 3000. The data were processed with Bruker Data Analysis 4.2.

Thermogravimetric analyses (TGA) were performed utilizing a Netzsch 209 F1 Iris device (N₂ atmosphere) in a temperature range from 20 °C to 550 °C. The heating rate was set constant as 20 K min⁻¹.

Differential scanning calorimetry (DSC) was measured in a Netzsch 204 F1 Phoenix device under N₂ atmosphere. The applied temperature program was set from -80 to 200 °C with a heating rate of 20 K min⁻¹ for the first and second heating run and 10 K min⁻¹ for the third heating run. The applied cooling rate in between the heating runs was set constant as -20 K min⁻¹.

Cyclic voltammetry was measured with a BioLogic VMP3 potentiostat. A glassy carbon electrode was used as working electrode, a platinum wire was used as counter electrode and a Ag/AgNO₃ in acetonitrile electrode was used as reference.

Monomer synthesis:

Synthesis of 3-ferrocene propionitrile (2)

According to a recently published procedure,^[1] the corresponding 3-ferroceneacrylnitrile (4 g, 16.87 mmol) was dissolved in ethyl acetate (40 mL). 1 g of activated Pd on charcoal (10 wt% Pd) was added. The hydrogenation proceeded at 40 °C at ca. 4 bar for 30 h, until TLC indicated complete consumption of the starting material. Charcoal was filtered off, and volatiles were removed under reduced pressure yielding **2** (3.96 g, 98 %) as a yellow solid.

¹H NMR (400 MHz, CDCl₃, the numbers indicate the assigned peaks in **Figure SI 1**): δ = 2.52 – 2.56 (t, J = 7.3 Hz, 2H, **H-1**), 2.72 – 2.76 (t, J = 7.3 Hz, 2H, **H-2**), 4.15 – 4.17 (m, 9 H, **H-3**).

Synthesis of 2-ferroceneethyl-2-oxazoline (**3**)

3-Ferrocene propionitrile (2 g, 8.4 mmol, 1 eq.) was placed in a two-necked round bottom flask, which was purged with argon. Dry chlorobenzene (5 mL) was added. Zn(OAc)₂ (0.32 g, 1.7 mmol, 0.2 eq.), NaOAc (0.69 g, 8.4 mmol, 1 eq.) and ethanolamine (1 mL, 16.7 mmol, 2 eq.) were added to the stirred solution. The mixture was refluxed for 24 hours. Subsequently, more ethanolamine (0.5 mL) was added. Heating was continued for 7 additional hours. After cooling to room temperature, CH₂Cl₂ (20 mL) and sat. aq. NaHCO₃ solution (20 mL) were added. The organic phase was separated and washed with sat. aq. NaHCO₃ (20 mL) twice, once with distilled water and once with sat. aq. NaCl. The organic layer was dried over Na₂SO₄. After filtration, CaH₂ was added. After hydrogen evolution ceased, the solvent was removed under reduced pressure and the remaining solid was transferred to a sublimator. The pure product was received after resublimation at 75 °C oil-bath temperature and 2 × 10⁻² mbar vacuum for two days as orange crystals (0.95 g, 40%).

¹H NMR (400 MHz, CD₂Cl₂, the numbers indicate the assigned peaks in **Figure SI 2**): δ = 2.45 – 2.49 (t, *J* = 7.2 Hz, 2H, **H-1**), 2.63 – 2.67 (t, *J* = 8.7 Hz, 2H, **H-2**), 3.75 – 3.80 (t, *J* = 9.6 Hz, 2H, **H-3**), 4.05 – 4.09 (m, 4H, **H-4**), 4.11 (s, 5H, **H-4'**), 4.18 – 4.22 (t, *J* = 9.6 Hz, 2H, **H-5**)

¹³C NMR (100 MHz, CD₂Cl₂): δ = 25.9 (Fc-C), 29.3 (C-Oxa), 54.6 (N-C), 67.1 (C₅H₄) 67.2 (O-C), 67.9 (C₅H₄), 68.5 (C₅H₅), 88.2 (C₅H₄R subst.), 167.8 (C(O)N)

Elemental analysis found (calc): C 63.88 (63.63), H 6.03 (6.05), N 5.11 (4.95)

HR-ESI m/z: [M+H]⁺ calcd. for [C₁₅H₁₇FeNO + H], 284.0732; found, 284.0719

Cationic ring-opening polymerization:

Kinetic study of the copolymerization of EtOx and FEtOx: A stock solution containing 25 mg (0.14 mmol, 1 eq.) of MeTos, 428 μ L (420 mg, 4.24 mmol, 30 eq.) of EtOx, 1.201 g (4.24 mmol, 30 eq.) of FEtOx and 8.05 mL of chlorobenzene were added to a pre-dried Schlenk flask under inert conditions. Subsequent to complete dissolution, 1 mL aliquots were transferred to pre-dried microwave vials under inert conditions and heated to 140 °C for varying reaction times in a the microwave synthesizer. The reaction solutions were analyzed by means of SEC and ^1H NMR spectroscopy to determine monomer conversions, molar masses and dispersity values. Subsequently, the samples were precipitated from -22 °C diethyl ether to analyze the copolymer composition by ^1H NMR spectroscopy.

Kinetic study of the copolymerization of MeOx and FEtOx: A stock solution containing 26 mg (0.14 mmol, 1 eq.) of MeTos, 359 μ L (360 mg, 4.24 mmol, 30 eq.) of MeOx, 1.208 g (4.24 mmol, 30 eq.) of FEtOx and 8.12 mL of chlorobenzene were added to a pre-dried Schlenk flask under inert conditions. Subsequently, the kinetic studies were performed as described above.

P1 (P(EtOx-co-FEtOx) 80%/20%): A pre-heated polymerization vessel was cooled to room temperature by a continuous argon stream. It was transferred to a glovebox, charged with 67 mg FEtOx (0.24 mmol, 5 eq.) and sealed. Subsequent to removal from the glovebox, 10 mg methyl tosylate (0.05 mmol, 1 eq.), 84 mg EtOx (0.85 mmol, 16 eq.) and 974 μ L acetonitrile were added under argon atmosphere. The polymerization proceeded at 140 °C for 15 min in a microwave reactor. 20 μ L acetic acid (0.35 mmol, 7 eq.) and 20 μ L triethylamine (0.14 mmol, 3 eq.) were added and the mixture was heated to 50 °C for 19 h with stirring. After removal of aliquots for ^1H -NMR spectroscopy and SEC, the mixture was diluted with dichloromethane (ca. 150 mL), washed twice with sat. aq. NaHCO_3 (à 200 mL) and once with sat. aq. NaCl (200 mL). The organic phase was dried over Na_2SO_4 and filtered. The volatiles were removed under

reduced pressure. The residue was precipitated from $-22\text{ }^{\circ}\text{C}$ diethyl ether and dried *in vacuo* yielding **P1** as a yellow solid.

DP NMR: EtOx/FEtOx = 15/5. Yield: 104 mg (65%), $M_{n, \text{NMR}} = 2,900\text{ g mol}^{-1}$, $M_{n, \text{SEC}} = 3,900\text{ g mol}^{-1}$, $\bar{D} = 1.13$, $^1\text{H-NMR}$ (CDCl_3 , the numbers indicate the assigned peaks in **Figure SI 5**): $\delta = 0.99 - 1.37$ (br, 45H, **H-6**), $2.02 - 2.12$ (br, 3H, **H-7**), $2.12 - 2.83$ (br, 50H, **H-4** and **H-5**), $2.91 - 3.09$ (br, 3H, **H-1**), $3.12 - 3.86$ (br, 80H, **H-2**), $3.97 - 4.47$ (br, 45H, **H-3** and **H-3'**).

General procedure for the cationic ring-opening polymerization without end-capping yielding P2-P4:

A pre-heated polymerization vessel was cooled to room temperature by a continuous argon stream. It was transferred to a glovebox, charged with FEtOx, and sealed. Subsequent to removal from the glovebox, methyl tosylate, EtOx or MeOx and the appropriate solvent were added under argon atmosphere. The polymerization proceeded at $140\text{ }^{\circ}\text{C}$ in a microwave reactor. Subsequent to analysis by SEC and $^1\text{H-NMR}$ spectroscopy, the reaction solvent was removed under reduced pressure. **P2–P4** were re-dissolved in dichloromethane and precipitated from $-22\text{ }^{\circ}\text{C}$ diethyl ether.

P2 (P(MeOx-co-FEtOx) 80%/20%): 54 mg FEtOx (0.19 mmol, 4 eq.), MeOx 67.7 μL (0.8 mmol, 16 eq.), MeTos 7.5 μL (0.05 mmol, 1 eq.) and 925 μL acetonitrile were used according to the general procedure. The polymerization proceeded for 45 min. To remove residual water after precipitation, **P2** was freeze-dried from dioxane.

