Electronic Supplementary Material (ESI) for Polymer Chemistry.

Visible-Light Reversible Photopolymerisation: Insights via Online Photoflow – Electrospray Ionisation – Mass Spectrometry

Matthias Van De Walle[a], Charlotte Petit[a], James P. Blinco*[a] and Christopher Barner-Kowollik*[a]
[a] Centre for Materials Science, School of Chemistry, Physics and Mechanical Engineering, Queensland University of Technology (QUT), 2 George St., Brisbane, QLD 4000, Australia.
* E-mail: christopher.barnerkowollik@qut.edu.au; j.blinco@qut.edu.au

Materials

1,10-dibromodecane (Merck); 1-pyrenecarboxaldehyde (Merck); acetonitrile (Fisher Scientific); acetovanillone (Merck); cesium carbonate (Fisher Scientific); dichloromethane (Fisher Scientific); dimethylformamide (Fisher Scientific); ethanol (Fisher Scientific); ethyl 4-bromobutyrate (Merck); hydrochloric acid, 32% (Fisher Scientific); magnesium sulfate (Merck); methanol, Optima grade (ThermoFisher Scientific); potassium carbonate (Chem-Supply); sodium bicarbonate (Merck); sodium hydroxide (Chem-Supply); sodium trifluoroacetate, HPLC grade (Chem-Supply); tetrahydrofuran, HPLC grade (Fisher Scientific)

