Supplementary Information for

Oxa-Michael polyaddition of vinylsulfonylethanol for aliphatic polyethersulfones

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Experimental part

Materials and Methods

All reagents and solvents were commercially purchased from Sigma-Aldrich, TCI Chemicals, and abcr. and were used without further purification. Vinylmercaptoethanol was provided by BASF SE.

^{1}H-NMR spectra were measured with a Bruker spectrometer (300 MHz) equipped with an Avance I console, a dual ^{1}H and ^{13}C sample head and a 60 x BACS automatic sample changer, and a Bruker spectrometer (400 MHz) equipped with an Avance III console, a BBFO sample head, and a 60 x BACS automatic sample changer. The chemical shifts of the peaks were determined by using the residual solvent signal as a reference and are given in ppm in comparison to TMS. Deuterated solvents were commercially purchased from EURISO-TOP GmbH.

Size-exclusion chromatography (SEC) of polymers was performed on an Agilent system (series 1200) equipped with a PSS degasser, a G1310A pump, a G1362A refractive index detector and a PSS GRAM 30 and 1000 column with DMAc (+ 0.21 wt.% LiCl) as eluent at a flow rate of 1 mL/min. The column oven was set to 40 °C and poly(ethylene glycol) (PEG) standards were used for calibration.

Matrix-assisted laser desorption ionization mass spectrometry (MALDI-MS) measurements were carried out using an Ultraflex III ToF/ToF instrument (Bruker Daltonics) equipped with an Nd-YAG laser. All these spectra were measured in the positive mode using alpha-Cyano-4-hydroxycinnamic acid (CHCA) as a matrix.

The differential scanning calorimetry (DSC) measurements were performed on a DSC 204 F1 Phoenix from Netzsch under a nitrogen atmosphere with a heating rate of 10 K/min. The thermal gravimetric analysis (TGA) was carried under nitrogen using a Netzsch TG 209F1.

The density and viscosity measurements were carried out on a Density meter: DMA 4100 M and an AMVn (Automated Micro Viscometer) from Anton Paar. A glass capillary with a diameter of 0.9 mm and a 0.3μ-gold plated ball (density 7.484 g/cm^3) with a diameter of 0.794 mm was used. All viscosity measurements were performed in DMSO.

The X-ray diffraction (XRD) measurements were performed on the STOE Transmission Diffractometer System STADI P with Cu-K_α radiation (40 kV, 15 mA, $\lambda = 1.5406$ Å).

The vapor pressure osmometry measurements were performed on the Vapor Pressure Osmometer K–7000 from Knauer. A calibration with PEG-standard (M_n =2800 g/mol) was executed and the polymer was measured in 4 different concentration. An extrapolation of the measurements data reveals the absolute molar mass of the polymers.

Synthetic procedures

Vinylsulfonylethanol: Vinylmercaptoethanol (30.00 g, 288 mmol, 1 eq.), sodium tungstate (0.04 g, 0.12 mmol, 0.0004 eq.) and hydroxyanisol (0.05 g, 0.40 mmol, 0.001 eq.) were dispersed in water (15 mL). Afterwards, 50% hydrogen peroxide solution (19.61 g, 288 mmol, 1 eq.) was added dropwise so that 40 °C was not exceeded. Then the solution was stirred for 1 h at 40 °C. Subsequently, 50% hydrogen peroxide solution (19.61 g, 288 mmol, 1 eq.) was added dropwise at 40 °C and then the solution was stirred overnight at 60 °C. Finally, manganese oxide was added, the solution was centrifuged and the solvent was removed in a gas flow at 40 °C.

^{1}H-NMR (300 MHz, DMSO): δ [ppm] = 6.93 (dd, J = 16.2, 9.8 Hz, 1H), 6.18 (dd, J = 12.7, 8.9 Hz, 2H), 5.06 (s, 1H), 3.74 (s, 2H), 3.24 (s, 2H).

^{13}C-NMR (75 MHz, DMSO) δ [ppm] = 138.09, 128.30, 56.19, 54.84.

General procedure for the bulk-polymerizations: Vinylsulfonylethanol (1 eq.) was added to the respective catalyst (0.1 eq.) and the reaction was agitated for 24 h at 40 °C. To monitor kinetics samples were taken at different time points. To quench the catalyst an excess of TFA was added. For purification, the polymer was subsequently dissolved in DMSO, precipitated in methanol and dried under vacuum. Details of the applied amounts can be found in Table S1.

Table S1: Applied amount of monomer and catalysts for the bulk polymerizations.

Polymer	Catalyst	$m_{catalyst}$ [g]	$n_{catalyst}$ [mmol]	$m_{monomer}$ [g]	$n_{monomer}$ [mmol]
P1	PPh_3	0.39	1.47	2.01	14.73
P2	TEDA	0.17	1.48	2.00	14.70
P3	DMAP	0.18	1.48	2.00	14.68

P4	DBU	0.22	1.47	2.00	14.68
P5	TBD	0.20	1.47	2.01	14.73
P6	K_2CO_3	0.20	1.47	2.00	14.69
P7	Cs_2CO_3	0.48	1.47	2.00	14.68

General procedure for the solution polymerization: The catalyst was dissolved in DMSO. Vinylsulfonylethanol (1 eq.) was added to the respective catalyst and the reaction was agitated for 24 h at 40 °C. To monitor kinetics samples were taken at different time points. To quench the catalyst an excess of TFA was added. For purification, the polymer was subsequently dissolved in DMSO, precipitated in methanol and dried under vacuum. Details of the applied amounts can be found in Table S2.

Table S2: Applied amount of monomer and catalysts for the solution polymerizations.

Polymer	Catalyst	$m_{catalyst}$ [mg]	$n_{catalyst}$ [mmol]	$m_{monomer}$ [mg]	$n_{monomer}$ [mmol]	m_{DMSO} [mg]
P8	PPh_3	58.0	0.22	302.9	2.22	471.1
P9	PPh_3	29.1	0.11	310.2	2.28	474.6
P10	PPh_3	15.1	0.06	310.1	2.28	470.3
P11	DMAP	26.9	0.22	303.1	2.22	476.0
P12	DBU	34.1	0.22	301.2	2.21	475.4
P13	DBU	34.1	0.22	306.5	2.23	341.7
P14	DBU	34.1	0.22	301.0	2.21	171.0
P15	DBU	10.1	0.07	302.8	2.22	474.9
P16	DBU	3.3	0.02	307.0	2.26	476.0

General procedure for the kinetic experiments in the NMR (solution-polymerizations using DBU as catalyst): Vinylsulfonylethanol (200 mg, 1.47 mmol, 1 eq.) and DBU were each dissolved in 0.15 mL DMSO-d_6. The solution was mixed in an NMR-tube and inserted into the preheated NMR-instrument at 40 °C. Every minute, an ^{1}H-NMR-spectrum was measured. Details of the applied amounts of catalyst are listed in Table S3.

Table S3: Applied amount of DBU for the NMR-experiments.

$m_{catalyst}$ [mg]	$n_{catalyst}$ [mmol]	Eq.
22.4	0.15	0.10

11.1	0.07	0.05
6.7	0.04	0.03
2.2	0.01	0.01

General procedure for the kinetic experiments in the NMR (solution-polymerizations using DMAP as catalyst): DMAP was dissolved in 0.3 mL DMSO-d_6. Vinylsulfonylethanol (200 mg, 1.47 mmol, 1 eq.) and the DMAP-solution were mixed in an NMR-tube and heated to 40 °C in an NMR-instrument. Every minute, an ^{1}H-NMR-spectrum was measured. Details of the applied amounts of catalyst are listed in S4.

Table S4: Applied amount of DMAP for the NMR-experiments.

$m_{catalyst}$ [mg]	$n_{catalyst}$ [mmol]	Eq.
18.0	0.15	0.10
8.9	0.07	0.05
5.4	0.04	0.03
1.7	0.01	0.01

Monomer

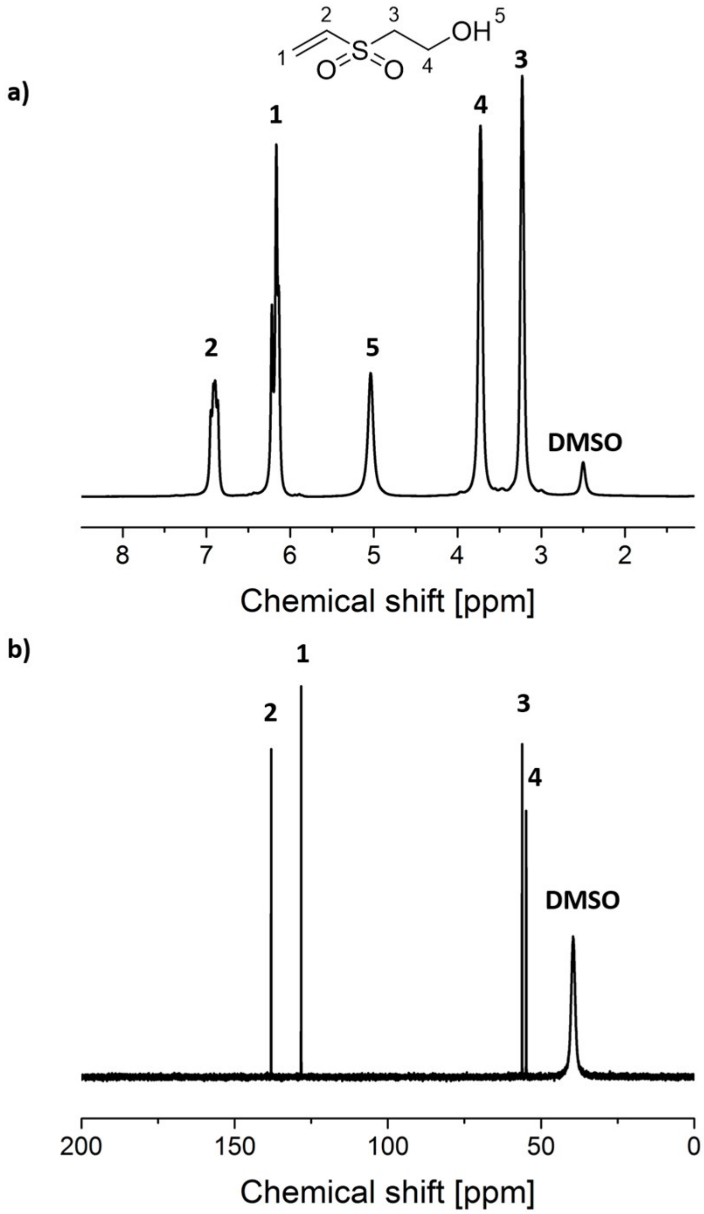

Figure S1: a) ^{1}H-NMR (300 MHz, DMSO-d_6) spectrum and b) ^{13}C-NMR (75 MHz, DMSO-d_6) spectrum of vinylsulfonylethanol.

Determination of conversion

The conversion of the end-groups was determined from the comparison of the NMR spectra before and after the reaction. Setting the integral of the signal at δ = 6.21 ppm to 2, which reflects protons in residual monomer and end-group, the integral of the second signal at δ = 3.42 ppm, which comprises only protons of the polymer chain, can be used to determine the conversion according to

$$conversion = \frac{I(polymer\ signal\ 3')/2}{I\ (end - group\ monomer\ signal\ 1) + I(polymer\ signal\ 3')/2}$$

The chemical shift of the water signal depends on the concentration of the compounds. Because of this, there may be an overlap between the water signal and the polymer signal at δ = 3.42 ppm. If this is the case, the other polymer signal δ = 3.80 ppm was used for the determination of the conversion. This signal comprises the protons of the polymer chain and the monomer and so the conversion was determined according to the following equation:

$$conversion = \frac{I(polymer\ signal\ 4' - 2)/2}{I\ (end - group\ monomer\ signal\ 1)\ + I(polymer\ signal\ 4' - 2)/2}$$

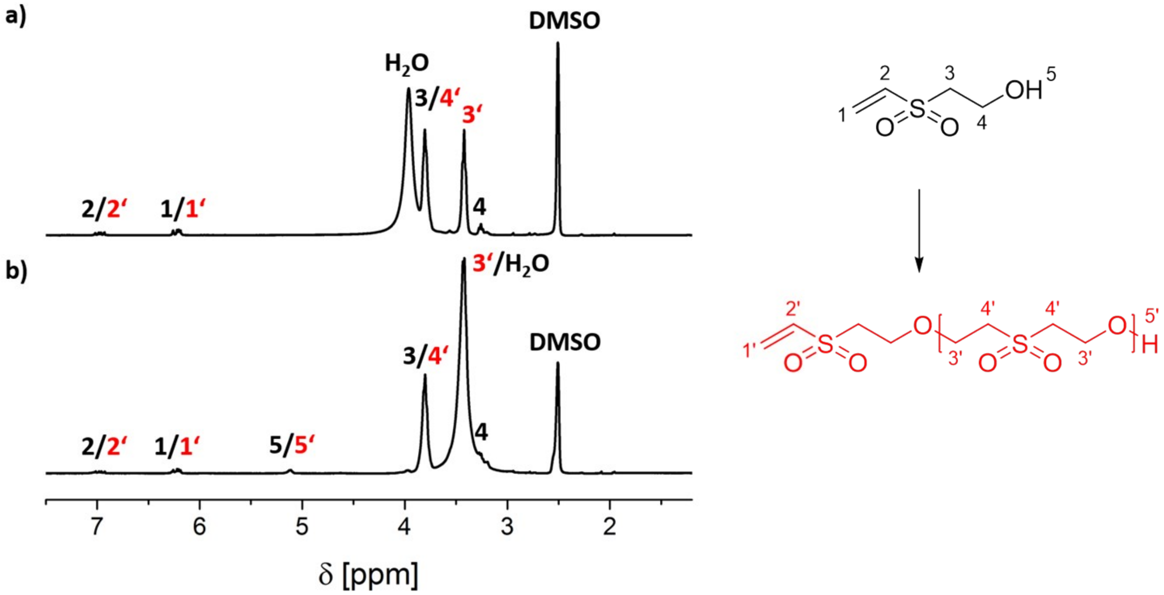

Figure S2: a) ^{1}H-NMR (300 MHz, DMSO-d_6) spectrum of the kinetic sample of the K_2CO_3-catalyzed polymerization after 3 h and b) ^{1}H-NMR (300 MHz, DMSO-d_6) spectrum of the kinetic sample of the PPh_3-catalyzed polymerization after 3 h.

Bulk-polymerization

Kinetic samples after 1 h

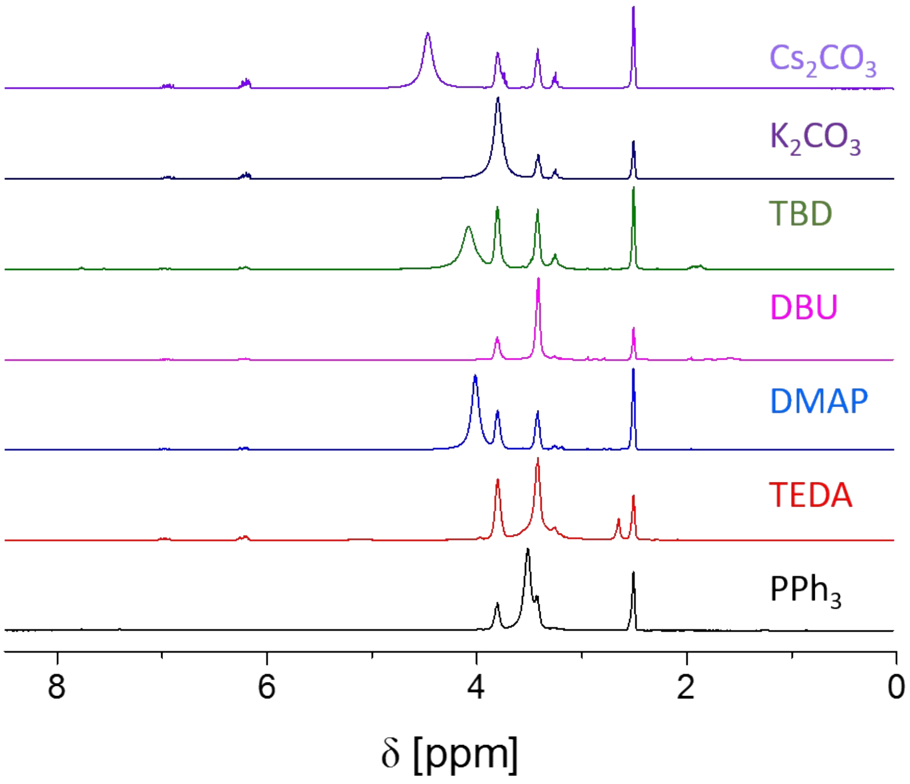

Figure S3: ^{1}H-NMR (300 MHz, DMSO-d_6) spectra of the polymerization with different catalysts after 1 h.