DP NMR: MeOx/FEtOx = 14/4. Yield: 66 mg (54%), $M_{n, \text{NMR}} = 2,300\text{ g mol}^{-1}$, $M_{n, \text{SEC}} = 3,900\text{ g mol}^{-1}$, $\bar{D} = 1.29$, $^1\text{H-NMR}$ (CDCl_3 , the numbers indicate the assigned peaks in **Figure SI 7**): $\delta = 1.91 - 2.28$ (br, 42H, **H-5**), $2.32 - 2.82$ (br, 16H, **H-4**), $2.93 - 3.10$ (br, 3H, **H-1**), $3.14 - 3.66$ (br, 72H, **H-2**), $3.97 - 4.29$ (br, 45H, **H-3** and **H-3'**).

P3 (EtOx-*co*-FETox 50%/50%): 607 mg FETox (2.14 mmol, 30 eq.), 210 mg EtOx (2.12 mmol, 30 eq.), 13 mg MeTos (0.07 mmol, 1 eq.) and 4025 μ L chlorobenzene were used were used according to the general procedure. The polymerization proceeded for 60 min.

Molar ratio NMR: EtOx/FETox = 52%/48%. Yield: 486 mg (59%), $M_{n,NMR} = 11,300 \text{ g mol}^{-1}$, $M_{n,SEC} = 11,300 \text{ g mol}^{-1}$, $\bar{D} = 1.16$, $^1\text{H-NMR}$ (CDCl_3 , the numbers indicate the assigned peaks in **Figure SI 9**): $\delta = 0.99 - 1.44$ (br, 90H, **H-6**), $2.00 - 2.86$ (br, 160H, **H-4** and **H-5**), $2.86 - 3.70$ (br, 220H, **H-2**), $3.89 - 4.33$ (br, 225H, **H-3** and **H-3'**).

P4 (MeOx-*co*-FETox 50%/50%): 712 mg FETox (2.52 mmol, 28 eq.), 210 mg MeOx (2.12 mmol, 27 eq.), 17 mg MeTos (0.09 mmol, 1 eq.) and 4740 μ L chlorobenzene were used were used according to the general procedure. The polymerization proceeded for 60 min.

Molar ratio NMR: MeOx/FETox = 53%/47%. Yield: 666 mg (71%), $M_{n,NMR} = 9,900 \text{ g mol}^{-1}$, $M_{n,SEC} = 10,200 \text{ g mol}^{-1}$, $\bar{D} = 1.13$, $^1\text{H-NMR}$ (CDCl_3 , the numbers indicate the assigned peaks in **Figure SI 11**): $\delta = 1.83 - 2.24$ (br, 90H, **H-5**), $2.24 - 2.81$ (br, 104H, **H-4**), $2.92 - 3.74$ (br, 224H, **H-2**), $3.81 - 4.70$ (br, 234H, **H-3** and **H-3'**).

NMR spectra

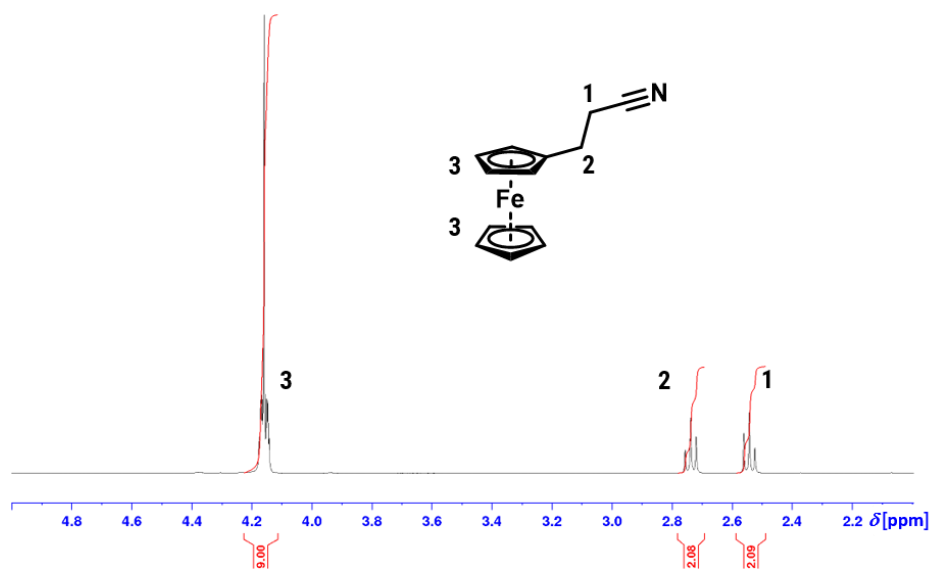


Figure SI 1. ¹H NMR spectrum (400 MHz, CD₂Cl₂) of **2** and assignment of the signals to the schematic representation of the chemical structure.

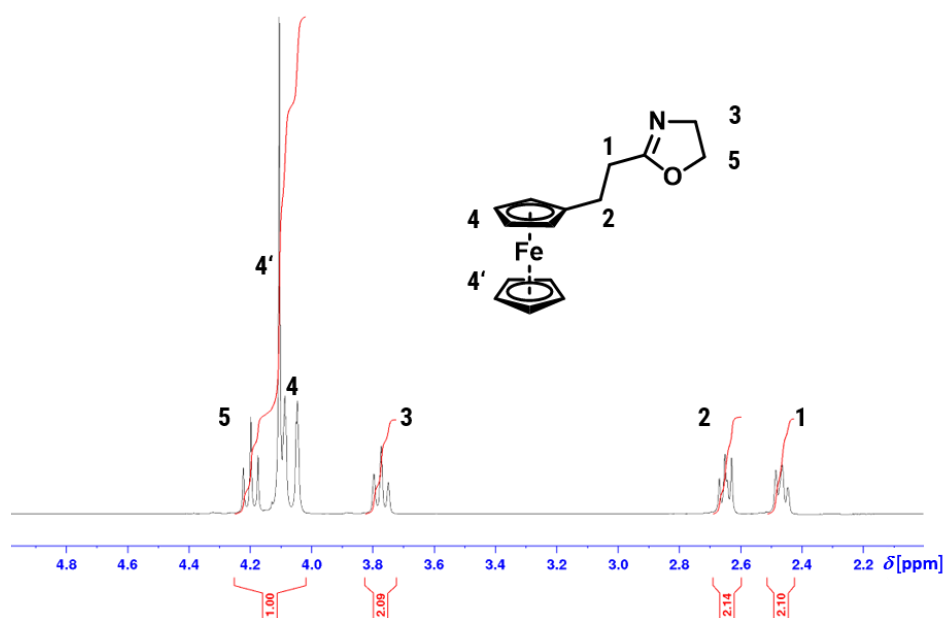


Figure SI 2. ¹H NMR spectrum (400 MHz, CD₂Cl₂) of **3** and assignment of the signals to the schematic representation of the chemical structure.

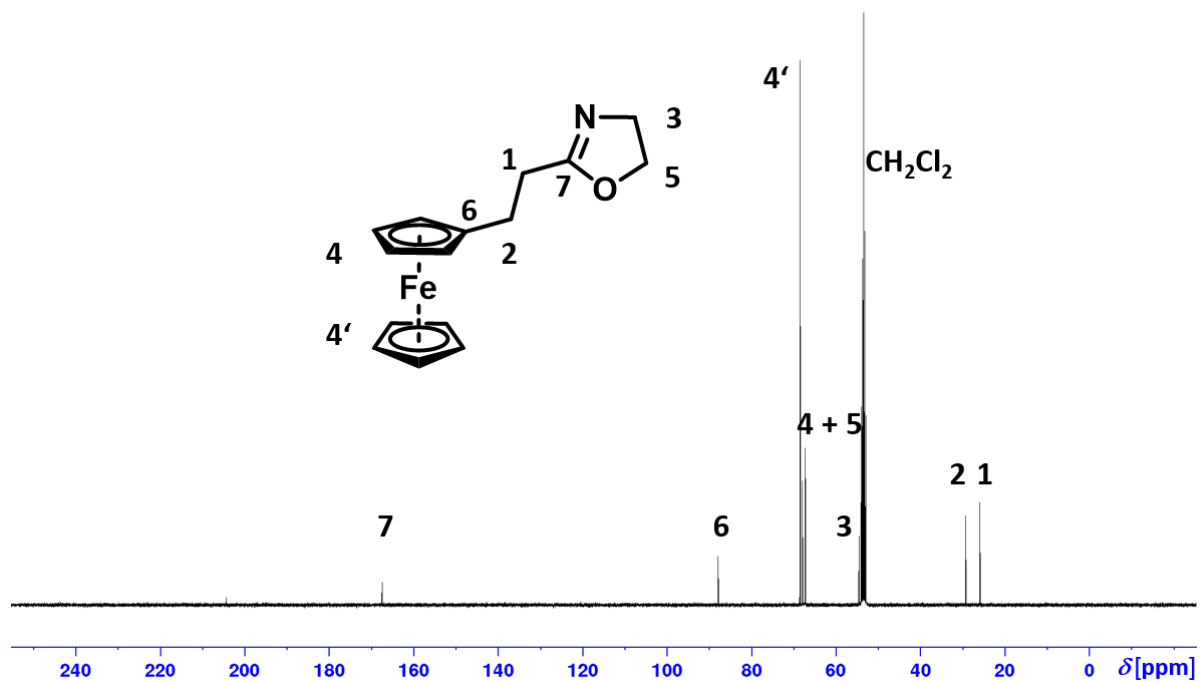


Figure SI 3. ¹³C NMR spectrum (100 MHz, CD₂Cl₂) of **3** and assignment of the signals to the schematic representation of the chemical structure.