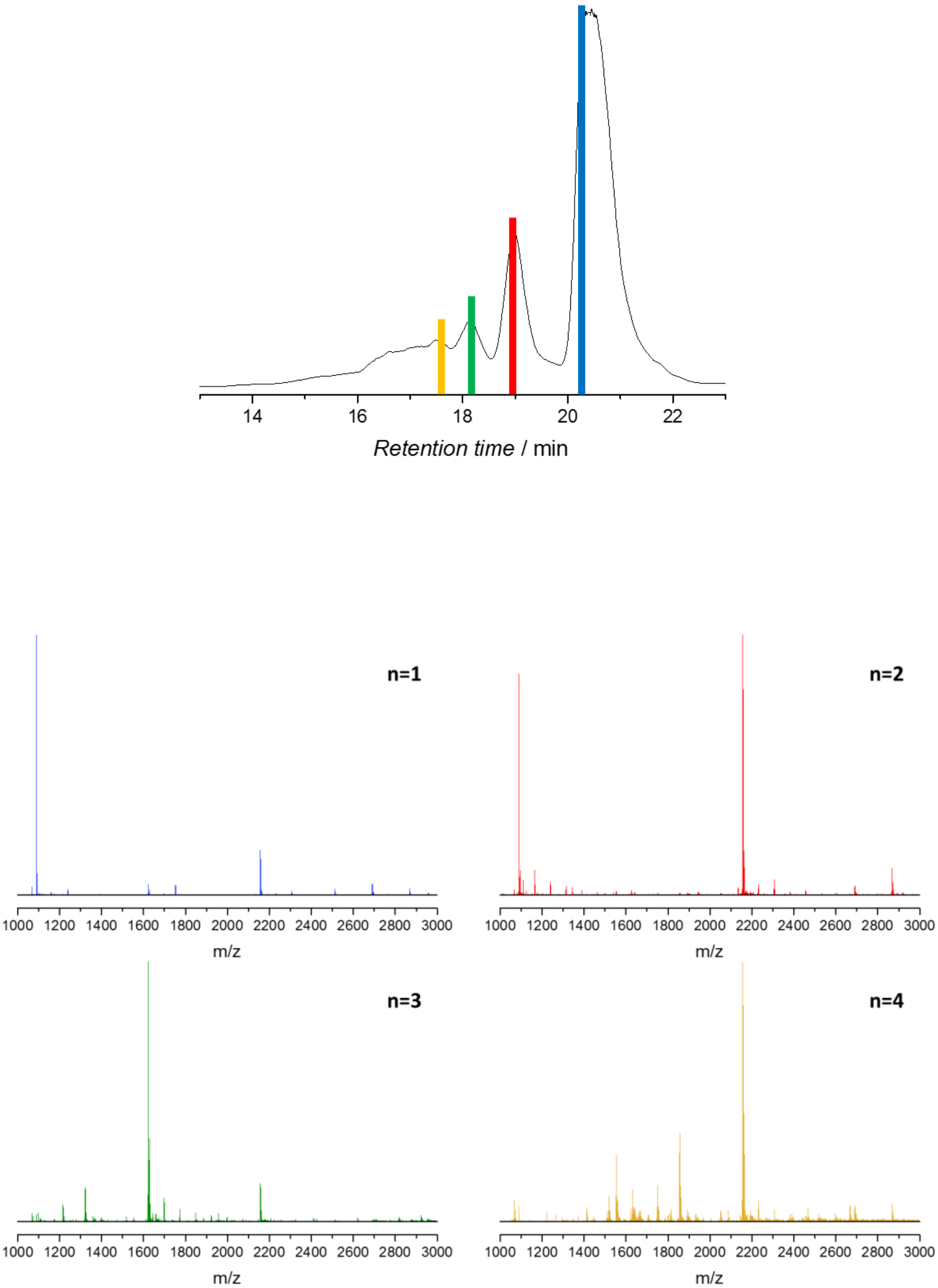

Figure S1: Top: SEC elugram of the photopolymerisation of bisPC. Small oligomers can be distinguished from each other. Bottom: individual mass spectra correlated to specific fractions of the SEC elugram. The m/z values match to the individual monomer (n=1), dimer (n=2), trimer (n=3) and tetramer (n=4).

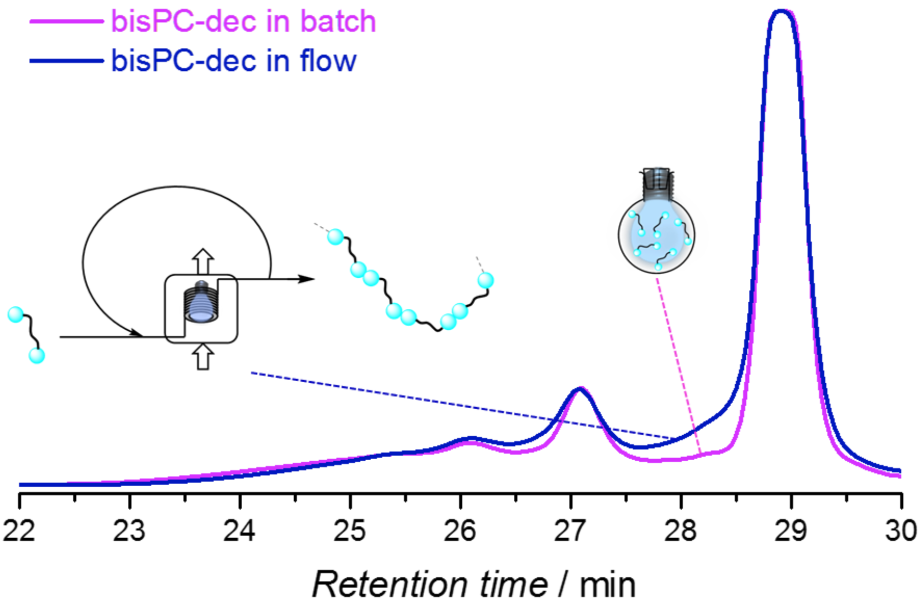

Figure S2: SEC chromatograms of poly(bisPC)$_{10}$ obtained in batch (pink curve) or via a looped photoflow setup (blue curve). No significant difference in the degree of polymerisation could be observed.

