Solvent-free macrocyclisation by nucleophilemediated Oxa-Michael addition polymerisation of divinyl sulfone and alcohols

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Electronic Supplementary Information (ESI)

General

DVS, DMAP and all alcohols used were purchased from Aldrich and were used as received. Only ethylene glycol was distilled prior to use and PEG300 was dried under oil-pump vacuum for 24h. Column chromatography was done using silica gel (60, 0.03-0.2 mm, product no. P090.5) purchased from Lactan, Austria. Aluminum sheets with silica gel (60 F254) for thin layer chromatography (TLC) were purchased from Merck KGaA, Germany.

Nuclear magnetic resonance experiments were done on a Bruker Avanze 300 MHz spectrometer (¹H: 300.36 MHz; ¹³C: 75.53 MHz) at 25 °C. Chemical shifts are given in ppm relative to a tetramethylsilan (TMS) standard. Deuterated solvents were obtained from Cambridge Isotope laboratories Inc. and spectra were referenced against the residual proton signals according to literature.¹

Thermogravimetric analyses (TGA) were performed with a Netzsch Simultaneous Thermal Analyzer STA 449C (crucibles: aluminium from Netzsch). A helium flow of 35 mL min⁻¹ was used in combination with a protective flow of helium of 8 mL min⁻¹. The heating rate until a final temperature of 550 °C was 10 °C min⁻¹.

Gel permeation chromatography (GPC) was carried out on a system provided by WGE Dr. Bures operated with THF (separating columns from MZ-Gel SD plus, linear 5µ; UV und RI detector SEC 3010). Poly(styrene) standards purchased from Polymer Standard Service were used for calibration.

Dynamic mechanical analyses (DMA) were measured on a DMA Q 800 from TA Instruments Waters GmbH in the 3-point bending mode (10 mm clamping lengths) of specimens with sample dimensions of 3 x 5 x 20 mm with a frequency of oscillation of 1 Hz and amplitude of 25 μ m in a temperature range from -4 to 50°C (heating rate: 3°C min⁻¹).

Differential scanning calorimetry (DSC) analyses were measured on a DSC 8500 instrument from Perkin Elmer in a temperature range from -20 to 100°C with a heating rate of 20°C/min for the first run and with 20°C/min in the second run (T_g values were retrieved from the second heating run).

Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectra were recorded on two different machines: a) on a Micromass TofSpec 2E Time-of-Flight Mass Spectrometer: Trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) was used as matrix substance and THF as solvent. Sample solutions have been prepared by mixing solutions of DCTB (10 mg/mL), sodium trifluoroacetate (1 mg/mL) and the samples (5 mg/mL) in a ratio of 7/2/2 (v/v/v). Calibration was done externally with polyethylene glycol standards (5 mg/mL). b) on a Waters Micromass MALDI micro MX Time-of-Flight Mass Spectrometer: 1,8,9-Anthracenetriol (Dithranol) was used as matrix substance and THF as solvent. Sample solutions of Dithranol (10 mg/mL), sodium trifluoroacetate (1 mg/mL) in a ratio of 7/2/2 (v/v/v). Calibration was used as matrix substance and THF as solvent. Sample solutions have been prepared by mixing solutions of Dithranol (10 mg/mL), sodium trifluoroacetate (1 mg/mL) and the samples (5 mg/mL Chloroform) in a ratio of 7/2/2 (v/v/v). Calibration with polyethylene glycol standards (5 mg/mL) and the samples (5 mg/mL Chloroform) in a ratio of 7/2/2 (v/v/v). Calibration was done externally with polyethylene glycol standards (5 mg/mL)

GC MS: Mass spectra were recorded on a Waters Micromass GCT Premier Mass Spectrometer internally calibrated with Heptacosa. Of a sample solution (1mg/mL) 1 μ L was injected into a gas chromatograph (Agilent, 7890A, operated with He, injection temperature: 300°C; split: 1:100; column: DB 5MS from J&W Scientific; temperature program: start at 40°C, heating rate 50°C/min, end temperature 300°C for 5 min.

¹ Fulmer, G. R.; Miller, A. J. M.; Sherden, N. H.; Gottlieb, H. E.; Nudelman, A.; Stoltz, B. M.; Bercaw, J. E.; Goldberg, K. I. Organometallics 2010, 29, 2176.