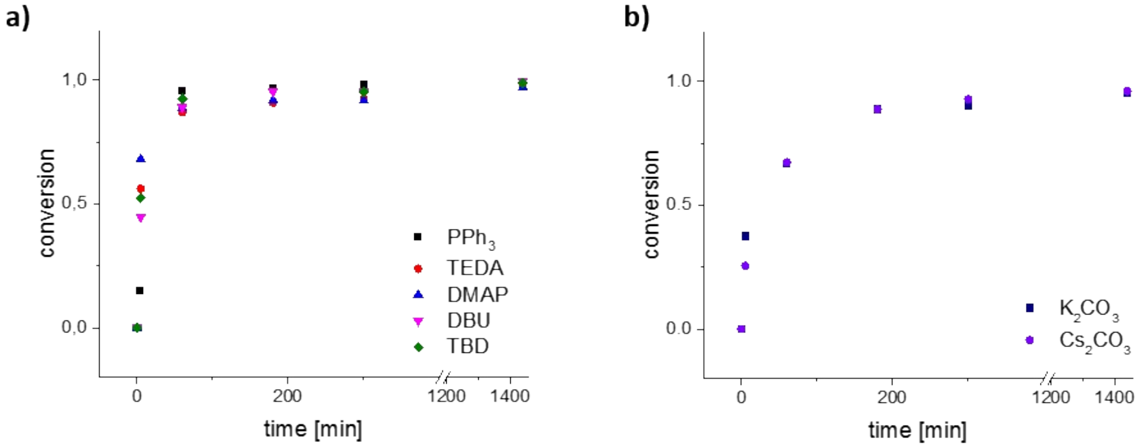

Figure S4: Conversion vs. reaction time for different polymerizations: a) comparison of different organic catalysts; b) comparison of different inorganic catalysts.

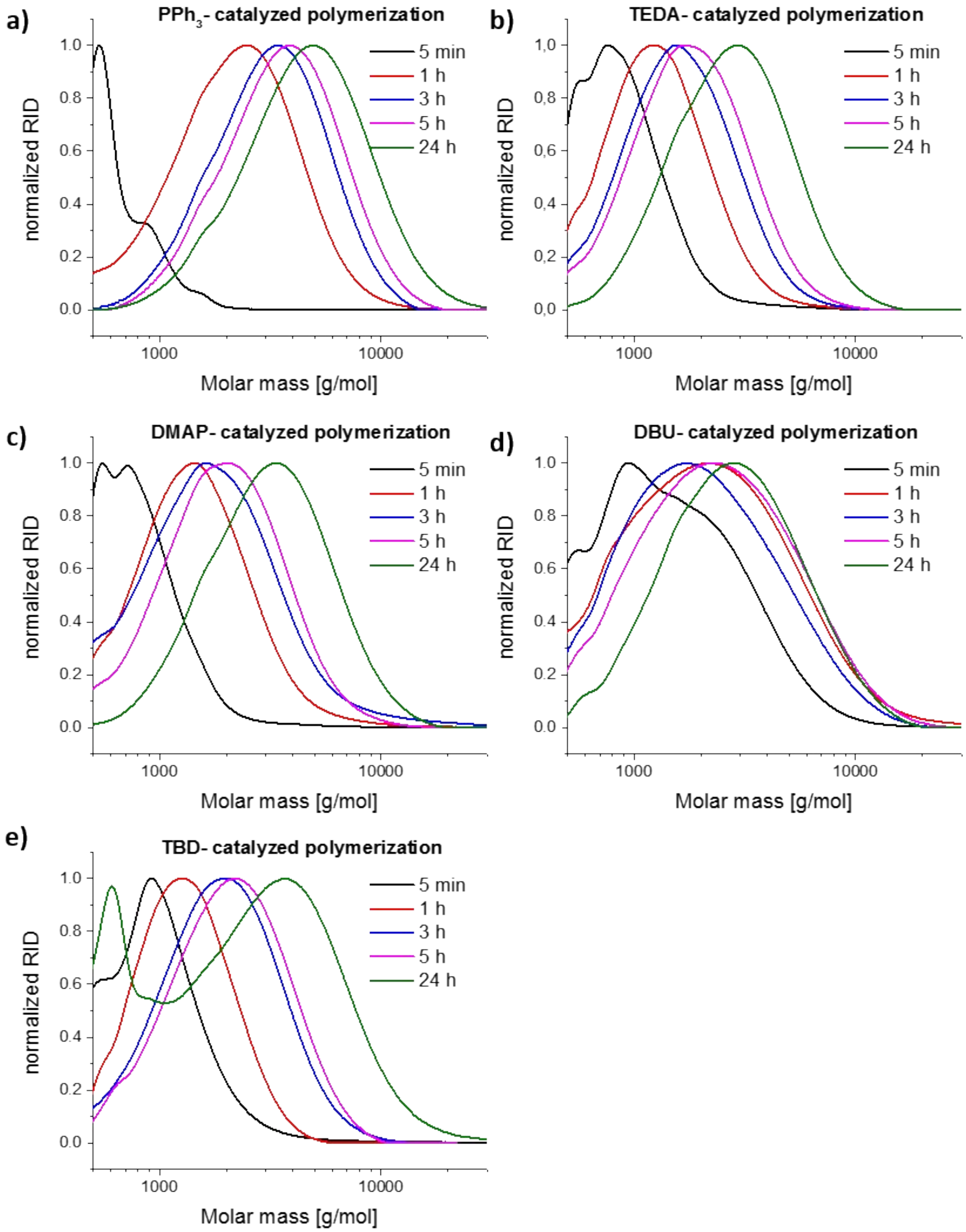

Figure S5: SEC (DMAc (+ 0.21 wt.% LiCl), PEG standards) traces of the kinetic samples taken after 5 min, 1 h, 3 h and 24 h of the polymerization catalyzed with a) triphenylphosphine, b) TEDA, c) DMAP, d) DBU, e) TBD.

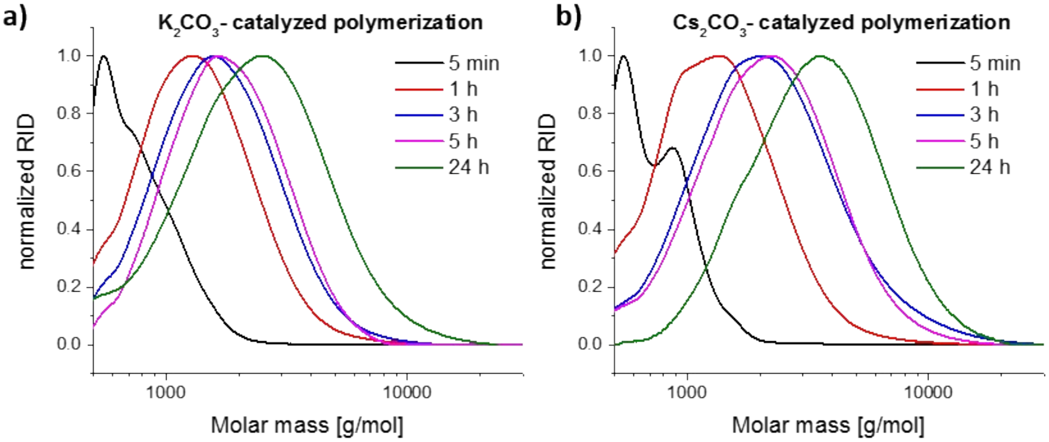

Figure S6: SEC (DMAc (+ 0.21 wt.% LiCl), PEG standards) traces of the kinetic samples taken after 5 min, 1 h, 3 h and 24 h of the polymerization catalyzed with a) K_2CO_3, and b) Cs_2CO_3

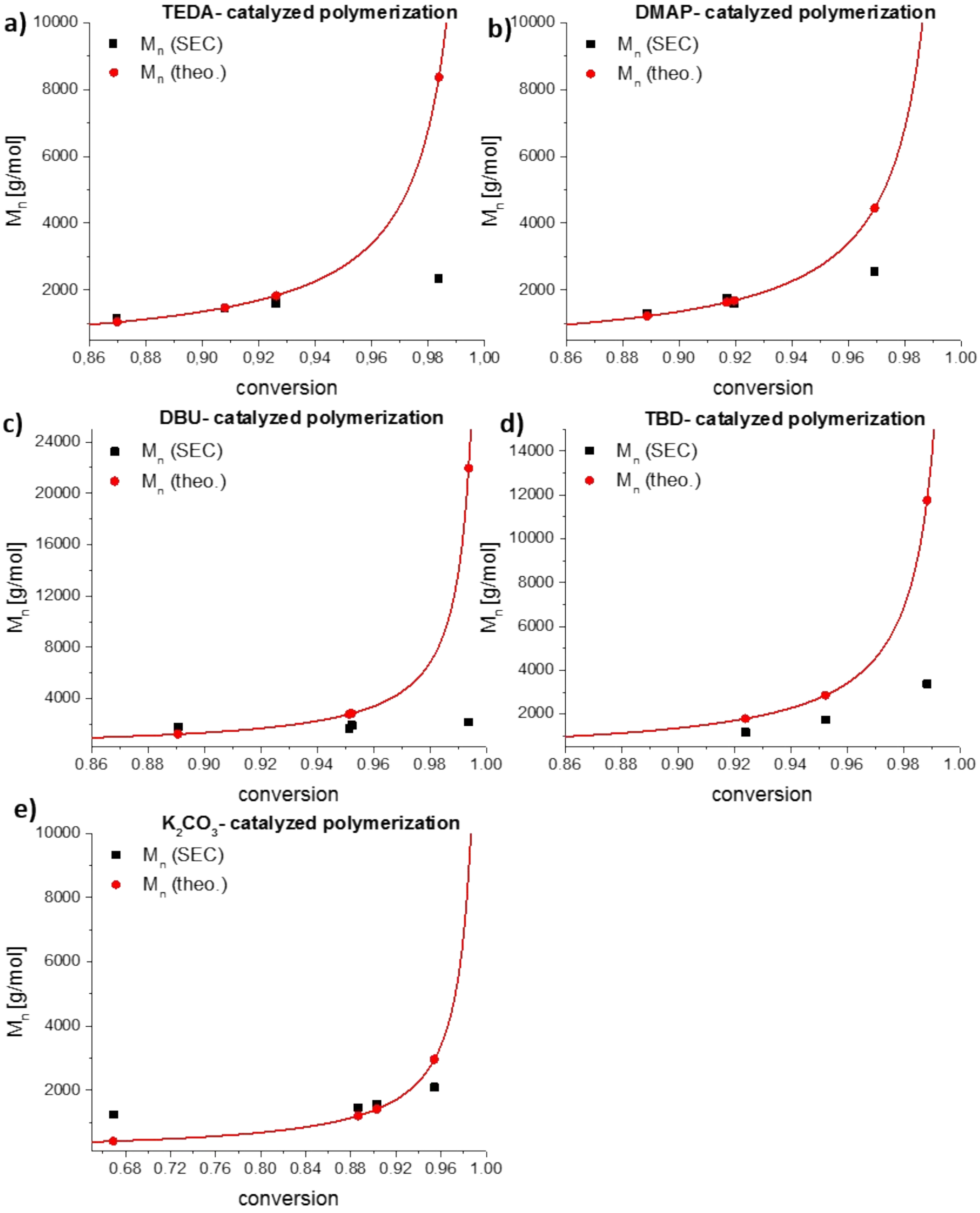

Figure S7: Plot of M_n versus conversion (red: theoretically values according to Carothers equation; black: experimental data from SEC measurements) for the polymerizations catalyzed by a) TEDA, b) DMAP, c) DBU, d) TBD, e) K_2CO_3.

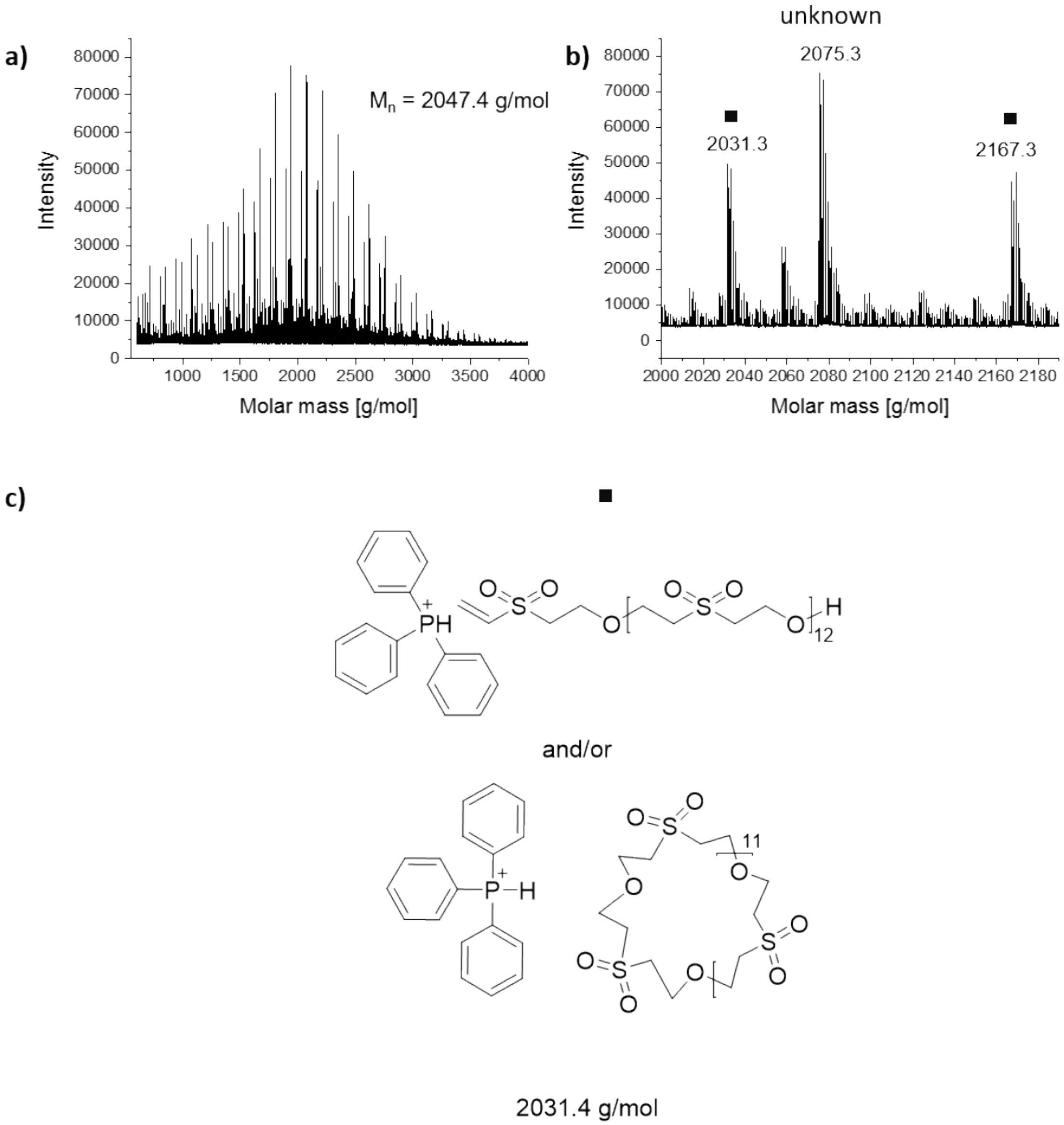

Figure S8: a) MALDI-ToF-spectrum of PPh$_3$-catalyzed polymer after 24 h; b) Enlarged section of the MALDI ToF-spectrum of PPh$_3$-catalyzed polymer after 24 h; c) potential chemical structures of detected species.

