Electronic Supplementary Material (ESI) for Polymer Chemistry.

Synthesis of a sulfonamide functionalized poly(styrene oxide) and illustration of a potential post-polymerization strategy

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1. GENERAL EXPERIMENTAL

All air and moisture sensitive compounds were prepared using standard *Schlenk* techniques with argon (99.996 vol.-%) from *Westfalen* as inert gas. Solvents were dried with the solvent purification system MB SPS-800 from *MBraun* or over activated alumina and stored over molecular sieve (3 or 4 Å). Deuterated solvents were purchased from *Sigma-Aldrich* and dried over activated 3 Å molecular sieve. Unless otherwise stated, all chemicals were purchased from *Sigma-Aldrich*, *ABCR GmbH* or *TCI Chemicals* and used without further purification.

Nuclear magnetic resonance spectroscopy (NMR). ^{1}H- and ^{13}C-NMR spectra were recorded on a *Bruker Ascend* 400 MHz NMR-spectrometer at 400 MHz (^{7}Li-NMR spectra measured at 300 MHz). All chemical shifts are given in parts per million (ppm) and referenced to the residual proton signal of the respective solvent. The NMR spectra were analyzed using the *MestReNova* software. Signal multiplicities are abbreviated as following: s - singlet, m – multiplet. **Thermogravimetric analysis (TGA).** For **2** (catalyst to monomer ratios 1:10, 1:50, 1:100, 1:200), 2 mg of sample was heated from room temperature to 1000 °C with a heating rate of 10 K/min under synthetic air on a TGA Q5000 by *TA Instruments.* Analysis of mass loss was done using *TA* Analysis software. For **3** (catalyst to monomer ratios 1:10, 1:50, 1:100, 1:200), 2 mg of sample was heated from 50 °C to 700 °C with a heating rate of 10 K/min under argon on a *Netzsch* TG 209 F1 Libra inside a glovebox. The data was processed with the software *Netzsch* Proteus 6. **Differential scanning calorimetry (DSC).** For **2** (catalyst to monomer ratios 1:10, 1:50, 1:100, 1:200), about 3-4 mg were weighed in a non-hermetic aluminum pan and measured in a range of -100 °C to 220 °C (depending on the sample) with a heating and cooling rate of 10 K/min on a DSC Q2000 by *TA Instruments.* Analysis was performed using *TA* Analysis software. The same procedure was

repeated for **3** (catalyst to monomer ratios 1:10, 1:50, 1:100, 1:200) in a hermetic set-up. Sample preparation was performed inside a glovebox. **Gel permeation chromatography (GPC).** Average absolute molecular weights and polydispersity of **2** were determined on an *Agilent* PL-GPC 50 with an integrated RI unit, two light scattering detectors (15° and 90°) and a differential pressure viscosimeter with two *Agilent* PolarGel M columns at 30 °C. 2 mg of sample were dissolved in DMF + 25 mmol/L LiBr. Absolute molecular weights and polydispersity were determined using the experimentally determined value for dn/dc of 0.152 mL g^{-1}. **Refractive index increment determination (dn/dc).** For dn/dc determination of **2**, a *WGE Dr. Bures* dn/dc-2010 from PSS equipped with a 620 nm light source was used. The measurements were performed in DMF with 25 mmol L^{-1} LiBr at 30 °C with 7 different polymer concentrations. **Energy-dispersive X-ray spectroscopy (EDX).** EDX measurements were conducted on a *Hitachi* table top scanning electron microscope with a 10.000 magnification and an accelerating voltage of 1 kV. **FTIR.** Measurements were performed on a nitrogen-cooled *Bruker Vertex* 70A spectroscope on an attenuated total reflection mode.

2. SYNTHESIS PROCEDURES

4-(2-BROMOETHYL)-BENZENE SULFONYL CHLORIDE (A)

The synthesis was conducted according to literature known chlorosulfonation reactions.[1] At 0 °C (2-bromoethyl)-benzene (20.5 mL, 150 mmol, 1.0 eq) in chloroform (50 mL) was added dropwise to a solution of chlorosulfonic acid (30.0 mL, 450 mmol, 3.0 eq.) in chloroform (35 mL). The solution was stirred for 15 min at 0 °C before it was warmed up to room temperature. After

stirring for 3 h at 25 °C, the solution was poured into ice and the aqueous phase was extracted with DCM (3 x 100 mL). The organic phase was washed with $NaHCO_3$ solution (3 x 150 mL) and brine (3 x 150 mL) and dried over Na_2SO_4. The crude product was purified via column chromatography (pentan/diethylether 10/1) to obtain **A** (32.3 g, 114 mmol, 76%).

^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 8.01 (d, *J* = 8.2 Hz, 2H), 7.48 (d, *J* = 8.2 Hz, 2H), 3.62 (t, *J* = 7.1 Hz, 2H), 3.30 (t, *J* = 7.1 Hz, 2H).

1-((4-VINYLPHENYL)SULFONYL)-PYRROLE (B)

To a solution of pyrrole (10.7 mL, 155 mmol, 2.2 eq.) in dry THF (100 mL), *n*-BuLi (2.5 M in hexane, 62.0 mL, 155 mmol, 2.2 eq.) was added dropwise at −78 °C and the reaction was stirred for 10 min at this temperature. The cooling bath was removed to warm up the solution to room temperature. **A** (20.0 g, 70.5 mmol, 1.0 eq.) was dissolved in dry THF (25 mL) and added dropwise to the solution over a period of 20 min at −78 °C. After stirring overnight and removing of the solvent, the residue was dissolved in dichloromethane (100 mL) and extracted with water (2 x 150 mL) and $NaHCO_3$ solution (2 x 150 mL). The organic phases were collected and dried over Na_2SO_4. The obtained brownish solid was sublimated twice resulting in **B** (12.8 g, 54.9 mmol, 78%).