Polyaddition of ethylene glycol (1) and DVS: poly1

DMAP (11.70 mg, 0.096 mmol, 0.053 equiv. in respect to DVS) was dissolved in ethylene glycol (109.43 mg, 1.763 mmol) and subsequently DVS (214.74 mg, 1.820 mmol) was admixed under stirring at room temperature. After 24 h an aliquot of the reaction mixture was removed and investigated by ¹H-NMR spectroscopy (sample poly1a) and the remaining reaction mixture was placed for 24 h in an oven at 80°C again an aliquot was removed and investigated by ¹H-NMR spectroscopy (sample poly1b). The remaining reaction mixture was dissolved in CH₂Cl₂ and was extracted with aqueous HCI (5 %). The organic phase was washed with water, dried over Na₂SO₄ and upon removal of the solvent and drying the residue was analyzed as follows:

¹H-NMR (300 MHz, CDCl₃, 25°C): δ 6.78 (dd, 1H, ${}^{3}J_{HH(E)}$ = 16.6 Hz, ${}^{3}J_{HH(Z)}$ = 9.9 Hz, CH), 6.39 (d, 1H, ${}^{3}J_{HH}$ = 16.6 Hz, $CH_{2}^{(E)}$), 6.12 (d, 1H, ${}^{3}J_{HH}$ = 9.9 Hz, $CH_{2}^{(Z)}$), **3.91 (t, 124H, -SO₂-CH₂CH₂-O-), 3.64 (s, 127H, -O-CH₂CH₂-O-), 3.35 (t, 123H, -SO₂-CH₂CH₂-O)**. Peaks assigned to the repeating group printed in bold.



Fig. S1: ¹H-NMR spectrum of **poly1** after workup.

Analysis of the ¹H-NMR spectrum: Assuming that the structure of the polymer contains equal amounts of $CH_2=CH-SO_2-CH_2CH_2$ - and $-O-CH_2CH_2-OH$ end-groups, the degree of polymerization was estimated according to the formula: **n** = [(Integral of the peak at 3.91 ppm)-2]/4 = 124/4 = **30.5±2**, whereby the proton of the $-SO_2-CH=CH_2$ at 6.78 was referenced to 1. The protons attached to the α -carbon of free alcohol (-O-CH₂CH₂-OH) are partly submersed under the signal for the $-O-CH_2CH_2-O$ - protons and were included in the integral for this group. As long as the integral value for this peak is not considerably higher than the one for the peaks at 3.91 and 3.35 the assumption mentioned in the first sentence of this paragraph holds true.



Cyclic structures were not considered in this calculation.

A similar evaluation of the samples removed from the reaction mixture after 24 h at room temperature (poly1a) and further 24 h at 80° C (poly1b) revealed n values of 9.5 ± 1 and 30.5 ± 2 .

A reproduction was carried out as described above using DMAP (14.30 mg, 0.117 mmol, 0.050 equiv. in respect to DVS) was dissolved in ethylene glycol (145.04 mg, 2.337 mmol) and subsequently DVS (286.57 mg, 2.353 mmol).

Analysis of the ¹H-NMR spectra removed from the reaction mixture after 24 h at room temperature and further 24 h at 80°C revealed n values of 12.5±1 and 15.3±2.

¹³C{¹H}-NMR (75 MHz, CDCl₃, 25°C): δ 138.0 (-SO₂-CH=CH₂), 129.2 (-SO₂-CH=CH₂), 72.7 (HO-CH₂CH₂-O-), **70.4** (-O-CH₂CH₂-O-), 70.1 (HO-CH₂CH₂-O-), **64.7** (-SO₂-CH₂CH₂-O-), 61.4 (-O-CH₂CH₂-SO₂-CH=CH₂), **55.0** (-SO₂-CH₂CH₂-O-), 53.6 (-O-CH₂CH₂-SO₂-CH=CH₂) ppm. Peaks assigned to the repeating group printed in bold.



Fig. S2: ¹³C{¹H}-NMR spectrum of **poly1** after workup.

GPC (in THF calibrated relative to polystyrene) gave a M_n value < 800 g/mol.







Fig. S4: MALDI-TOF mass spectrum of poly1 after workup (detail).

Alternative structures included in series D may comprise:



TGA: 2% weight loss at 293°C; 3% weight loss at 300°C; 3% char residue at 500°C.



DSC (20°C/min): T_g at -16.2°C and -8.4°C.

Fig. S5: DSC curve of poly1 after workup (detail).

Snapshots of the composition of the reaction mixture at 30 min at room temperature and 16 h at 80°C

To a mixture of ethylene glycol (200.63 mg, 3.232 mmol) and DVS (382.35 mg, 3.236 mmol) DMAP (39.49 mg, 0.323 mmol, 0.10 equiv. in respect to DVS) was admixed under stirring at room temperature. After 30 min an aliquot of the reaction mixture (150.8 mg) was removed and immediately investigated by ¹H-NMR spectroscopy (sample poly1c was characterized by an apparent n value of 3 ± 1) and subsequently submitted to column chromatography (silica; eluent: cyclohexane:ethyl acetate = 1:1). A single spot eluted (R_f = 0.22 in cyclohexane:ethyl acetate = 1:1) which was sampled and dried. Yield: 1.6 mg (1 %).

¹H-NMR (300 MHz, CDCl₃, 25°C): δ 4.03 (bt, 4H, -SO₂-CH₂CH₂-O-), 3.62 (bs, 4H, -O-CH₂CH₂-O-), 3.37 (bs, 4H, -SO₂-CH₂CH₂-O).

GC-MS: 180.05 M⁺; 137; 122; 101; 75; 73; 72; 70; 58; 57 m/z.

