Supporting Information

Wavelength-Gated Photoreversible Polymerization and Topology Control

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Table of Contents

1. Additional Experiments

1.1 Cyclization of L1

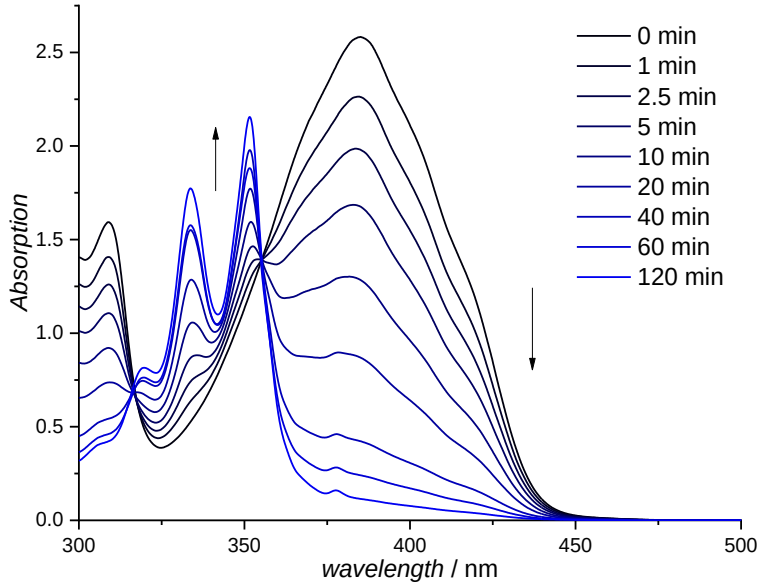


Figure S1.1.1 UV/Vis spectra of L1 in THF (0.05 mg mL^{-1}) after blue light irradiation (refer to section 3 for details).

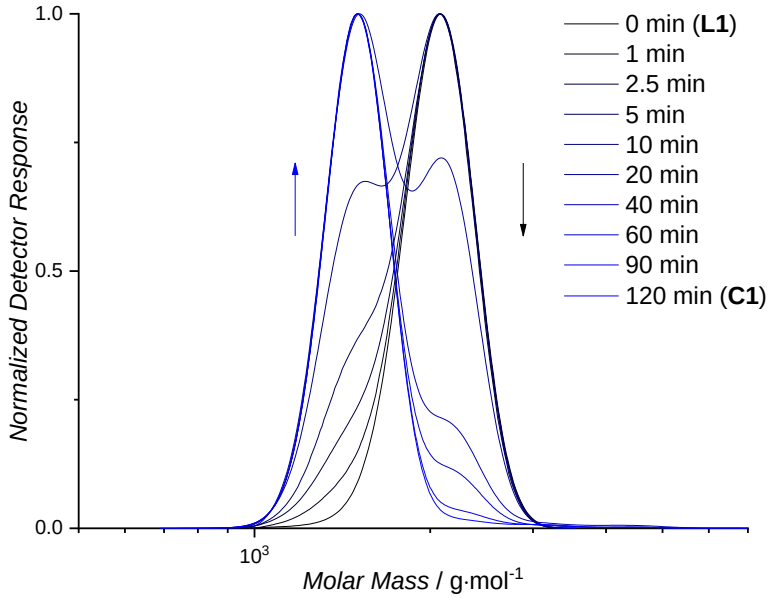


Figure S1.1.2 SEC traces of L1 in THF after blue light irradiation as also shown in Figure 1. A) of the main manuscript (refer to section 3 for details).

1.2 Cycloreversion of C1

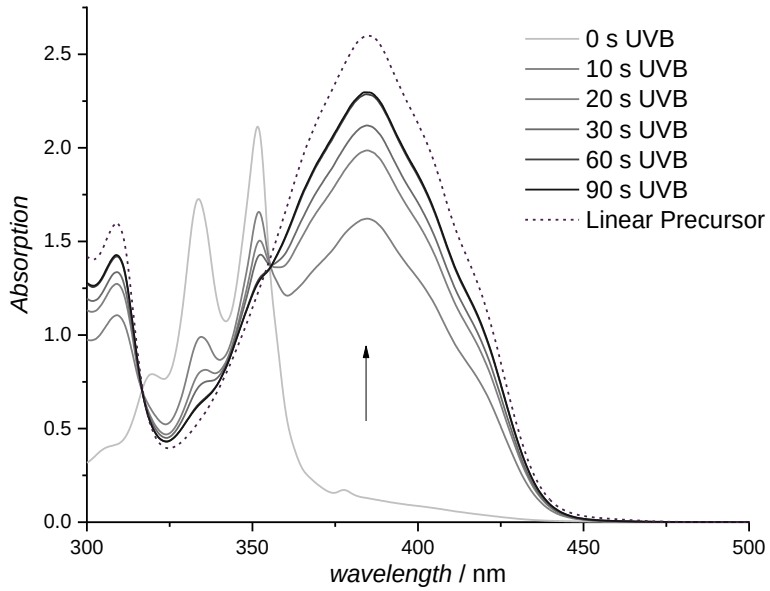


Figure S1.2.1 UV/Vis spectra of C1 in THF (0.05 mg mL^{-1}) after UVB light irradiations (refer to section 3.2 for details).

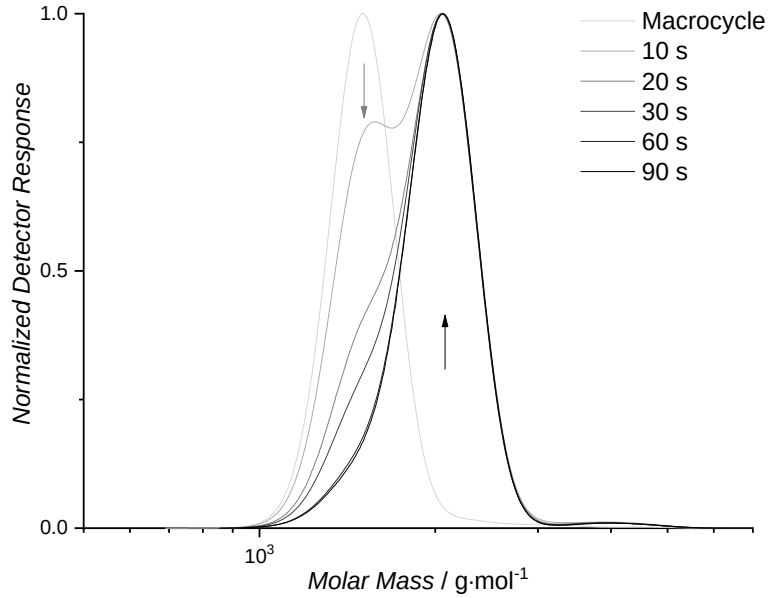


Figure S1.2.2 SEC traces of C1 in THF (0.05 mg mL^{-1}) after UVB light irradiations as also shown in Figure 1. B) of the main manuscript (refer to section 3.2 for details).

1.3 Photopolymerization of L1

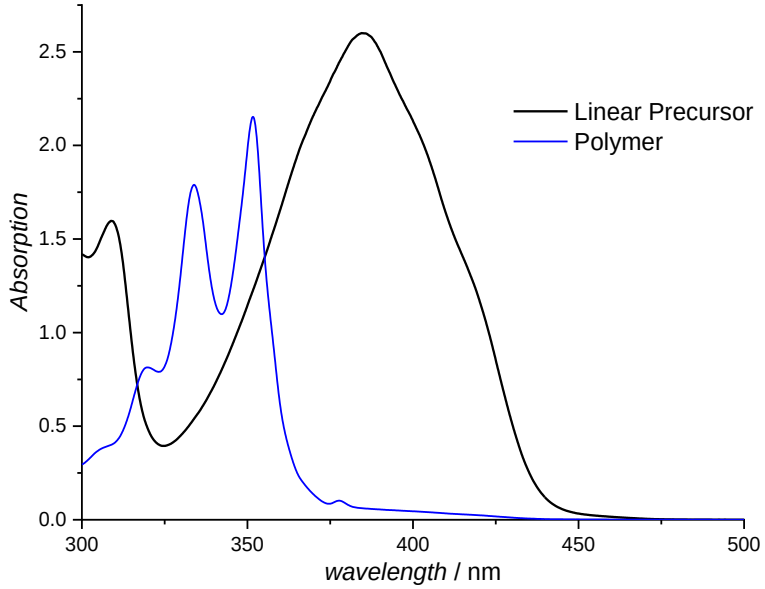
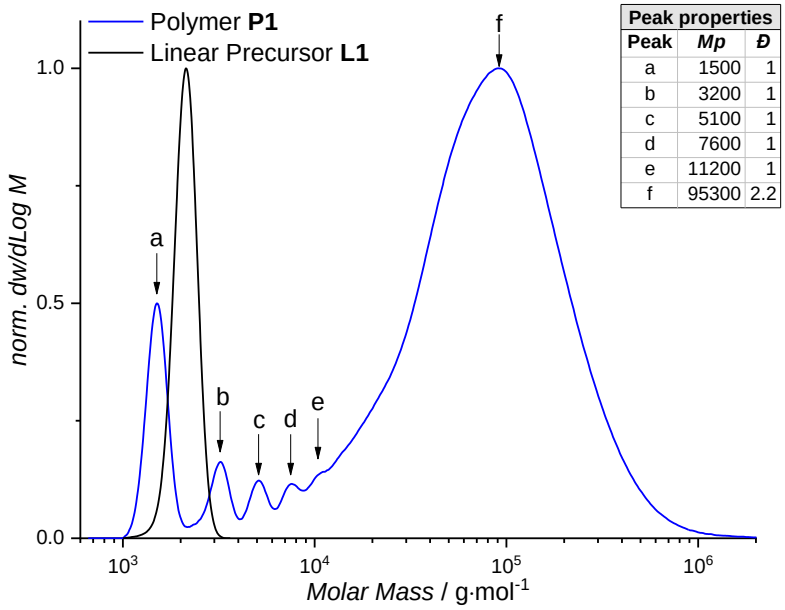


Figure S1.3.1 UV/Vis spectra of L1 and P1 after visible light photopolymerization in THF (0.05 mg mL^{-1}, refer to section 3.3 for details).



Peak properties		
Peak	*Mp*	*Đ*
a	1500	1
b	3200	1
c	5100	1
d	7600	1
e	11200	1
f	95300	2.2

Figure S1.3.2 SEC traces of L1 and P1 after visible light photopolymerization in THF (0.05 mg mL^{-1}, refer to section 3.3 for details).

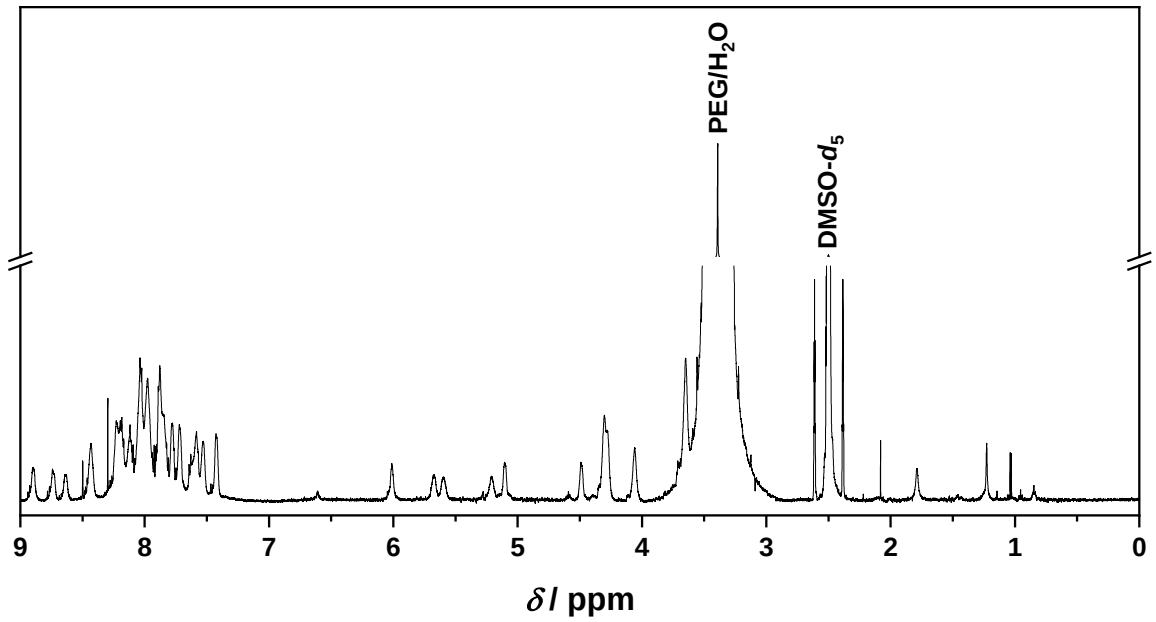


Figure S1.3.3. ^{1}H-NMR spectrum of P1 in DMSO-d_6.

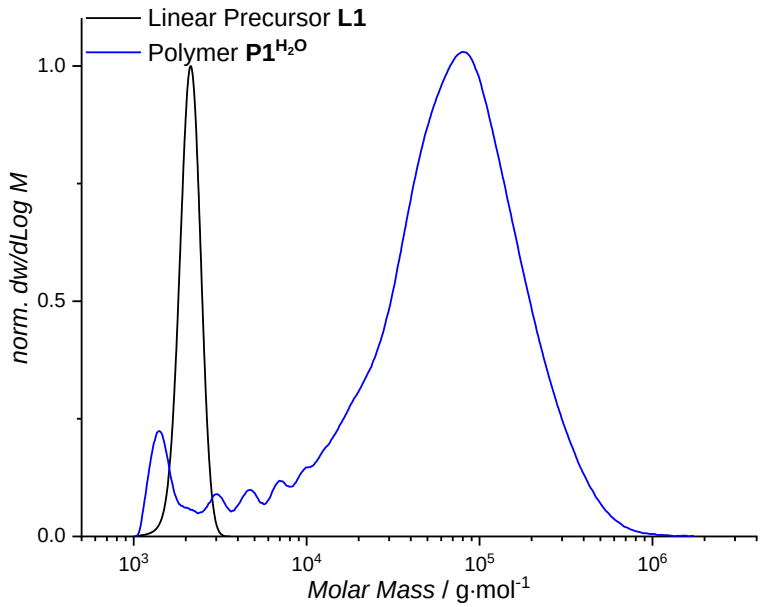


Figure S1.3.4 SEC traces of L1 and P1^{H_2O} after visible light photopolymerization in water (20% DMSO) (50 mg mL^{-1}, refer to section 3.3 for details).