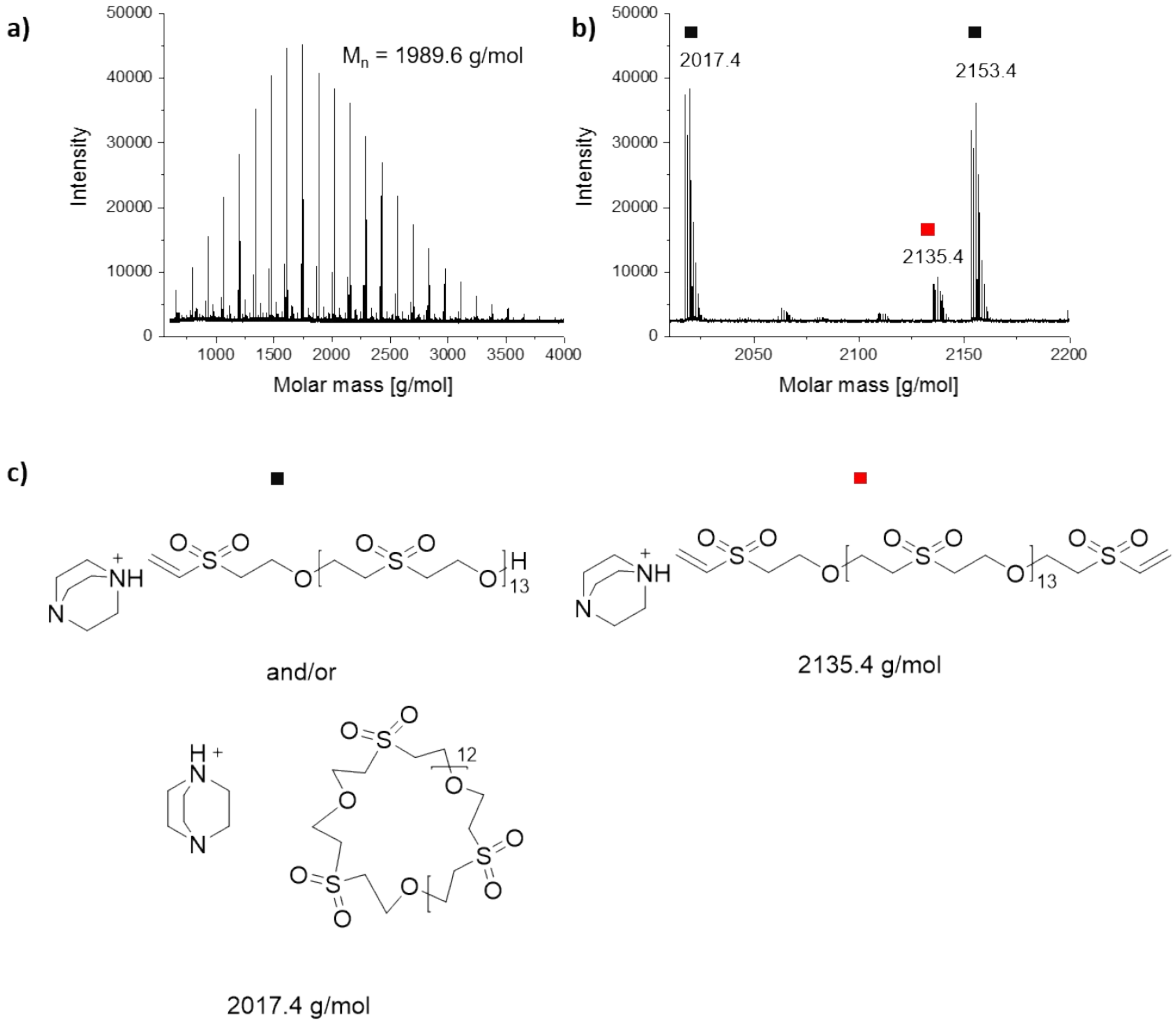

Figure S9: a) MALDI-ToF-spectrum of TEDA-catalyzed polymer after 24 h; b) Enlarged section of the MALDI ToF-spectrum of TEDA-catalyzed polymer after 24 h; c) potential chemical structures of detected species.

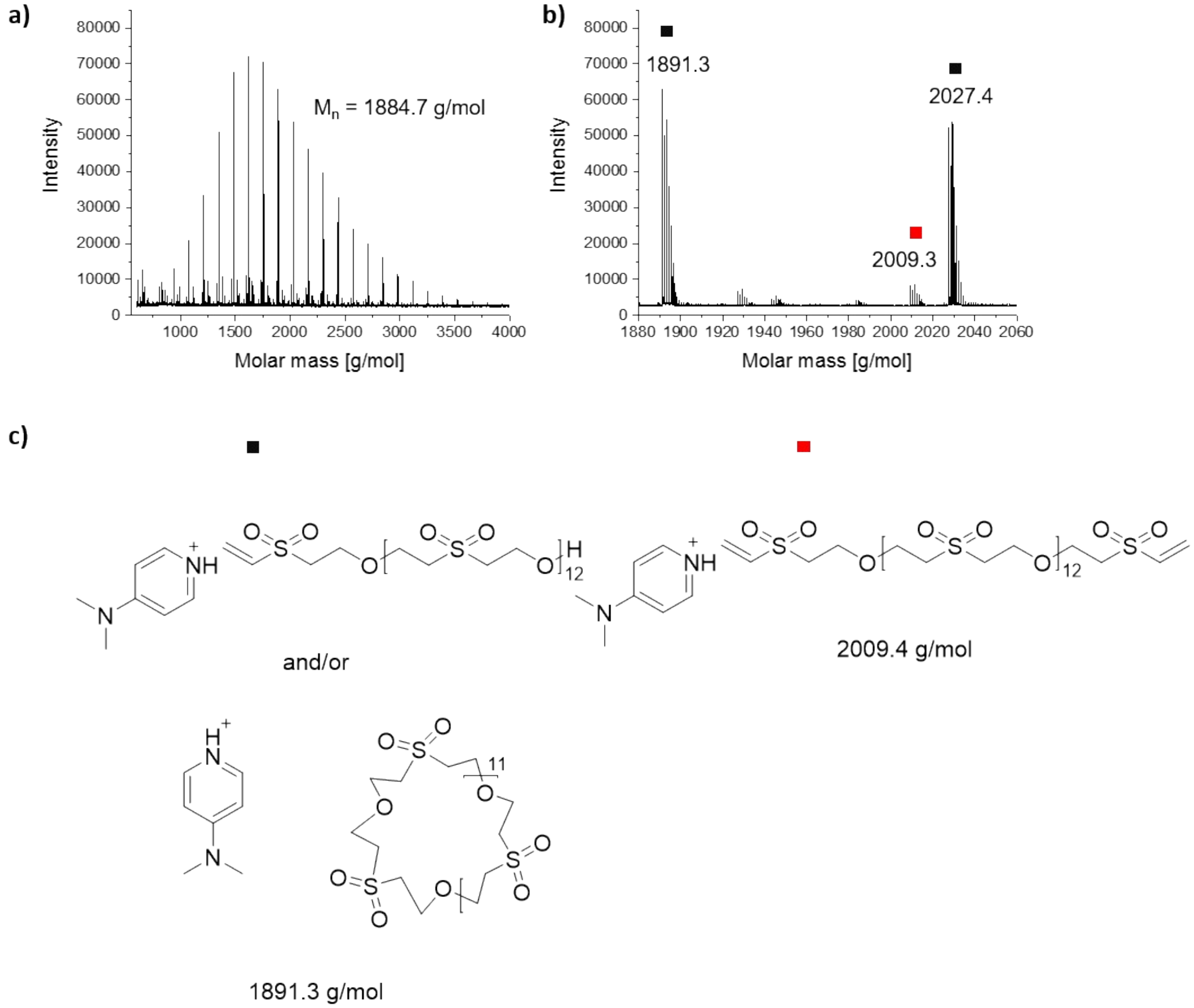

Figure S10: a) MALDI-ToF-spectrum of DMAP-catalyzed polymer after 24 h; b) Enlarged section of the MALDI ToF-spectrum of DMAP-catalyzed polymer after 24 h; c) potential chemical structures of detected species.

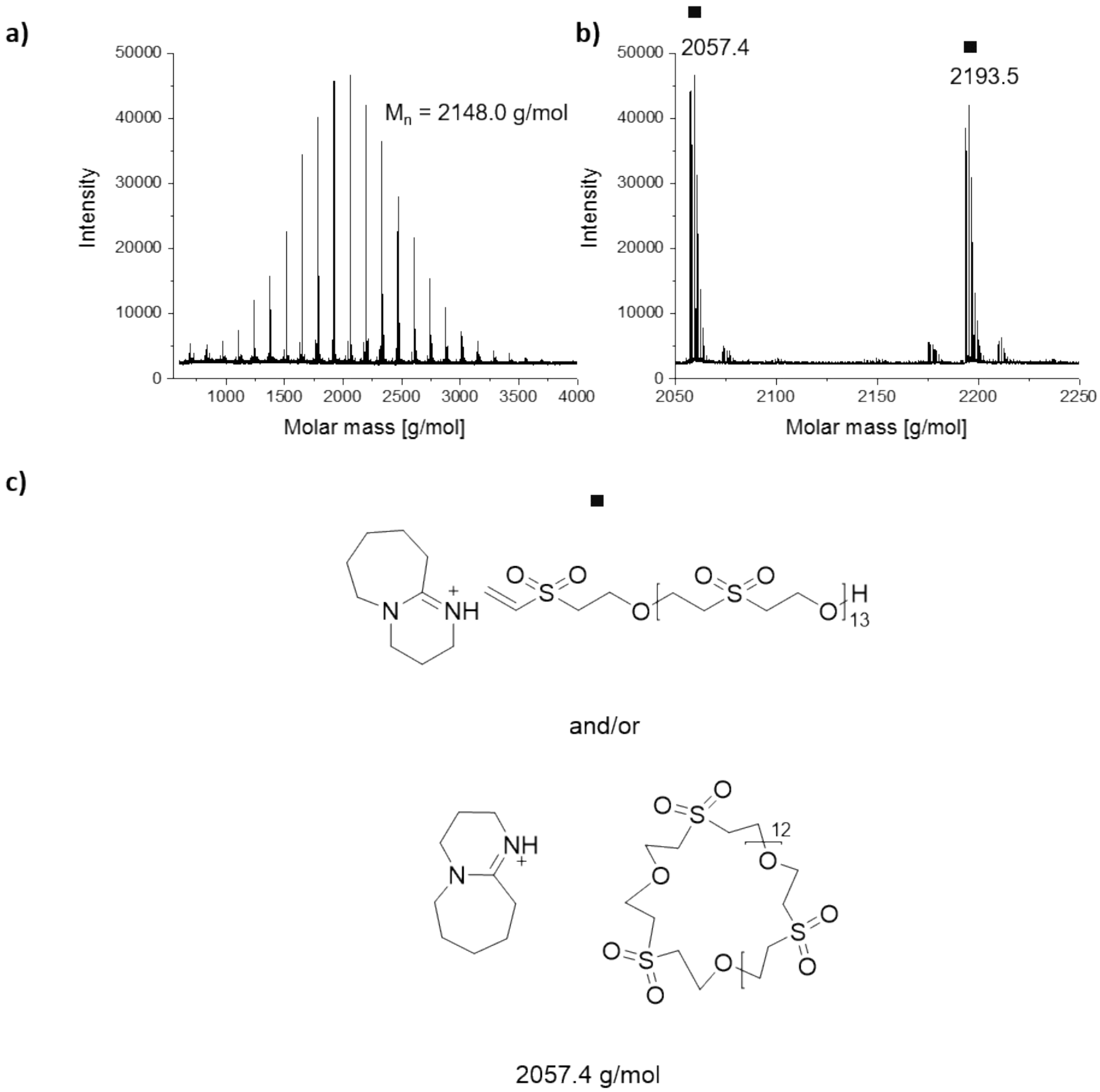

Figure S11: a) MALDI-ToF-spectrum of DBU-catalyzed polymer after 24 h; b) Enlarged section of the MALDI ToF-spectrum of DBU-catalyzed polymer after 24 h; c) potential chemical structures of detected species.

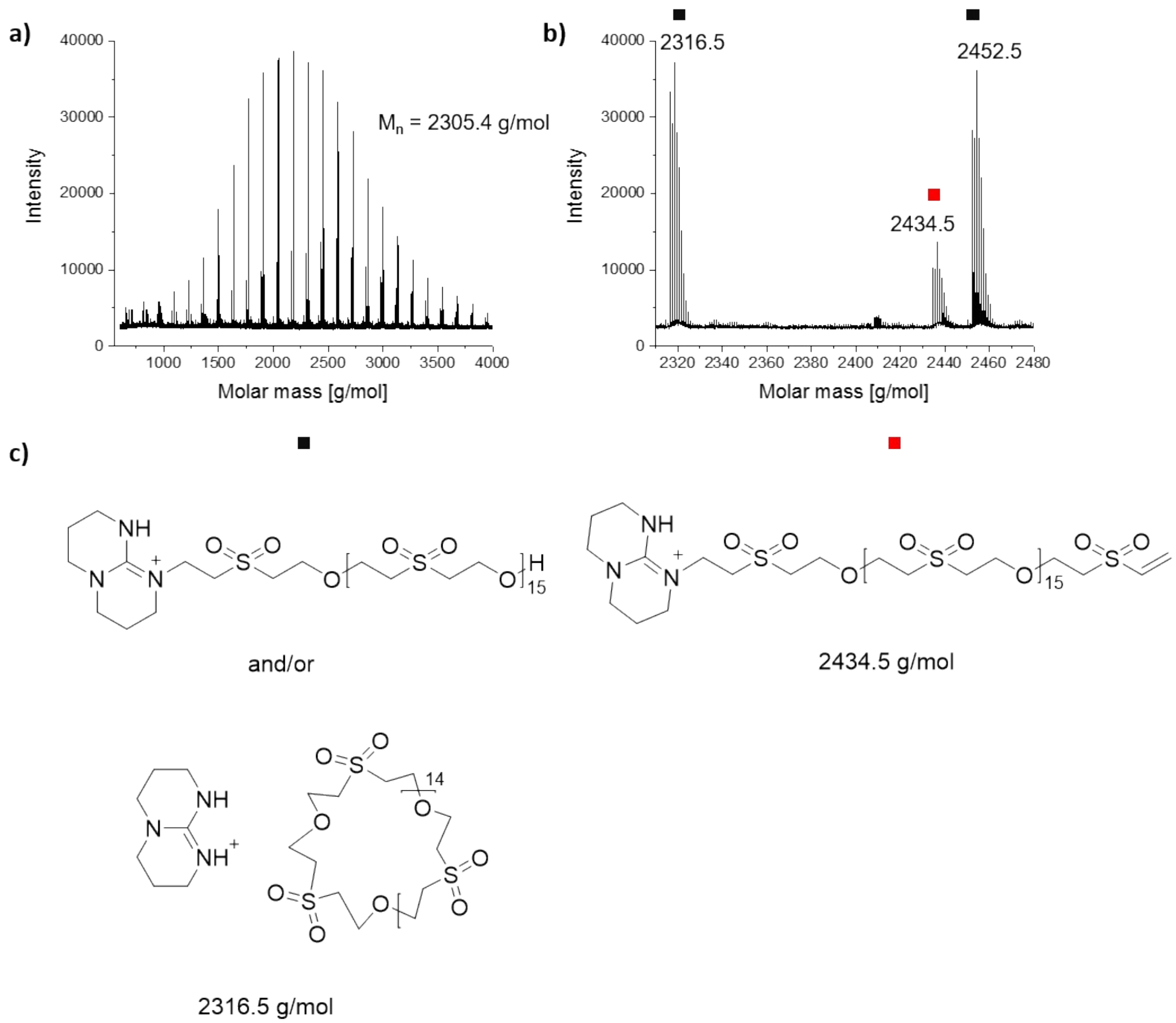

Figure S12: a) MALDI-ToF-spectrum of TBD-catalyzed polymer after 24 h; b) Enlarged section of the MALDI ToF-spectrum of TBD-catalyzed polymer after 24 h; c) potential chemical structures of detected species.