Data suggest that this product is 1,4,7-dioxathionane-7,7-dioxide.

The eluent was changed to dichloromethane:methanol = 10:1 and several spots in the R_{f^-} range of 0.8-0.53 were isolated. Upon drying 123.2 mg material were recovered (82%; this fraction of poly1 was characterized by an apparent n value of 3.7±1).

The remaining reaction mixture was heated for 16h at 80°C and work-up was done as described above using 153.4 mg of the reaction mixture. ¹H-NMR spectroscopy directly after quenching the reaction revealed an apparent n value of 12.5 ± 1.5 . Chromatographic purification released 120.1 mg (78%) of a polymer characterized by an apparent n value of

21±2. A similar amount of 1,4,7-dioxathionane 7,7-dioxide as in case of the room temperature fraction was obtained.



Fig. S6: ¹H-NMR spectrum of 1,4,7-dioxathionane 7,7-dioxide.



Fig. S7: GC of 1,4,7-dioxathionane-7,7-dioxide.



Fig. S8: Mass spectrum of 1,4,7-dioxathionane-7,7-dioxide



Fig. S9: Overlay of the NMR spectra of 1,4,7-dioxathionane-7,7-dioxide (blue) and poly1c (red, the reaction mixture before column chromatography).

Reaction of 1 and DVS in CDCI₃ using 1 equiv. DMAP

To a mixture of ethylene glycol (28.39 mg, 0.457 mmol) and DVS (49.08 mg, 0.415 mmol) DMAP (50.75 mg, 0.415 mmol, 1.0 equiv. in respect to DVS) and 1 mL CDCl₃ was admixed at room temperature. ¹H-NMR spectra were recorded after 2 h and after 26 h revealing almost complete consumption of DVS after 2 h (8±4% DVS left) and 26 h (2±2% DVS left). **1** was not completely consumed (singlet at 3.60 ppm), which was expected because of the slight excess of **1** used. Noticeable is a distinct decrease of the integral value (0.16) expected for the proton attached to the α -carbon of the vinyl-group (SO₂-CH=CH₂) when compared to the integral values for the terminal vinyl-protons (0.79). Similarly, signal of the protons at the α -C in the SO₂CH₂CH₂O moiety is smaller (0.75) when compared to the signal for the β -protons (2.13).



Fig. S10: ¹H-NMR spectrum of the reaction mixture after 26 h.



Fig. S11: ¹³C{¹H}-NMR spectrum of the reaction mixture after 26 h

The residue was submitted to column chromatography (silica; eluent: cyclohexane:ethyl acetate = 1:1). A single spot eluted ($R_f = 0.22$ in cyclohexane:ethyl acetate = 1:1) which was sampled and dried. Yield: 1.1 mg (1.4 %).

¹H-NMR (300 MHz, CDCl₃, 25°C): δ 4.02 (s, 4H, -SO₂-CH₂CH₂-O-), 3.62 (bs, 4H, -O-CH₂CH₂-O-), 3.49 (bs, 1H, -SO₂-CH₂CH₂-O). ¹³C{¹H}-NMR (75 MHz, CDCl₃, 25°C): δ 70.6 (-O-CH₂CH₂-O-), 66.46, 66.40 (- D_{1.5} O D_{1.5} SO₂-CH/D₂CH₂-O-), 55.08, 54.79, 54.52 (-SO₂-CH/D₂CH₂-O-) ppm.

The spectra suggest the compound to be 1,4,7-dioxathionane 7,7-dioxide-6,8-d₃

The eluent was changed to dichloromethane:methanol = 10:1 and the spot with $R_f = 0.89$ (dichloromethane:methanol = 1:1) was isolated. Upon drying 10.2 mg material was obtained (13%).

¹H-NMR (300 MHz, CDCl₃, 25°C): δ 6.78 (dd, 0.24H, ³J_{HH(E)} = 16.3 Hz, ³J_{HH(Z)} = 9.6 Hz, *CH*), 6.40 (1H, *CH*₂^(*E*)), 6.12 (1H, *CH*₂^(*Z*)), 3.91 (14.7H, -SO₂-CH₂CH₂-O-), 3.73 (3.7H, HO-CH₂CH₂-O-), 3.65 (14.7H, -O-CH₂CH₂-O-), 3.35 (3.4H, -SO₂-CH₂CH₂-O), 3.26 (0.6H, H₂C=CH-SO₂-CH₂CH₂-O) ppm. ¹³C{¹H}-NMR (75 MHz, CDCl₃, 25°C): δ 138.0-137.3 (-SO₂-CH/D=CH₂), 129.17, 129.07 (-SO₂-CH/D=CH₂), 72.87, 72.73 72.66 (HO-CH₂CH₂-O-), 70.4 (-O-CH₂CH₂-O-), 70.1 (HO-CH₂CH₂-O-), 64.8-64.1 (-SO₂-CH/D₂CH₂-O-), 61.4 (HO-CH₂CH₂-O-), 55.2-54.2 (-SO₂-CH/D=CH₂)

 $CH/D_2CH_2-O-)$ ppm.