1.4 Stability of P1 under blue irradiation

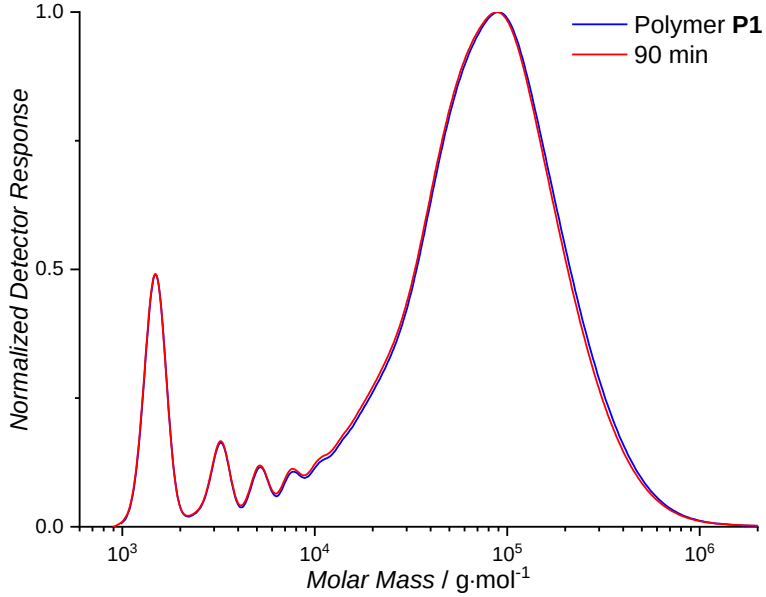


Figure S1.4.1 P1 before and after irradiation with blue light (460 nm) for 90 min.

1.5 Depolymerization of P1

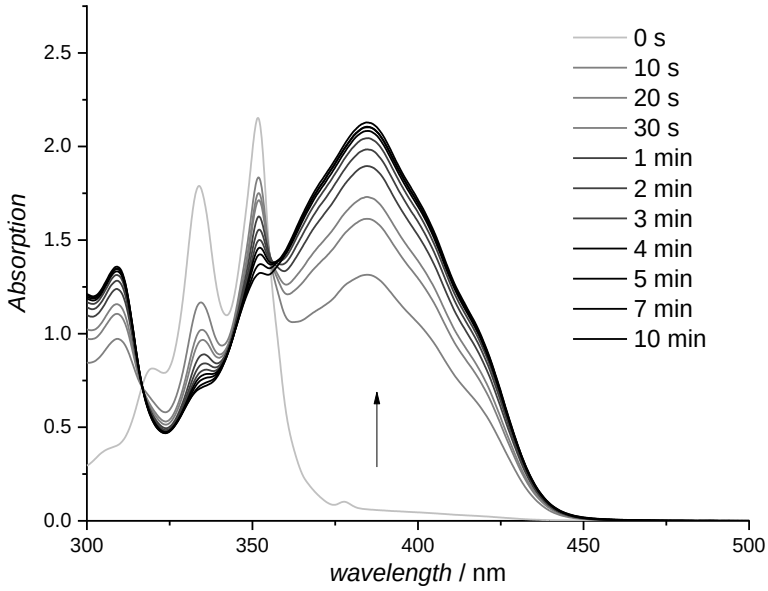


Figure S1.5.1 UV/Vis spectra of P1 in THF (0.05 mg mL^{-1}) after UVB light irradiations (refer to section 3.2 for details).

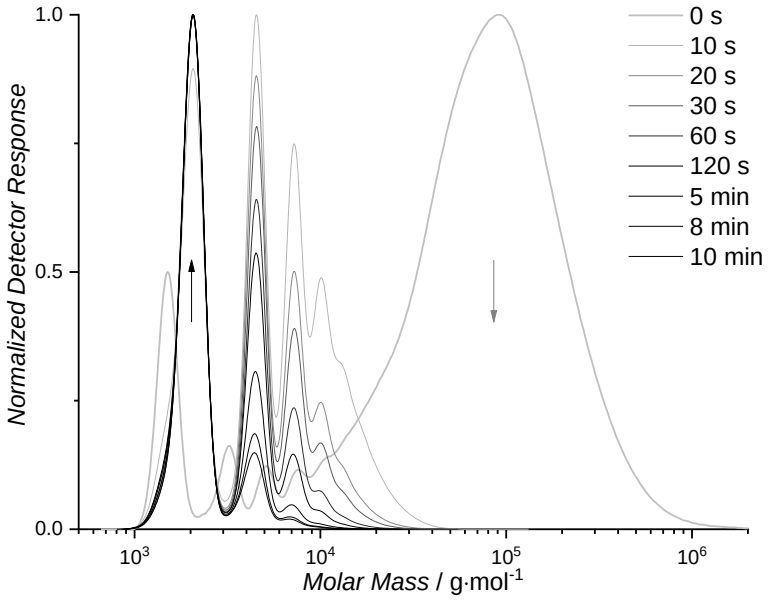


Figure S1.5.2 SEC traces of P1 in THF (0.05 mg mL^{-1}) after UVB light irradiations (refer to section 3.2 for details).

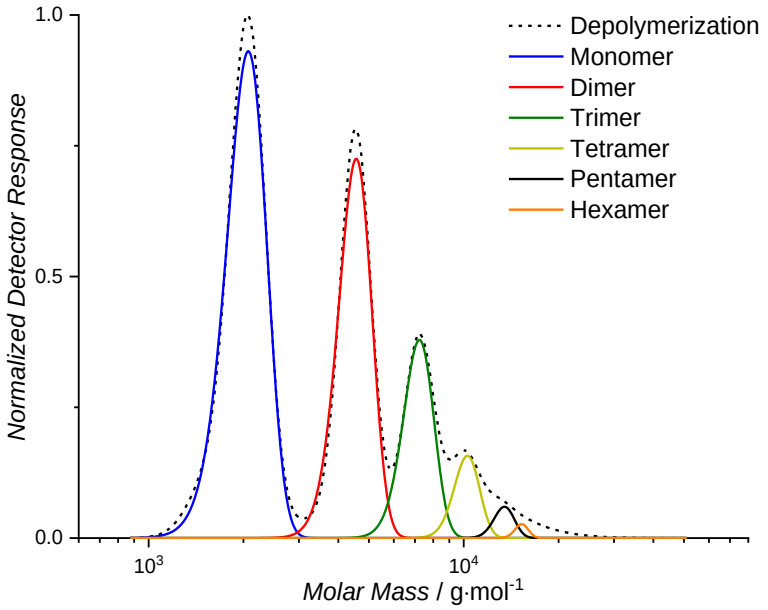


Figure S1.5.3 Deconvolution of the SEC traces of the depolymerization after 30 s to distinguish linear oligomers up to a hexamer.

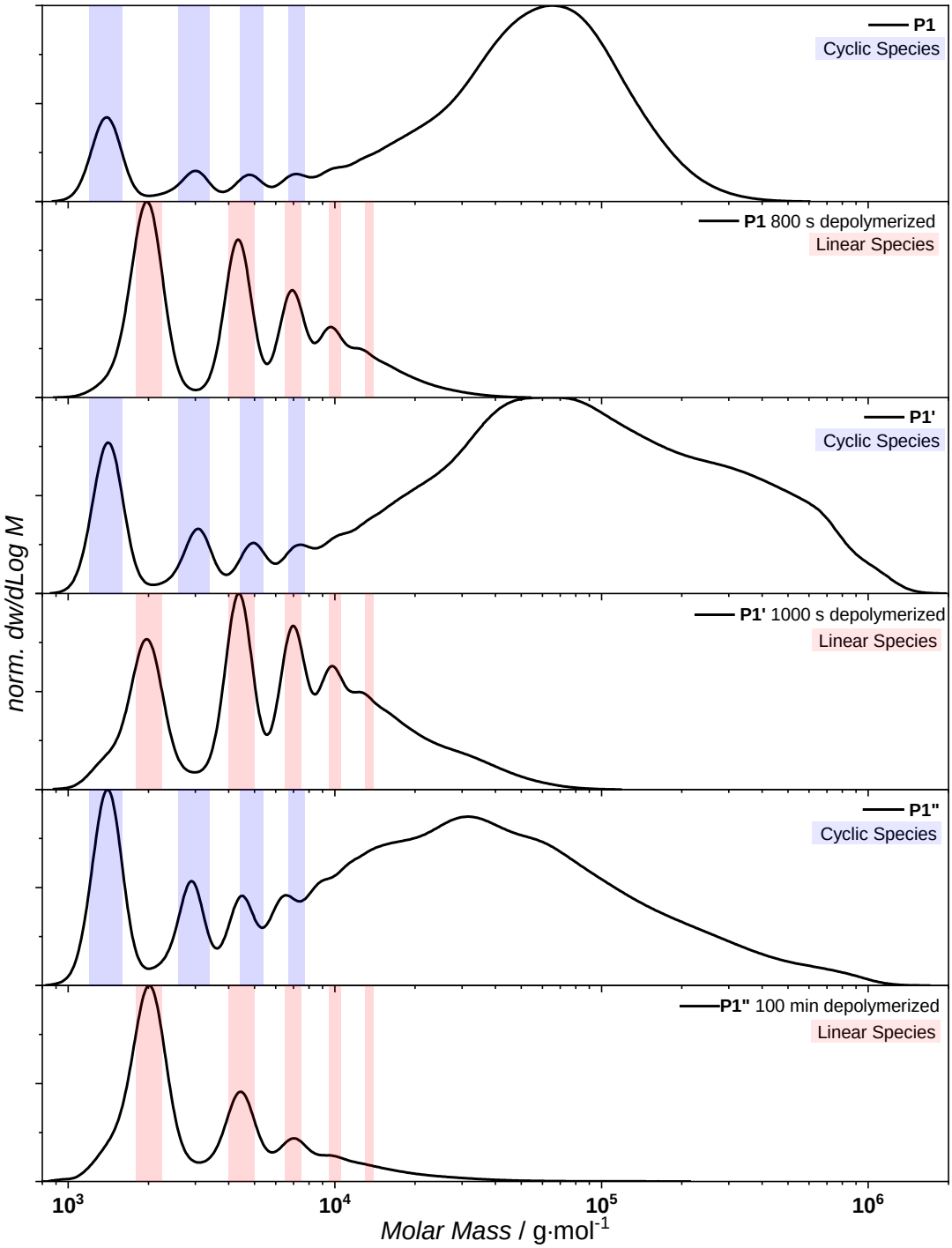


Figure S1.5.4 Three cycles of polymerization and depolymerization of P1, utilizing the photopolymerization procedure described (refer to section 3.3) and the depolymerization procedure developed for higher concentrations (refer to section 3.1.1.).

1.6 Cyclodepolymerization of P1

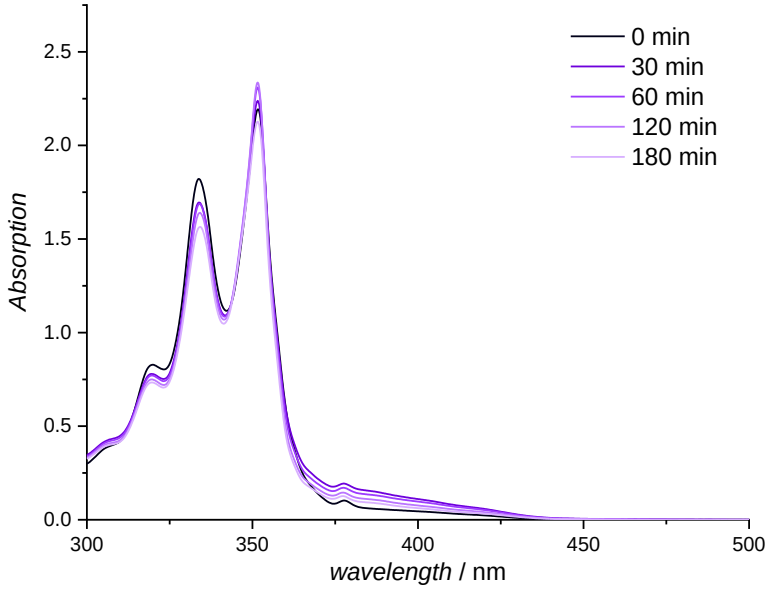


Figure S1.6.1 UV/Vis spectra of P1 in THF (0.05 mg mL^{-1}) after violet light irradiations (refer to section 3 for details).

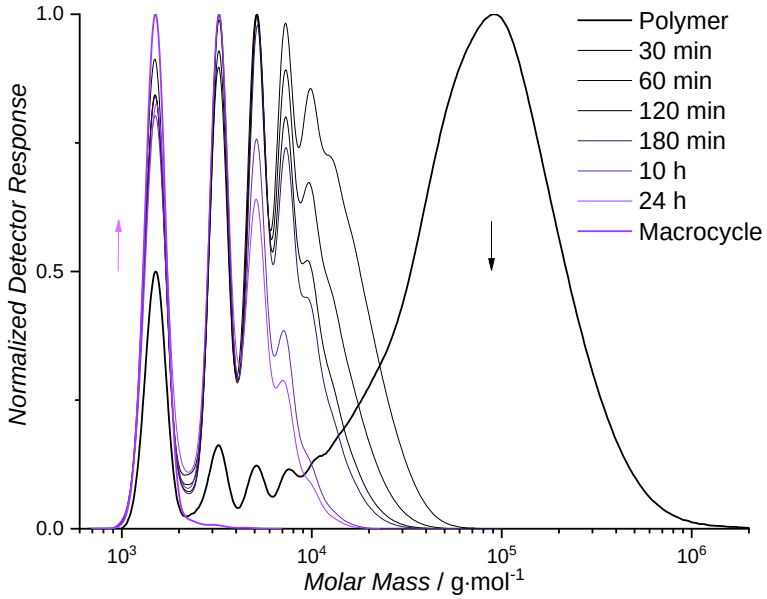


Figure S1.6.2 SEC traces of P1 in THF (0.05 mg mL^{-1}) after violet light irradiations (refer to section 3 for details).