^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.92 (d, *J* = 8.6 Hz, 2H), 7.57 (d, *J* = 9.0 Hz, 2H), 7.30 – 7.21 (m, 2H), 6.80 (dd, *J* = 17.6, 10.9 Hz, 1H), 6.43 – 6.36 (m, 2H), 5.96 (d, *J* = 17.6 Hz, 1H), 5.52 (d, *J* = 11.0 Hz, 1H).

1-((4-(OXIRAN-2-YL)PHENYL)SULFONYL)-1*H*-PYRROLE (1)

The synthesis was conducted according to a published epoxidation strategy of *Jacobsen et al.*[2] **B** (4.02 g, 17.3 mmol, 1.0 eq.), *N*-methylmorpholine *N*-oxide (10.1 g, 86.2 mmol, 5.0 eq.) and (*R,R*)-(–)-[1,2-cyclohexanediamino-*N,N'*-bis-(3,5-di-*t*-butylsalicycliden)]-mangan(III)-chlorid (438 mg, 689 µmol, 4 mol%) were dissolved in dry dichloromethane (400 mL) and the reaction mixture was cooled to −78 °C. After the addition of *m*CPBA (8.50 g, 34.5 mmol, 2.0 eq.) in small portions the reaction is stirred at −78 °C for 45 min. The reaction solution was mixed with 1 M NaOH (380 mL) and the aqueous phase was extracted with DCM (3 x 150 mL). The combined organic layers were washed with brine (3 x 150 mL) and dried over Na_2SO_4. The crude product was purified via column chromatography (pentan/ethyl acetate 10/1) and sublimated to obtain **1** (2.74 g, 11.0 mmol, 64%).

^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.83 (d, J = 8.2 Hz, 2H), 7.40 (d, J = 8.2 Hz, 2H), 7.15 (m, 2H), 6.30 (m, 2H), 3.89 (m, 1H), 3.21 – 3.14 (m, 1H), 2.72 (m, 1H).

^{13}C-NMR (101 MHz, $CDCl_3$): δ (ppm) = 144.4, 138.7, 127.1, 126.4, 120.8, 113.8, 77.2, 51.6, 51.5.

TGA: $T_{d,\ onset}$ = 195 °C.

DSC: T_m = 108 °C.

3. POLYMERIZATION PROCEDURE

POLY(1-((4-(OXIRAN-2-YL)PHENYL)SULFONYL)-1*H*-PYRROLE) (2)

In an argon atmosphere, **1** was dry mixed with (1S,2S)-(+)-[1,2-cyclohexanediamino-*N,N*'-bis(3,5-di-*t*-butylsalicylidene)]-chromium(III)chloride in different catalyst to monomer ratios (1:10, 1:50, 1:100, 1:200) and heated up to 115 °C for 3 days. After the completion of polymerization, the

solid mixture was dissolved in dichloromethane and precipitated in pentane. The solid was centrifugated and again precipitated three times to separate the polymer from the monomer and catalyst residues. The received polymer is dried in vacuum at 50 °C for 24 h to obtain **2** in powder form (93-97%).

^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 8.03 – 7.30 (m, 4H), 7.22 – 7.06 (m, 2H), 6.46 – 6.20 (m, 2H), 5.25 – 3.06 (m, 3H).

X = 93-97%.

$M_{n,abs}$ = 14.2-113 kg mol^{-1}.

Đ = 1.3-2.6.

I_e: 18-43%.

TGA: $T_{d,\ onset}$ = 290-310 °C.

DSC: T_g = 68-73 °C.

4. POST-POLYMERIZATION FUNCTIONALIZATION

POLY(LITHIUM 4-OXIRAN-2-YL)BENZENESULFONATE (3)

In a glovebox, elemental lithium (10 eq. per monomer unit) is dissolved in dry MeOH. A solution of **2** (in different catalyst to monomer ratios 1:10, 1:50, 1:100, 1:200) in dry DCM is added and refluxed for 3 d at 65 °C. After evaporation of the solvent, the solid is dissolved in water and dialyzed against 2 L of water. The purified polymer is dried in vacuum to yield **3** in 40-45% yield.

^{1}H-NMR (400 MHz, D_2O): δ (ppm) = 8.38 – 6.89 (m, 4H), 4.90 – 2.82 (m, 3H).

^{7}Li-NMR (156 MHz, D_2O): δ (ppm) = 0.16 (s).

TGA: $T_{d,\ onset}$ = 280-310 °C.