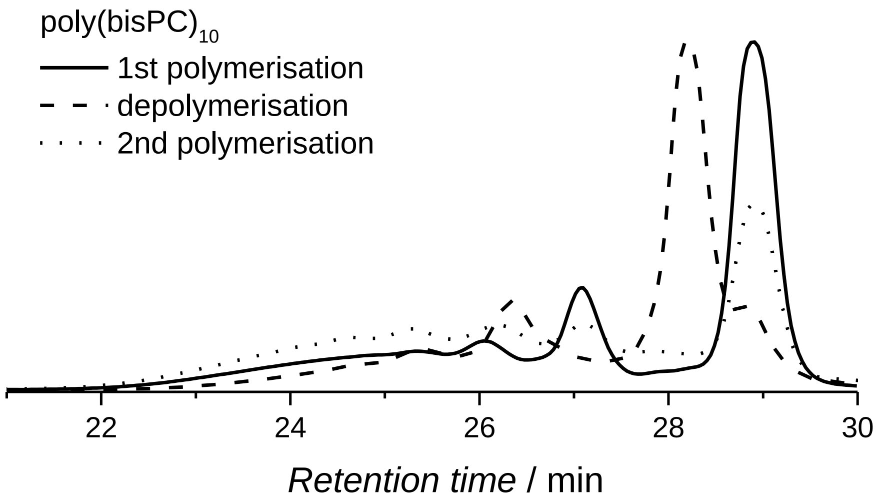

Figure S3: SEC elugrams of poly(bisPC)10 after 1^{st} visible light irradiation (full line ——), after UV-B irradiation (dashed line ----) and after 2^{nd} visible light irradiation (dotted line …..).

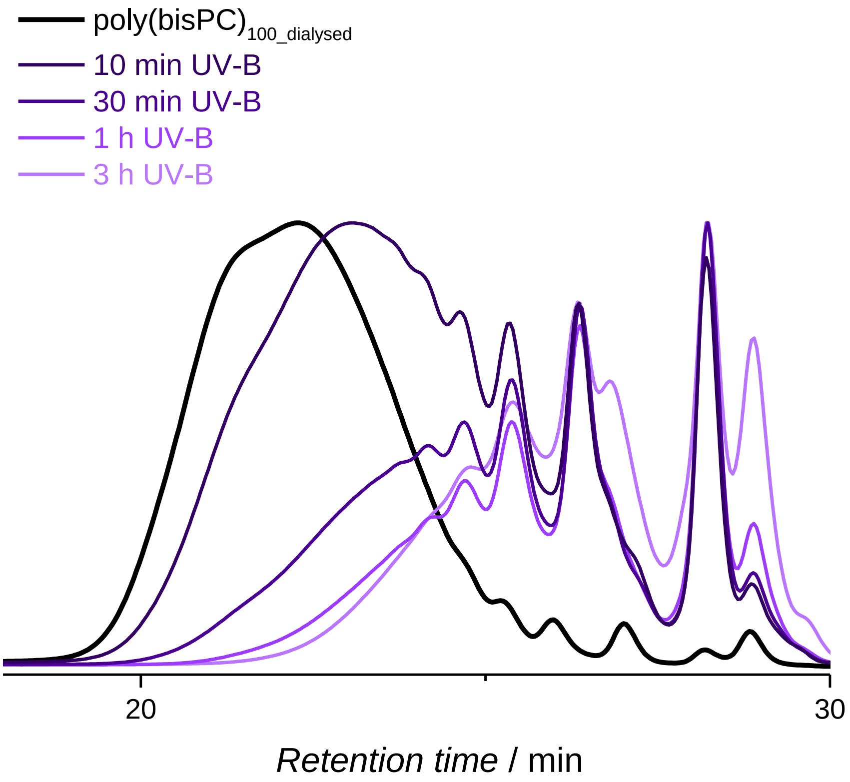

Figure S4: SEC elugrams of poly(bisPC)$_{100\_dialysed}$ and the corresponding degradation products after 10 min, 30 min, 1 h and 3h of UV-B irradiation.