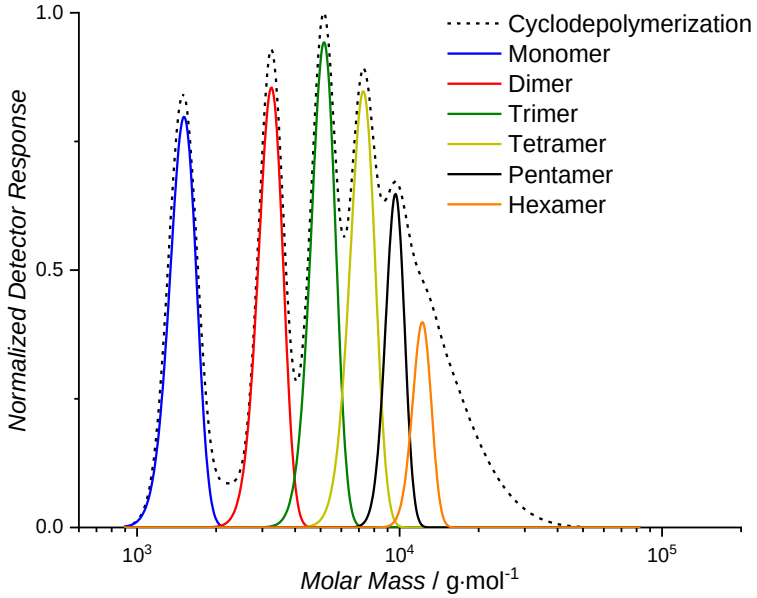


Figure S1.6.3 Deconvolution of the SEC traces of the cyclodepolymerization after 60 min to distinguish cyclic oligomers up to a hexamer.

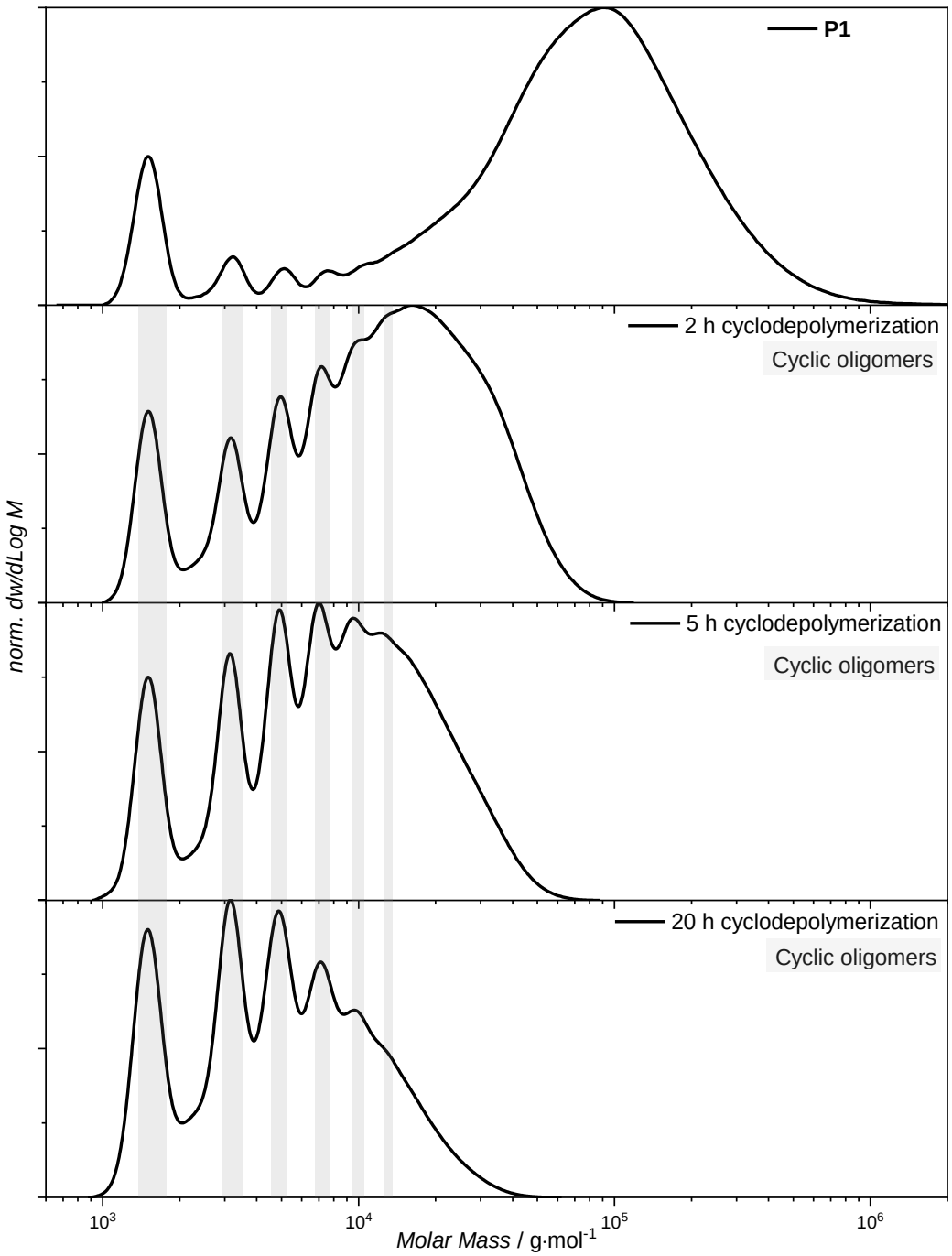


Figure S1.6.4 Cyclic depolymerization at higher concentrations (refer to section 3.1.1).

1.7 Depolymerization of P1 under sun light

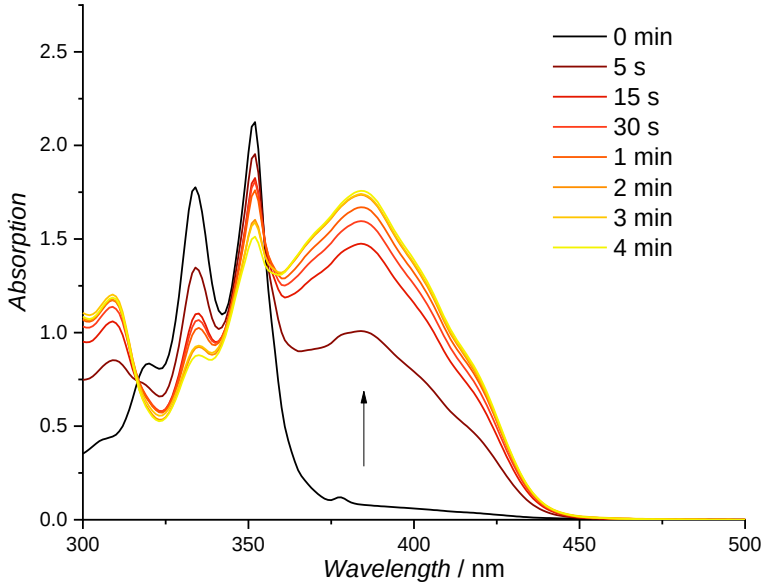


Figure S1.7.1 UV/Vis spectra of P1 in THF (0.05 mg mL^{-1}) after sun light irradiation (refer to section 3.4 for details).

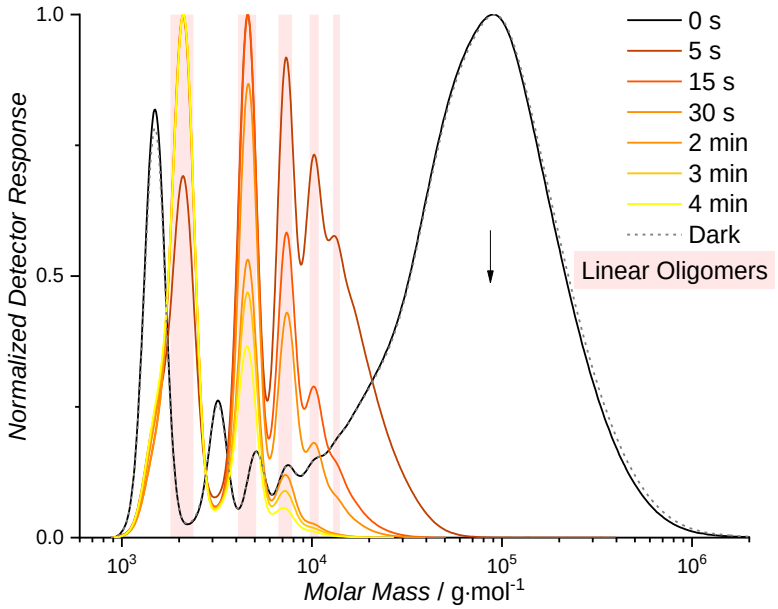


Figure S1.7.2 SEC traces of P1 in THF (0.05 mg mL^{-1}) after sun light irradiation (refer to section 3.4 for details).

1.8 Depolymerization of P1 under ambient light

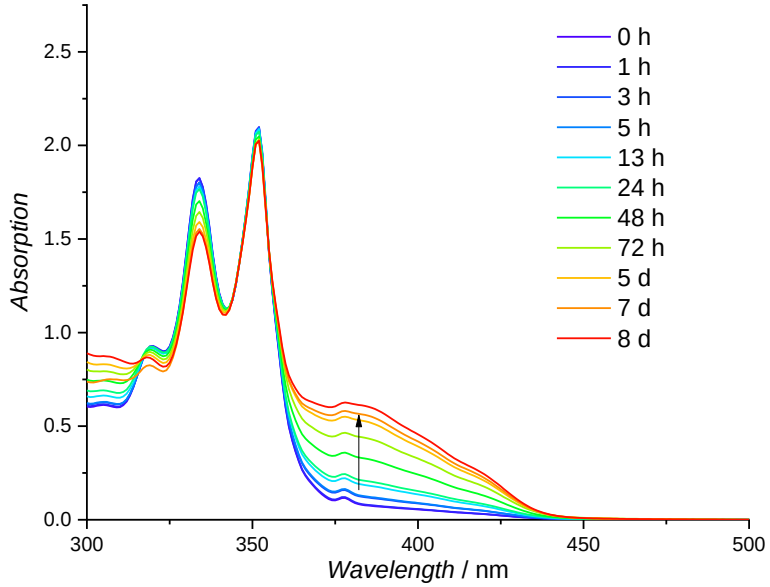


Figure S1.8.1 UV/Vis spectra of P1 in THF (0.05 mg mL^{-1}) after ambient light irradiation (refer to section 3.5 for details).

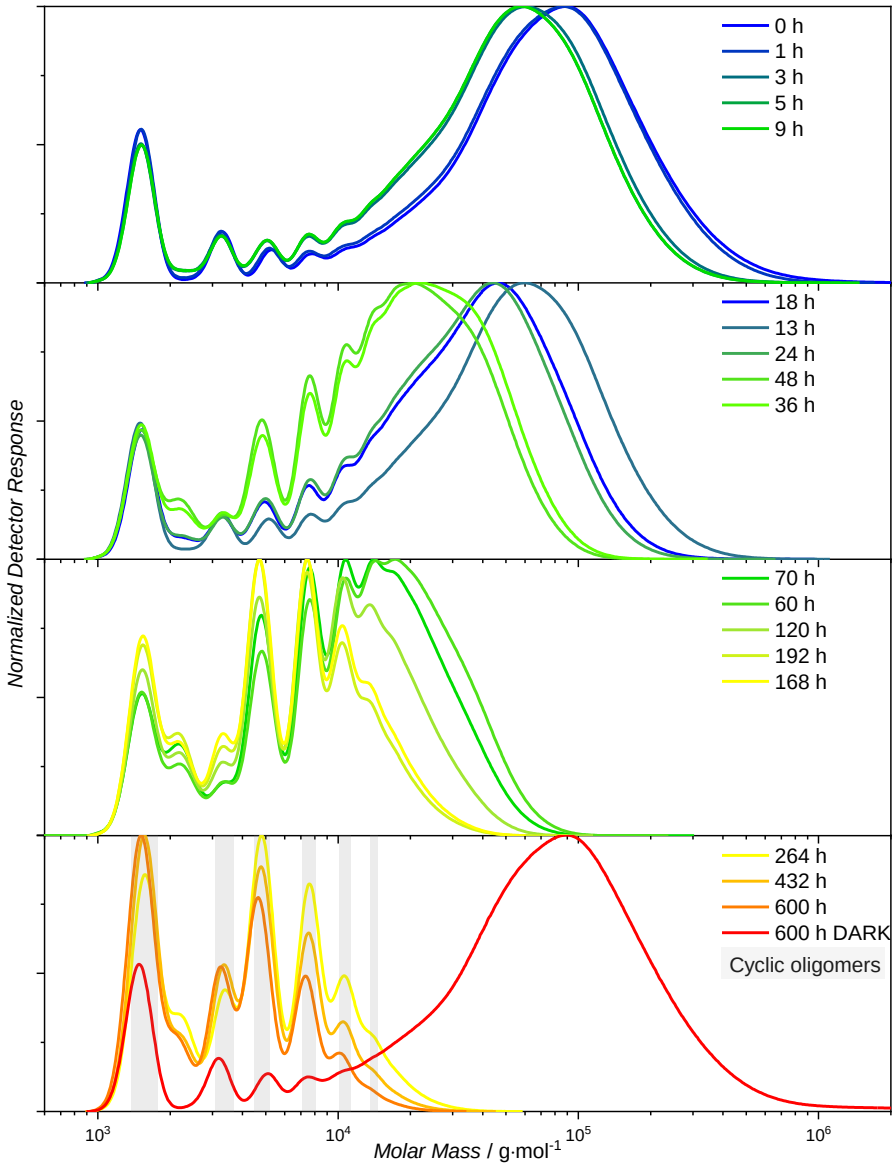


Figure S1.8.2 SEC traces of P1 in THF (0.05 mg mL^{-1}) after ambient light irradiation (refer to section 3.5 for details).

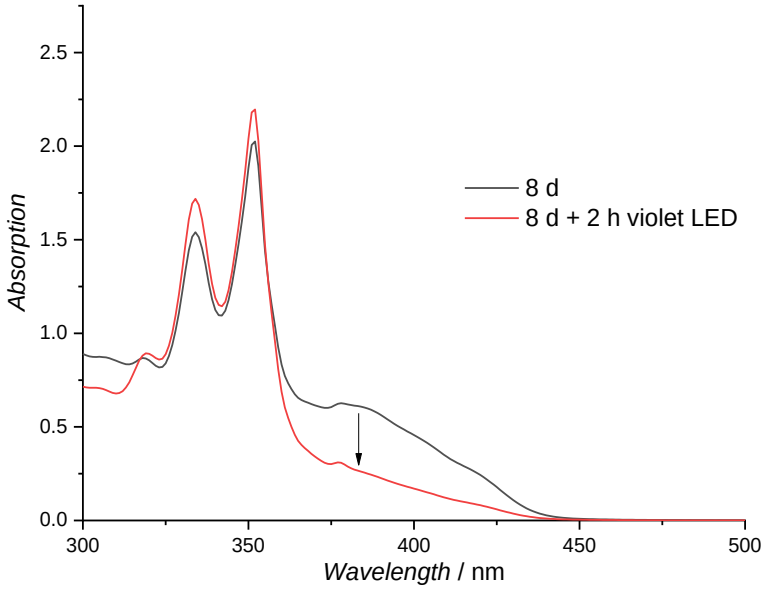


Figure S1.8.3 UV/Vis spectra of P1 in THF (0.05 mg mL^{-1}) after 8 d of ambient light irradiations (black, irradiation as described in 3.5) and subsequent irradiation with violet light to cyclize the linear fragments (red, irradiation as described in 3).