The spectra suggest a mixture of the following compounds in a ratio of 1:0.7:



In the next fractions DMAP was recovered ($R_f = 0.76$ (dichloromethane:methanol = 1:1)). Subsequently the eluent was changed to dichloromethane:methanol = 1:1. The final fractions containing any poduct ($R_f = 0.15-0.10$ (dichloromethane:methanol = 1:1)) were sampled containing approx. 3 mg. The composition of this residue could not be identified. Some evidence for the presence of pyridinium species could be gained.



Fig. S12: ¹H-NMR spectrum of 1,4,7-dioxathionane 7,7-dioxide-6,8-d₃



Fig. S14: ¹H-NMR spectrum of the oligomers



Fig. S16: ${}^{13}C{}^{1}H$ -NMR spectrum of the oligomers - Detail

Polyaddition of ethylene glycol (1) and DVS followed by the reaction with propargylic alcohol

DMAP (66.52 mg, 0.544 mmol, 0.100 equiv. in respect to DVS) was dissolved in **1** (337.96 mg, 5.445 mmol) and subsequently DVS (643.64 mg, 5.448 mmol) was admixed under stirring at room temperature. The reaction mixture was stirred and heated to 80°C and kept at this temperature for 8 h. Afterwards the reaction mixture was allowed to cool to room temperature and an aliquot (237.76 mg) was removed. To this aliquot propargylic alcohol (70 μ L, 1.211 mmol) was added and the reaction mixture was stirred at 80°C for further 8 h. From both reaction mixtures MALDI-TOF MS measurements were performed:



Fig. S17: MALDI-TOF mass spectra of **poly1** without propargylic alcohol addition (above) and **poly1** after reaction with propargylic alcohol (below).

Polyaddition of 1,4-butanediol (2) and DVS: poly2

DMAP (11.56 mg, 0.095 mmol, 0.046 equiv. in respect to DVS) was dissolved in **2** (175.45 mg, 1.947 mmol) and subsequently DVS (241.87 mg, 2.047 mmol) was admixed under stirring at room temperature. After 24 h an aliquot of the reaction mixture was removed and investigated by ¹H-NMR spectroscopy (sample poly2a) and the remaining reaction mixture was placed for 24 h in an oven at 80°C again an aliquot was removed and investigated by ¹H-NMR spectroscopy (sample poly 2b). The remaining reaction mixture was dissolved in CH₂Cl₂ and was extracted with aqueous HCI (5 %). The organic phase was washed with water, dried over Na₂SO₄ and upon removal of the solvent and drying the residue was analyzed as follows:

¹H-NMR (300 MHz, CDCl₃, 25°C): δ 6.71 (dd, 1H, ³J_{HH} = 16.7 Hz, ³J_{HH} = 9.9 Hz, CH), 6.39 (d, 1H, ³J_{HH} = 16.7 Hz, CH₂^(E)), 6.09 (d, 1H, ³J_{HH} = 9.9 Hz, CH₂^(Z)), **3.84 (t, 31H, -SO₂-CH₂CH₂-O-**), 3.63 (t, 1.4H, CH₂CH₂CH₂CH₂-OH), **3.48 (s, 31H, -O-CH₂CH₂CH₂CH₂-O-**), **3.30 (t, 31H, -SO₂-CH₂CH₂-O)**, **1.63 (s, 31H, -O-CH₂CH₂CH₂-O-**). Peaks assigned to the repeating group printed in bold.

Analysis of the ¹H-NMR spectrum: Assuming that the structure of the polymer contains equal amounts of CH₂=CH-SO₂-CH₂CH₂- and -O-CH₂CH₂CH₂CH₂-OH end-groups, the degree of polymerization was estimated according to the formula: **n** = [(Integral of the peak at 3.84 ppm)-2]/4 = 29/4 = **7.3±1**, whereby the proton of the $-SO_2$ -CH=CH₂ at 6.71 was referenced to 1. The protons attached to the α -carbon of free alcohol (-O-CH₂CH₂CH₂CH₂-OH) gave an integral value of 1.42 (at 3.63 ppm) for this group, meaning that there are more vinyl-sulfone end-groups.



Cyclic structures were not considered in this calculation.

A similar evaluation of the samples removed from the reaction mixture after 24 h at room temperature (poly2a) and further 24 h at 80°C (poly2b) revealed n values of 2.5 ± 0.5 and 5.5 ± 2 .

A reproduction was carried out as described above using DMAP (12.17 mg, 0.103 mmol, 0.051 equiv. in respect to DVS), **2** (179.052 mg, 1.992 mmol) and DVS (244.03 mg, 2.003 mmol). Analysis of the ¹H-NMR spectra removed from the reaction mixture after 24 h at room temperature and further 24 h at 80°C revealed n values of 3.3 ± 0.5 and 6 ± 2 .