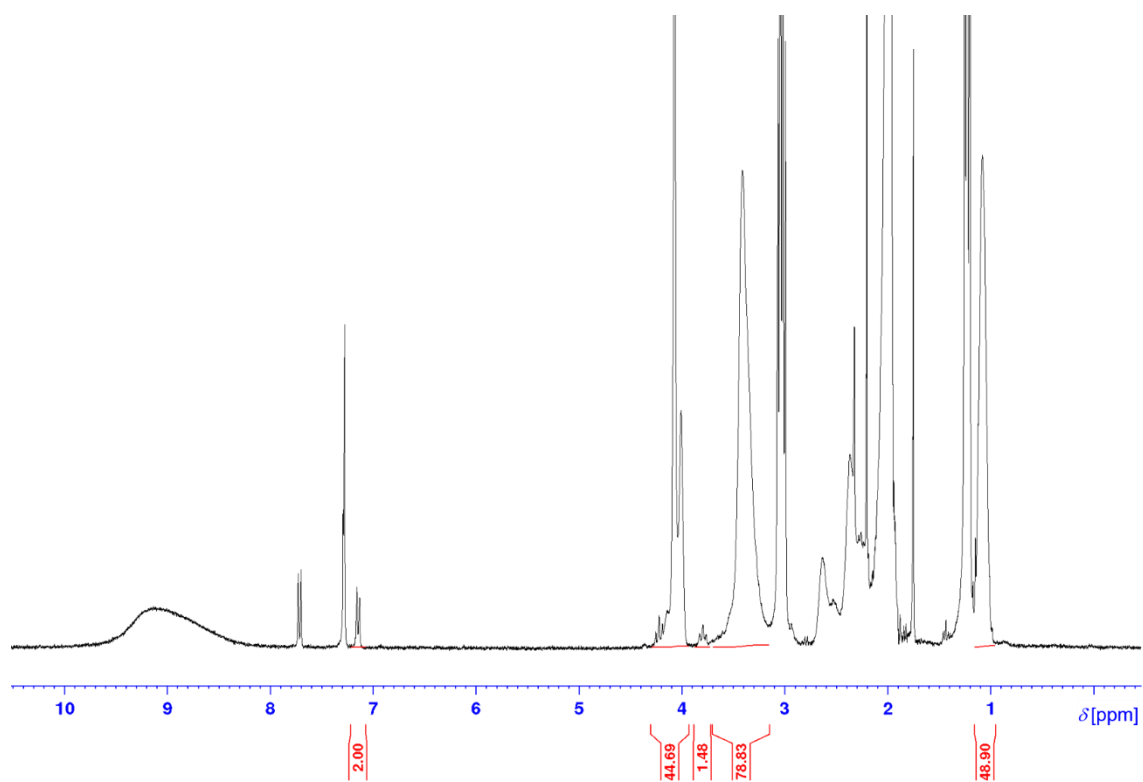


Figure SI 4. ¹H NMR spectrum (300 MHz, CDCl₃) of the reaction mixture yielding **P1**.

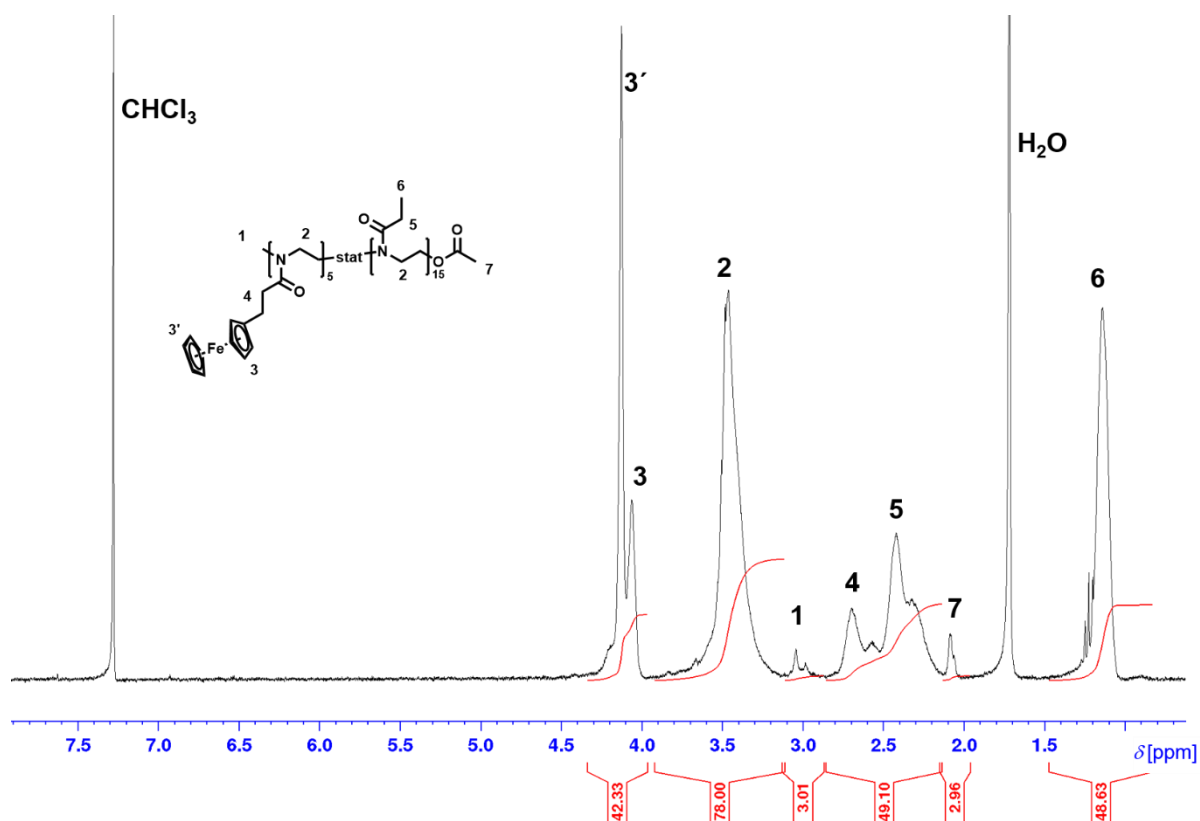


Figure SI 5. ^1H NMR spectrum (300 MHz, CDCl_3) of the purified copolymer **P1** and assignment of the signals to the schematic representation of the chemical structure of **P1**.

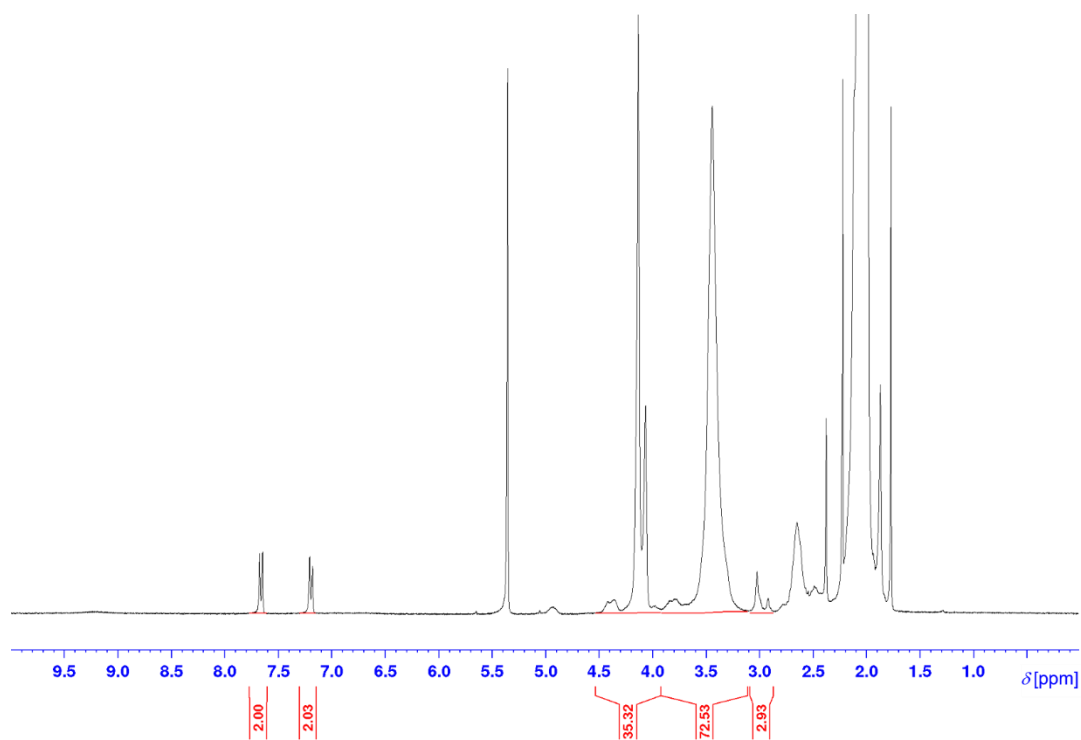


Figure SI 6. ^1H NMR spectrum (300 MHz, CD_2Cl_2) of the reaction mixture yielding **P2**.