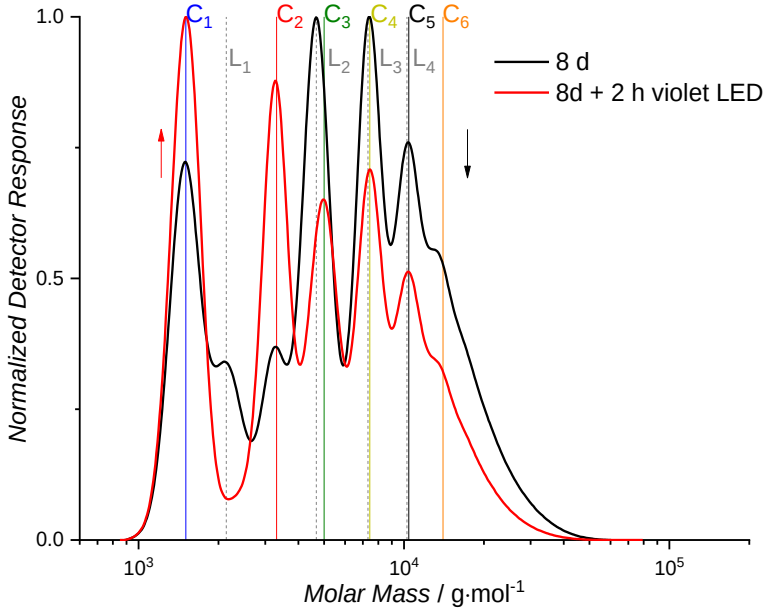


Figure S1.8.4 SEC traces of P1 in THF (0.05 mg mL^{-1}) after 8 d of ambient light irradiations (black, irradiation as described in 3.5) and subsequent irradiation with violet light to cyclize the linear fragments (red, irradiation as described in 3).

1.9 Ion Mobility

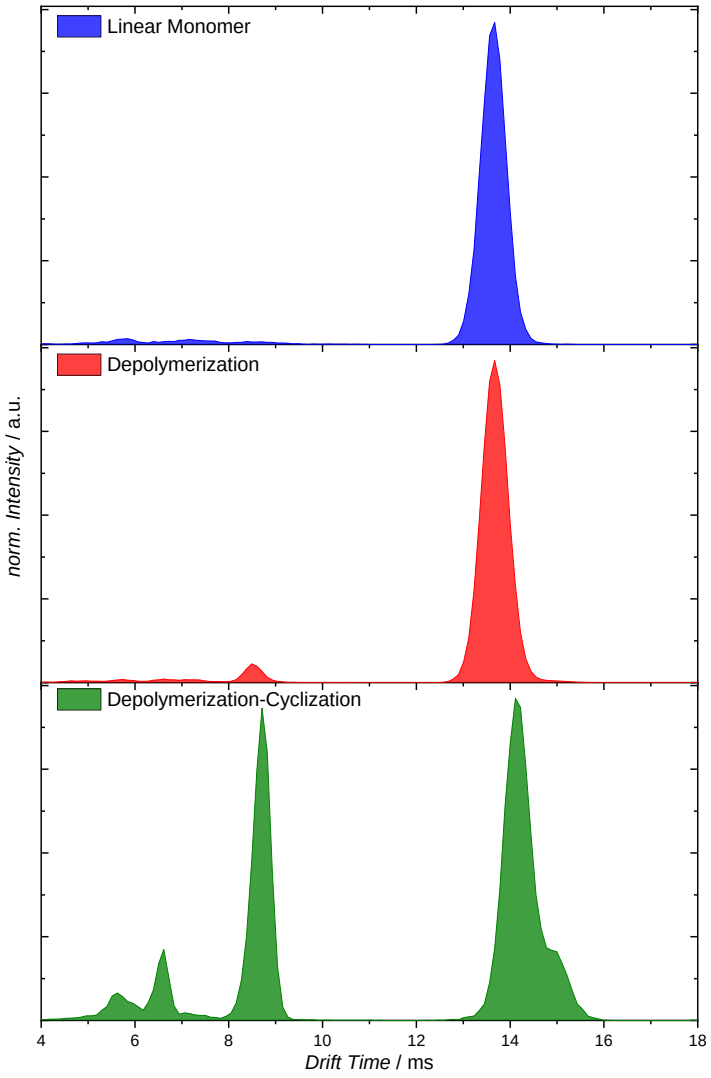


Figure S1.9.1 Drift time distributions of the linear monomer (blue), depolymerization (20 s, red) and cyclodepolymerization (60 min, green).

1.10 XI Extracted-ion chromatography (XIC)

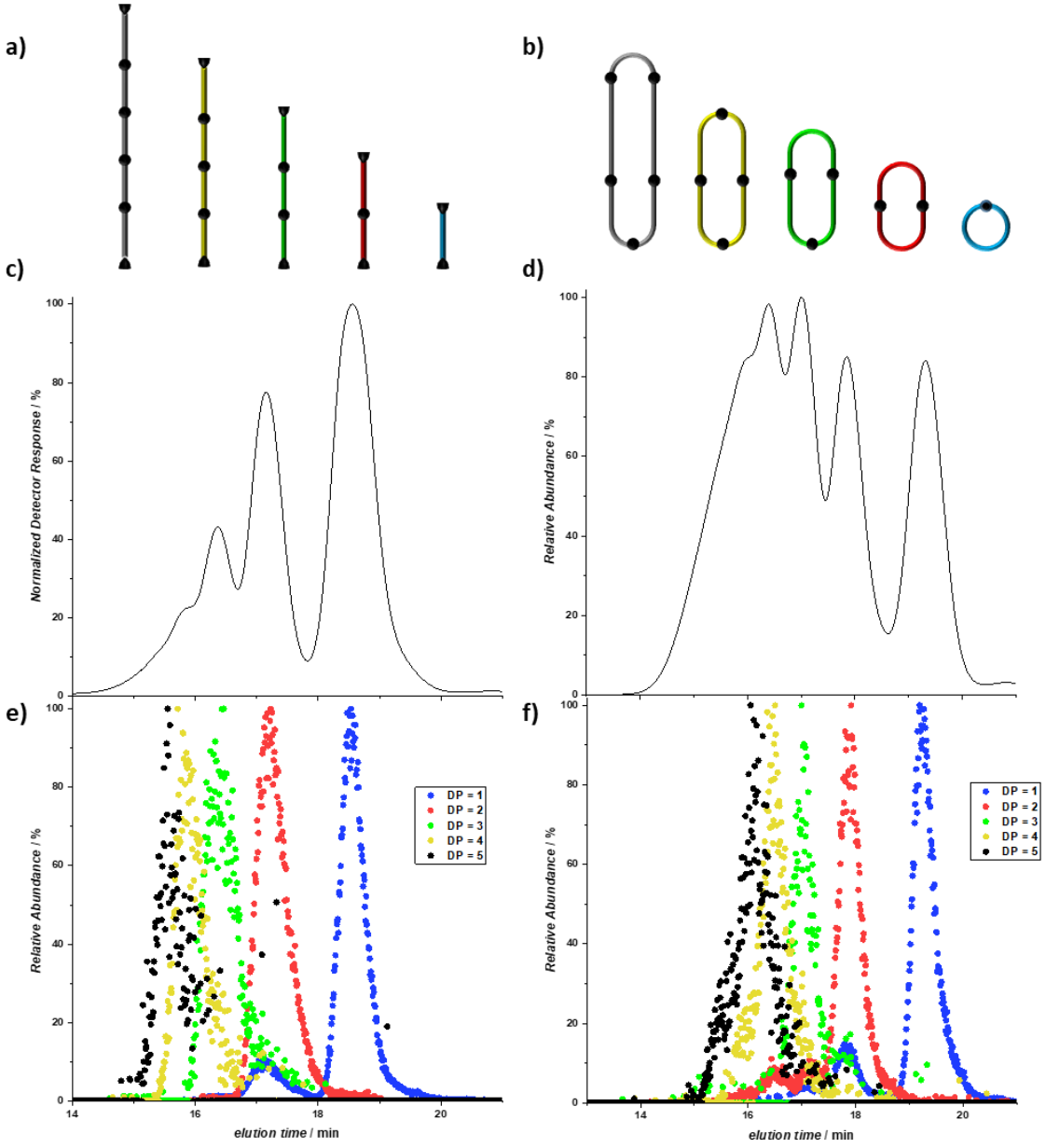


Figure S1.10.1 TOP: Schematic representation of the linear (a) and cyclic (b) oligomers form upon depolymerization of P1. Middle: Normalized SEC traces of the oligomer mixtures obtained after 5 s of UVB (c) or 30 min of blue light irradiation (d). Bottom: XIC traces of the different oligomers (*DP* = 1-5) obtained from UVB (e) or violet light irradiation (f), see Fig S1.102-6 for details of the traced ions.

DP = 1

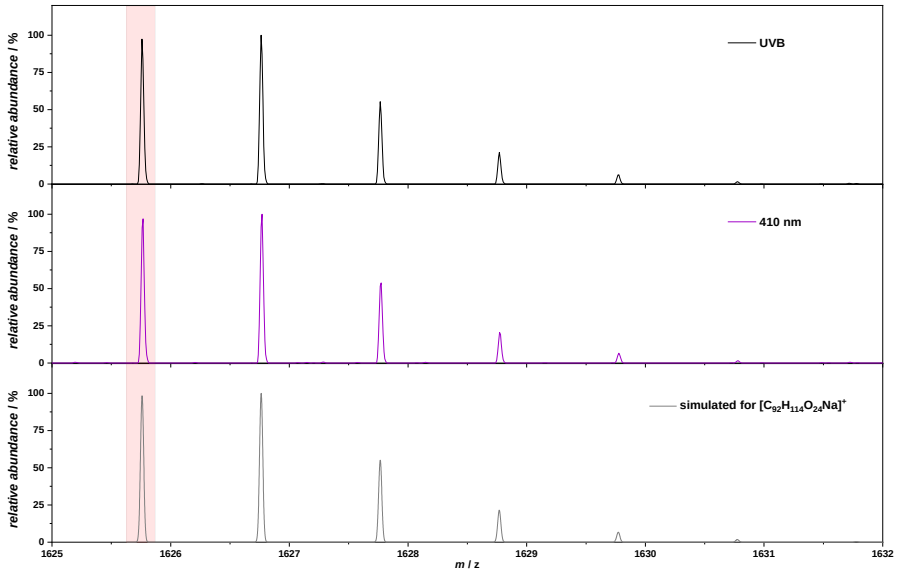


Figure S1.10.2 SEC ESI mass spectra of L1 obtained by irradiation with UVB (top), C1 obtained by irradiation with violet light (middle) and the simulated isotopic patter for $[C_{92}H_{114}O_{24}Na]^+$ corresponding to DP = 1. The *m/z* range followed in the XIC (1625.63-1625.87) is highlighted in red.

DP = 2

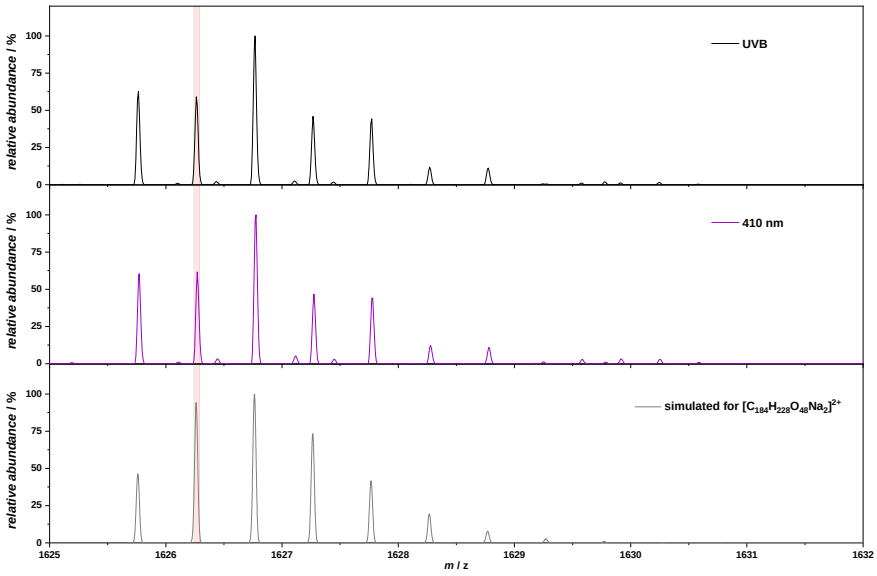


Figure S1.10.3. SEC ESI mass spectra of L2 obtained by irradiation with UVB (top), C2 obtained by irradiation with violet light (middle) and the simulated isotopic patter for $[C_{184}H_{228}O_{48}Na_2]^{2+}$ corresponding to DP = 2. The *m/z* range followed in the XIC (1626.24-1626.29) is highlighted in red.

DP = 3

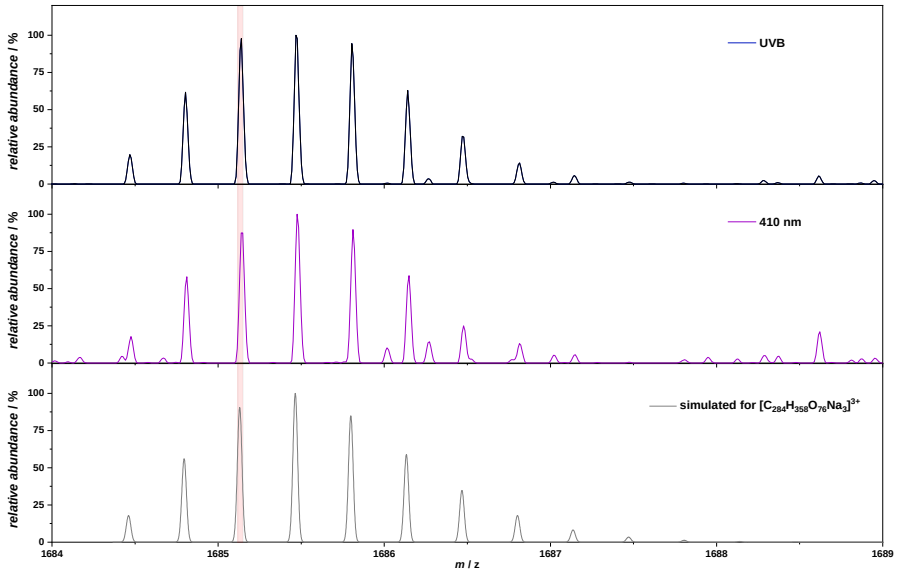


Figure S1.10.4 SEC ESI mass spectra of L3 obtained by irradiation with UVB (top), C3 obtained by irradiation with violet light (middle) and the simulated isotopic patter for $[C_{284}H_{358}O_{76}Na_3]^{3+}$ corresponding to DP = 3. The *m/z* range followed in the XIC (1685.12-1685.15) is highlighted in red.