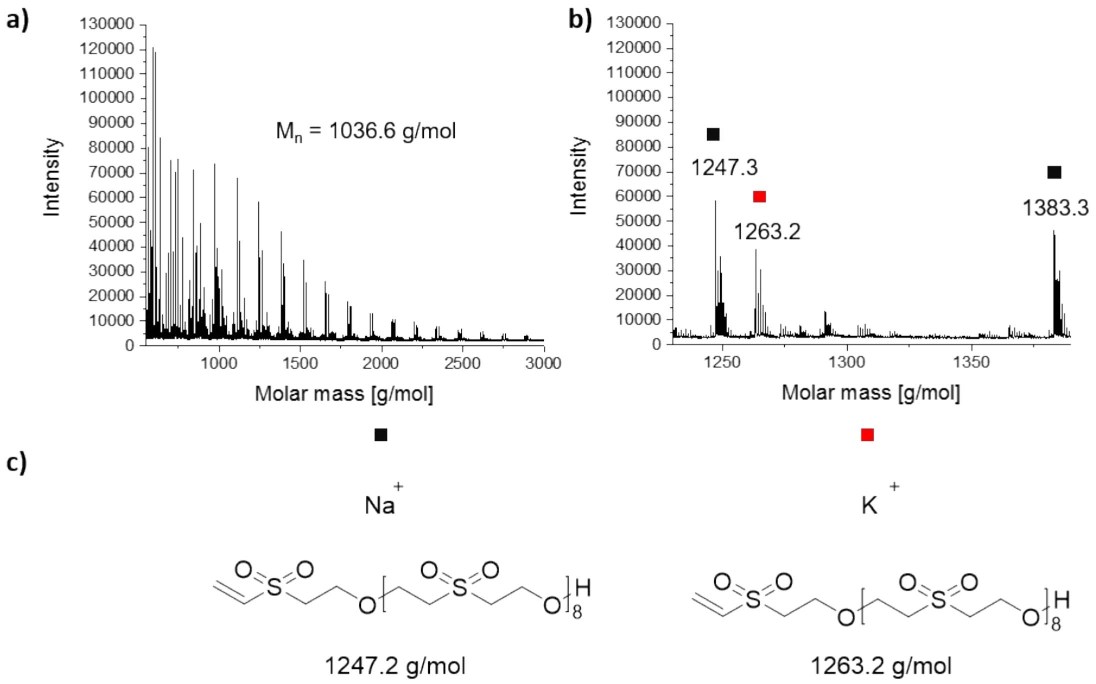

Figure S13: a) MALDI-ToF-spectrum of K_2CO_3-catalyzed polymer after 24 h; b) Enlarged section of the MALDI ToF-spectrum of K_2CO_3-catalyzed polymer after 24 h; c) potential chemical structures of detected species.

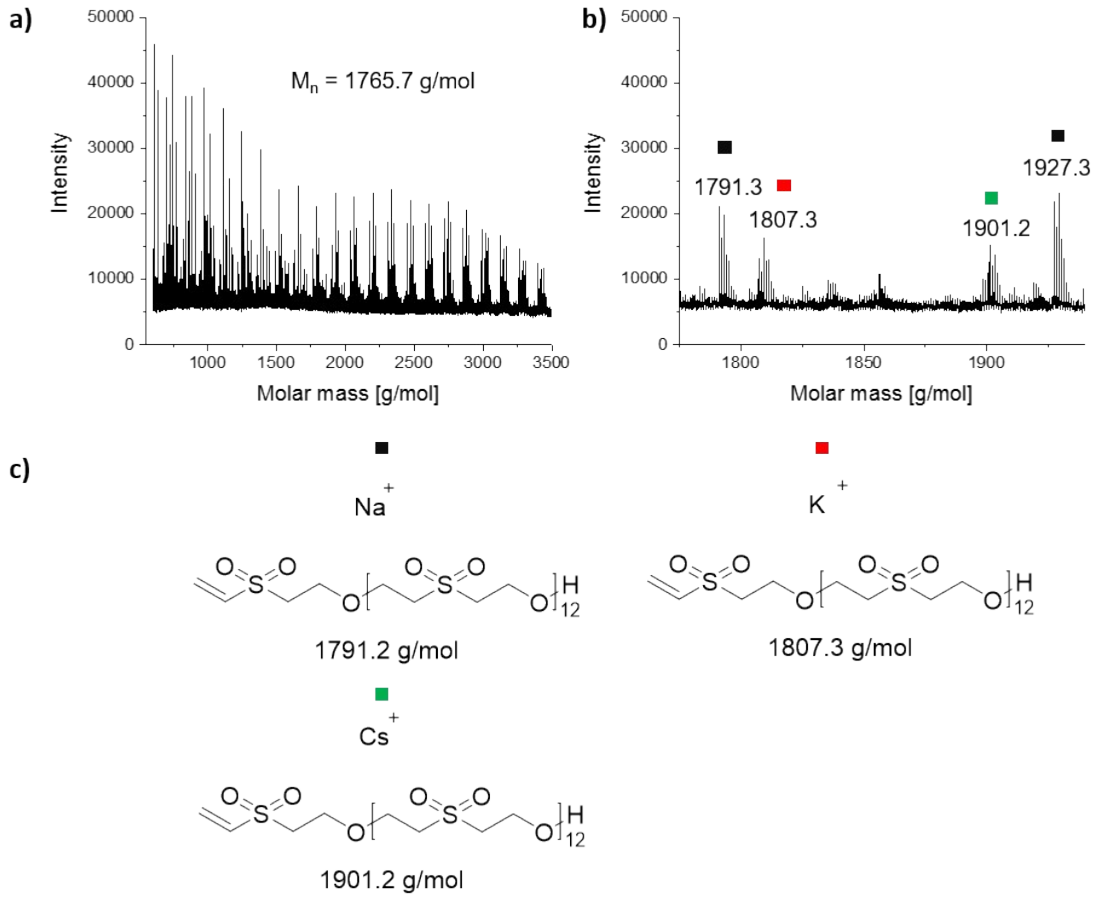

Figure S14: a) MALDI-ToF-spectrum of Cs_2CO_3-catalyzed polymer after 24 h; b) Enlarged section of the MALDI ToF-spectrum of Cs_2CO_3-catalyzed polymer after 24 h; c) potential chemical structures of detected species.

Purified Polymers (2^{nd} batch)

Polymer P1 (PPh_3):

^{1}H-NMR (300 MHz, DMSO-d_6) δ [ppm] = 7.99 – 7.71 (m), 6.98 (dd, J = 16.6, 10.0 Hz), 6.31 – 6.17 (m), 5.08 (s), 3.81 (t, J = 5.2 Hz), 3.43 (t, J = 5.3 Hz).

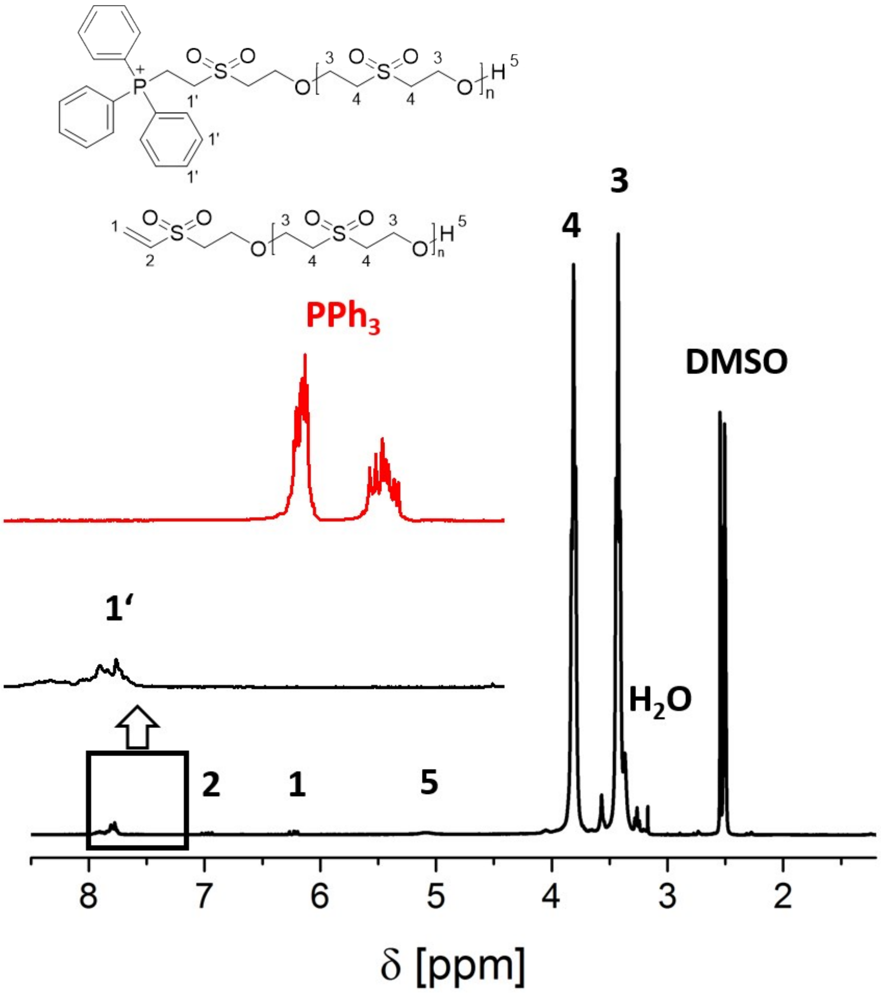

Figure S15: ^{1}H-NMR-spectrum (300 MHz, DMSO-d_6) of P1 (black) and PPh_3 (red).

MALDI-ToF-MS:

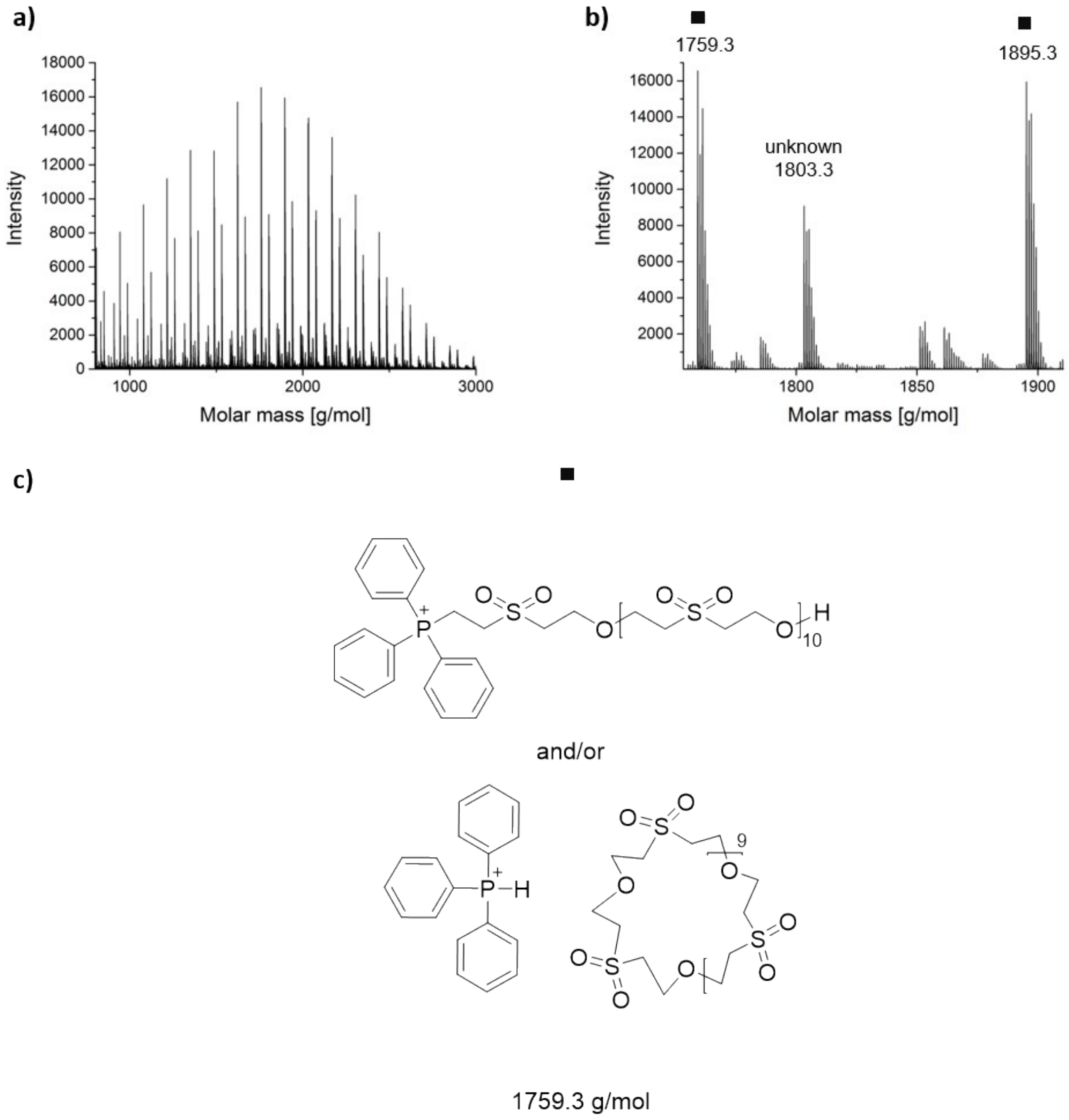

Figure S16: a) MALDI-ToF-spectrum of P1; b) Enlarged section of the MALDI ToF-spectrum of P1; c) potential chemical structures of detected species for P1 with consideration of the ^{1}H-NMR spectrum.

Polymer P2 (TEDA):

^{1}H-NMR (300 MHz, DMSO-d$_6$) δ [ppm] = 6.98 (dd, J = 16.6, 10.0 Hz), 6.22 (dd, J = 13.3, 8.0 Hz), 5.09 (t, J = 5.0 Hz), 3.81 (t, J = 5.2 Hz), 3.43 (t, J = 5.2 Hz), 3.26 (t, J = 5.8 Hz), 3.05 (s).

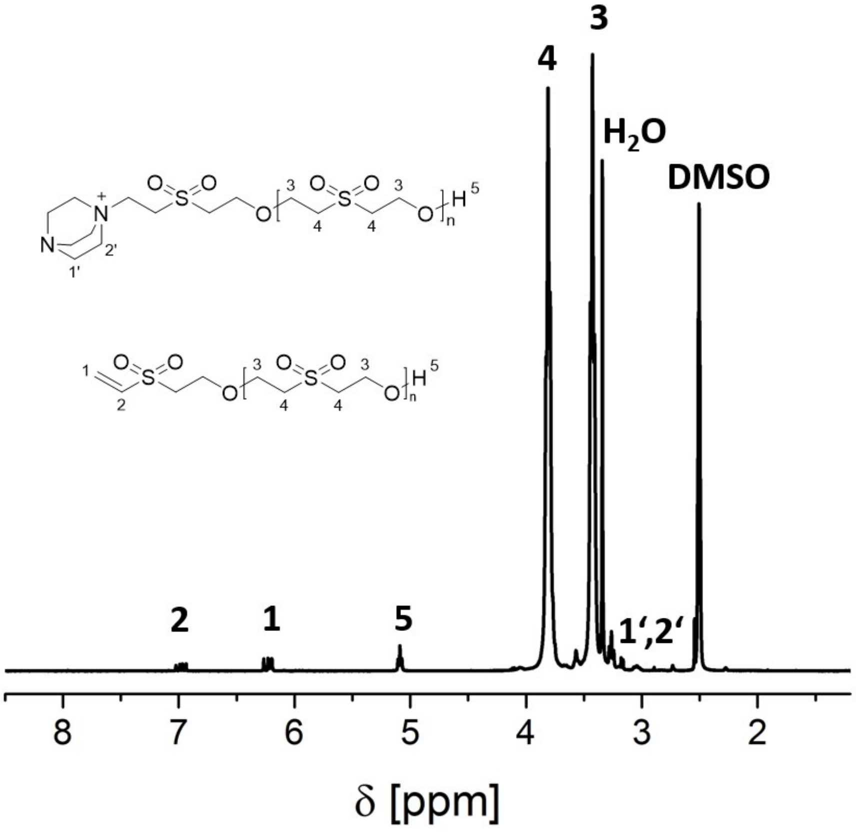

Figure S17: ^{1}H-NMR-spectrum (300 MHz, DMSO-d$_6$) of P2.