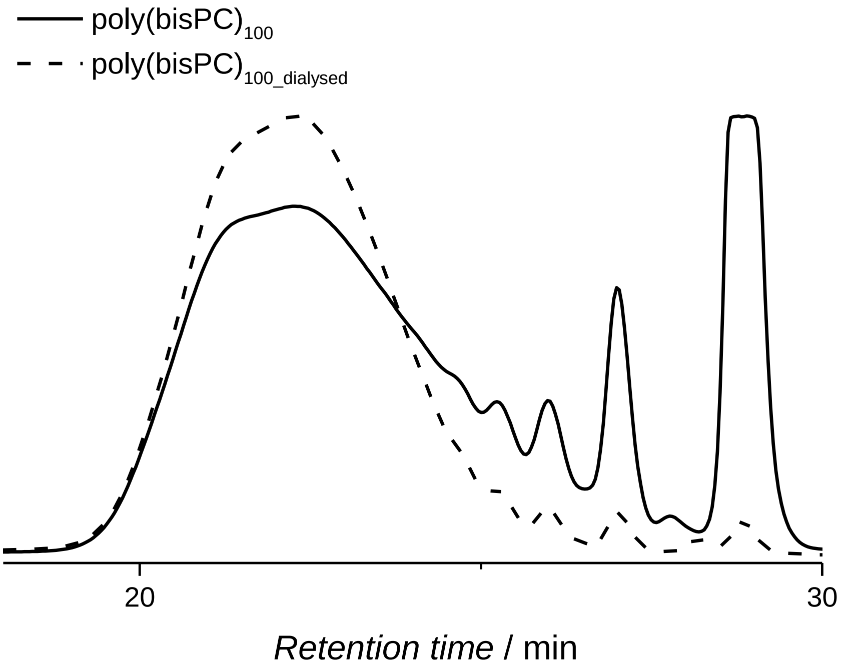

Figure S5: SEC elugrams of poly(bisPC)$_{100}$ before and after dialysis against THF with Spectrum^{TM} RC dialysis membrane, pre-wetted, 10 kDa MWCO.

Table S1: Ion counts for monomer, 2-, 3-, 4-, 5- and, 6-mer species after 0 to 70 s of UV irradiation, obtained via mass spectrometry single ion monitoring with a m/z range centred on the nominal mass value ±50. Top: Original values. Bottom: Ion counts values relative to the monomer used to plot Figure 3b. The most abundant isotope signal was used, representing the double sodium adduct with charge 2+ ($[M+2Na]^{2+}$)** or single charged sodium species ($[M+Na]^{+}$)*.

Time / s	Monomer*	2*-&4**-mer	3**-mer	5**-mer	3*-&6**-mer
0	1.229E+07	7363879	5.526E+06	9.036E+05	1.144E+06
5	1.338E+08	28527106	3.480E+06	1.434E+05	1.866E+06
10	1.044E+08	14152077	1.623E+06	1.029E+05	7.143E+05
35	1.604E+08	14133743	7.430E+05	2.751E+04	3.860E+05
70	146222880	10063632	245222.3	0.0[1]	0.01

Time / s	Monomer*	2*-&4**-mer	3**-mer	5**-mer	3*-&6**-mer
0	100.00	59.91	44.96	7.35	9.31
5	100.00	21.32	2.60	0.11	1.39
10	100.00	13.55	1.55	0.10	0.68
35	100.00	8.81	0.46	0.02	0.24
70	100.00	6.88	0.17	0.00	0.00

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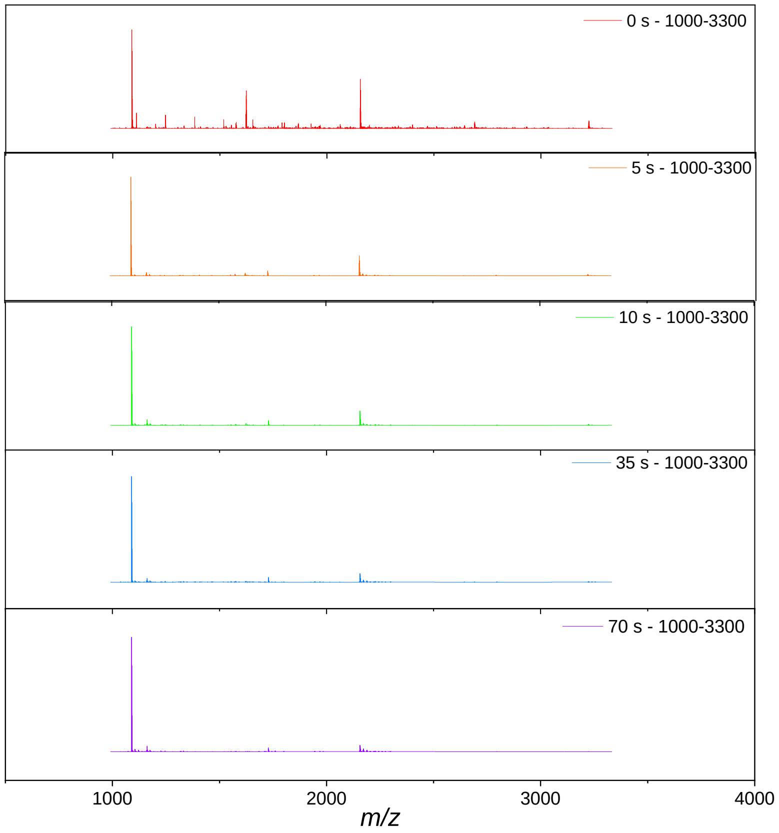
[1] The ion counts intensity was not significant enough to be distinguished from the background, therefore set to zero.