DP = 4

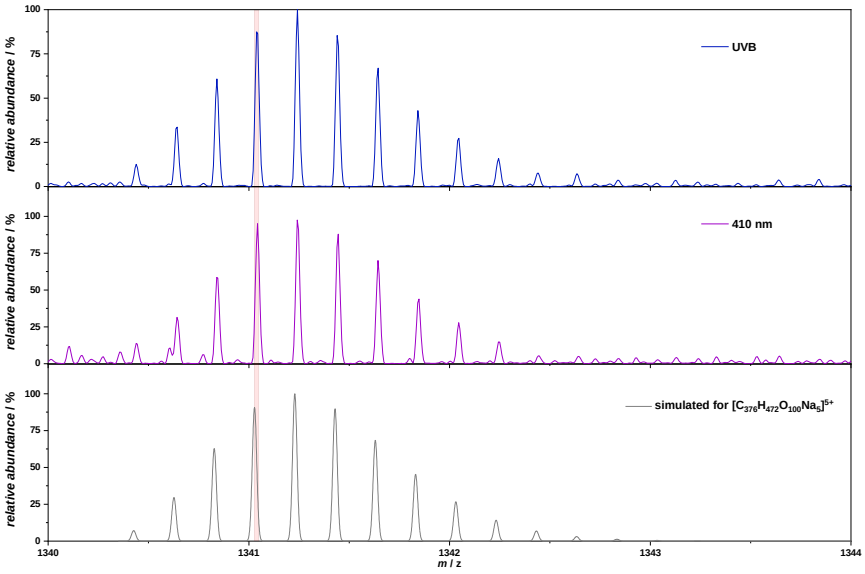


Figure S1.10.5 SEC ESI mass spectra of L4 obtained by irradiation with UVB (top), C4 obtained by irradiation with violet light (middle) and the simulated isotopic patter for $[C_{376}H_{472}O_{100}Na_5]^{6+}$ corresponding to DP = 4. The *m/z* range followed in the XIC (1341.03-1341.05) is highlighted in red.

DP = 5

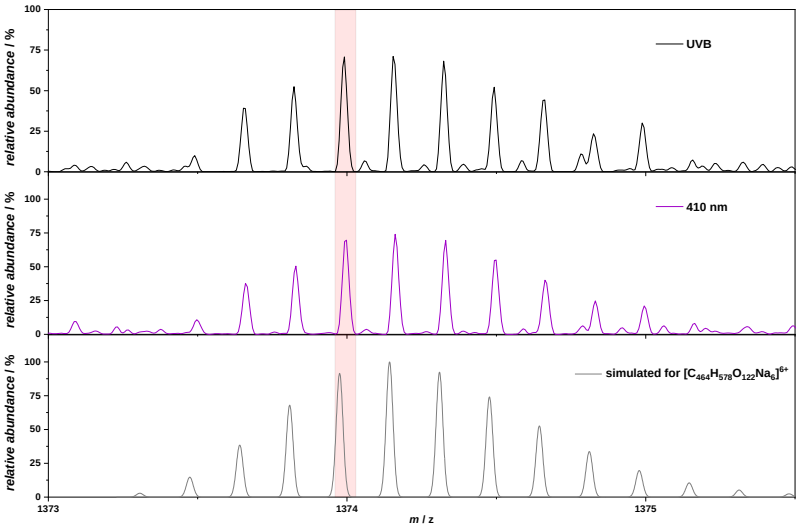


Figure S1.10.6 SEC ESI mass spectra of L5 obtained by irradiation with UVB (top), C5 obtained by irradiation with violet light (middle) and the simulated isotopic patter for $[C_{464}H_{578}O_{122}Na]^{6+}$ corresponding to DP = 5. The *m/z* range followed in the XIC (1373.96-1374.03) is highlighted in red.

1.11 Hydrodynamic radius of oligomers from size exclusion chromatography

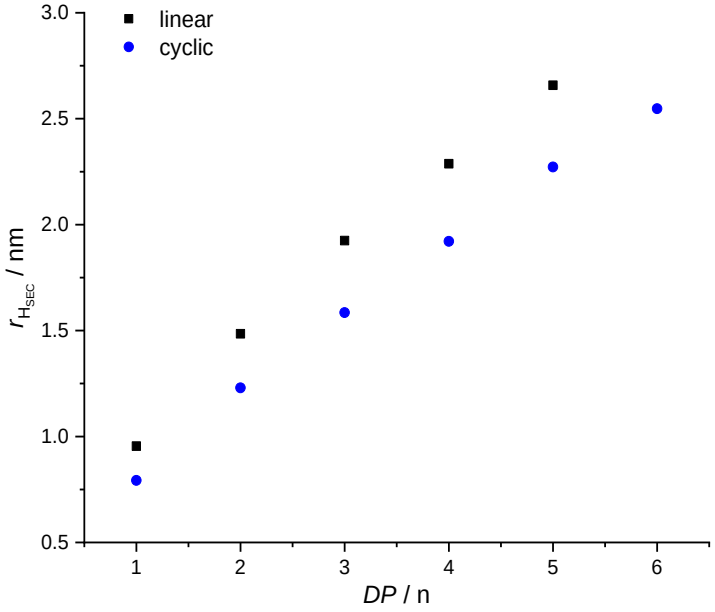


Figure S1.11.1 Hydrodynamic radius via SEC of the linear (black) and cyclic (blue) oligomers.

2. Experimental details

2.1 SEC-ESI-MS

Spectra were recorded on a Q Exactive Plus (Orbitrap) mass spectrometer (Thermo Fisher Scientific, San Jose, CA, USA) equipped with an HESI II probe. The instrument was calibrated in the m/z range 74-1822 using premixed calibration solutions (Thermo Scientific) and for the high mass mode in the m/z range of 600-8000 using ammonium hexafluorophosphate solution. A constant spray voltage of 3.5 kV, a dimensionless sheath gas and a dimensionless auxiliary gas flow rate of 10 and 0 were applied, respectively. The capillary temperature was set to 320 °C, the S-lens RF level was set to 150 and the aux gas heater temperature was set to 125 °C. The Q Exactive was coupled to an UltiMate 3000 UHPLC System (Dionex, Sunnyvale, CA, USA) consisting of a pump (LPG 3400SD), autosampler (WPS 3000TSL), and a temperature controlled column department (TCC 3000). Separation was performed on two mixed bed size exclusion chromatography columns (Agilent, Mesopore 250 × 4.6 mm, particle diameter 3 µm) with a precolumn (Mesopore 50 × 7.5 mm) operating at 30 °C. THF at a flow rate of 0.30 mL·min^{-1} was used as eluent. The mass spectrometer was coupled to the column in parallel to an UV-detector (VWD 3400, Dionex), and a RI-detector (RefractoMax520, ERC, Japan) in a setup described earlier.[1] 0.27 mL·min^{-1} of the eluent were directed through the UV- and RI-detector and 30 µL·min^{-1} were infused into the electrospray source after post-column addition of a 50 µM solution of sodium iodide in methanol at 20 µL·min^{-1} by a micro-flow HPLC syringe pump (Teledyne ISCO, Model 100DM). A 100 µL aliquot of a polymer solution with a concentration of 2 mg·mL^{-1} was injected into the SEC system.

2.2 THF-SEC

The SEC measurements were conducted on a *PSS* SECurity2 system consisting of a *PSS* SECurity Degasser, *PSS* SECurity TCC6000 Column Oven (35 °C), *PSS* SDV Column Set (8 x 150 mm 5 µm Precolumn, 8 x 300 mm 5 µm Analytical Columns, 100000 Å, 1000 Å and 100 Å) and an *Agilent* 1260 Infinity Isocratic Pump, *Agilent* 1260 Infinity Standard Autosampler, *Agilent* 1260 Infinity Diode Array and Multiple Wavelength Detector (A: 254 nm, B: 360 nm), *Agilent* 1260 Infinity Refractive Index Detector (35 °C). HPLC grade THF, stabilized with BHT, is used as eluent at a flow rate of 1 mL·min^{-1}. Narrow disperse linear poly(methyl methacrylate) (M_n: 202 g·mol^{-1} to 2.2x10^6 g·mol^{-1}) standards (*PSS* ReadyCal) were used as calibrants. All samples were passed over 0.22 µm PTFE membrane filters. Molecular weight and dispersity analysis was performed in *PSS* WinGPC UniChrom software (version 8.2).

2.3 Hydrodynamic radius from SEC

Due to the separation mechanism the primary result in SEC is the hydrodynamic volume of the analytes. For practical reasons this is generally transformed to molar mass equivalents via a calibration with standards of known molar masses. In the same manner one can calibrate the elution volume (V_E) in respect of r_H via literature values for the calibrants. Narrow disperse linear poly(styrene) (PS) standards (M_P: 266 g·mol^{-1}, 370 g·mol^{-1}, 474 g·mol^{-1}, 578 g·mol^{-1}, 682 g·mol^{-1}, 1306 g·mol^{-1}, 2280 g·mol^{-1}, 3470 g·mol^{-1}, 4920 g·mol^{-1}, 6540 g·mol^{-1}, 8680 g·mol^{-1}, 15700 g·mol^{-1}, 17600 g·mol^{-1}, 25500 g·mol^{-1}, 34800 g·mol^{-1}, 42400 g·mol^{-1}, 66000 g·mol^{-1}, 130000 g·mol^{-1}, 277000 g·mol^{-1}, 552000 g·mol^{-1}, 1210000 g·mol^{-1}, 2520000 g·mol^{-1})) were used to calibrate the column set (see 2.2) in respect of PS molar mass equivalents and k (125.8 ml·g^{-1}) and α (0.715)[2] were used to calculate the rH of said standards via the Mark-Houwink equation (**1**) and the relation of the hydrodynamic volume and molar mass (Equation **2**) 1 to gain polymer independent r_H (**4**) from V_E.

1 $$k \cdot M^{\alpha} = [\eta]$$

2 $$k \cdot M \cdot [\eta] = V_H$$

3 $$V_H = \frac{4}{3}\pi r_H^3$$

4 $$\sqrt[3]{\frac{V_H}{\frac{4}{3}\pi}} = r_H$$

2.4 1D NMR Measurements

^{1}H- and ^{13}C-spectra were recorded on a *Bruker* System 600 Ascend LH, equipped with a BBO-Probe (5 mm) with z-gradient (^{1}H: 600.13 MHz, ^{13}C: 150.90 MHz,) or a Bruker 400 UltraShield spectrometer equipped with a Quattro Nucleus Probe (QNP) with an operating frequency of 400 MHz (^{1}H). All measurements were carried out in deuterated solvents. The chemical shift (δ) is recorded in parts per million (ppm) and relative to the residual solvent protons.[3] The measured coupling constants were calculated in Hertz (Hz). To analyze the spectra the software MESTRENOVA 11.0 was used. The signals were quoted as follows: s = singlet, bs = broad singlet, d = doublet, t = triplet and m = multiplet.

2.5 UV-VIS Spectroscopy

UV/vis spectra were recorded on a *Shimadzu* UV-2700 spectrophotometer equipped with a CPS-100 electronic temperature control cell positioner. Samples were prepared in THF and measured in *Hellma Analytics* quartz high precision cells with a path length of 10 mm at ambient temperature.

2.6 ATR-FTIR Spectroscopy

FT-IR spectra were recorded on a *Thermo Fisher* Nicolet iS50-FTIR using a germanium ATR crystal from 4000 cm^{-1} to 400 cm^{-1}. Data recording and manipulation was performed in *Thermo Fisher* Omnic 9 v9.6. Spectra are reported from low to high wavenumbers, evaluation was conducted with *OriginLab* OriginPro2017. Bands are characterized regarding their intensity (*I*) as strong (s, $I > \frac{2}{3}I_{Strongest}$), medium (m, $\frac{1}{3}I_{Strongest} < I < \frac{2}{3}I_{Strongest}$) and weak (w, $\frac{1}{3}I_{Strongest} > I$) after baseline correction (10 points, spline fit).

2.7 Ion mobility

Ion-mobility measurements were carried out using a traveling wave ion mobility mass spectrometer fitted with an electrospray ionisation source (SYNAPT G2-S*i*, Waters, Wilmslow, UK). Mass spectra were acquired between *m/z* 500 – 5000, and all ion mobility spectra were acquired in successive runs on the same day to minimise any effects of temperature or humidity changes on the measured arrival time distribution. Samples were prepared in methanol and directly infused at a rate of 20 μL min^{-1}, with source settings: ESI capillary voltage +0.5kV, desolvation temperature 250 ºC and source temperature 100 ºC. Gas flow rates for the cone and desolvation gasses were set at 50 and 600 L hr^{-1}, respectively. For IMS separation, a Travelling Wave velocity of 650 ms^{-1} and amplitude of 40 V were used. To minimise TOF pusher aliasing, the Transfer wave velocity was set to 111 ms^{-1}. All other parameters relating to the travelling wave ion optics were set to their default values. The arrival time distributions of $[C_{86}H_{102}O_{21}Na]^+$, (*m/z* 1493) was used to infer the arrival time distribution of the respective samples.

3. Photochemical Procedures

3.1 Cyclization of L1 / photocyclodepolymerization of P1 (λ = 410 nm)

Solutions of **L1** or **P1** in THF (0.05 mg mL^{-1}) were irradiated in a fluorescence cuvette with a 10 W LED provided by Future Eden Ltd. UV/Vis spectra were recorded and the same cuvette and SEC traces were recorded at the same concentration.