MALDI-ToF-MS:

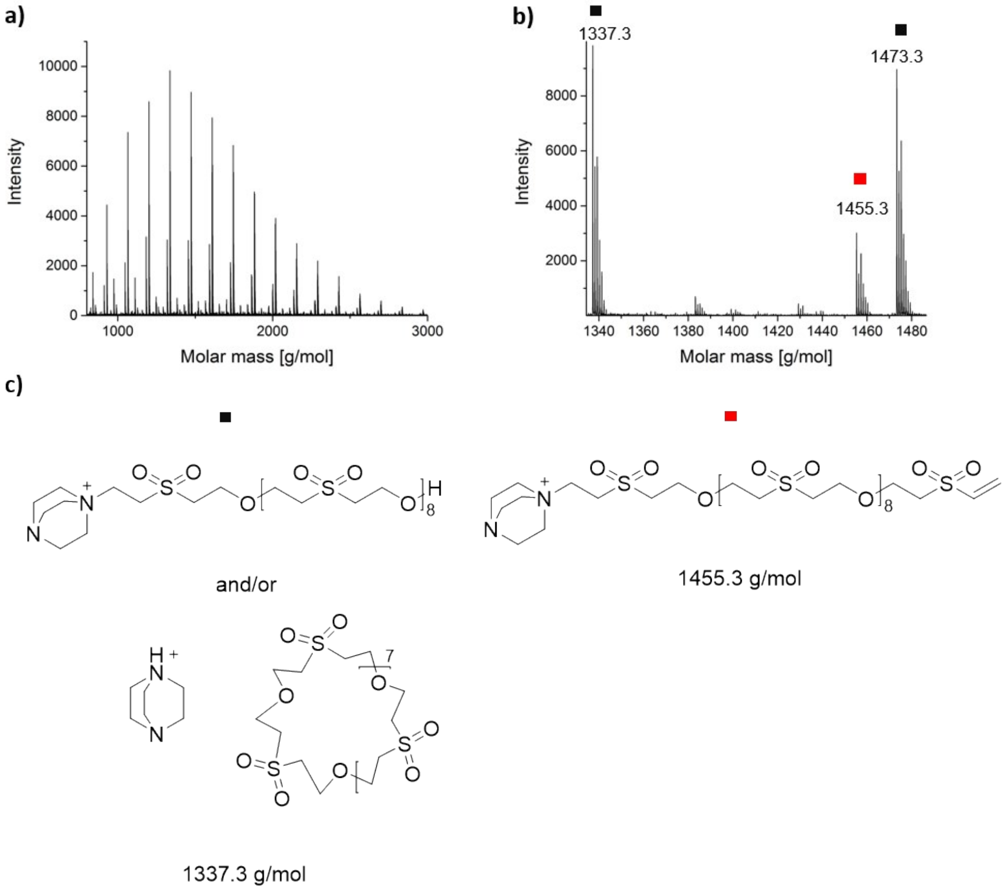

Figure S18: a) MALDI-ToF-spectrum of P2 b) Enlarged section of the MALDI ToF-spectrum of P3 c) potential chemical structures of detected species for P2 with consideration of the ^{1}H-NMR spectrum.

Polymer P3 (DMAP):

^{1}H-NMR (300 MHz, DMSO-d$_6$): δ [ppm] = 8.28 (s), 7.08 – 6.89 (m), 6.22 (dd, J = 13.3, 8.4 Hz), 5.08 (t, J = 5.0 Hz), 3.80 (t, J = 5.2 Hz), 3.42 (t, J = 5.2 Hz).

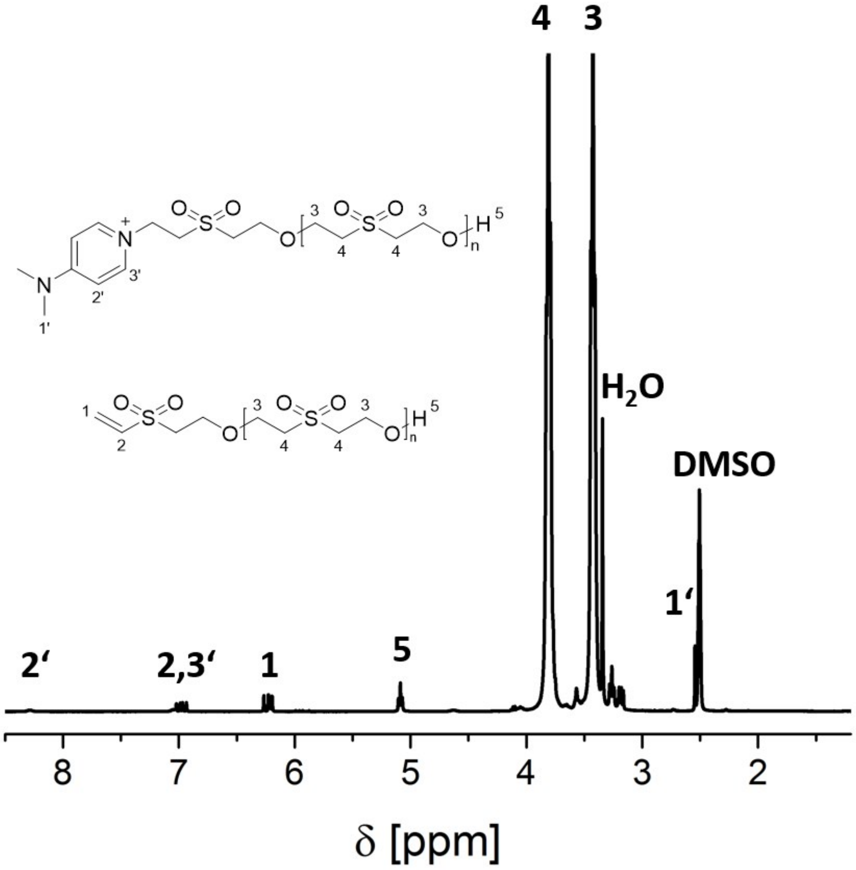

Figure S19: ^{1}H-NMR-spectrum (300 MHz, DMSO-d$_6$) of P3.

MALDI-ToF-MS:

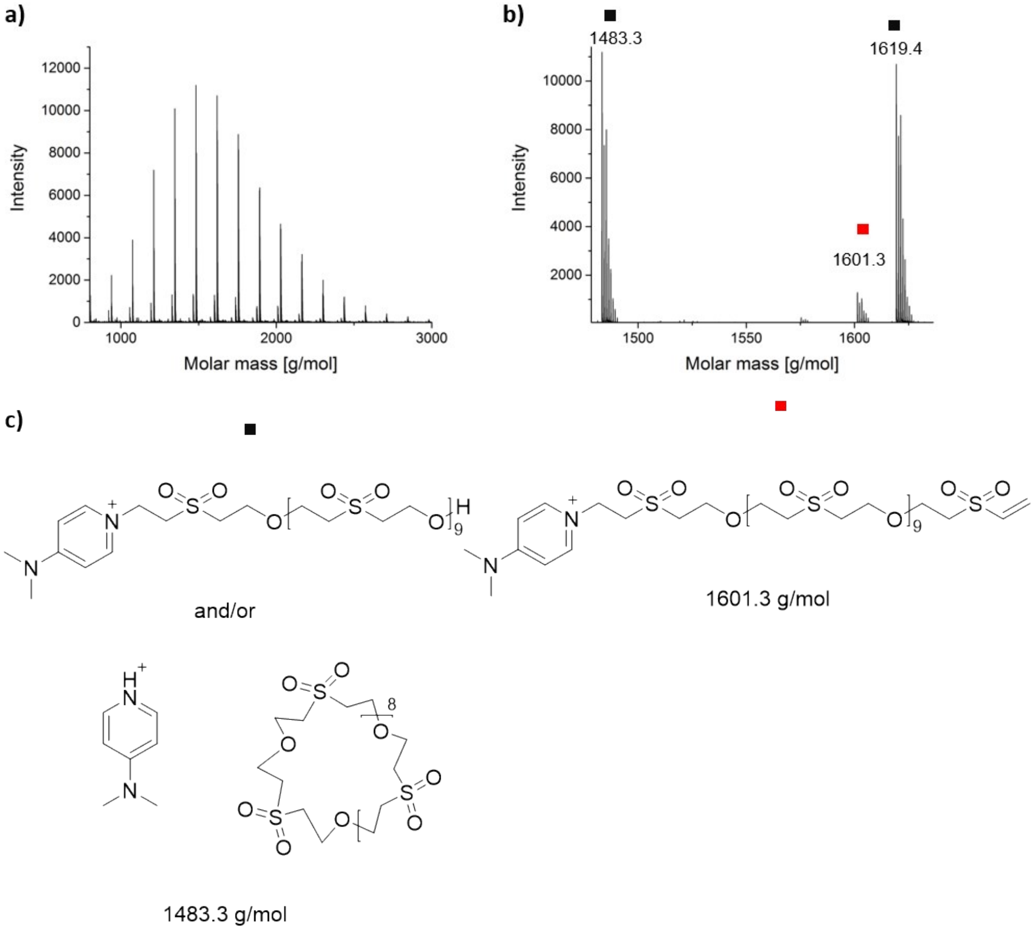

Figure S20: a) MALDI-ToF-spectrum of P3 b) Enlarged section of the MALDI ToF-spectrum of P3 c) potential chemical structures of detected species for P3 with consideration of the ^{1}H-NMR spectrum.

Polymer P4 (DBU):

^{1}H-NMR (300 MHz, DMSO-d$_6$) δ [ppm] = 7.10 – 6.91 (m), 6.22 (dd, J = 13.3, 8.1 Hz), 5.09 (t, J = 4.9 Hz), 3.81 (t, J = 5.2 Hz), 3.43 (t, J = 5.3 Hz).

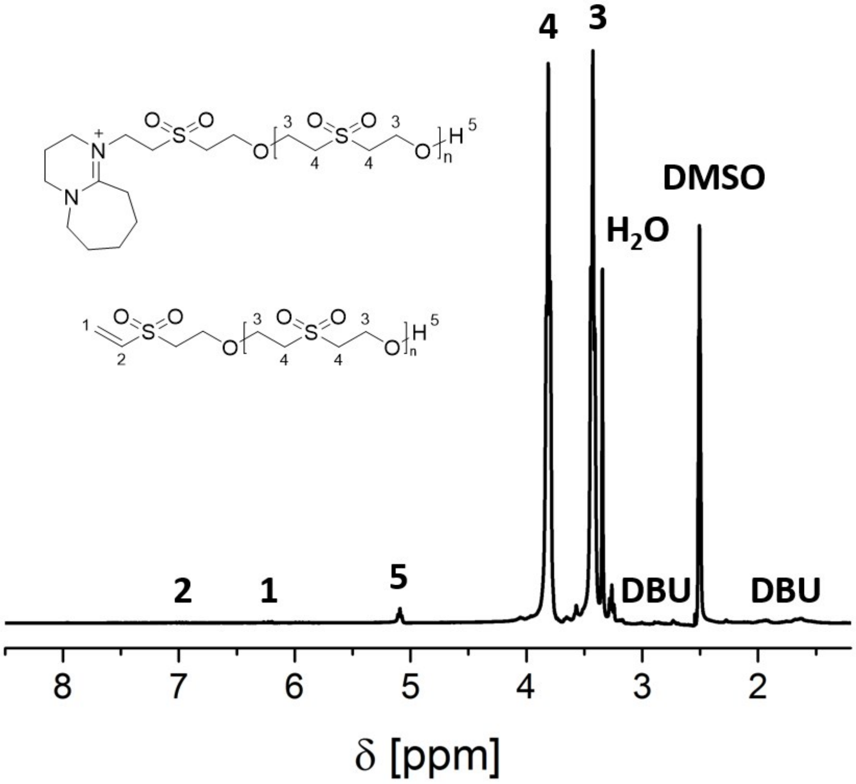

Figure S21: ^{1}H-NMR-spectrum (300 MHz, DMSO) of P4.

MALDI-ToF-MS:

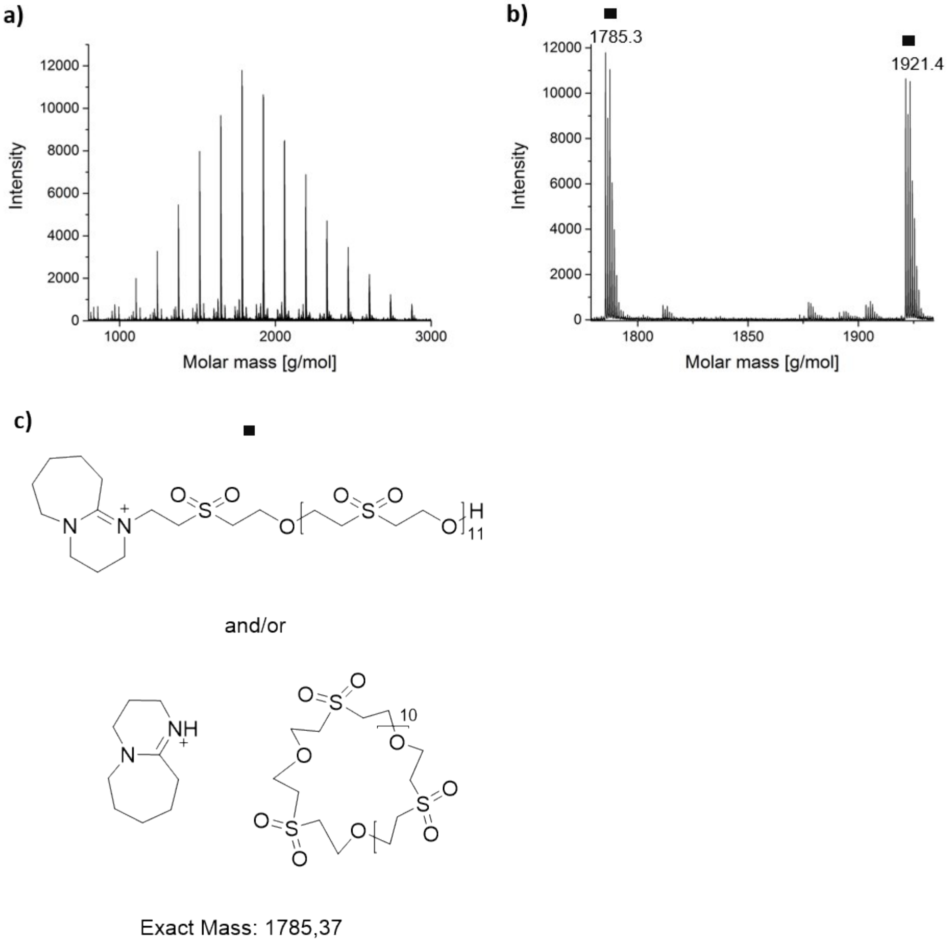

Figure S22: a) MALDI-ToF-spectrum of P4 b) Enlarged section of the MALDI ToF-spectrum of P4 c) potential chemical structures of detected species for P4 with consideration of the ^{1}H-NMR spectrum.

Polymer P5 (TBD):

^{1}H-NMR (300 MHz, DMSO-d$_6$) δ [ppm] = 6.98 (dd, J = 16.6, 9.9 Hz), 6.22 (dd, J = 13.3, 8.0 Hz), 5.09 (s), 3.81 (t, J = 5.1 Hz), 3.43 (t, J = 5.3 Hz).

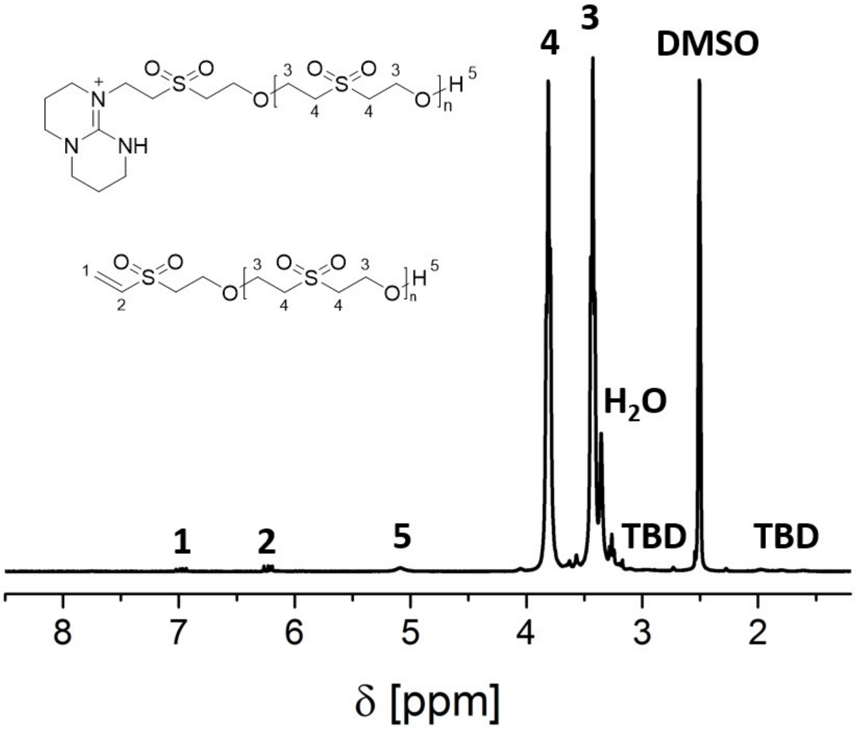

Figure S23: ^{1}H-NMR-spectrum (300 MHz, DMSO-d$_6$) of P5.