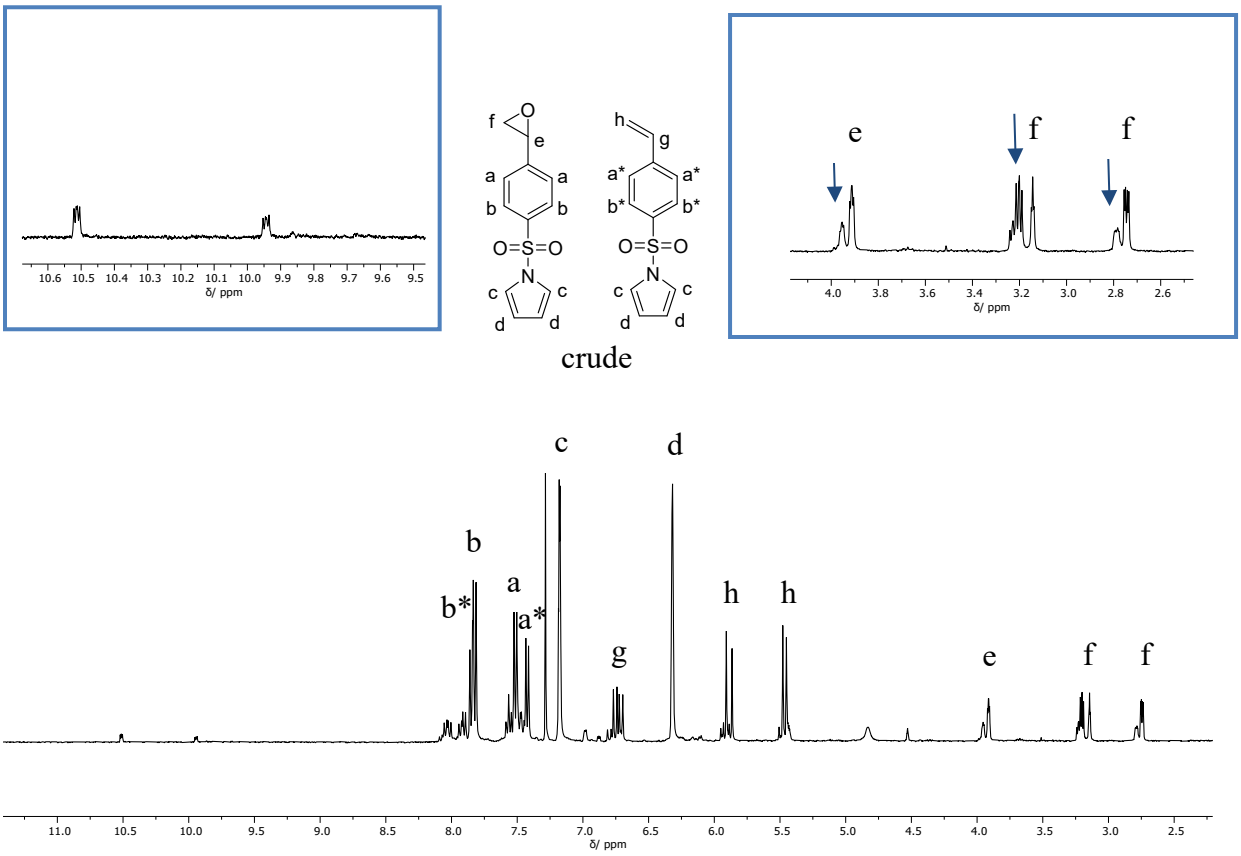
DSC: T_g = 18-20 °C.

5. ADDITIONAL DATA

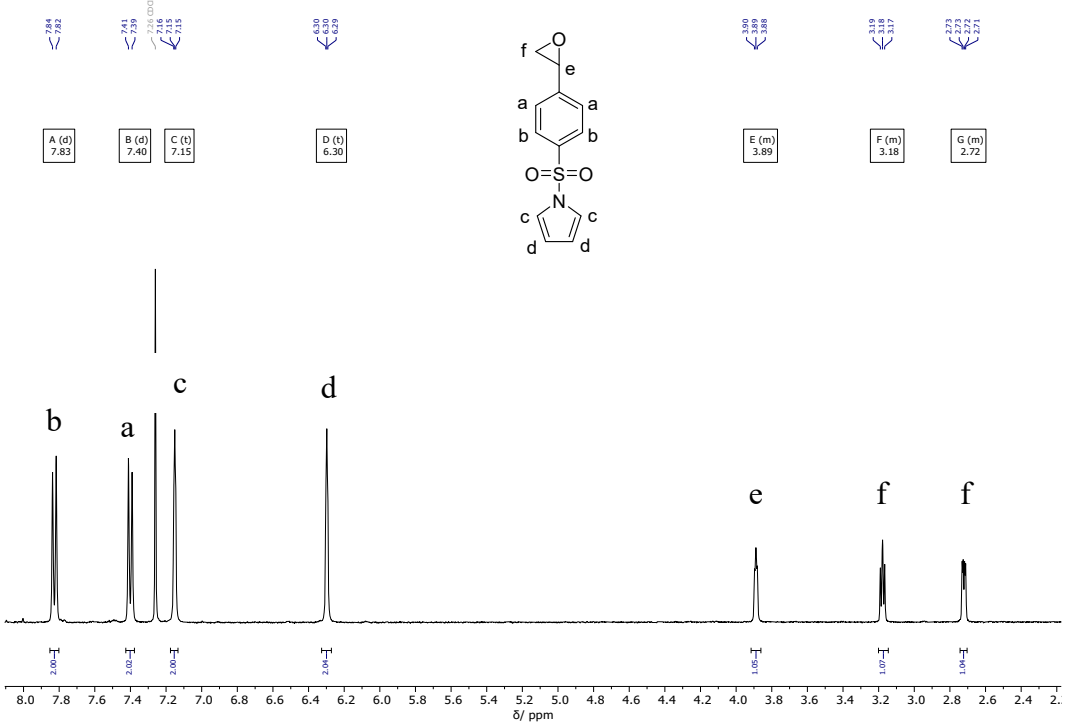
S1 Overview of different epoxidation strategies converting **B** into **1**; Reaction conditions: 1 eq. of **B** reacts with the respective amount of epoxidation reagent in a certain temperature range with varying reaction times.