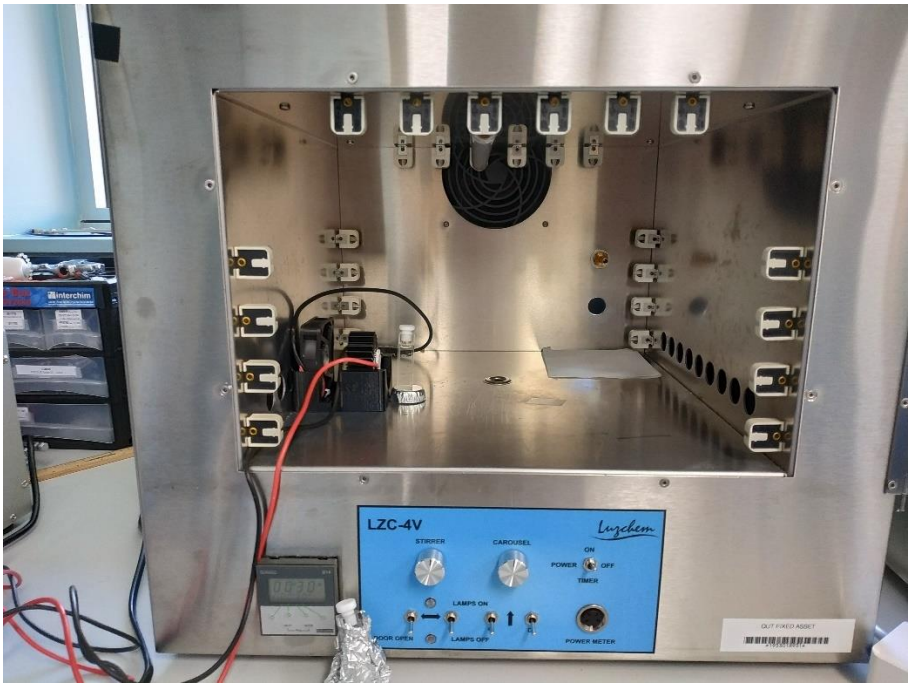


Figure S3.1.1 Irradiation setup used for irradiation at λ = 410 nm.

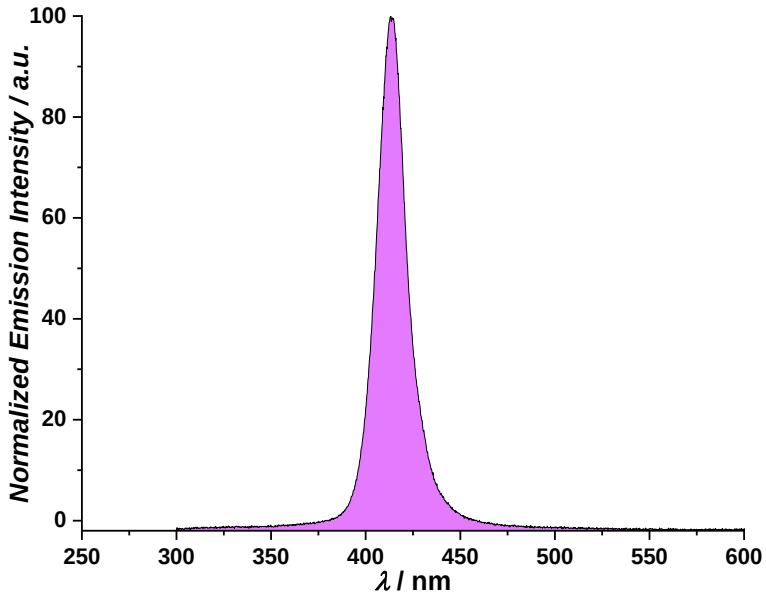


Figure S3.1.2 Emission spectrum of the violet LED.

3.1.1 Photocyclodepolymerization of P1 at higher concentrations

Solutions of **P1** in THF (20 mg mL^{-1}) were irradiated in closed glass vials and irradiated with a 10 W LED provided by Future Eden Ltd. while stirring.

Figure S3.1.1.1 Irradiation set-up employed for irradiation at λ = 410 nm at 20 mg mL^{-1}.

3.2 Decyclization of L1/ depolymerization of P1

Solutions of **C1** or **P1** in THF (0.05 mg mL^{-1}) were irradiated in a UV/Vis cuvette in a Luzchem photoreactor, equipped with two UVB lamps yielding an irradiance of 1.1 mW cm^{-2} at the position of the sample.

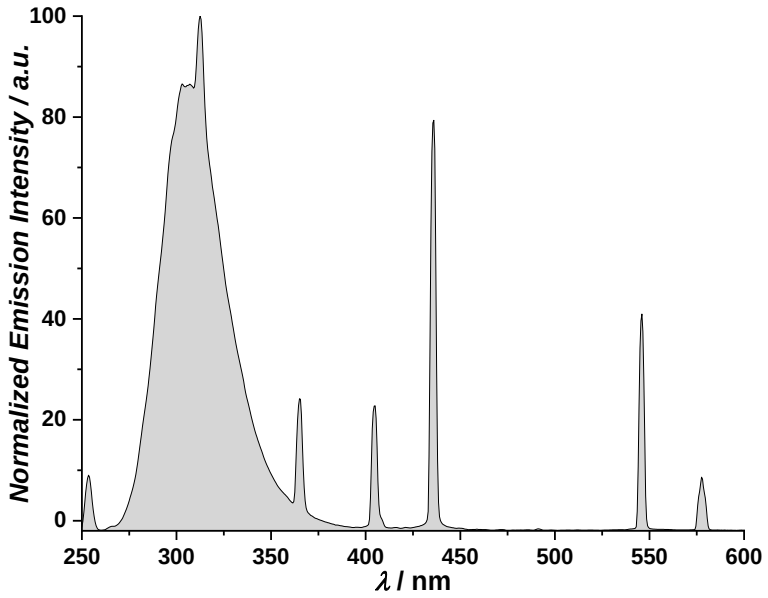


Figure S3.2.1 Emission spectrum of the LZC-UVB lamps.

Figure S3.2.2 Irradiation setup used for the decyclization of L1 and depolymerization of P1 under UVB light irradiation.

3.2.1 Photodepolymerization of P1 at higher concentrations

Solutions of **P1** in THF (20 mg mL^{-1}) were irradiated in a closed glass vials in a Luzchem photoreactor, equipped with two UVB lamps while stirring.

Figure S3.2.1.1 Irradiation setup used for irradiation with UVB light at 20 mg mL^{-1}.

3.3 Photopolymerization of L1

8 mg of **L1** were dissolved in 30 µL THF (266 mg mL^{-1}) in a glass vial. The solution was purged with argon for 5 min and placed in a Luzchem photoreactor with an irradiance of 1.7 mW cm^{-2} at the position of the sample. After irradiation overnight, the solvent was removed under reduced pressure to obtain **P1**. For polymerizations in aqueous media (20% DMSO in H_2O), the reaction mixture (50 mg mL^{-1}) was stirred during irradiation.

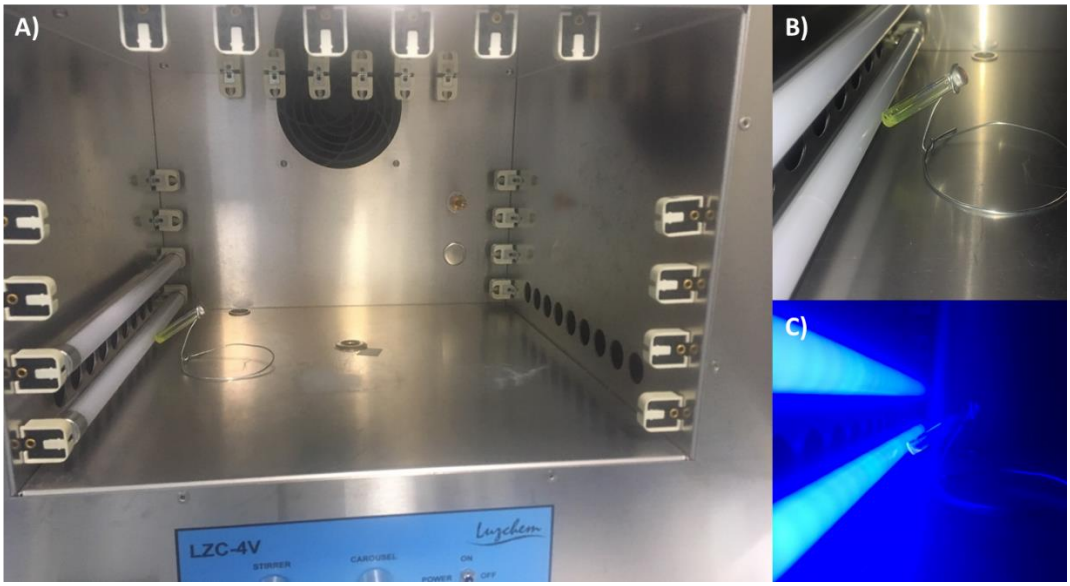


Figure S3.3.1 Irradiation setup used for the photopolymerization of L1 (A). Close up of the glass vial with LEDs turned off (B) and on (C).

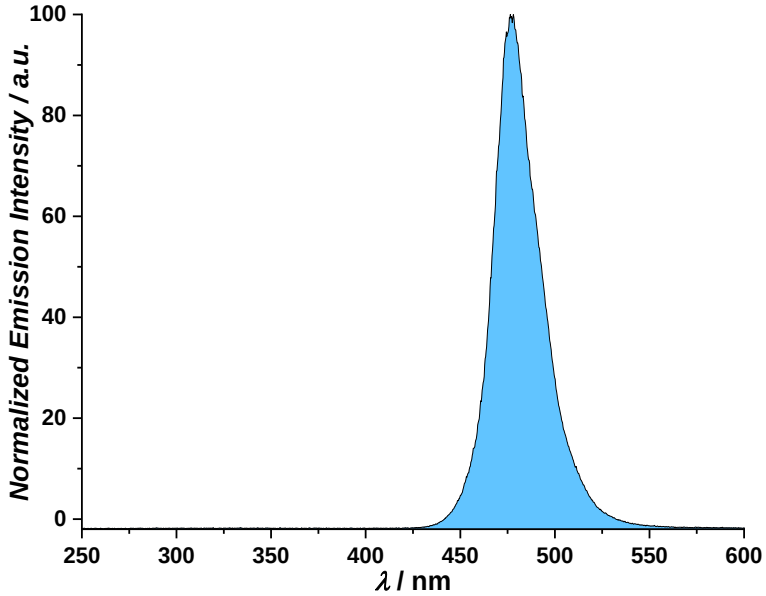


Figure S3.3.2 Emission spectrum of the blue LED used for the photopolymerization.

3.4 Photodepolymerization under sun light irradiation

Solutions of **P1** in THF (0.05 mg mL^{-1}) were placed in fluorescence cuvettes on top of a small box covered in aluminum foil directly into the sun (see figure below). All experiments were carried out on the 30th of July 2019 on a clear Queensland winter day between 09:00 and 12:00 (27.477331°S; 153.029053°E, daily solar exposure 15.7 MJ m^{-2} as provided by the Bureau of Meteorology).

Figure S3.4.1 A) Irradiation setup used for sun light experiments. B) Perspective of the cuvettes facing the sun.

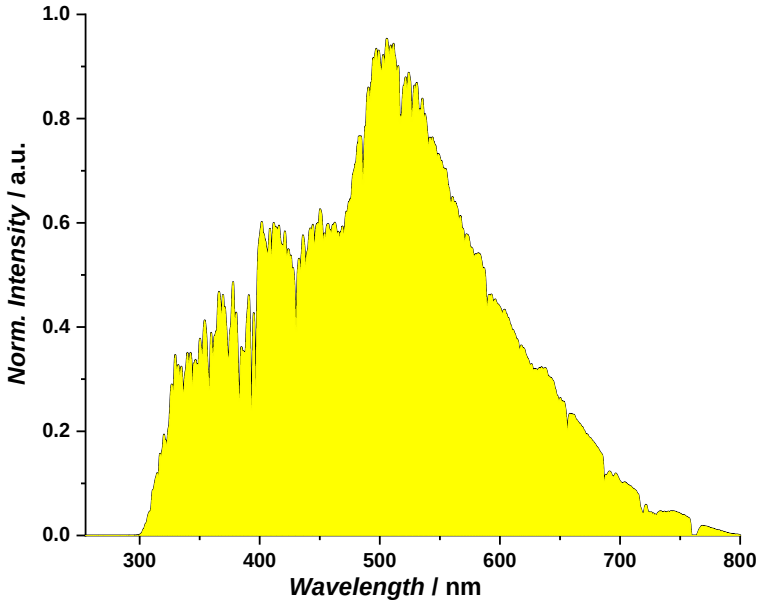


Figure S3.4.2 Emission spectrum of sunlight measured during the experiments next to the cuvettes, facing the same direction recorded on the 30th of July 2019.

3.5 Photodepolymerization under ambient light irradiation

Solutions of **P1** in THF (0.05 mg mL^{-1}) were placed in fluorescence cuvettes on top of a small box covered in aluminum foil in the laboratory (refer to the figure below). The lighting of the laboratory was on for day and night to allow for a constant irradiation of the sample under laboratory ambient conditions yielding an irradiance of 0.2 mW cm^{-2} at the position of the sample.

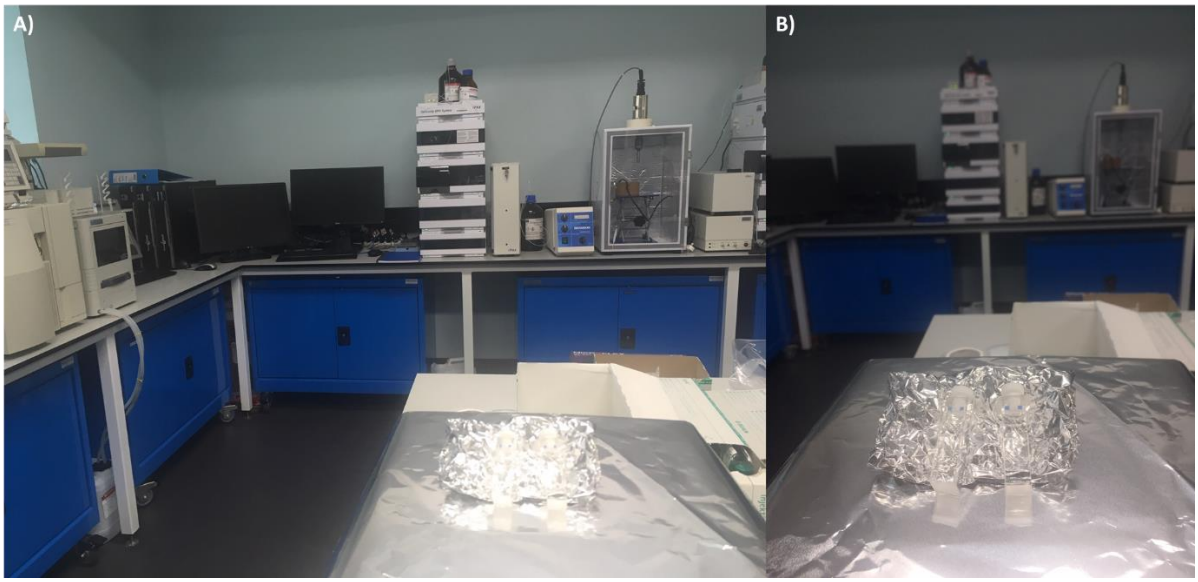


Figure S3.5.1 A) Irradiation setup used for ambient light experiments. B) Close up of the cuvettes.