¹³C{¹H}-NMR (75 MHz, CDCl₃, 25°C): δ 137.9 (-SO₂-CH=CH₂), 129.0 (-SO₂-CH=CH₂), 71.4 (HO-CH₂CH₂CH₂CH₂-O-), 71.1 (-O-CH₂CH₂CH₂CH₂-O-), 64.3 (-SO₂-CH₂CH₂-O-), 62.5 (HO-CH₂CH₂CH₂-O-), 55.1 (-SO₂-CH₂CH₂-O-), 29.7 (-O-CH₂CH₂CH₂-O-), 26.2 (-O-CH₂CH₂CH₂-O-) ppm. Peaks assigned to the repeating group printed in bold.



GPC (in THF calibrated relative to polystyrene) gave: M_n = 1400 g/mol, PDI = 1.6.





Fig. S20: MALDI-TOF mass spectrum of poly1 after workup.



Fig. S21: MALDI-TOF mass spectrum of poly1 after workup (detail).

TGA: 3% weight loss at 278°C; 3% char residue at 500°C.

DSC (20°C/min): T_g at -31.7°C.



Polyaddition of (Z)-2-butene-1,4-diol (3) and DVS: poly3

DMAP (12.99 mg, 0.106 mmol, 0.050 equiv. in respect to DVS) was dissolved in **3** (191.24 mg, 2.064 mmol) and subsequently DVS (259.04 mg, 2.127 mmol) was admixed under stirring at room temperature. After 24 h an aliquot of the reaction mixture was removed and investigated by ¹H-NMR spectroscopy (sample poly3a) and the remaining reaction mixture was placed for 24 h in an oven at 80°C again an aliquot was removed and investigated by ¹H-NMR spectroscopy (sample poly3b):

¹H-NMR (300 MHz, CDCl₃, 25°C): δ 8.21 (d, 1.3H, residual DMAP), 6.71 (dd, 1H, ³J_{HH} = 16.6 Hz, ³J_{HH} = 9.9 Hz, CH), 6.48 (d, 1.3H, residual DMAP), 6.40 (d, 1H, ³J_{HH} = 16.6 Hz, CH₂^(E)), 6.10 (d, 1H, ³J_{HH} = 9.9 Hz, CH₂^(Z)), **5.72 (s, 36.9H, -CH₂CH=CHCH₂-)**, 4.19 (d, 1.8H, HO-CH₂CH=CHCH₂-), **4.09 (d, 72.7H, -O-CH₂CH=CHCH₂-O-)**, **3.85 (t, 72.3H, -SO₂-CH₂CH₂-O-)**, **3.32 (s, 72.6H, -SO₂-CH₂CH₂-O)**, 2.99 (d, 4.6H, residual DMAP). Peaks assigned to the repeating group printed in bold.

Analysis of the ¹H-NMR spectrum of poly3b: Assuming that the structure of the polymer contains equal amounts of CH₂=CH-SO₂-CH₂CH₂- and -O-CH₂CH=CHCH₂-OH end-groups, the degree of polymerization was estimated according to the formula: **n** = [(Integral of the peak at 3.85 ppm)-2]/4 = 72.3/4 = **17.6±2**, whereby the proton of the $-SO_2$ -CH=CH₂ at 6.71 was referenced to 1. The protons attached to the α -carbon of free alcohol (-O-CH₂CH=CHCH₂-OH) gave an integral value of 1.8 (at 4.19 ppm) for this group, meaning that there are slightly more vinyl-sulfone end-groups.



Cyclic structures were not considered in this calculation.

A similar evaluation of the samples removed from the reaction mixture after 24 h at room temperature (poly3a) revealed an n value of 10.6 ± 2 .

¹³C{¹H}-NMR (75 MHz, CDCl₃, 25°C): δ 149.8 (DMAP), 137.9 (-SO₂-CH=CH₂), 133.3 (HO-CH₂CH=CHCH₂-O-), **129.3** (-O-CH₂CH=CHCH₂-O-), 129.1 (-SO₂-CH=CH₂), 127.2 (HO-CH₂CH=CHCH₂-O-), 106.7 (DMAP), **66.9** (-O-CH₂CH=CHCH₂-O-), **63.9** (-SO₂-CH₂CH₂CH₂-O-), 58.6 (-CH₂-SO₂-CH=CH₂), **55.1** (-SO₂-CH₂CH₂-O-), 39.1 (DMAP) ppm. Peaks assigned to the repeating group printed in bold.

GPC (in THF calibrated relative to polystyrene) gave a M_n value < 1000 g/mol.



Fig. S22: ¹H-NMR spectrum of poly3b.



Fig. S23: ${}^{13}C{}^{1}H$ -NMR spectrum of **poly3b**.



Fig. S24: MALDI-TOF mass spectrum of poly3b.



Fig. S25: MALDI-TOF mass spectrum of poly3b (detail).

TGA: 3% weight loss at 224°C; 2% char residue at 500°C.



DSC (20°C/min): T_g at -20.4°C.