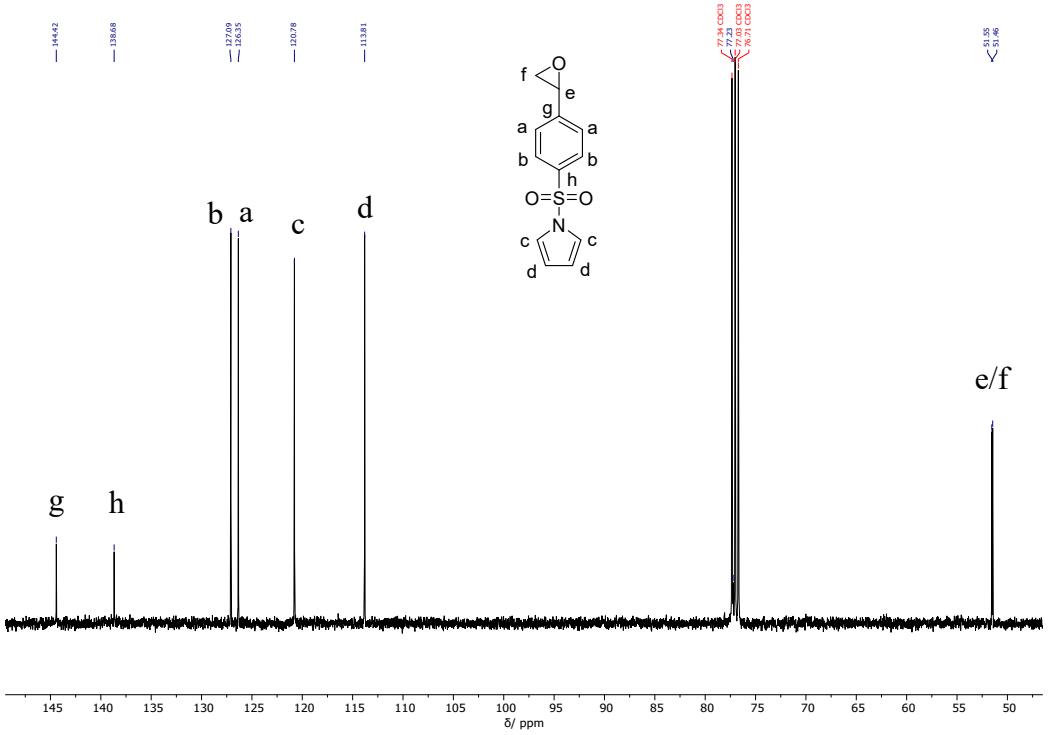
reagent	equivalents	temperature	reaction time	yield
m-CPBA (70%)	2.0-5.0 eq.	–78 °C to RT	2 h-1 d	–
H_2O_2 (35%)	1.5-2.0 eq.	0 °C to RT	1-5 d	–
NaOCl	1.5-2.0 eq.	0 °C to 40 °C	1-5 d	–
DMDO (c = 0.1 M)	2.0-5.0 eq.	0 °C to RT	2-6 d	15-20%

S2 ^{1}H-NMR spectrum of unpurified **1** in $CDCl_3$ (δ = 7.26 ppm) at 400 MHz; epoxidation parameters: 1.3 eq. DMDO (c = 0.1 M), 0 °C, in DCM, reaction time 5 d; marked in blue: isomerization signals produced by related aldehydes of **1**.

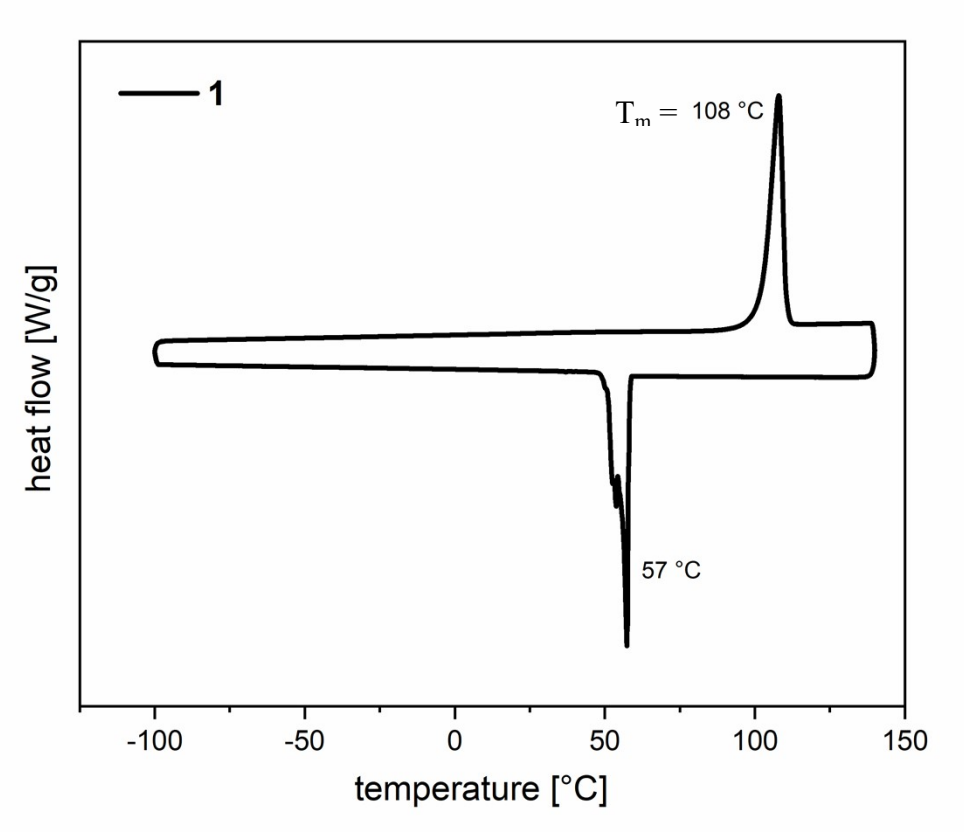


S3 ^{1}H- and ^{13}C-NMR spectra of **1** in $CDCl_3$ (δ = 7.26 ppm) at 400 MHz.