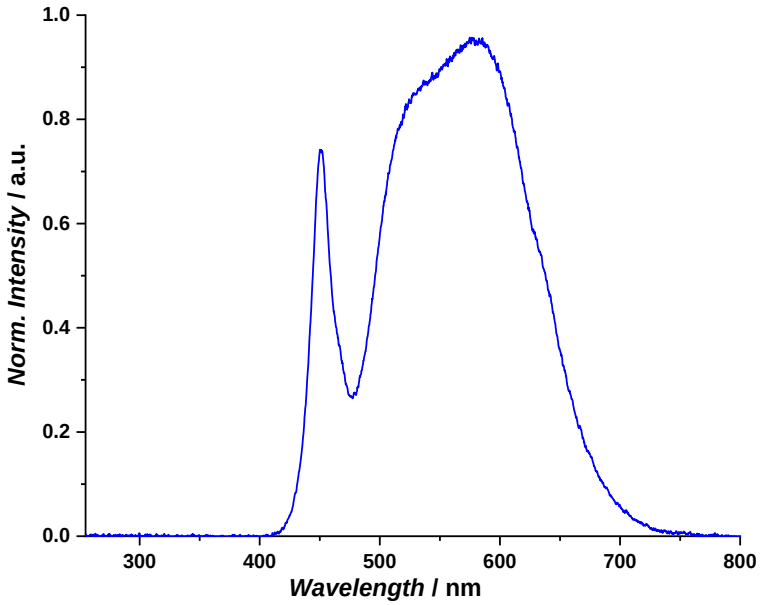


Figure S3.5.2 Emission spectrum of the laboratory light.

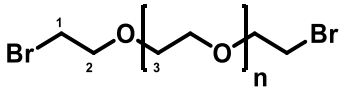
4. Synthetic procedures

4.1 Materials

Unless stated otherwise, all chemicals and solvents were used as received from the supplier without further purification.

Poly(ethylene glycol) 1000 (Merck), N-bromosuccinimide (Merck), triphenylphosphine (Chemsupply), Cs_2CO_3(Thermo Fisher Scientific), THF (Thermo Fisher Scientific.), dichloromethane (Thermo Fisher Scientific, after drying and purification with SP-1 Stand Alone Solvent Purification System LC Technology Solutions Inc.), methanol (Thermo Fisher Scientific), dichloromethane-d_2 (Sigma-Aldrich), DMSO-d_6 (Sigma-Aldrich).

4.2 Poly(ethylene glycol) bis(bromine)



PEG (1000 g·mol^{-1}, 2.0896 g, 2.1 mmol, 1 eq.) and PPh_3 (2.6539 g, 10 mmol, 5 eq.) were dissolved in DCM (25 mL) in a round bottom flask at 35 °C. To this mixture a solution of NBS (1.7801 g, 10 mmol, 5 eq.) in DCM (50 mL) was added dropwise within 20 min, changing color to a dark brown, and the reaction was allowed to stir at 35 °C over night. The organic phase was washed with a small amount of saturated $NaHCO_3$, changing the color to green, 1 M HCl, saturated Na_2SO_3 and brine turning the color to dark blue. The organic phase was filtered over dry $MgSO_4$ which also absorbed the color. The solvent was evaporated under reduced pressure to yield PEG-bis(bromine)

Yield: 1.3426 g (57 %, 1.2 mmol, pale yellow waxy solid).

SEC-ESI-MS: Calculated for $C_{42}H_{84}Br_2O_{20}Na^+$: 1626.76258; found: 1626.76656.

^{1}H NMR (600 MHz, Dichloromethane-d_2) δ / ppm = 3.83 (t, 4H, CH-2) 3.71-3.66 (m, 78H, CH-3) 3.49 (t, 4H, CH-1).

^{13}C NMR (600 MHz, Chloroform-d) δ / ppm = 71.3 (s, C-2) 70.7-70.6 (m, C-3) 30.4 (s, C-1).

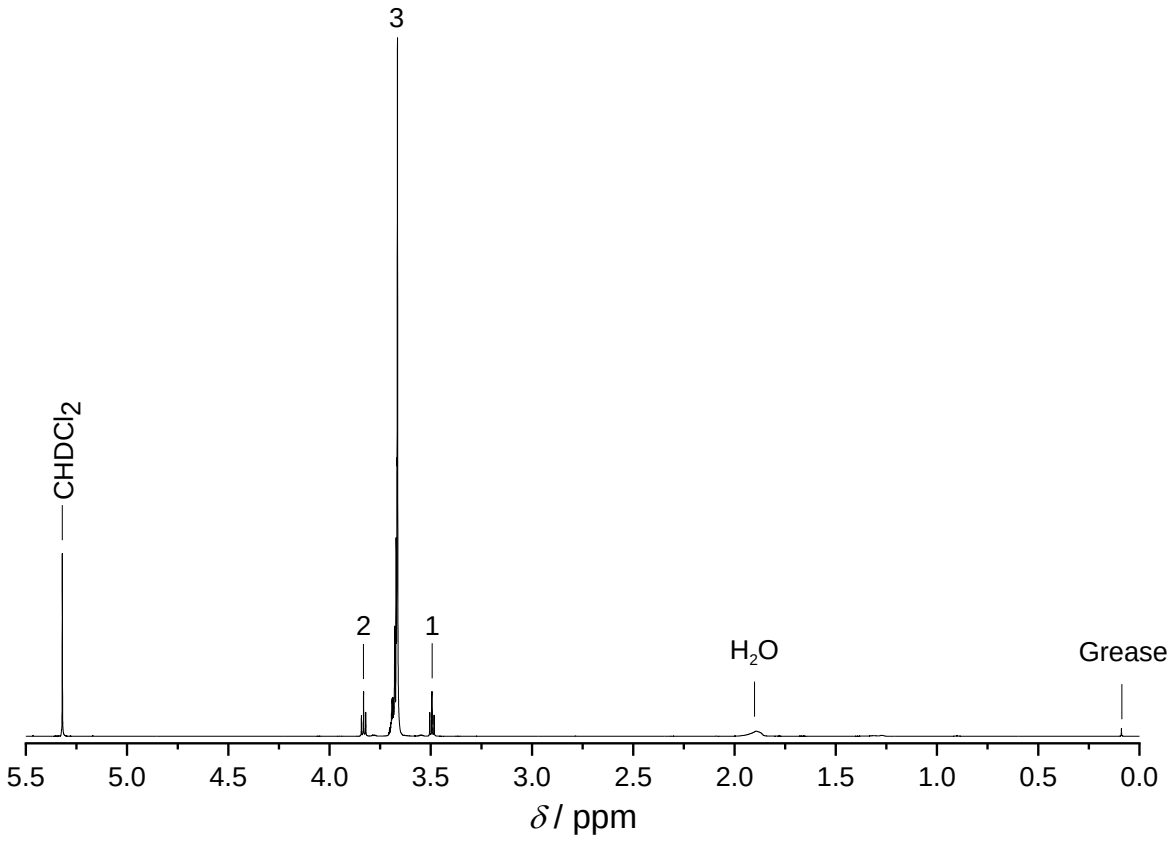


Figure S4.2.1 ^{1}H-NMR spectrum of PEG-bis(bromine) in CD_2Cl_2.

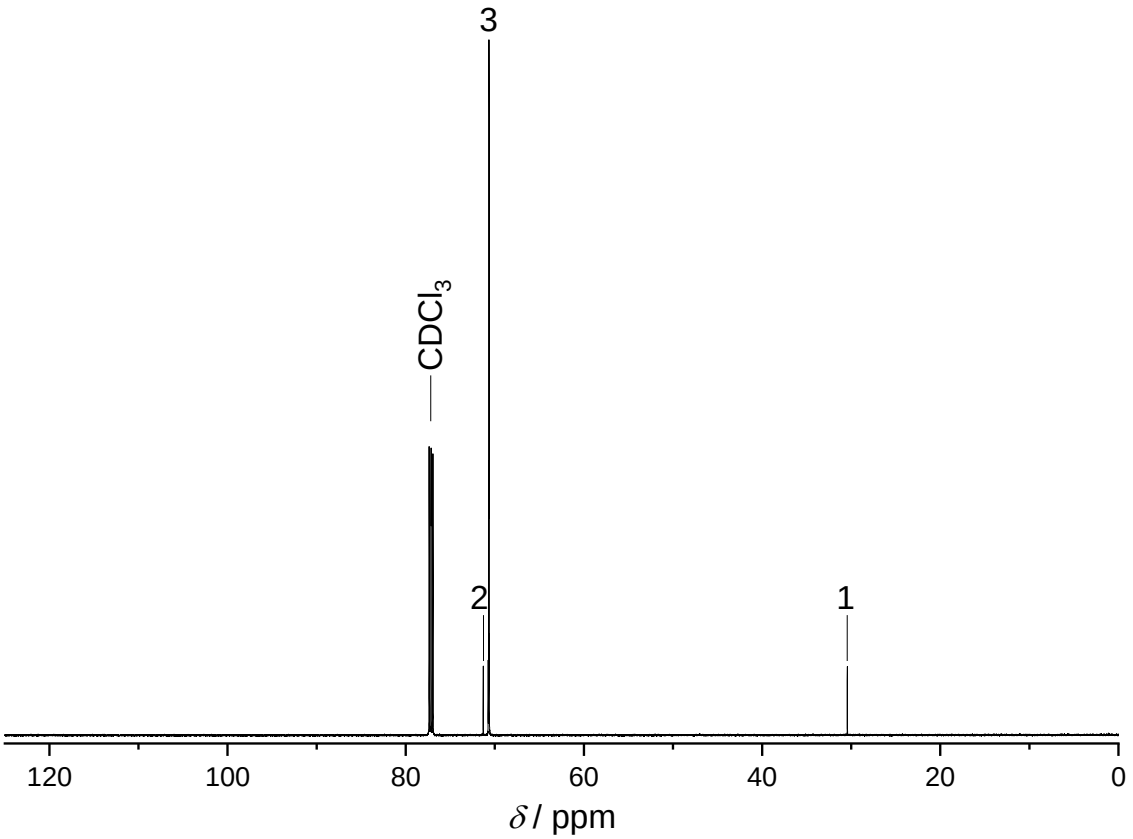


Figure S 4.2.2 ^{13}C-NMR spectrum of PEG-bis(bromine) in $CDCl_3$.

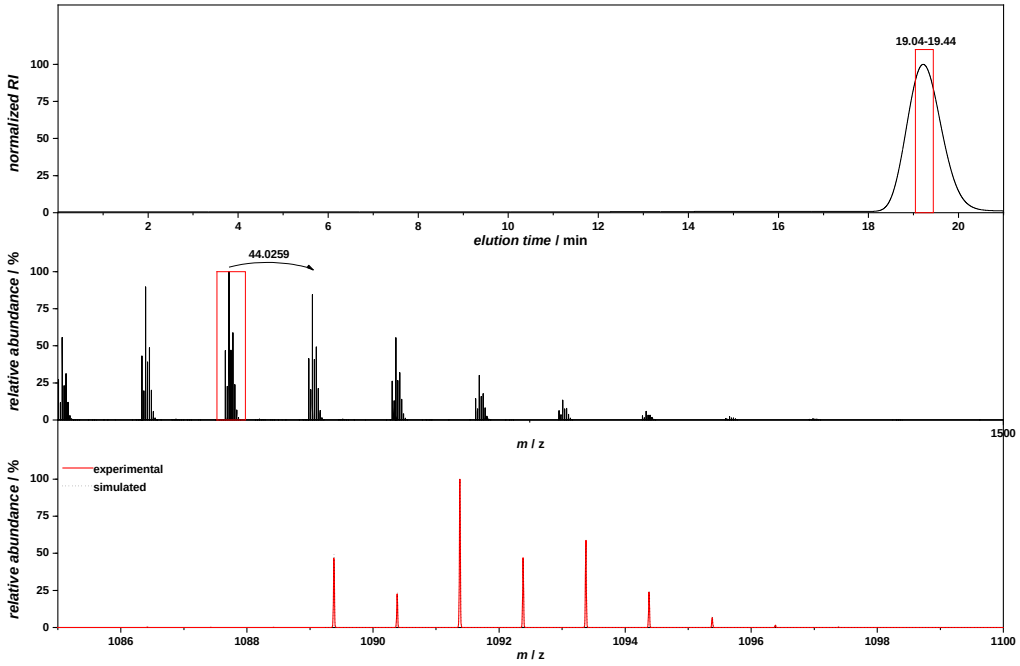
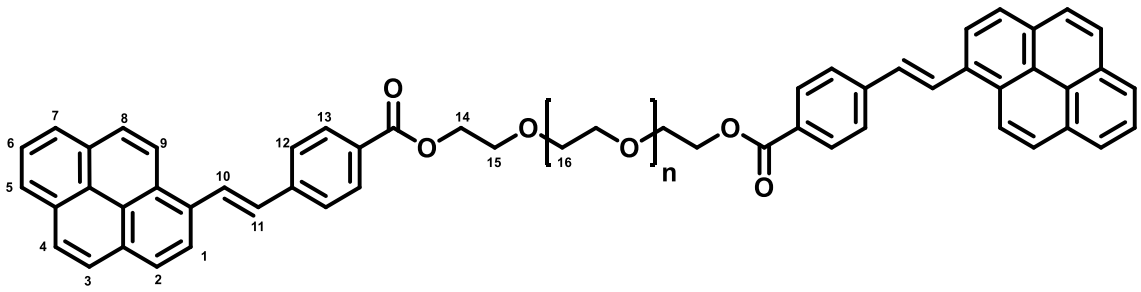


Figure S4.2.3 SEC-ESI-MS of Poly(ethylene glycol) bis(bromine). (Top) SEC trace in THF. (Middle) ESI-MS of the elution time 19.04-19.44 min. (Bottom) Zoom into the mass region of the most abundant signal (m/z = 1085 to 1100) showing the measured and simulated isotope pattern for $C_{42}H_{84}Br_2O_{20}Na$.

4.3 L1 (Poly(ethylene glycol) bis(styrylpyrene ester)



Poly(ethylene glycol) bis(bromine) (100 mg, 0.10 mmol, 1.0 eq.), carboxy styrylpyrene[4] (140 mg, 0.40 mmol, 4.0 eq.), Cs_2CO_3 (300 mg, 0.09 mmol, 0.9 eq.) were dissolved in dry deuterated DMSO under an atmosphere of N_2 in a Glovebox and stirred for 10 h at 70 °C until full consumption of the Poly(ethylene glycol) bis(bromine) was reached. The reaction mixture was filtrated over a short plug of SiO_2 (DCM → DCM / MeOH = 9/1). The crude product was purified using preparative size exclusion chromatography (Sephadex LH-20 in MeOH).