Polyaddition of 2-butyne-1,4-diol (4) and DVS: poly4

Poly4 was prepared analogously to **poly3** using DMAP (10.03mg, 0.082 mmol, 0.049 equiv. in respect to DVS), **4** (143.14 mg, 1.663 mmol) and DVS (196.52 mg, 1.663 mmol) as the starting materials.

¹H-NMR (300 MHz, CDCl₃, 25°C): δ 8.20 (d, 2.2H, residual DMAP), 6.73 (dd, 1H, ³*J*_{HH} = 16.6 Hz, ³*J*_{HH} = 9.9 Hz, C*H*), 6.48 (d, 2.2H, residual DMAP), 6.41 (d, 1H, ³*J*_{HH} = 16.6 Hz, C*H*₂^(E)), 6.11 (d, 1H, ³*J*_{HH} = 9.9 Hz, C*H*₂^(Z)), **4.25 (s, 160.3H, -O-CH**₂C≡CCH₂-O-), included in the integral before 4.29 (HO-CH₂C≡CCH₂-O-), **3.96 (t, 155H, -SO**₂-CH₂CH₂-O-), **3.35 (s, 156H, -SO**₂-CH₂CH₂-O), 2.99 (d, 4.6H, residual DMAP). Peaks assigned to the repeating group printed in bold.

Analysis of the ¹H-NMR spectrum of ploy4b: Assuming that the structure of the polymer contains equal amounts of $CH_2=CH-SO_2-CH_2CH_2$ - and $-O-CH_2C\equiv CCH_2-OH$ end-groups, the degree of polymerization was estimated according to the formula: **n** = [(Integral of the peak at 3.96 ppm)-2]/4 = 153/4 = **38±2**, whereby the proton of the $-SO_2-CH=CH_2$ at 6.11 was referenced to 1. The protons attached to the α -carbon of free alcohol (- $O-CH_2C\equiv CCH_2-OH$) gave an integral value of ≈4 (detracting the integral value of the peak at 3.96 ppm from the one of the pak at 4.25 ppm) for this group, meaning that in this sample more alcohol bearing end-groups are present).



Cyclic structures were not considered in this calculation.

A similar evaluation of the samples removed from the reaction mixture after 24 h at room temperature (poly4a) revealed an n value of 17.5 ± 2 .

¹³C{¹H}-NMR (75 MHz, CDCl₃, 25°C): δ 149.7 (DMAP), 137.8 (-SO₂-CH=CH₂), 129.5 (-SO₂-CH=CH₂), 127.2 (HO-CH₂CH=CHCH₂-O-), 106.7 (DMAP), 86.2 (HO-CH₂C≡CCH₂-O-), 82.5 (-O-CH₂C≡CCH₂-O-), 80.5 (HO-CH₂C≡CCH₂-O-), 63.4 (-O-CH₂C≡CCH₂-O-), 58.7 (-SO₂-CH₂CH₂-O-), 54.9 (-SO₂-CH₂CH₂-O-), 50.9 (HO-CH₂C≡CCH₂-O-), 39.1 (DMAP) ppm. Peaks assigned to the repeating group printed in bold.

GPC (in CHCl₃/Et₃N calibrated relative to polystyrene): $M_n = 8000 \text{ g/mol}$; PDI = 1.8.





Fig. S28: MALDI-TOF mass spectrum of poly4b.



Fig. S29: MALDI-TOF mass spectrum of poly4b (detail).

TGA: 3% weight loss at 186°C; 18% char residue at 500°C.



DSC (20°C/min): T_g at -1.8°C.

Polyaddition of PEG300 (5) and DVS: poly5

Poly5 was prepared similar to **poly4** using DMAP (12.39 mg, 0.101 mmol, 0.047 equiv. in respect to DVS), **5** (608.60 mg, 2.029 mmol) and DVS (255.44 mg, 2.162 mmol) as the starting materials. The reaction mixture was heated to 80°C before DMAP was added. After heating the stirred reaction mixture for 2 h at 80°C, an aliquot was removed and investigated with ¹H-NMR spectroscopy.

¹H-NMR (300 MHz, CDCl₃, 25°C): δ 6.82 (dd, 1H, ³J_{HH} = 16.6 Hz, ³J_{HH} = 9.9 Hz, CH), 6.39 (d, 1H, ³J_{HH} = 16.6 Hz, CH₂^(E)), 6.09 (d, 1H, ³J_{HH} = 9.9 Hz, CH₂^(Z)), 3.90 (t, 4.9H, -SO₂-CH₂CH₂-O-), 3.64 (s, 39.7H, PEG300), 3.35 (t, 2.9H, -SO₂-CH₂CH₂-O), 3.00 (t, 2.2H, H₂C=CH-SO₂-CH₂CH₂-O).

The spectrum is represented by the structure drawn below.



To the rest of the reaction mixture, propargylic alcohol (125 μ L, 2.162 mmol) was added and the reaction was stirred for further 2 h at 80°C. An aliquot was removed and investigated with ¹H-NMR spectroscopy.