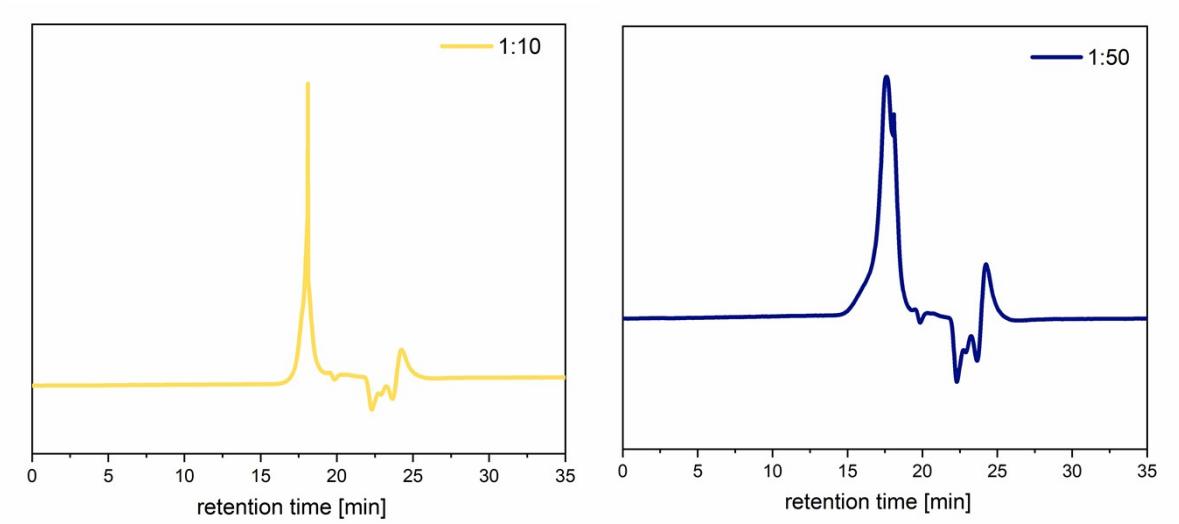


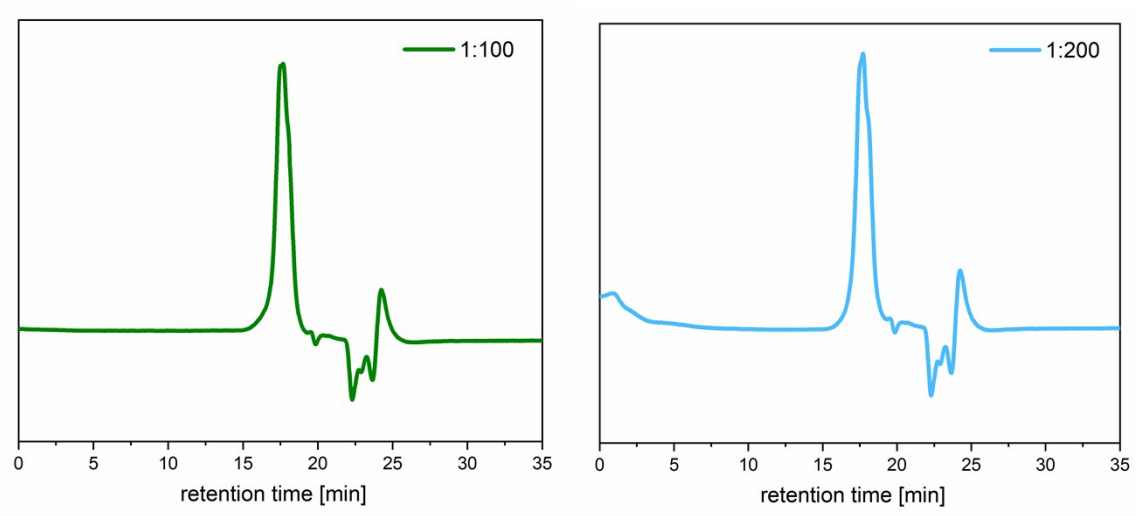


S4 DSC measurement of **1** measured in three cycles; depicted here: first cooling cycle and second heating cycle, plotted in exo down mode, 10 K/min heating rate, non-hermetic set-up.