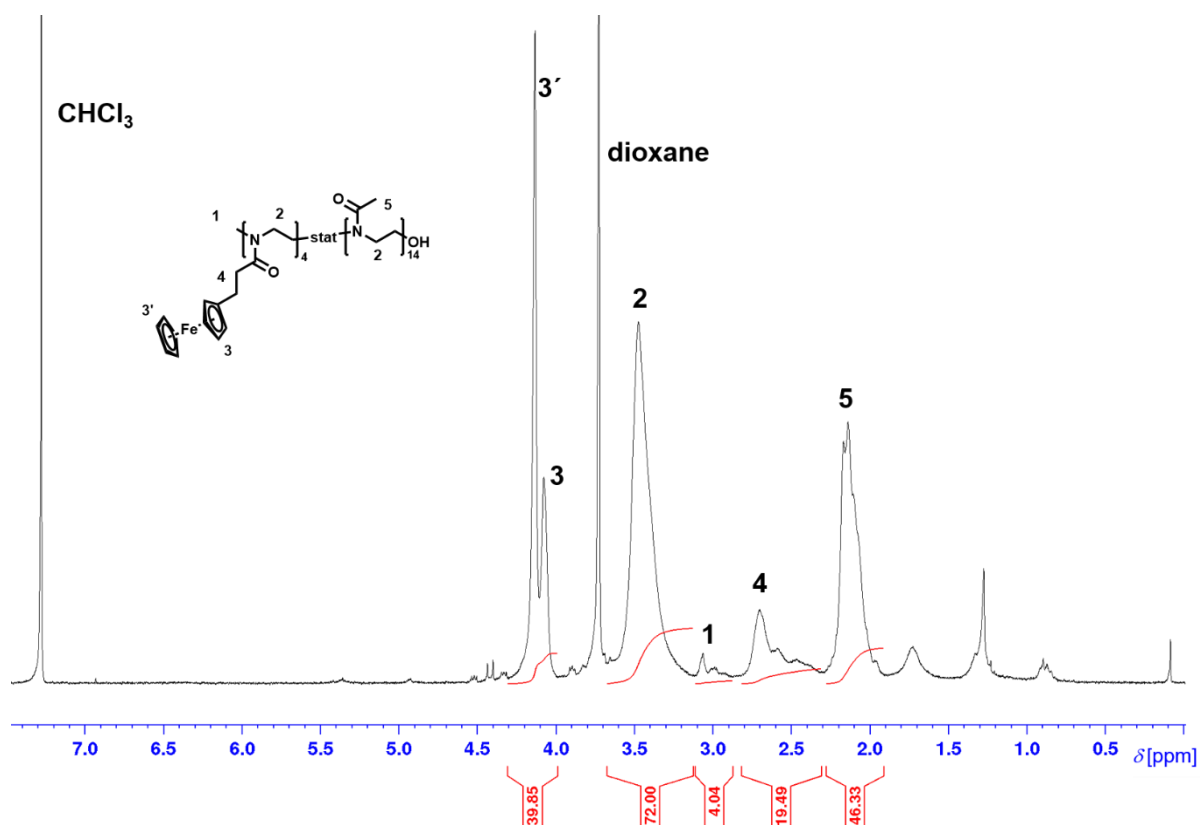


Figure SI 7. ¹H NMR spectrum (300 MHz, CDCl₃) of the purified copolymer **P2** and assignment of the signals to the schematic representation of the chemical structure of **P2**.

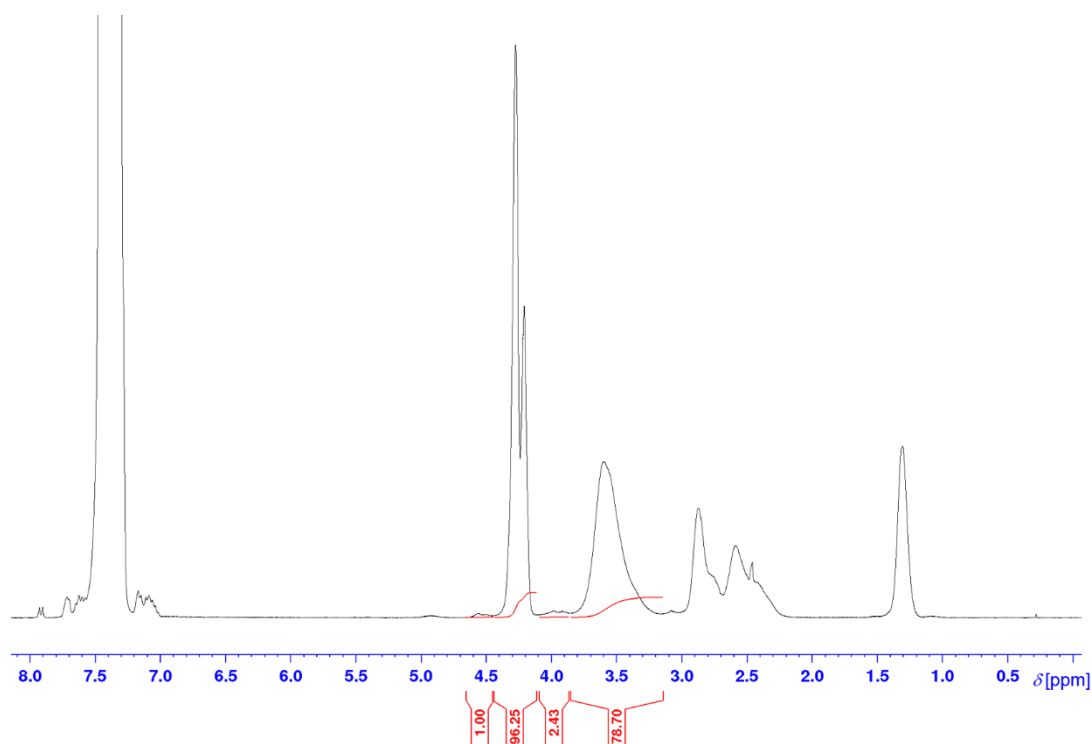


Figure SI 8. ¹H NMR spectrum (300 MHz, CDCl₃) of the reaction mixture yielding **P3**.