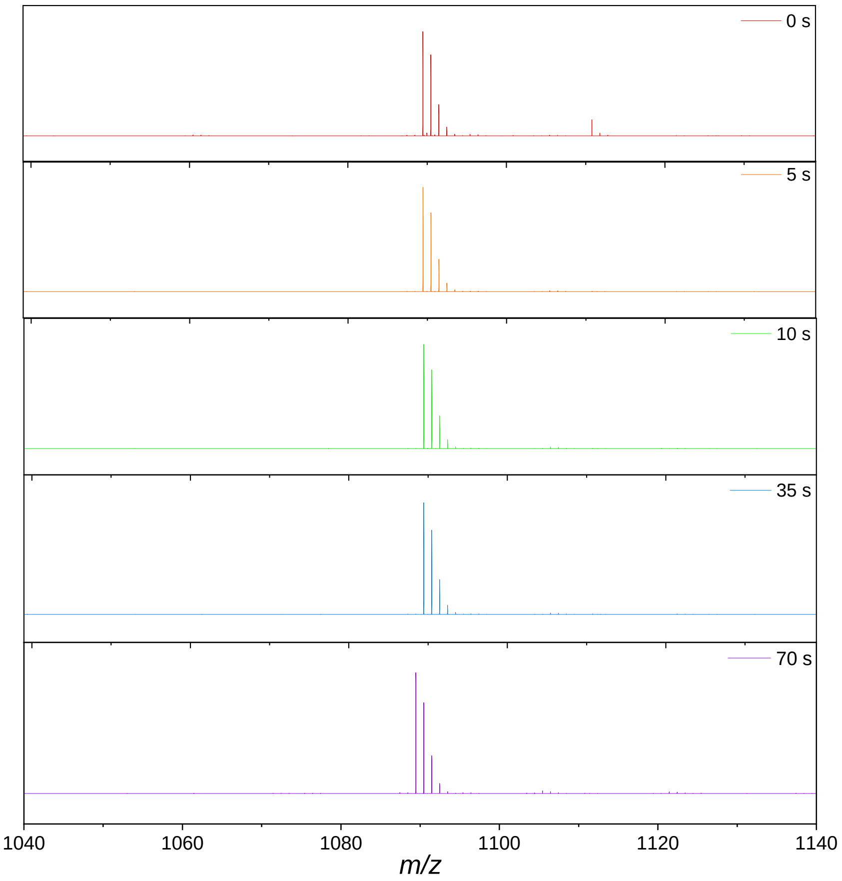
Table S2: Overview of the experimental mass versus the theoretical mass for each i-mer (i= 1, 2, 3, 4, 5 or 6) at different irradiation times. The most abundant isotope signal was used, representing the double sodium adduct with charge 2+ ([M+2Na]$^{2+}$)** or single charged sodium species ([M+Na]$^{+}$)*.

Tracked species / m/z$_{th}$	*Reaction time* / s	m/z$_{exp}$	$\Delta_{m/z}$ / ppm
Monomer* / 1089.4548	0	1089.4564	1.5
	5	1089.4596	4.4
	10	1089.4598	4.6
	35	1089.4592	4.0
	70	1089.4595	4.3
3**-mer / 1623.6910	0	1623.7009	6.1
	5	1623.7018	6.7
	10	1623.7025	7.1
	35	1623.7029	7.3
	70	1623.7040	8.0
2*-&4**-mer / 2156.9238	0	2156.9397	7.4
	5	2156.9367	6.0
	10	2156.9385	6.8
	35	2156.9372	6.2
	70	2156.9387	6.9
5**-mer / 2691.1599	0	2691.1782	6.8
	5	2691.1782	6.8
	10	2691.1791	7.1
	35	2691.177	6.4
	70	n/a	n/a
3*-&6**-mer / 3224.3927	0	3224.4209	8.7
	5	3224.4249	10.0
	10	3224.4268	10.6
	35	3224.4246	9.9
	70	n/a	n/a