¹H-NMR (300 MHz, CDCl₃, 25°C): δ 4.28 (d, 0.36H, HC=CCH₂OH), 4.20 (d, 1.8H, HC=CCH₂OCH₂CH₂-), 4.02-3.85 (m, 7.0H, -SO₂-CH₂CH₂-O-), 3.64 (s, 39.7H, PEG300), 3.46-3.28 (m, 7.1H, -SO₂-CH₂CH₂-O).

The spectrum is represented by the structure drawn below.



 $n = 0.7 \pm 0.4$; $m \approx 7$ (in average)



Fig. S30: ¹H-NMR spectrum of **poly5** before reaction with propargylic alcohol.



Fig. S31: ¹H-NMR spectrum of **poly5** after reaction with propargylic alcohol.



Fig. S32: MALDI-TOF mass spectrum of poly5 after reaction with propargylic alcohol.



Fig. S32: MALDI-TOF mass spectrum of poly5 after reaction with propargylic alcohol (detail).

Polyaddition of ethylene glycol (1), 1,4-phenylenedimethanol (6) and DVS: poly6

Poly6 was prepared similar to **poly4** using DMAP (15.29 mg, 0.125 mmol, 0.050 equiv. in respect to DVS), **1** (129.31 mg, 2.083 mmol), **6** (57.62 mg, 0.417 mmol), and DVS (296.79 mg, 2.512 mmol) as the starting materials. The reaction mixture was heated to 60°C before DMAP was added. After heating the stirred reaction mixture for 2 h at 80°C, an aliquot was removed and investigated with ¹H-NMR spectroscopy.

¹H-NMR (300 MHz, CDCl₃, 25°C): δ 8.18 (DMAP), 6.76 (dd, 1H, ³J_{HH(E)} = 16.6 Hz, ³J_{HH(Z)} = 9.9 Hz, CH), 6.46 (DMAP), 6.38 (d, 1H, ³J_{HH} = 16.6 Hz, CH₂^(E)), 6.10 (d, 1H, ³J_{HH} = 9.9 Hz, CH₂^(Z)), 4.53 (s, 16.6H, -O-CH₂-C₆H₄-CH₂-O-), 3.89 (s, 119H, -SO₂-CH₂CH₂-O-), 3.63 (s, 105H, -O-CH₂CH₂-O-), 3.33 (t, 121H, -SO₂-CH₂CH₂-O), 2.98 (DMAP). Peaks assigned to the repeating group printed in bold.

Assuming that the structure of the polymer contains equal amounts of $CH_2=CH-SO_2-CH_2CH_2$ and alcohol end-groups, the degree of polymerization was estimated according to the formula: **n** = [(Integral of the peak at 3.89 ppm)-2]/4 = 117/4 = **29±2**, whereby the proton of the $-SO_2-CH=CH_2$ at 6.76 was referenced to 1.



Fig. S33: ¹H-NMR spectrum of poly6.

¹³C{¹H}-NMR (75 MHz, CDCl₃, 25°C): δ 149.8 (DMAP), 138.0 (-SO₂-CH=CH₂), 137.2 (Ph^{1,4}), 129.1 (-SO₂-CH=CH₂), 128.0 (Ph^{2,3,5,6}), 106.7 (DMAP), 72.7 (HO-CH₂CH₂-O-), **73.1 (-O-CH₂C₆H₄-CH₂-O-)**, **70.4 (-O-CH₂CH₂-O-)**, 70.1 (HO-CH₂CH₂-O-), **64.7 (-SO₂-CH₂CH₂CH₂-O-CH₂CH₂), 63.9 (-SO₂-CH₂CH₂-O-CH₂C₆H₄-)**, **55.0 (-SO₂-CH₂CH₂-O-)**, 39.1 (DMAP) ppm. Peaks assigned to the repeating group printed in bold.



GPC (in THF calibrated relative to polystyrene) gave a M_n value < 1000 g/mol.

TGA: 3% weight loss at 224°C; 5% char residue at 500°C.



Polyaddition of glycerol (7) and DVS: poly7

Typically **Poly7** was prepared by addition of DMAP (99.84 mg, 0.817 mmol, 0.049 equiv. in respect to DVS) to a mixture of **7** (1.024 g, 11.123 mmol) and DVS (1.974 g, 16.705 mmol) as the starting materials. Upon dissolution of DMAP the reaction mixture became hot and viscosity was increasing fast. Complete dissolution of DMAP could not be assured. After approx. 20 sec the reaction mixture solidifies. The reaction mixture was transferred into a mould (transferring to a mould has to be done within the first 20 sec after DMAP addition) and was heated there for 16 h at 80°C.

Samples with a DMAP loading of 2, 5 and 10 mol% were prepared and investigated by DMA, TGA and DSC.



Fig. S35: DMA measurements of poly7 prepared with different DMAP loadings.