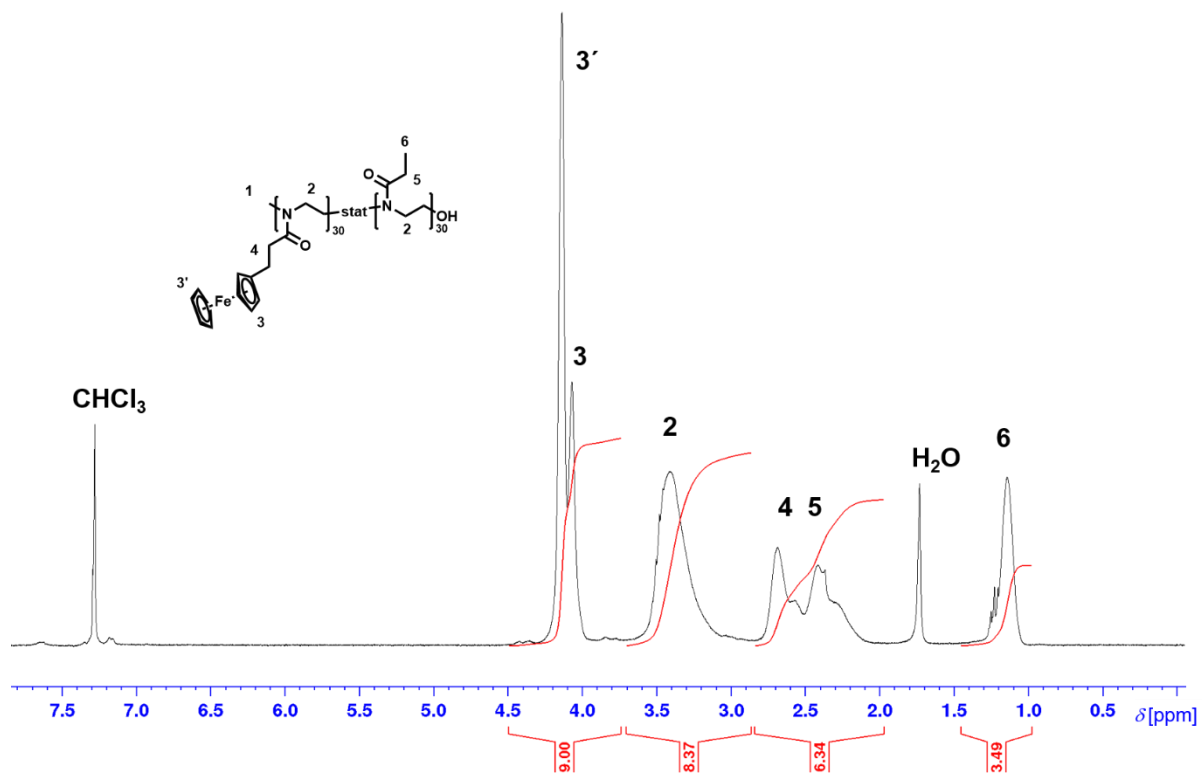


Figure SI 9. ¹H NMR spectrum (300 MHz, CDCl_3) of the purified copolymer **P3** and assignment of the signals to the schematic representation of the chemical structure of **P3**.

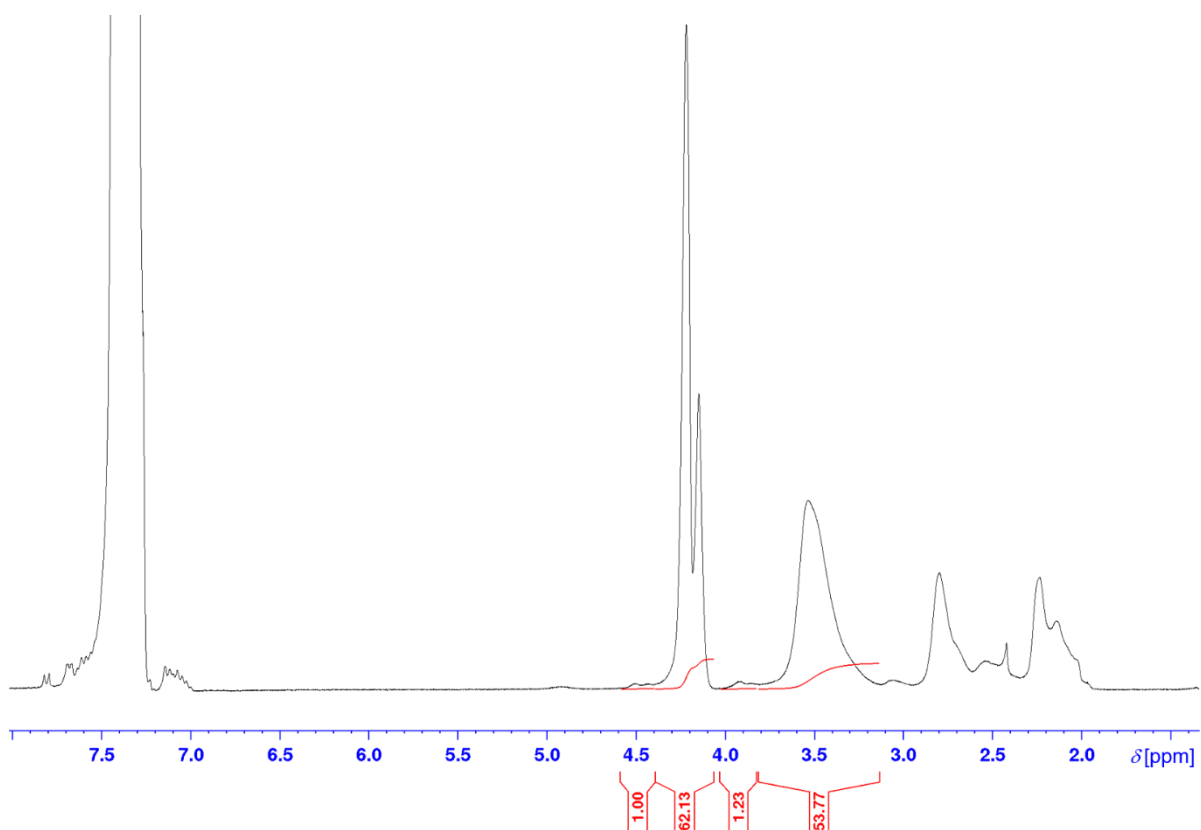


Figure SI 10. ^1H NMR spectrum (300 MHz, CDCl_3) of the reaction mixture yielding **P4**.

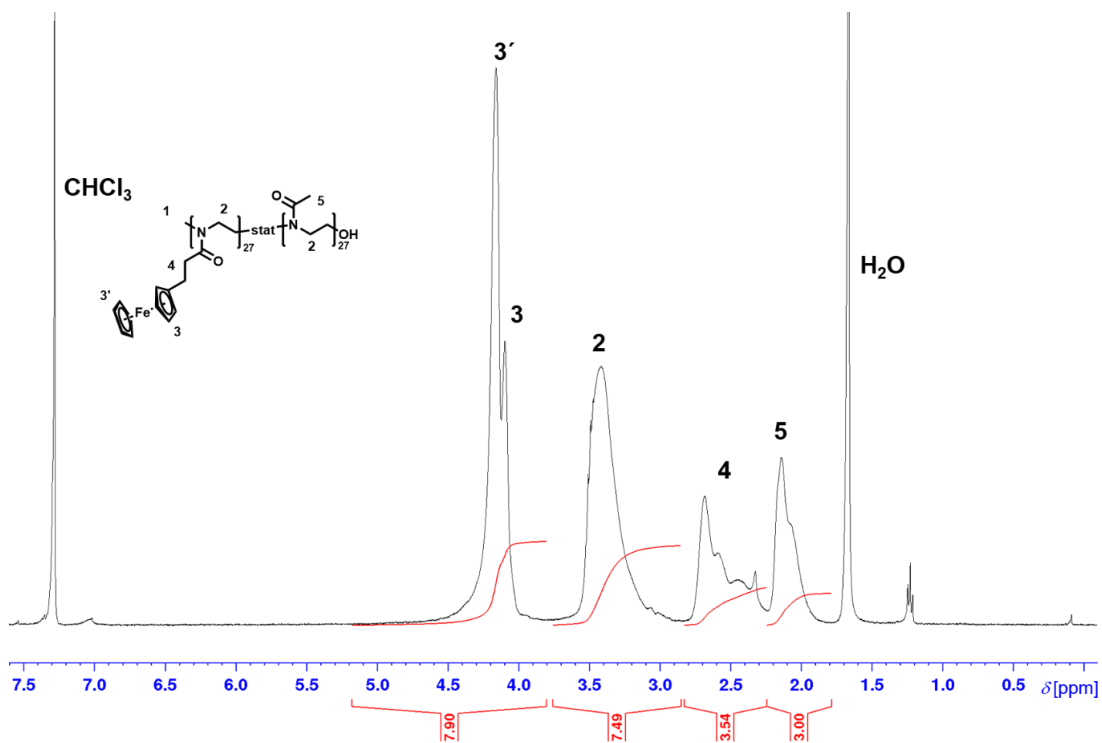


Figure SI 11. ^1H NMR spectrum (300 MHz, CDCl_3) of the purified copolymer **P4** and assignment of the signals to the schematic representation of the chemical structure of **P4**.