MALDI-ToF-MS:

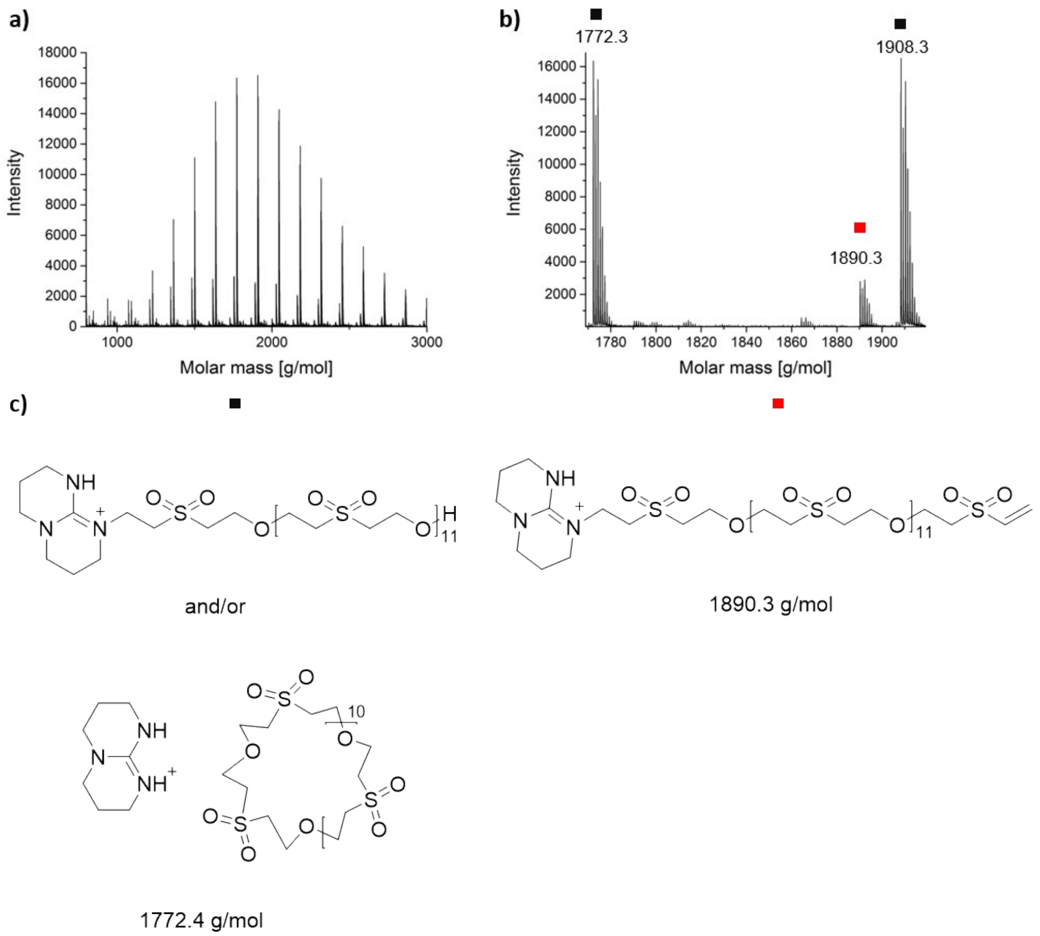

Figure S24: a) MALDI-ToF-spectrum of P5 b) Enlarged section of the MALDI ToF-spectrum of P5 c) potential chemical structures of detected species for P5 with consideration of the ^{1}H-NMR spectrum.

Polymer P6 (K_2CO_3):

^{1}H-NMR (300 MHz, DMSO-d_6) δ [ppm] = 6.98 (dd, J = 16.6, 10.0 Hz), 6.22 (dd, J = 13.3, 8.1 Hz), 5.09 (t, J = 4.9 Hz), 3.81 (t, J = 5.1 Hz), 3.43 (t, J = 5.1 Hz).

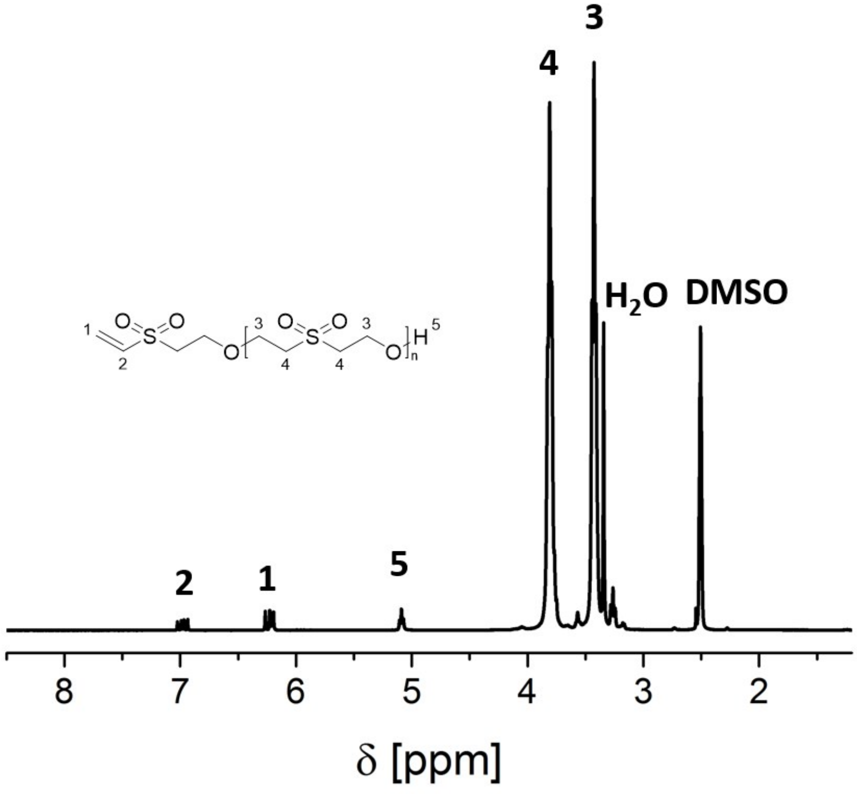

Figure S25: ^{1}H-NMR-spectrum (300 MHz, DMSO-d_6) of P6.

MALDI-ToF-MS:

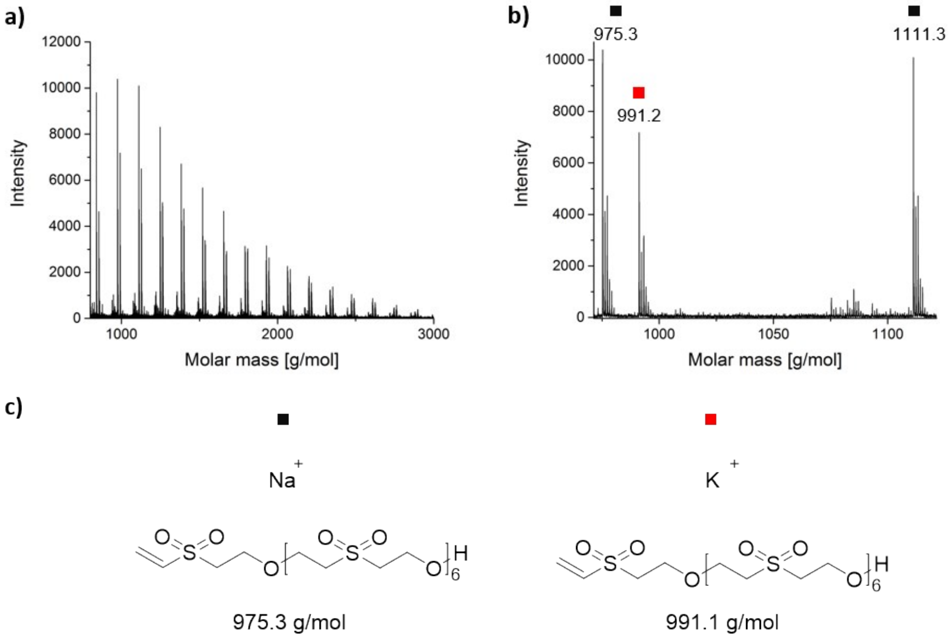

Figure S26: a) MALDI-ToF-spectrum of P6 b) Enlarged section of the MALDI ToF-spectrum of P6 c) potential chemical structures of detected species for P6.

Vapor pressure osmometry:

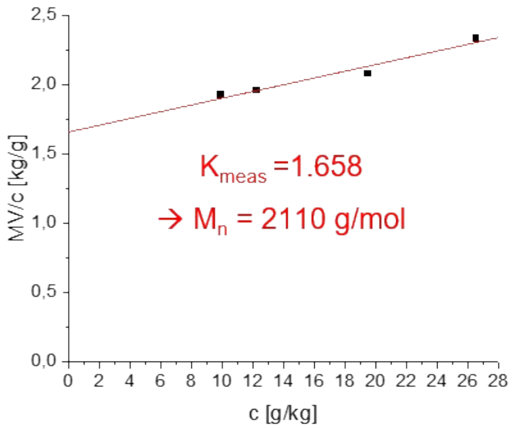

Figure S27: Plot of the vapor pressure osmometry measurement (PEG M_n = 2800 g/mol was used for the calibration)

Polymer P7 (Cs_2CO_3):

^{1}H-NMR (300 MHz, DMSO-d_6) δ [ppm] = 6.98 (dd, J = 16.6, 10.0 Hz), 6.22 (dd, J = 13.3, 8.0 Hz), 5.09 (t, J = 5.0 Hz), 3.81 (t, J = 5.2 Hz), 3.43 (t, J = 5.2 Hz).

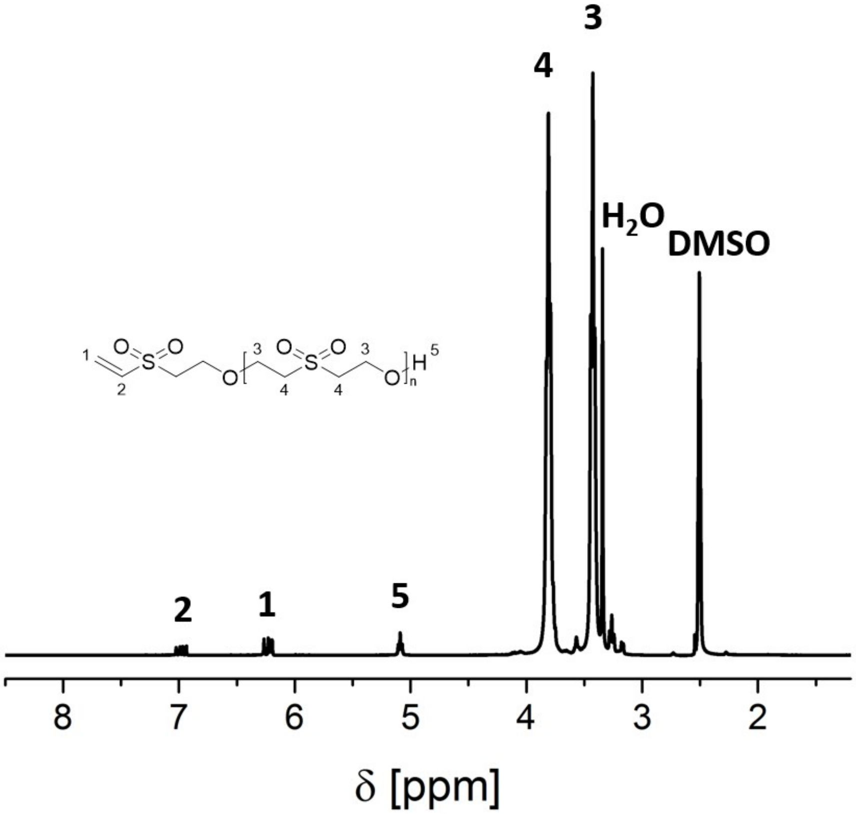

Figure S28: ^{1}H-NMR-spectrum (300 MHz, DMSO-d_6) of P7.

MALDI-ToF-MS:

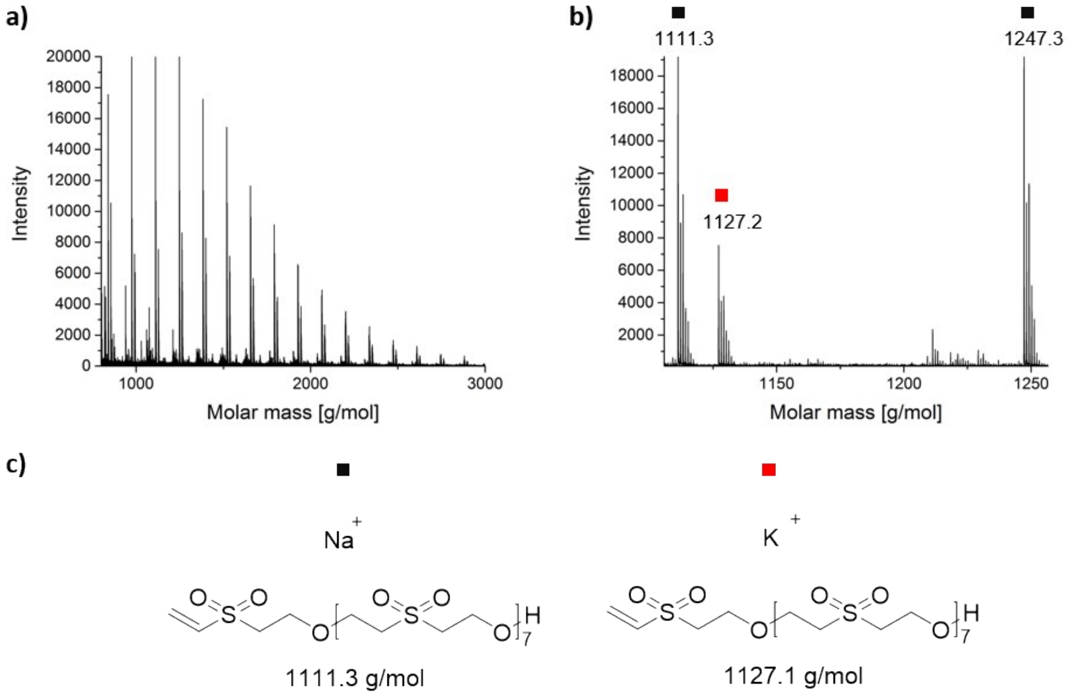

Figure S29: a) MALDI-ToF-spectrum of P7 b) Enlarged section of the MALDI ToF-spectrum of P7 c) potential chemical structures of detected species for P7.