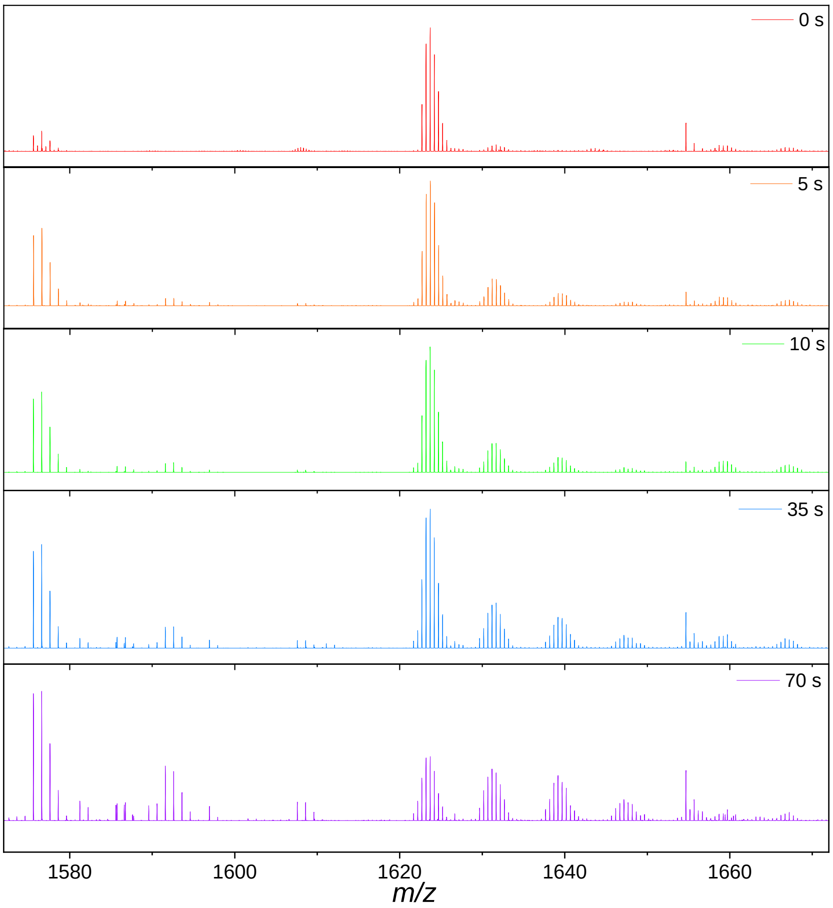
a)


0 s - 1000-3300
5 s - 1000-3300
10 s - 1000-3300
35 s - 1000-3300
70 s - 1000-3300
1000
2000
3000
4000
m/z