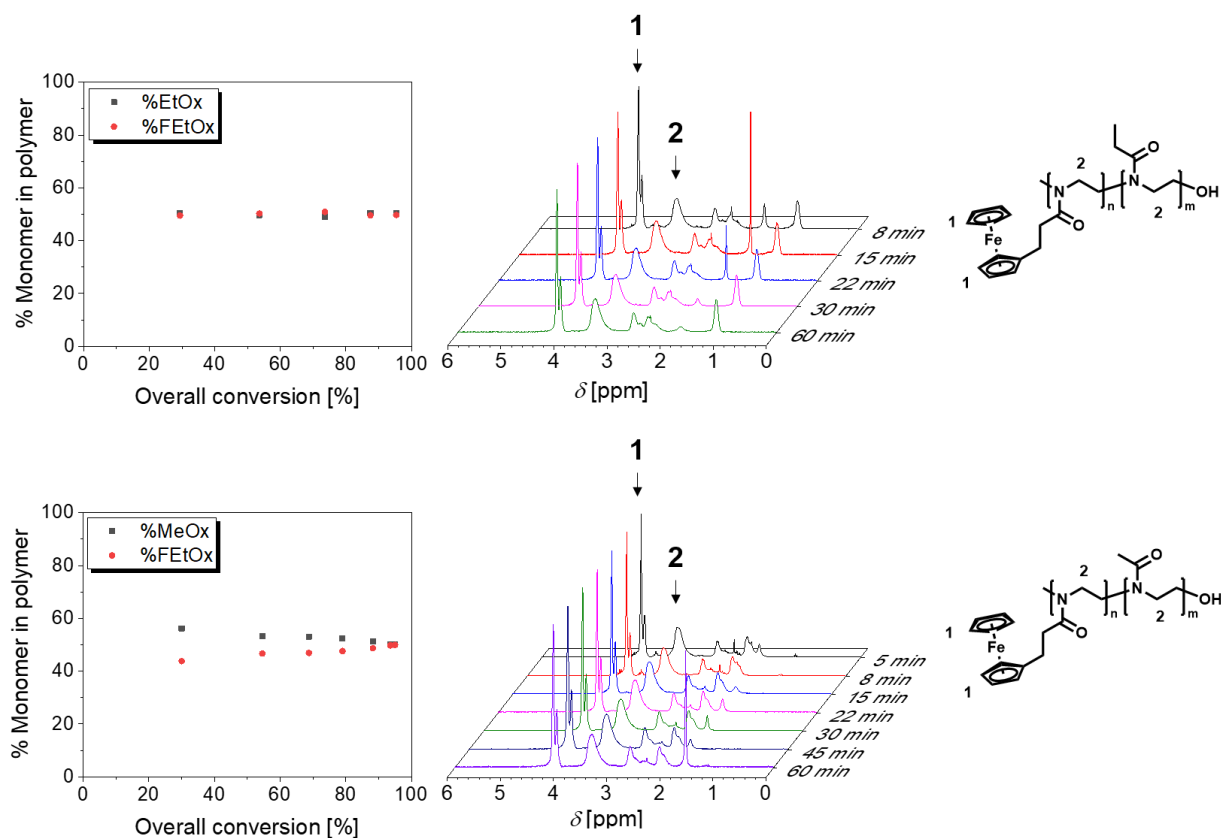


Figure SI 12. Left: Molar ratios of FEtOx and the corresponding comonomer (**Top:** EtOx, **Bottom:** MeOx) obtained by integration of the Cp signals (**1**) and the POx backbone (**2**) in the $^1\text{H-NMR}$ spectra of the precipitated kinetics samples. **Right:** Overlay of the $^1\text{H-NMR}$ spectra (300 MHz, CDCl_3) along with the schematic representation of the chemical structure of the copolymers.

Mass spectrometry

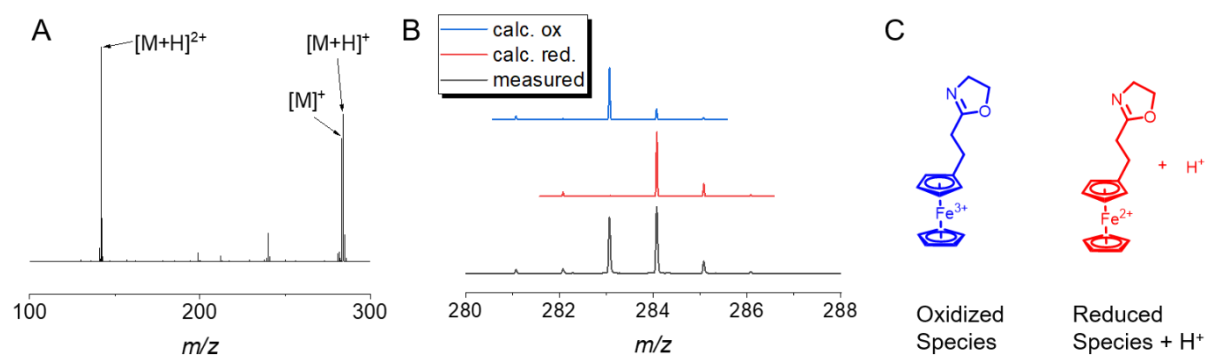


Figure SI 13. Mass spectrometric analysis of the monomer **2**. **A)** HR-ESI mass spectrum (ACN). **B)** Overlay of the observed and calculated isotopic patterns of [M]⁺ and [M+H]⁺. **C)** Schematic representation of the oxidized species [M]⁺ and the proton adduct of the reduced species [M+H]⁺.

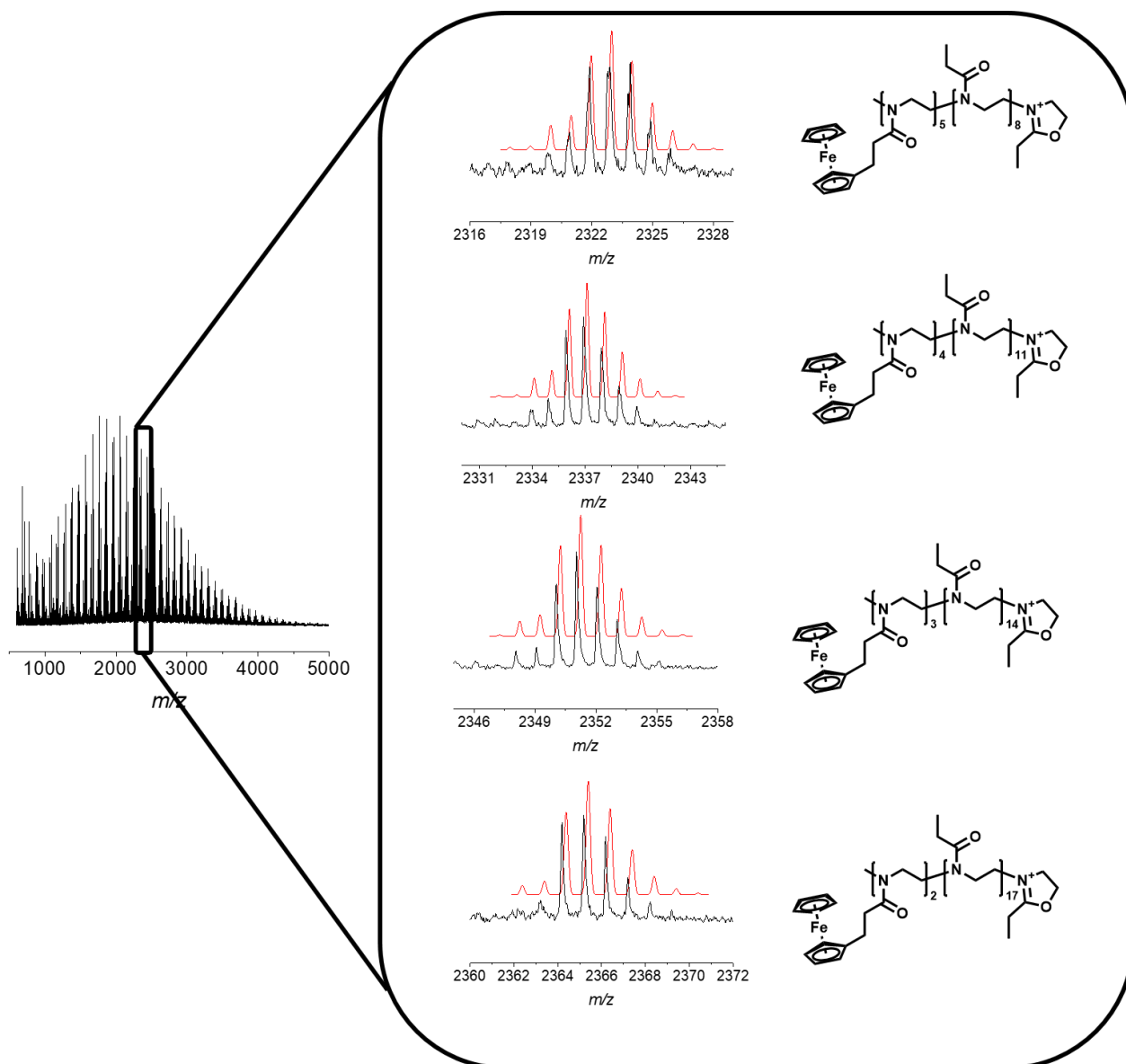


Figure SI 14. Full MALDI mass spectrum (dithranol) of **P1** and overlay of the individual measured and calculated isotopic patterns displayed in **Figure 2** in the main manuscript including the schematic representations of the chemical structures.