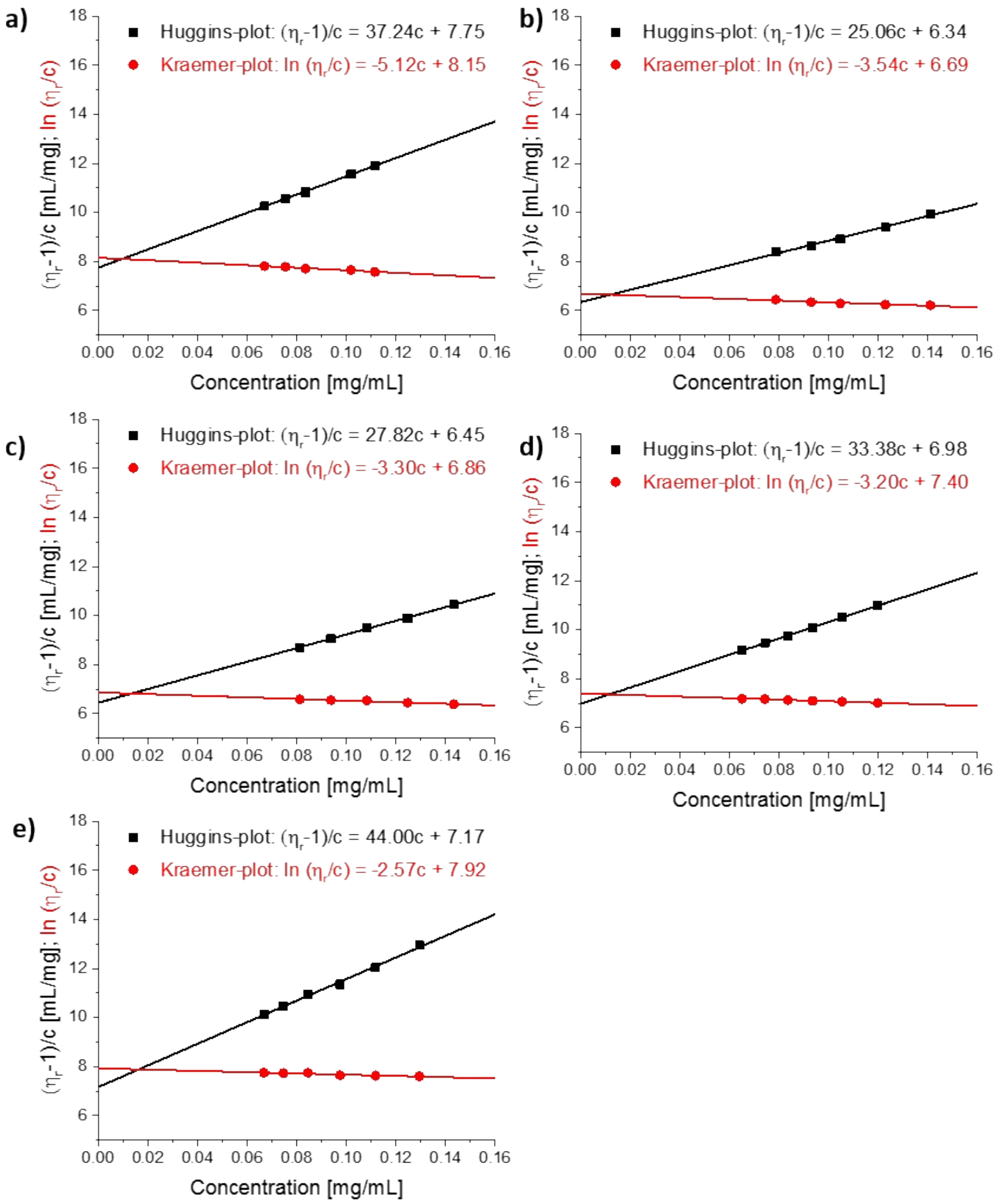

Figure S30: Huggins (black dots and line) and Kraemer (red dots and line) plots for the viscosity measurements of different concentrations of a) P1 b) P2 c) P3 d) P4 e) P5 in DMSO.

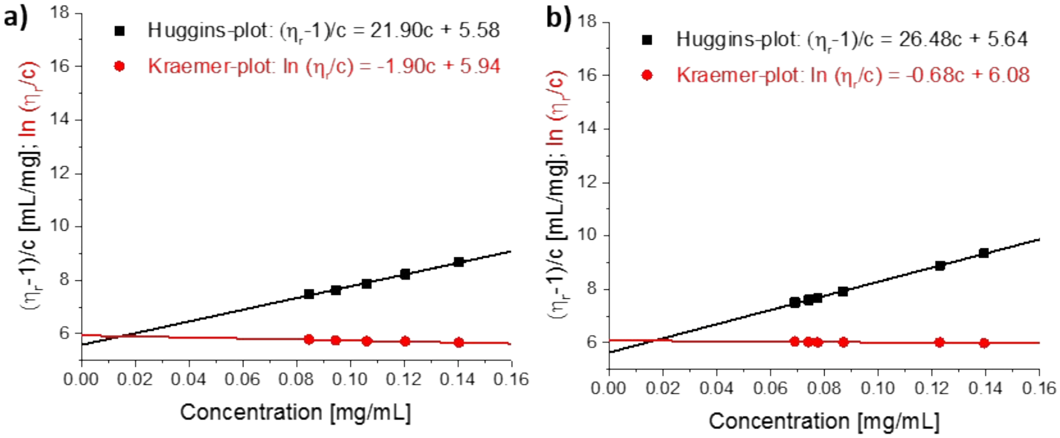

Figure S31: Huggins (black dots and line) and Kraemer (red dots and line) plots for the viscosity measurements of different concentrations of a) P6 b) P7 in DMSO.

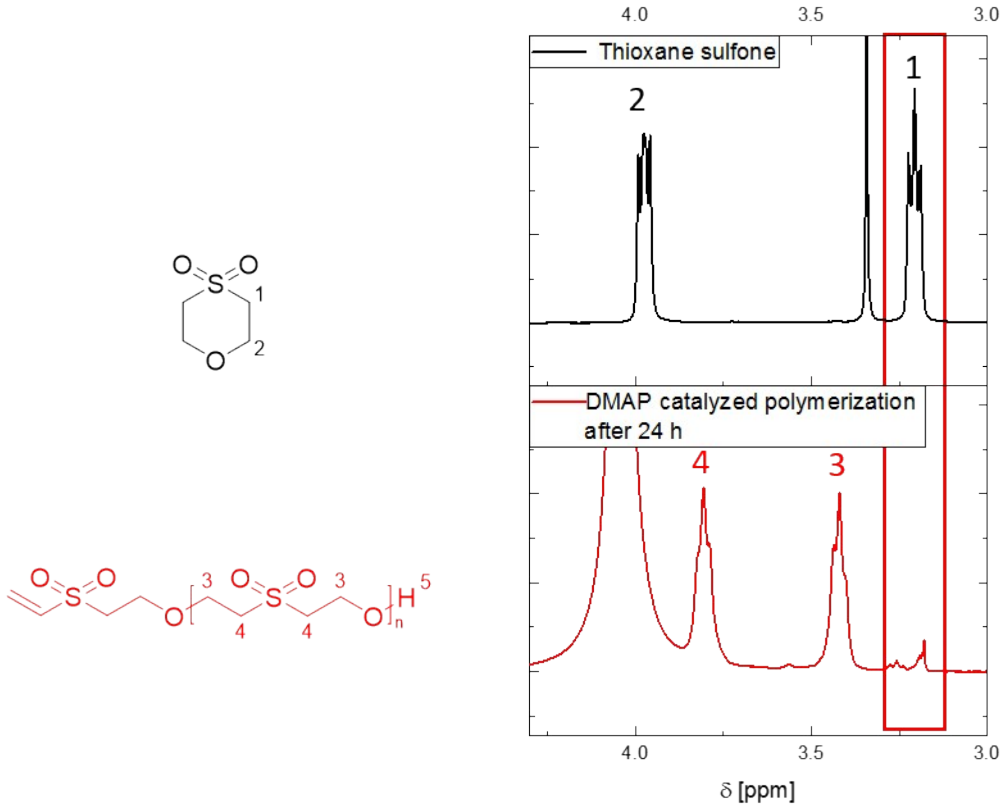

Figure S32: ^{1}H-NMR (300 MHz, DMSO-d_6) spectra of thioxane sulfone and the kinetic sample of the DMAP- catalyzed polymerization after 24 h.

Table S5: SEC-data and thermal properties of the purified polymers.

Polymer	M_n (SEC) [g/mol] [a]	Đ [a]	M_n (MALDI) [g/mol] [b]	5% mass loss [°C] [c]	5% mass loss [°C] [d]	T_g [°C] [e]
P1	3750	1.49	1890	213	213	13.6
P2	2750	1.40	1790	295	281	14.5
P3	2750	1.41	1680	265	261	10.3
P4	3120	1.40	2080	217	217	21.7
P5	3200	1.56	2230	217	224	18.6
P6	2230 (2110) [f]	1.56	1780	310	298	17.1
P7	2730	1.64	1680	318	313	12.6

[a] SEC (DMAc (+ 0.21 wt.% LiCl), PEG standards); [b] Determination from MALDI-ToF-spectra; [c] Determination from TGA measurements (N_2); [d] Determination from TGA measurements (Air); [e] Determination from DSC measurements; [f] the absolute M_n for P6 was exemplarily determined by vapor pressure osmometry.

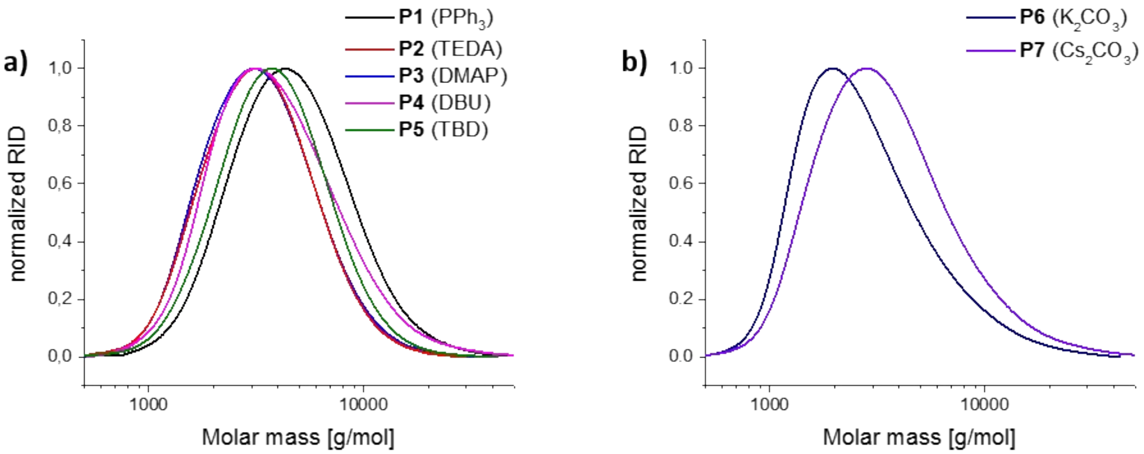

Figure S33: SEC (DMAc (+ 0.21 wt.% LiCl), PEG standards) traces of the purified polymers a) P1-P5 and b) P6/P7.

Solution-polymerization

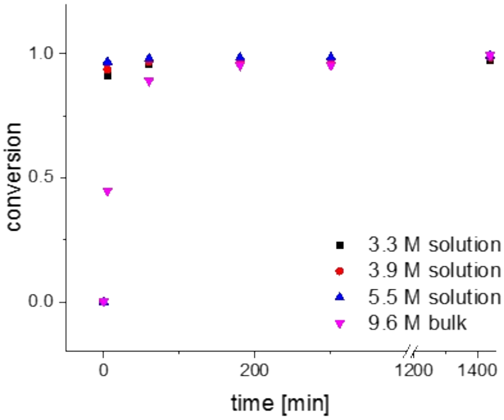

Figure S34: Conversion *vs.* reaction time for polymerizations with different monomer concentrations (catalyst: DBU)

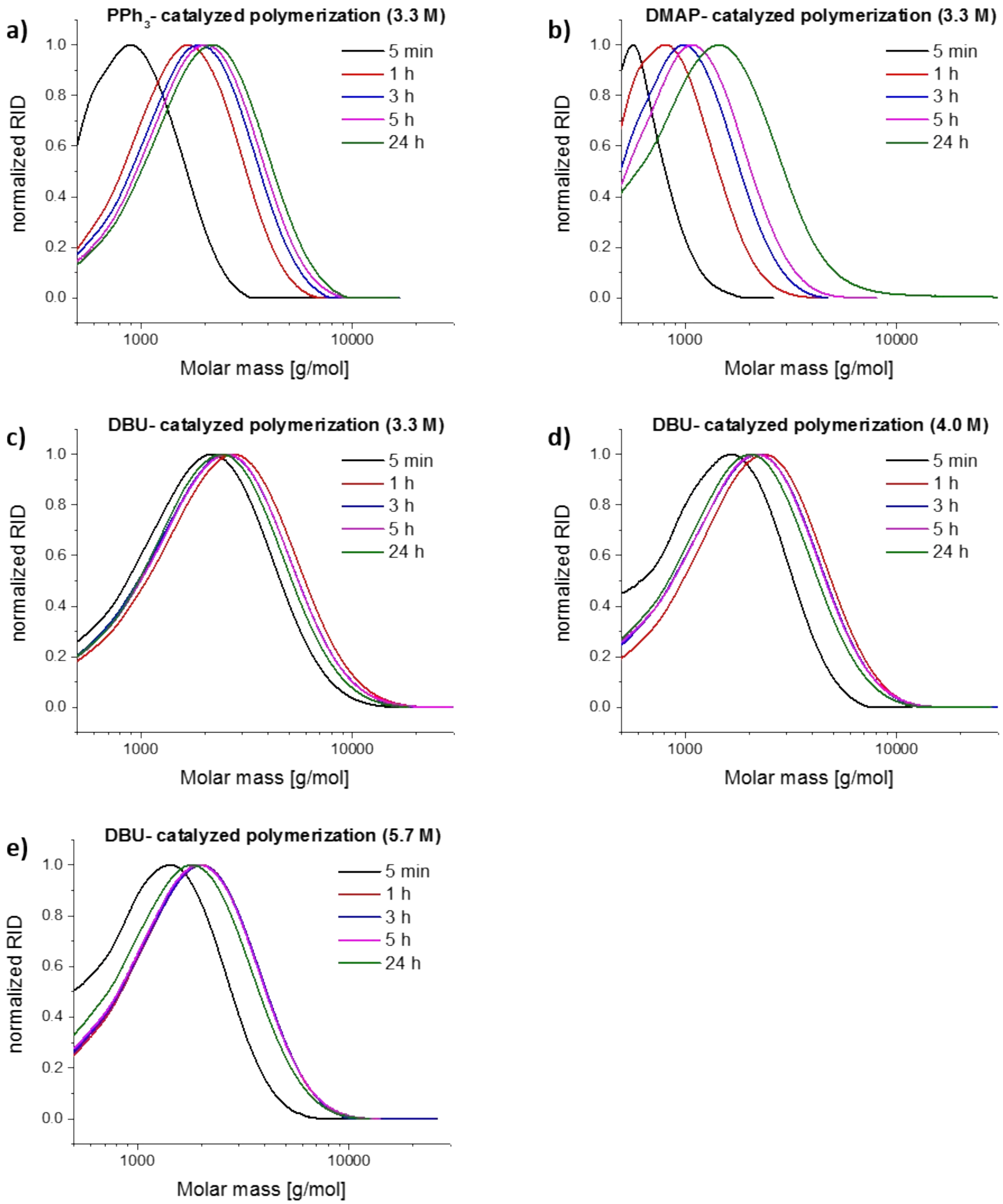

Figure S35: SEC (DMAc (+ 0.21 wt.% LiCl), PEG standards) traces of the kinetic samples taken after 5 min, 1 h, 3 h and 24 h of the polymerization catalyzed with a) PPh_3 (3.3 M) b) DMAP (3.3 M), c) DBU (3.3 M), d) DBU (4.0 M), e) DBU (5.7 M) in DMSO.

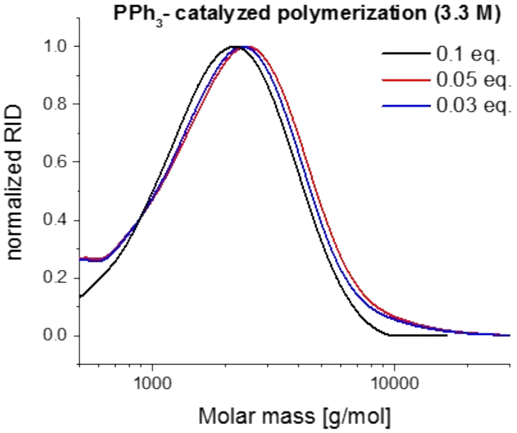

Figure S36: SEC (DMAc (+ 0.21 wt.% LiCl), PEG standards) traces of the kinetic samples taken after 24 h of the polymerization catalyzed with PPh_3 in DMSO.