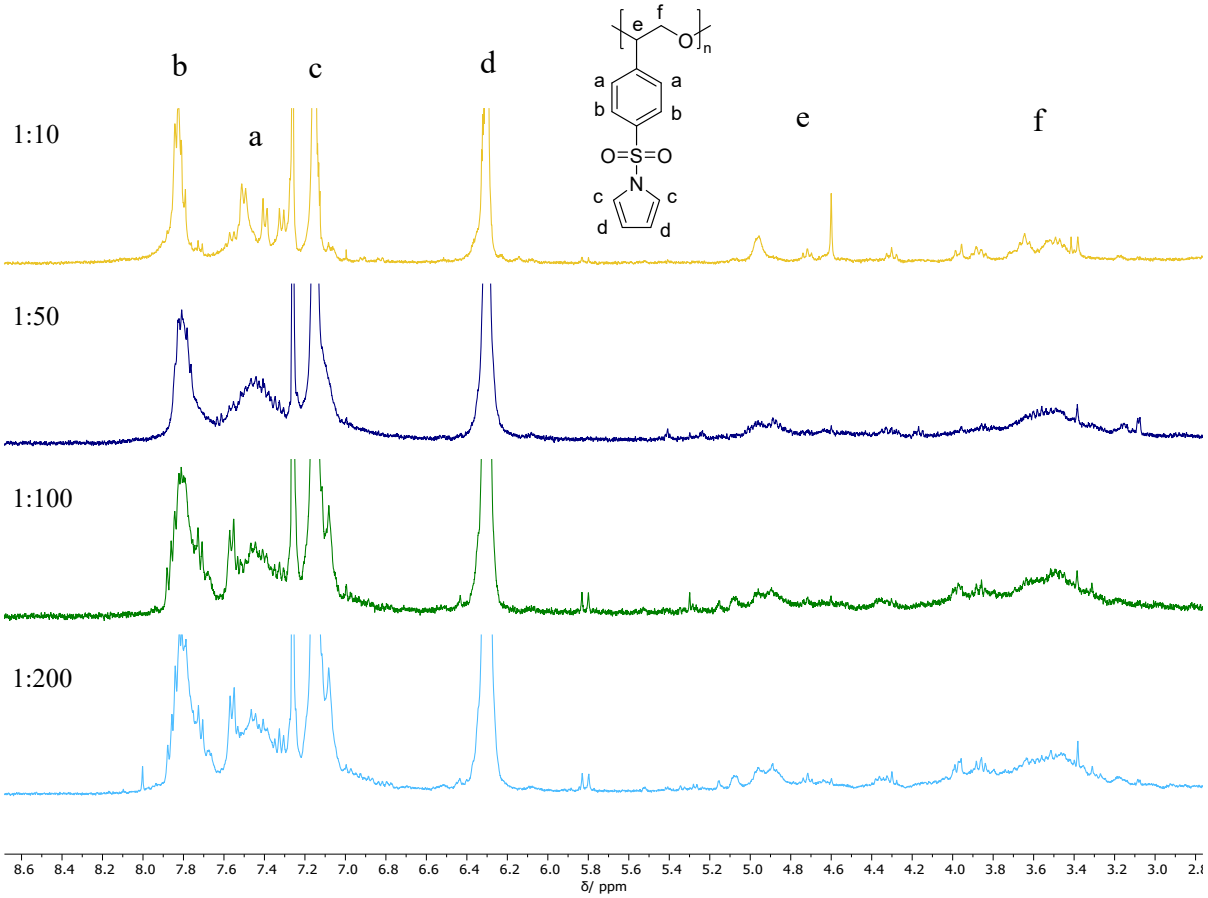


S5 GPC traces of **2** for different catalyst to monomer ratios (1:10, 1:20, 1:100, 1:200); DMF + 25 mmol L^{-1} LiBr as solvent, *dn/dc* = 0.152 mL g^{-1}, absolute determination of molecular weights and polydispersity at 30 °C.



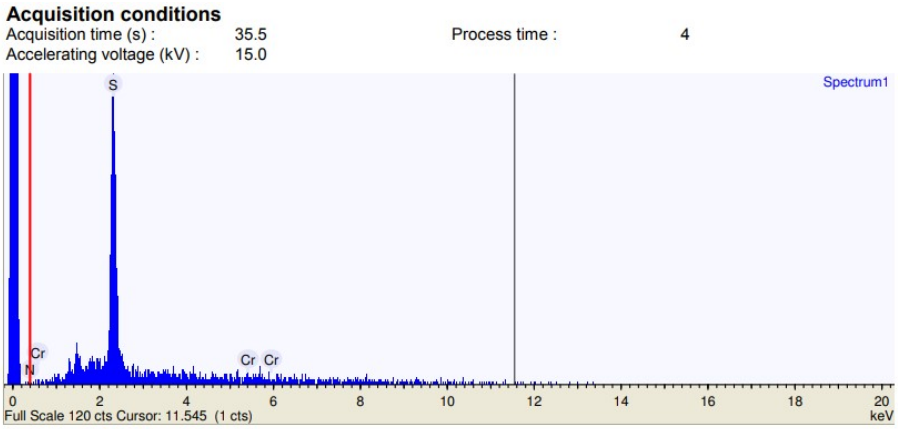


S6 ^{1}H-NMR spectra of **2** in $CDCl_3$ (δ = 7.26 ppm) at 400 MHz for different catalyst to monomer ratios (1:10 (yellow line), 1:50 (dark blue line), 1:100 (green line), 1:200 (light blue line)).



S7 EDX data of **2** (catalyst to monomer ratio 1:100) before and after the precipitation in pentane.

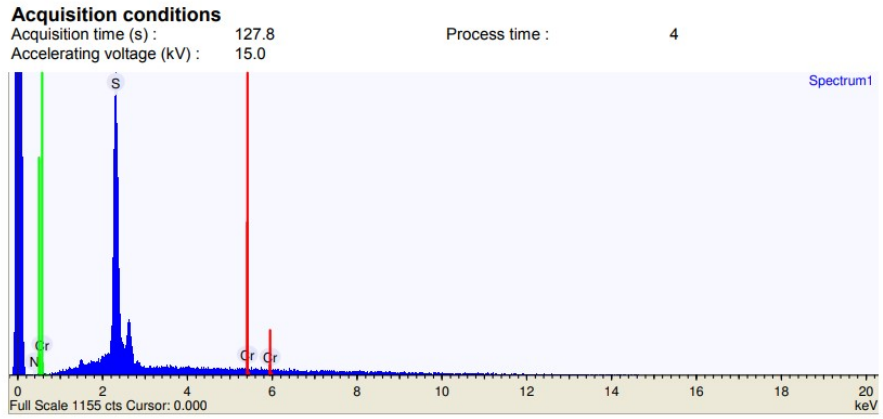
before precipitation:



Quantification Settings
Quantification method : All elements (normalised)

element	**weight %**
sulfur	93.8
chromium	6.2

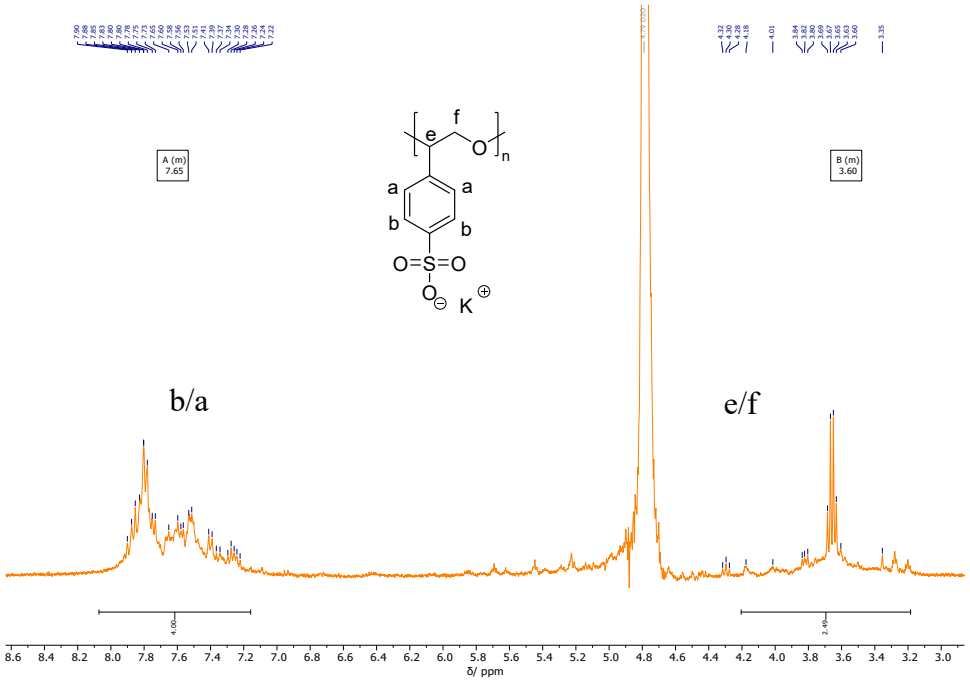
after precipitation:



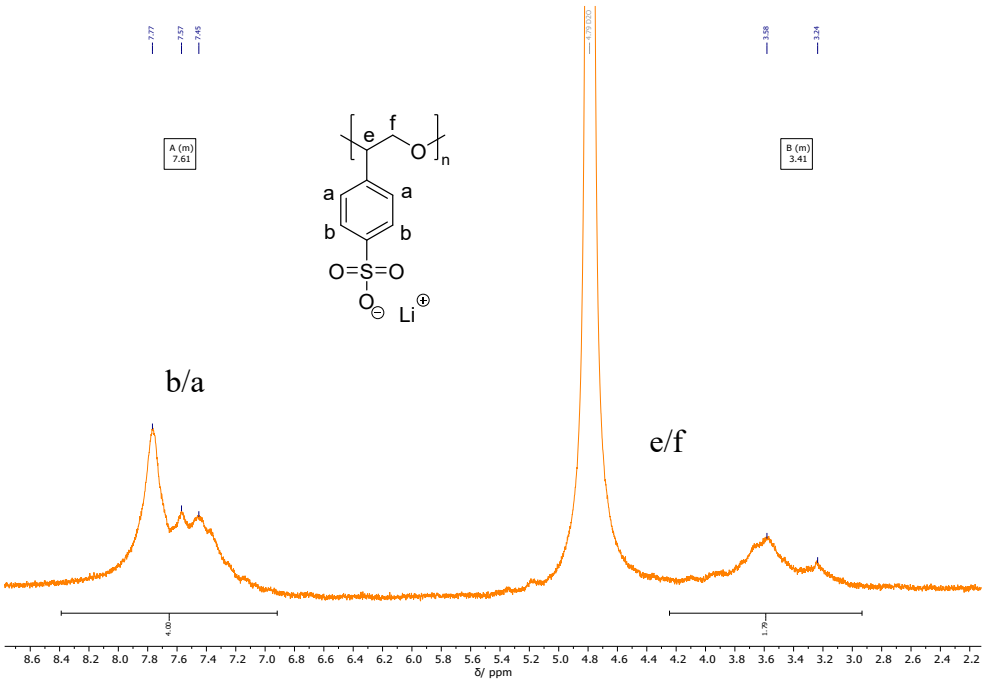
Quantification Settings
Quantification method : All elements (normalised)

element	**weight %**
sulfur	100
chromium	0.0

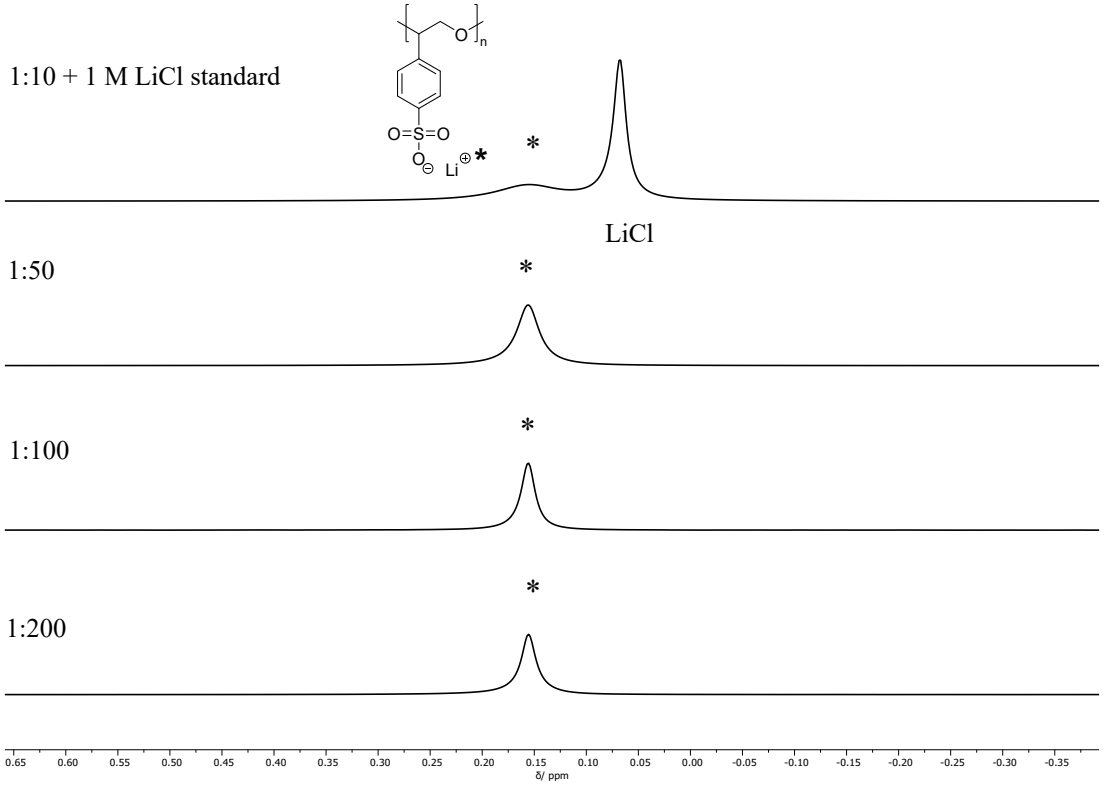
S8 ^{1}H-NMR spectrum of **3** (catalyst to monomer ratio 1:100) in D_2O (δ = 4.79 ppm) at 400 MHz using KOH as deprotecting reagent; reaction conditions: 10 eq. KOH per monomer unit, in EtOH, 80 °C, 3 d.