Yield: 100 mg (62%, 62 µmol, yellow viscous oil).

SEC-ESI-MS: Calculated for $C_{92}H_{114}O_{24}Na^+$: 1626.76258; found: 1626.76656.

^{1}H NMR (600 MHz, DMSO-*d6*) δ / ppm = 8.81 – 8.75 (m, 1H, CH-9), 8.60 – 8.49 (m, 2H, CH-1,11), 8.35 – 8.23 (m, 4H, CH-2,5,7,8), 8.21 – 8.15 (m, 2H, CH-3,4), 8.08 (t, *J* = 7.6 Hz, 1H, CH-6), 8.04 – 7.94 (m, 4H, CH-12,13), 7.62 (d, *J* = 15.7 Hz, 1H, CH-10), 4.43 – 4.38 (m, 2H, CH_2-14), 3.80 – 3.74 (m, 2H, CH_2-15), 3.64 – 3.28 (m, 133H, CH_2-16/H_2O).

^{13}C NMR (600 MHz, DMSO-*d6*) δ / ppm = 165.5 (C-4), 142.2 (C-7), 131.0-130.5 (m, C-12/13/20/22), 130.4 (C-10), 129.6 (C-5/6), 128.4 (C-15), 128.2 (C-21), 127.8-127.4 (C-16/19/23/24), 127.1 (C-6/8), 126.4 (C-11), 125.6-125.3 (C-25/26/27), 124.3 (C-14), 124.0 (C-3), 123.6 (C-17), 123.3 (C-18), 69.-69.7 (m, C-30), 68.4 (C-29), 64.1 (C-28).

ATR-FTIR Bands / cm^{-1} = 3046 (w), 2867 (m), 1712 (m), 1604 (m), 1274 (s) 1100 (s), 846 (m)

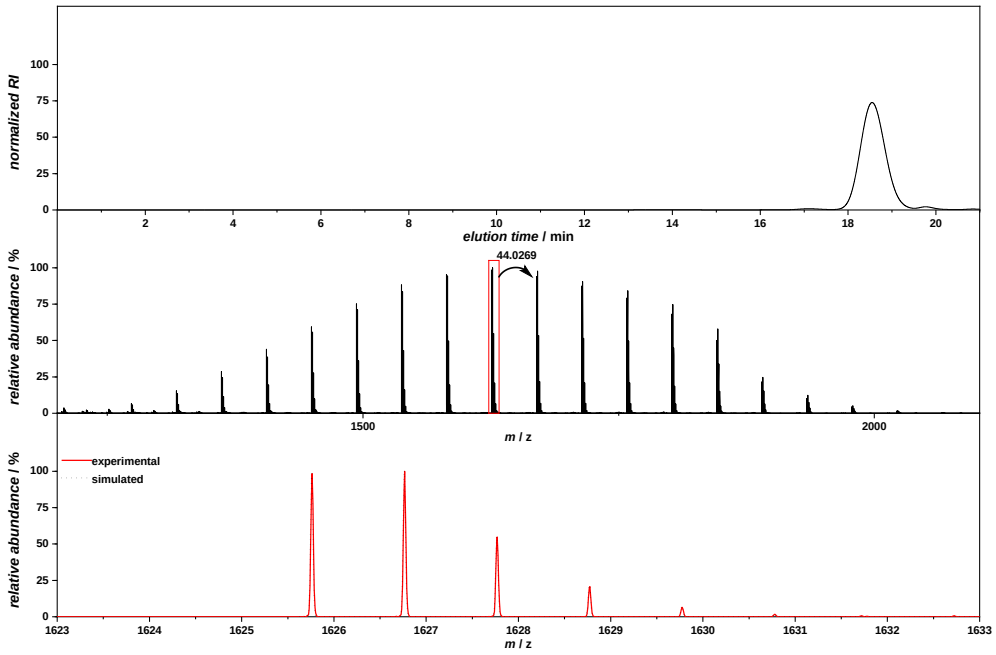


Figure S4.3.1. SEC-ESI-MS of L1. (Top) SEC trace in THF. (Middle) ESI-MS of the elution time 17.76-19.41 min. (Bottom) Zoom into the mass region of the most abundant signal (m/z = 1623 to 1633) showing the measured and simulated isotope pattern for $C_{92}H_{114}O_{24}Na$.

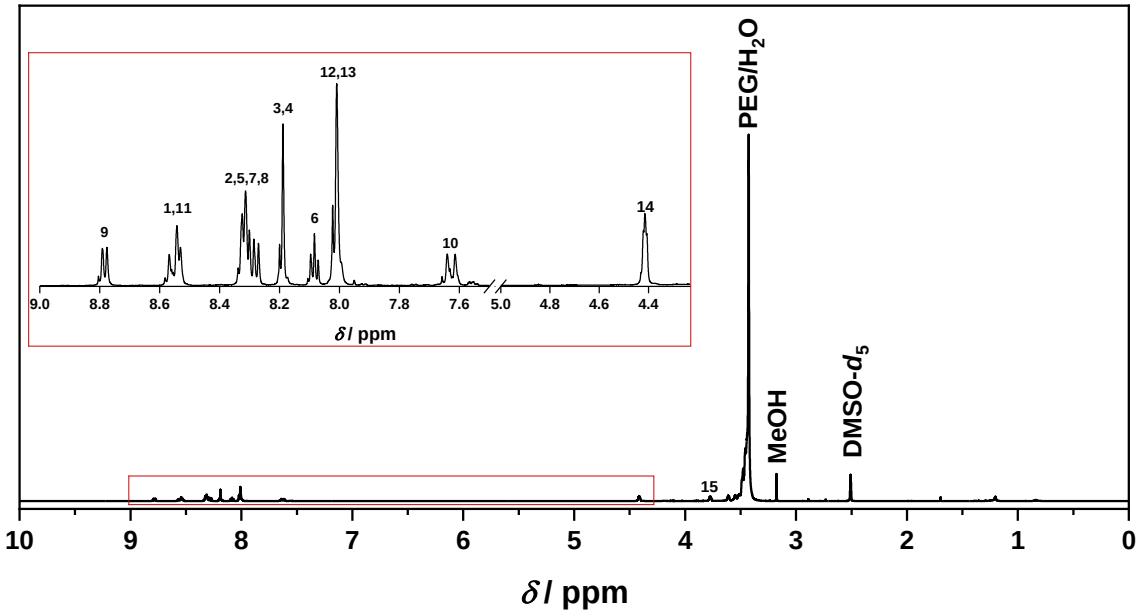


Figure S4.3.2. ^{1}H-NMR spectrum of L1 in DMSO-d_6.

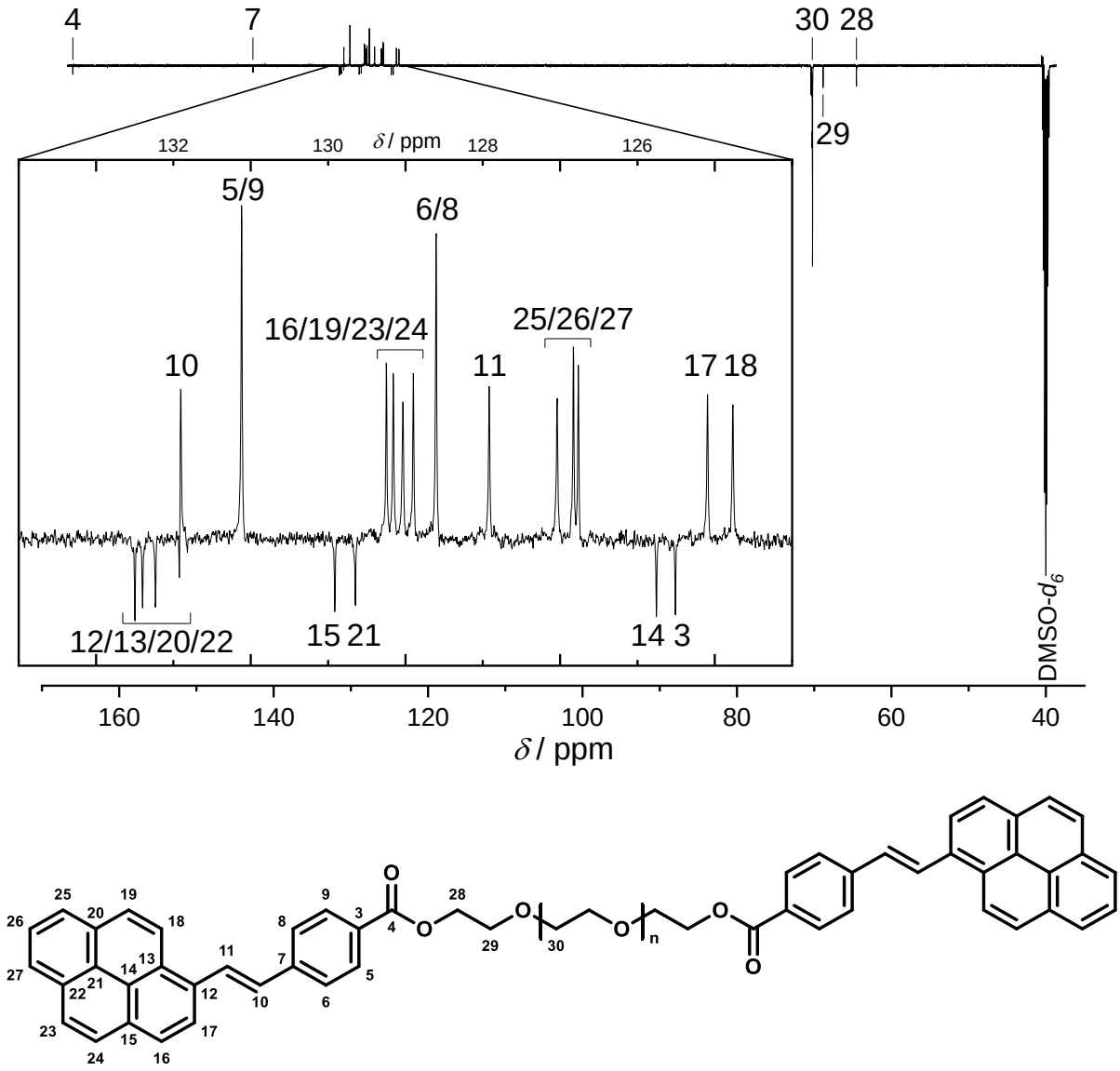


Figure S4.3.3 ^{13}C-DEPTQ-NMR spectrum of L1 in DMSO-d_6 and corresponding structure.

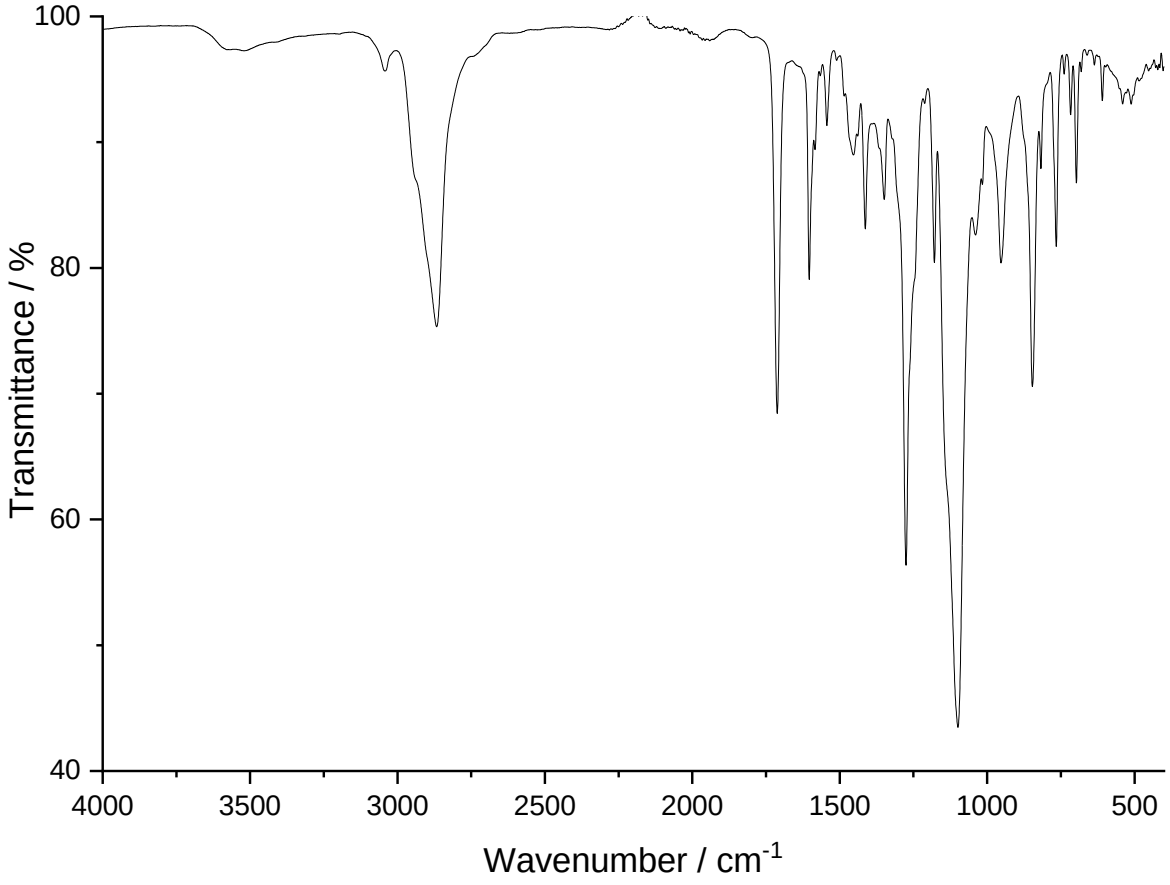


Figure S4.3.4 ATR-FTIR of L1.

5. References

[1] Gruendling, T., Guilhaus, M., Barner-Kowollik, C., *Macromolecules* ***2009***, *42*, 6366–6374.

[2] Mori, S., Barth, H.G., *Size Exclusion Chromatography*, Springer Berlin Heidelberg, Berlin, Heidelberg, ***1999***.

[3] 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*, 2176–2179.

[4] Marschner, D.; Frisch, H.; Offenloch, J. T.; Tuten, B. T.; Becer, R.; Walther, A.; Goldmann, A. S.; Tzvetkova, P.; Barner-Kowollik, C., *Macromol.* ***2018***, *51*, 3539–3896.