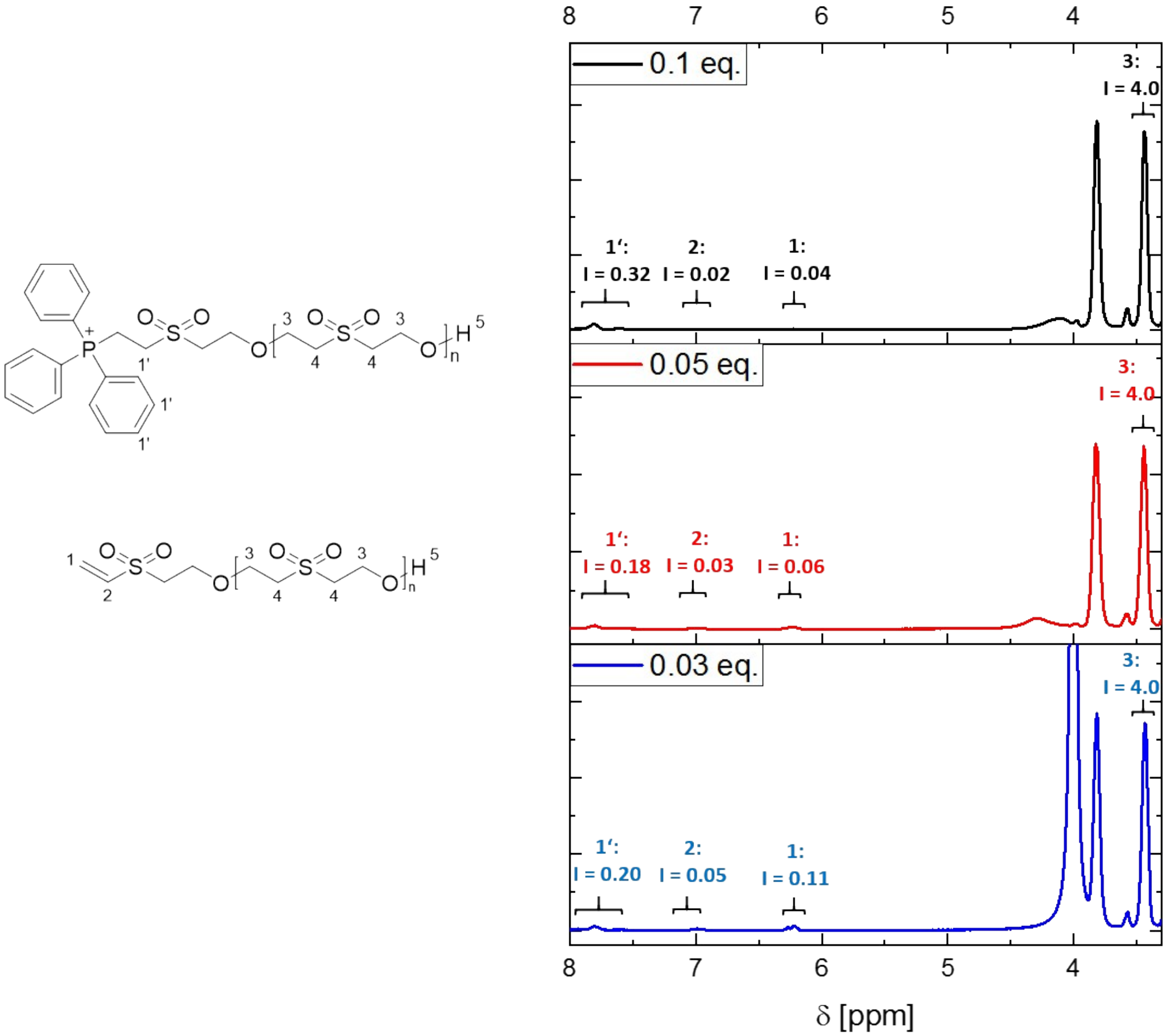

Figure S37: ^{1}H-NMR (300 MHz, DMSO-d_6) spectra of the PPh$_3$- catalyzed polymers with different amounts of PPh$_3$ after precipitation.

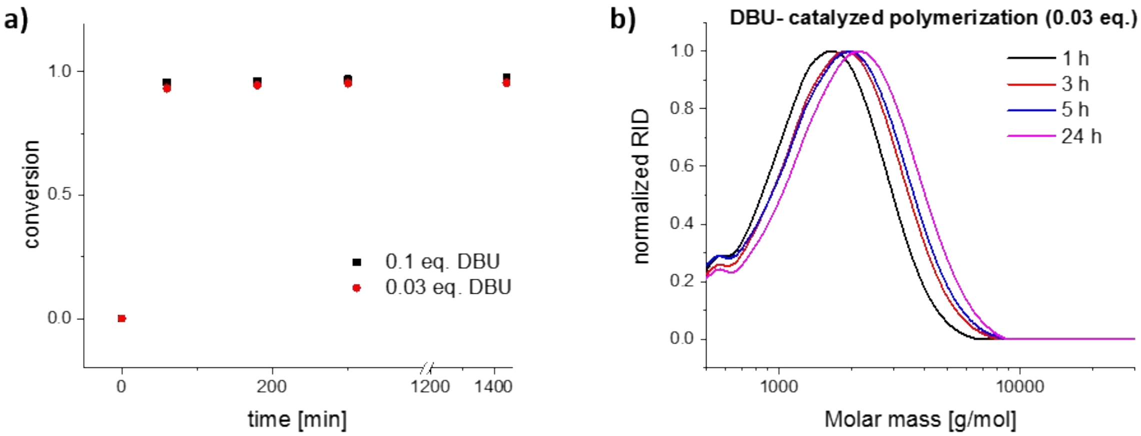

Figure S38: a) Conversion vs. reaction time for different polymerizations: comparison of different amount of catalyst (catalyst: DBU) b) SEC (DMAc (+ 0.21 wt.% LiCl), PEG standards) traces of the kinetic samples taken after 1 h, 3 h and 24 h of the polymerization catalyzed with 0.03 eq. DBU in DMSO.

Thermal properties of the polymers

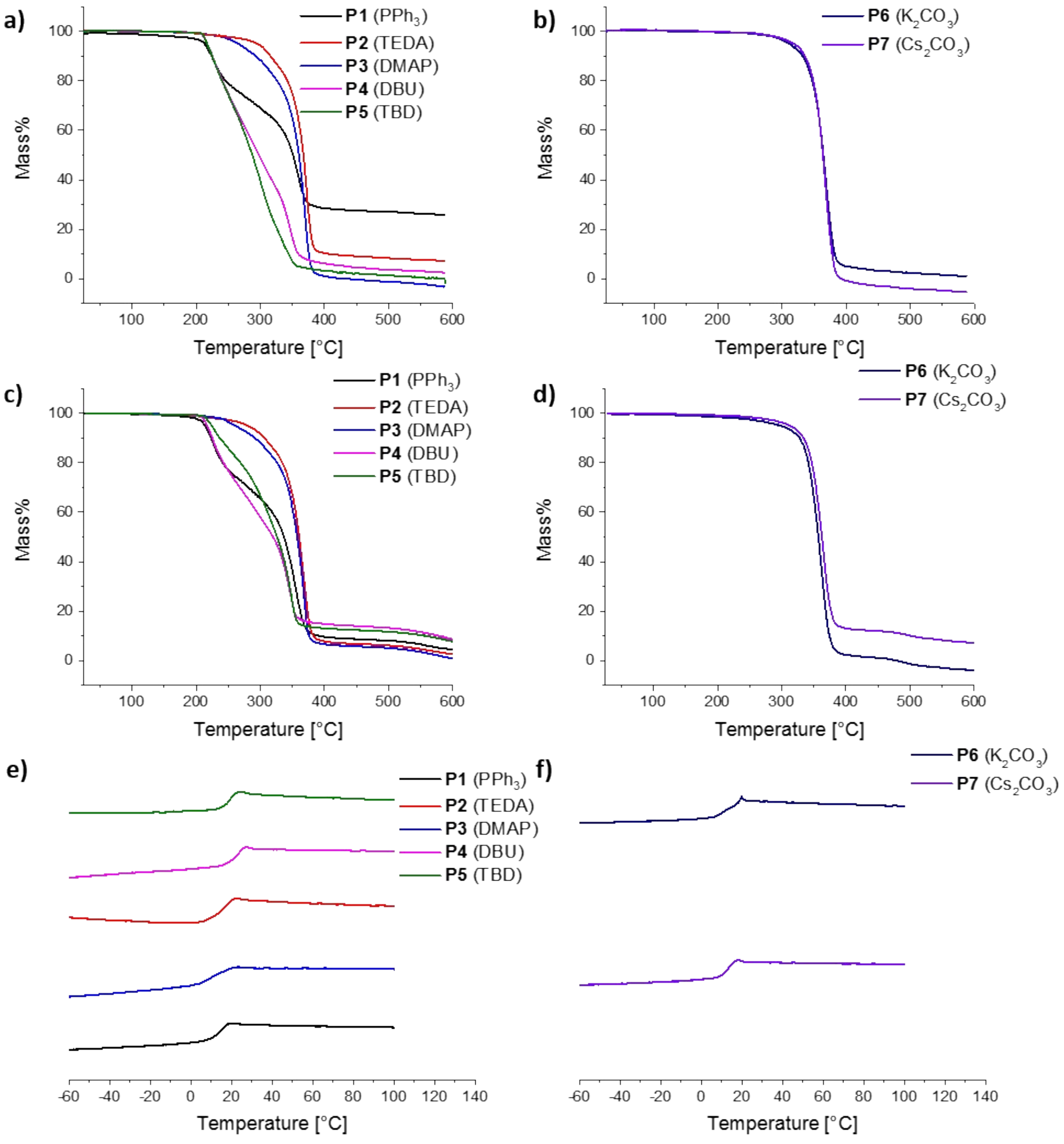

Figure S39: a) TGA-data of the polymers P1-P5 (N_2) b) TGA-data of the polymers P6/P7 (N_2) c) TGA-data of the polymers P1-P5 (Air) d) TGA-data of the polymers P6/P7 (Air) e) DSC-data of the polymers P1-P5 f) DSC-data of the polymers P6/P7.

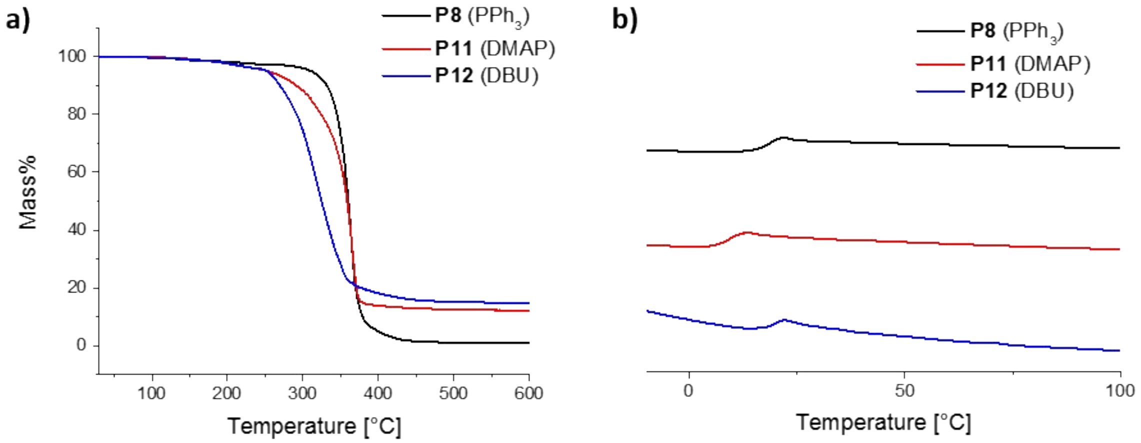

Figure S40: a) TGA-data of the polymers P8/11/12 (N_2) b) DSC-data of the polymers P8/11/12.

Table S6: SEC-data and thermal properties of the purified polymers.

Polymer	5% mass loss [°C] [b]	T_g [°C] [d]
P8	311	17.8
P11	253	9.2
P12	252	18.2

[a] Determination from TGA measurements (N_2) [b] Determination from DSC measurements.

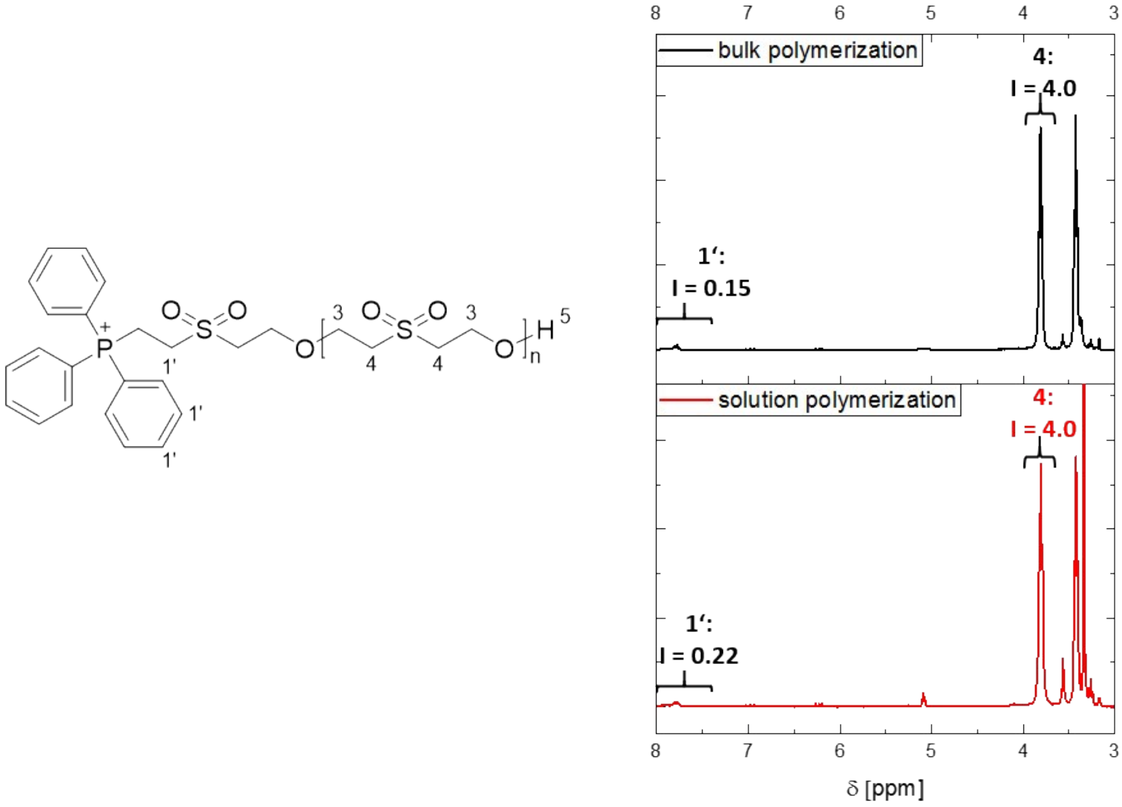

Figure S41: ^{1}H-NMR (300 MHz, DMSO-d6) spectra of the PPh$_3$- catalyzed polymers *via* bulk- and solution polymerization after precipitation.

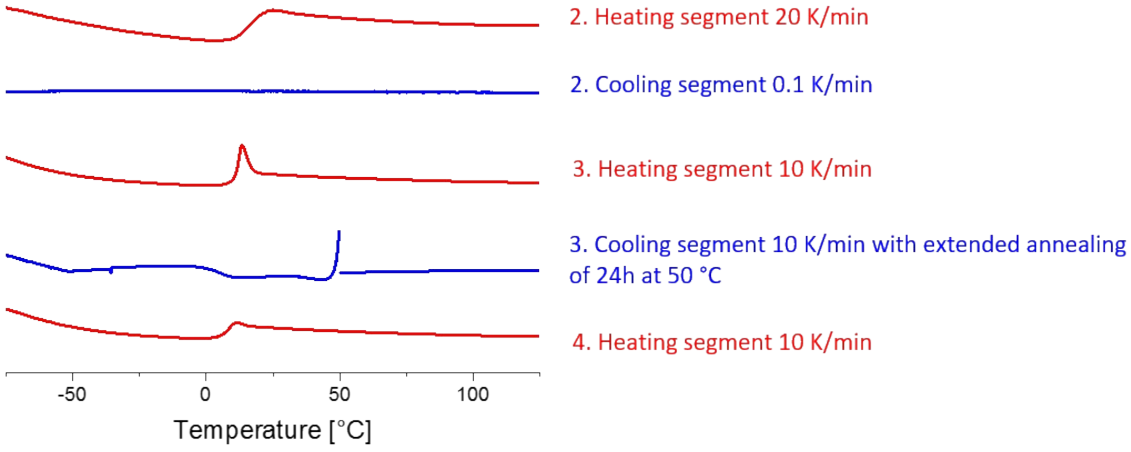

Figure S42: DSC-traces of P1 with different heating and cooling rates.