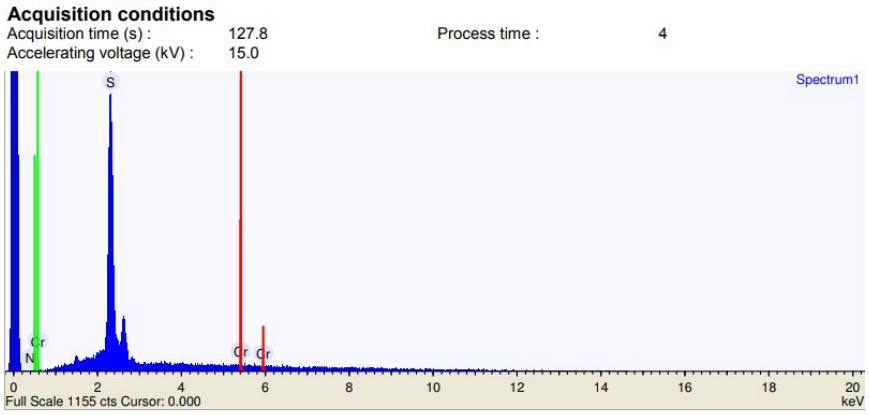
S9 Full ^{1}H-NMR spectrum of **3** (catalyst to monomer ratio 1:100) in D_2O (δ = 4.79 ppm) at 400 MHz using elemental Li as deprotecting reagent; reaction conditions: 10 eq. Li per monomer unit, in MeOH/DCM, 65 °C, 3 d.



S10 ^{7}Li-NMR spectrum of **3** in D_2O (δ = 4.79 ppm) at 300 MHz for different catalyst to monomer ratios (1:10, 1:20, 1:100, 1:200); as reference, a 1 M LiCl standard is added to the first sample.



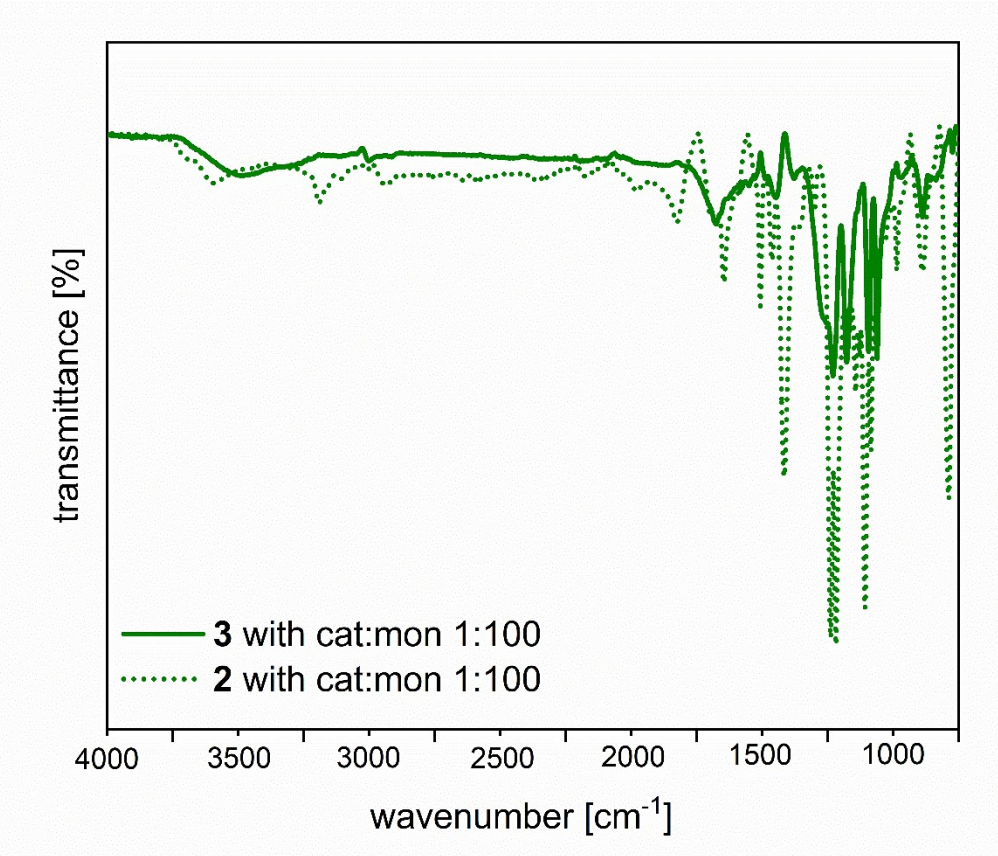
S11 EDX data of **3** (catalyst to monomer ratio 1:100) after dialysis.



Quantification Settings
Quantification method : All elements (normalised)

element	**weight %**
sulfur	100
chromium	0.0

S12 IR-spectra of **2** (catalyst to monomer ratio 1:100) and **3** (catalyst to monomer ratio 1:100); IR-spectra of **3** clearly shows the vanishing of the pyrrole related vibration modes.



6. REFERENCES

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2. M. Palucki, P. J. Pospisil, W. Zhang and E. N. Jacobsen, *Journal of the American Chemical Society*, 1994, **116**, 9333-9334.