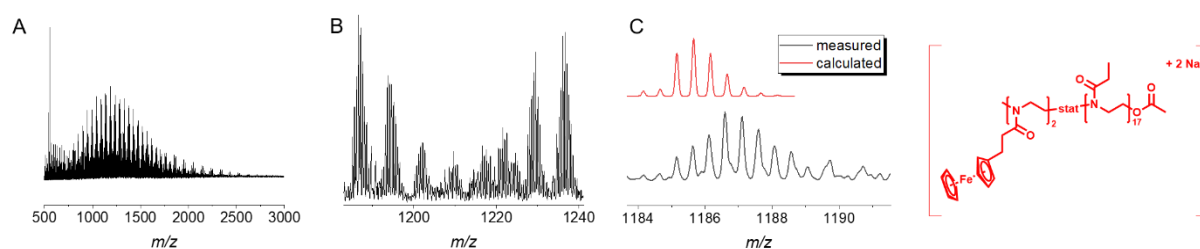


Figure SI 15. ESI mass spectrum of the copolymer **P1**. A) Full spectrum. B) Zoom into selected m/z regions displaying one EtOx repeating unit ($\Delta m/z = 49.5$). C) Overlay of measured and calculated isotopic patterns and schematic representation of the chemical structure of the copolymer ion adduct utilized for subsequent tandem MS analysis (compare **Figure SI 14**).

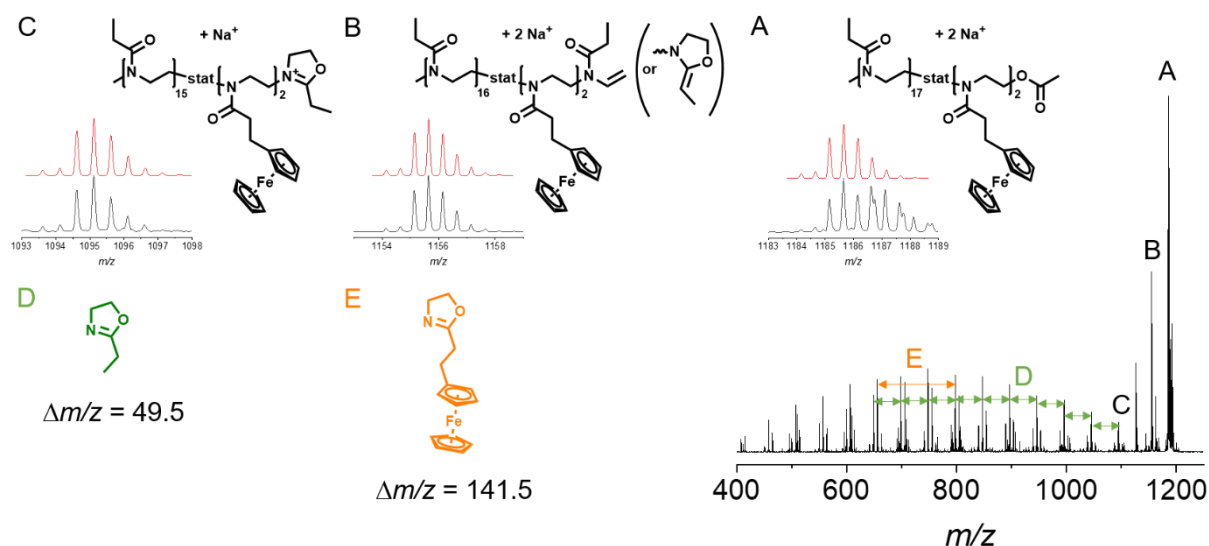


Figure SI 16. ESI tandem mass spectrum of a selected ion ($m/z = 1185.64$) derived from **P1** and assignment of fragmented species. A) Parent peak. B) Remaining fragment after abstraction of acetic acid. C) Remaining fragment after abstraction of sodium acetate and one EtOx unit. D) Schematic representation of the chemical structure of one EtOx unit fragmenting from the oxazolinium chain end. E) Schematic representation of the chemical structure of one FEtOx unit fragmenting from the oxazolinium chain end.

Size exclusion chromatography

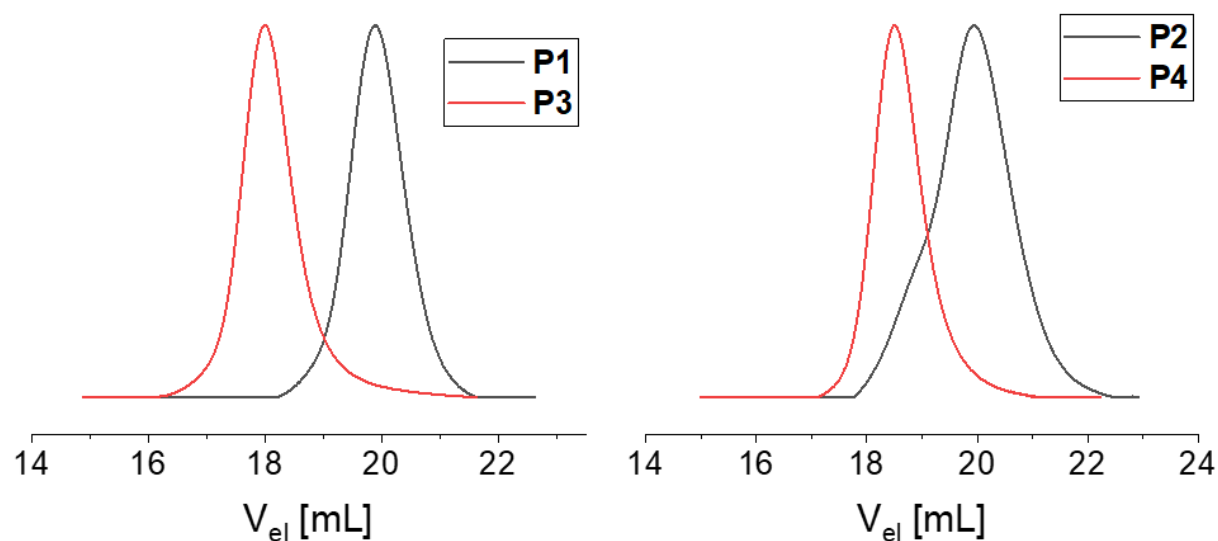


Figure SI 17. Overlay of the SEC elugrams (DMAc, 0.21 wt.% LiCl, RI detection) of the copolymers **P1** to **P4**. Left: Copolymers **P1** and **P3** composed of FEtOx and EtOx. Right: Copolymers **P2** and **P4** composed of FEtOx and MeOx.

Thermal analysis

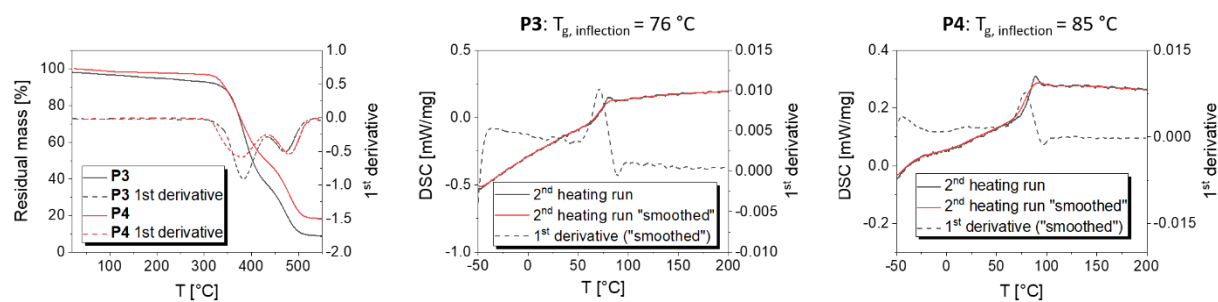


Figure SI 18. Thermal analysis of the copolymers **P3** and **P4**. Left: Thermogravimetric analysis (20 K min⁻¹, N₂ atmosphere). Middle: DSC thermogram of the EtOx based copolymer **P3** derived from the second heating run (20 °C min⁻¹, N₂ atmosphere). Right: DSC thermogram of the MeOx based copolymer **P4** derived from the second heating run (20 °C min⁻¹, N₂ atmosphere).

UV-Vis supported oxidation/reduction experiments in water

A solution of **P2** with a concentration of 1 mg mL^{-1} in deionized and degassed water was, a solution of 60 mg silver triflate in deionized water (1 mL, 0.24 M) and a solution of 47 mg sodium ascorbate in deionized water (1 mL, 0.24 M) were prepared.

The UV-VIS spectrometer was calibrated against blank water. The polymer solution was filtered and the absorption was measured from 400 nm to 800 nm. Afterwards, 10 μL of the AgOTf solution were added. The formed silver was removed by filtration and an absorption spectrum of the remaining blue solution was measured. Then, 10 μL of the sodium ascorbate solution were added. The silver was filtered off and the yellowish solution was measured. This procedure was repeated three times. For the last oxidation, 20 μL silver triflate solution were used.