Sample	Storage Modulus at 25°C [GPa]	T _g [°C] (Peak Loss modulus)	T _g [°C] (DSC)	3% / 5% / 50% mass loss [°C] (TGA)
poly7 – 2mol% DMAP	3.65±1.35	39±1	32.0	251 / 298 / 364
poly7 – 5mol% DMAP	2.4±0.6	40±1	27.3	224 / 260 / 369
poly7 – 10mol% DMAP	3.3±0.7	37±2.5	30.6	151 / 193 / 354









Polyaddition of 2-ethyl-2-(hydroxymethyl)propane-1,3-diol (8) and DVS: poly8

Typically **Poly8** was prepared by addition of DMAP (58.90 mg, 0.482 mmol, 0.048 equiv. in respect to DVS) to a mixture of **8** (890.58 g, 6.638 mmol) and DVS (1.182 g, 10.002 mmol) at 60°C. Upon dissolution of DMAP the reaction mixture was transferred into moulds and was heated there for 16 h at 80° C.

Samples with a DMAP loading of 2, 5 and 10 mol% were prepared and investigated by DMA, TGA and DSC. It was not possible to obtain test-specimen suited for DMA measurements when using a 2 mol% DMAP loading.



Fig. S37: DMA measurements of poly7 prepared with different DMAP loadings.

Sample	Storage	T _g [°C]	T _g [°C]	3% / 5% /	Extractable
	Modulus	(Peak Loss	(ĎSC)	50% mass	Content [wt%]
	at 25°C	modulus)		loss [°C]	
	[GPa]			(TGA)	
poly8 – 2mol%	-	-	12.8	325 / 338 /	-
DMAP				364	
poly8 – 5mol%	1.75±0.05	33.5±0.6	21.5	247 / 283 /	11.1 (CH ₂ Cl ₂)
DMAP				368	10.2 (acetone)
poly8 – 10mol%	1.87±0.05	32.6±0.3	20.5	145 / 201 /	10.0 (CH ₂ Cl ₂)
DMAP				364	8.2 (acetone)

Determination of extractable content

Moulded material (**poly8** – 5mol% DMAP, 438.93 mg) was extracted at room temperature under gentle shaking for 24 h with dichloromethane (10 mL). Afterwards the liquid was transferred into a flask, dichloromethane was removed and residual solid dried under vacuum. Yield: 40.72 mg (9.28 wt%). To the solid residue from above again dichloromethane (10 mL) were added and a second extraction was done as described above. Yield: 7.86 mg (1.79 wt%). The two extracts amount to 48.58 mg (11.1wt%).

Another extraction was done as described above but using acetone instead of dichloromethane.

The extracted residues were analysed by ¹H-NMR spectroscopy. Acetone and dichloromethane extracts are very similar. Only the dichloromethane extracts of **poly8** – 5mol% DMAP and **poly8** – 10mol% DMAP are discussed in the following:

The extract of **poly8** – 5mol% DMAP is characterized by a molar DMAP : oligomerised **8** ratio of 1:2. Oligomerised **8** features a **8**:DVS ratio of approx. 2:3. Neither unreacted **8** nor unreacted DVS could be observed. If DMAP is completely extracted, recovery of approx. 11 mg DMAP is expected accounting for approx. 22% of the mass of the residue.

The extract of **poly8** – 10mol% DMAP (300 mg sample were used) is characterized by a molar DMAP: oligomerised **8** ratio of 2.3:1. Oligomerised **8** features again a **8**:DVS ratio of approx. 2:3. Neither unreacted **8** nor unreacted DVS could be observed. If DMAP is completely extracted, recovery of approx. 15 mg DMAP is expected accounting for approx. 50% of the mass of the residue.

Accordingly, the use of more DMAP leads to a lower amount of extractable oligomers.



Fig. S38: ¹H-NMR spectrum of the first extract of **poly8** – 5mol% DMAP.





Fig. S40: TGA measurements of poly8 prepared with different DMAP loadings.



Reversibility of the reaction



To a mixture of 3-(2-((2-(prop-2-yn-1-yloxy)ethyl)sulfonyl)ethoxy)prop-1-yne (49.05 mg, 0.217 mmol), DVS (18.21 mg, 0.15412 mmol) and benzyl alcohol (48.1 μ L, 0.4624 mmol) DMAP (1.88 mg, 0.0154 mmol) was added. The reaction mixture was stirred for 2 h at room temperature and then 16 h at 80°C. The reaction mixture was cooled to room temperature and investigated by ¹H-NMR spectroscopy in CDCl₃. Results revealed the formation of the diadduct of benzyl alcohol along with small amounts of the corresponding mono-adduct. The vast majority of the di-adduct of propargylic alcohol remained unchanged. A minor amount of propargylic alcohol was observed (CH₂-group at 4.17 ppm; for reference spectra see: S. Strasser and C. Slugovc, *Catal. Sci. Technol.*, 2015, **5**, 5091-5094.); further heating of the reaction mixture for 6 d at 80°C did not change the outcome.





Fig. S41: ¹H-NMR spectrum of DVS