Cyclic voltammetry

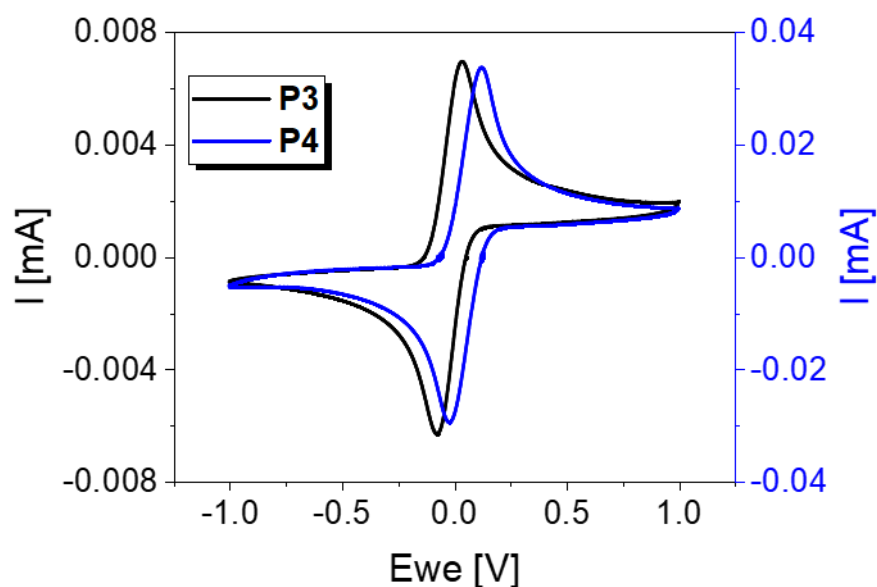


Figure SI 19. Cyclic voltammetry of the polymers **P3** and **P4**. Few milligrams of polymer were dissolved in propylene carbonate. Tetrabutylammonium hexafluorophosphate was used as conducting salt. Ag/AgNO₃ in CH₃CN served as reference electrode, glassy carbon and a

platinum wire were used as working electrode and counter electrode, respectively. The measurements were conducted from 0 to +1 V to -1 V with 200 mV s⁻¹.

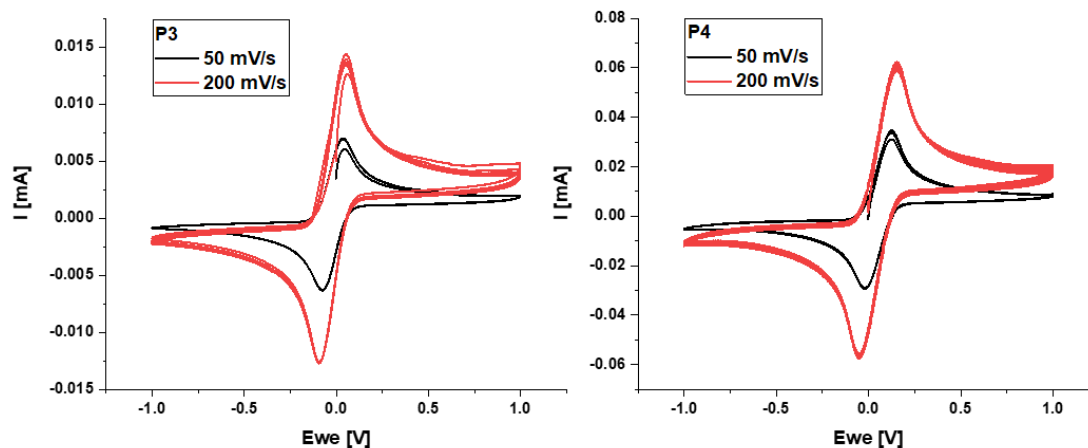


Figure SI 20. Cyclic voltammograms of **P3** and **P4** in propylene carbonate. Five cycles per scanning speed are depicted. Ag/AgNO₃ in CH₃CN served as reference electrode, glassy carbon and a platinum wire were used as working electrode and counter electrode, respectively. The measurements were conducted from 0 to +1 V to -1 V with the given scanning speed.

Other 2-oxazolines for bond-length comparison in the solid state

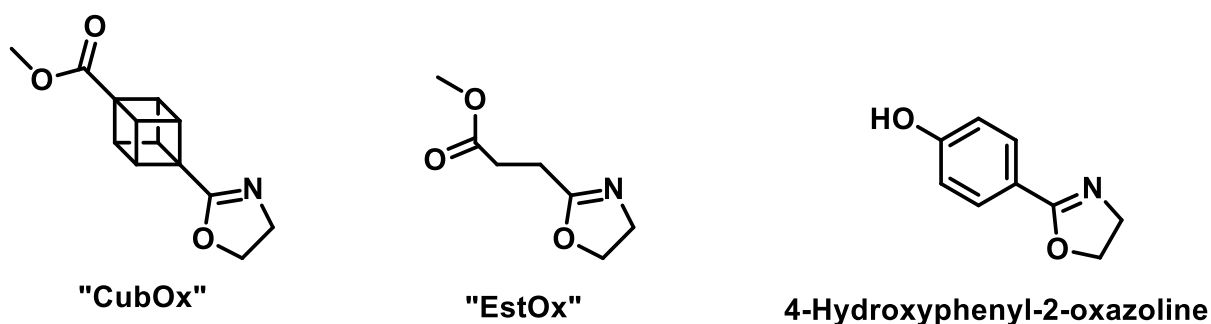


Figure SI 21. Schematic representation of the chemical structures of other 2-oxazolines with reported bond lengths used for comparison with FEtOx.^[2-4]

Crystal Structure Determination

The intensity data were collected on a Nonius KappaCCD diffractometer, using graphite-monochromated Mo-K α radiation. Data were corrected for Lorentz and polarization effects; absorption was taken into account on a semi-empirical basis using multiple-scans.^[5-7]

The structures were solved by direct methods (SHELXS^[8]) and refined by full-matrix least squares techniques against Fo² (SHELXL-2018^[8]). All hydrogen atoms were located by difference Fourier synthesis and refined isotropically. All non-hydrogen atoms were refined anisotropically.^[8]

MERCURY^[9] was used for structure representations.

Crystal Data for 2: C₁₃H₁₃FeN, Mr = 239.09 g mol⁻¹, yellow prism, size 0.102 x 0.092 x 0.078 mm³, monoclinic, space group P 2₁/c, a = 13.6413(4), b = 7.5242(2), c = 10.9536(3) Å, β = 106.566(1)°, V = 1077.61(5) Å³, T = -140 °C, Z = 4, $\rho_{\text{calcd.}}$ = 1.474 g cm⁻³, μ (Mo-K α) = 13.61 cm⁻¹, multi-scan, transmin: 0.6998, transmax: 0.7456, F(000) = 496, 7855 reflections in h(-17/17), k(-9/9), l(-14/14), measured in the range 3.116° ≤ Θ ≤ 27.466°, completeness Θ_{max} = 99.6%, 2460 independent reflections, R_{int} = 0.0220, 2317 reflections with F_o > 4 σ (F_o), 188 parameters, 0 restraints, R_{1obs} = 0.0233, wR_{2obs}² = 0.0543, R_{1all} = 0.0253, wR_{2all}² = 0.0555, GOOF = 1.050, largest difference peak and hole: 0.307 / -0.223 e Å⁻³.

Crystal Data for FEtOx: C₁₅H₁₇FeNO, Mr = 283.14 g mol⁻¹, yellow-orange prism, size 0.088 x 0.082 x 0.080 mm³, monoclinic, space group P 2₁/c, a = 15.1868(16), b = 7.6541(8), c = 10.6947(11) Å, β = 101.639(6)°, V = 1217.6(2) Å³, T = -140 °C, Z = 4, $\rho_{\text{calcd.}}$ = 1.545 g cm⁻³, μ (Mo-K α) = 12.24 cm⁻¹, multi-scan, transmin: 0.4424, transmax: 0.7455, F(000) = 592, 8428

reflections in h(-19/16), k(-8/9), l(-12/13), measured in the range $2.739^\circ \leq \Theta \leq 27.481^\circ$, completeness $\Theta_{\max} = 99.9\%$, 2760 independent reflections, $R_{\text{int}} = 0.0836$, 2394 reflections with $F_o > 4\sigma(F_o)$, 231 parameters, 0 restraints, $R1_{\text{obs}} = 0.0449$, $wR^2_{\text{obs}} = 0.1097$, $R1_{\text{all}} = 0.0528$, $wR^2_{\text{all}} = 0.1159$, GOOF = 1.067, largest difference peak and hole: 0.666 / -0.660 e \AA^{-3} .

Crystallographic data (excluding structure factors) has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC-2013191 for **2**, and CCDC-2013192 for **FEtOx**. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [E- mail: deposit@ccdc.cam.ac.uk].

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