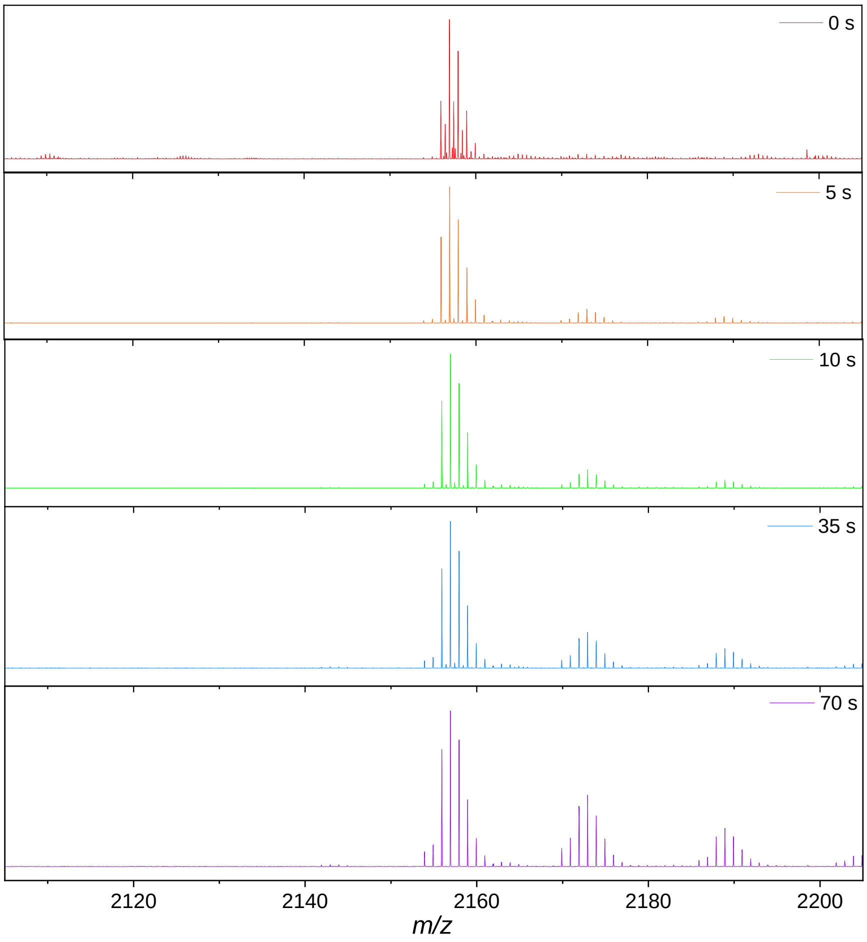
b)



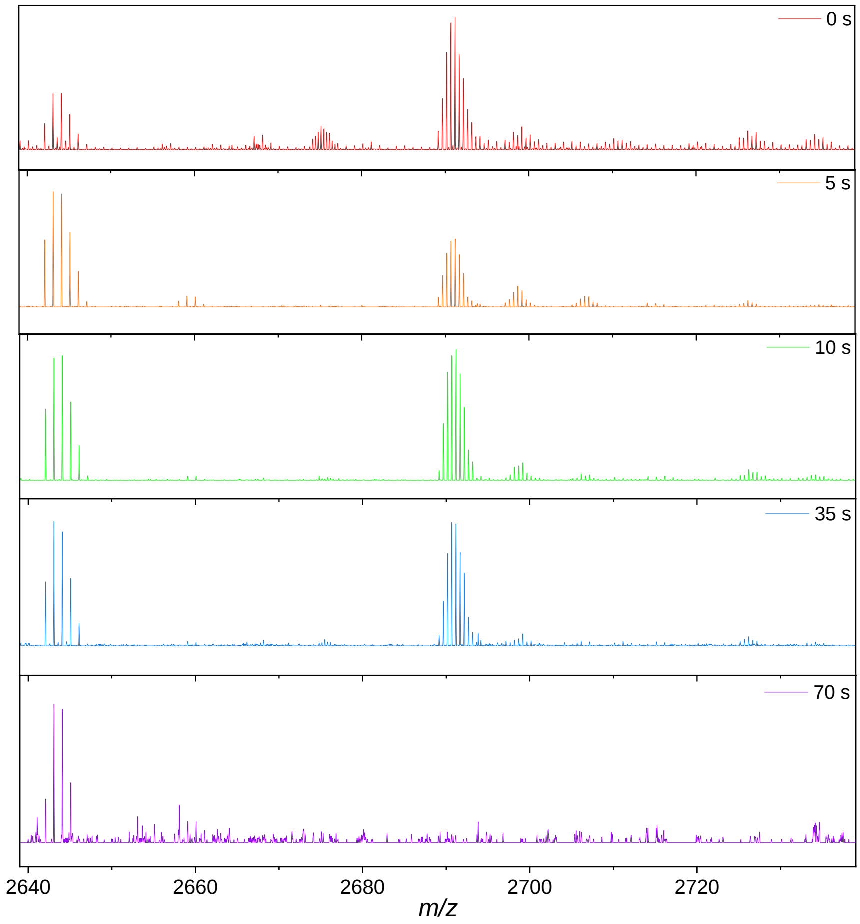
c)



d)



e)



f)

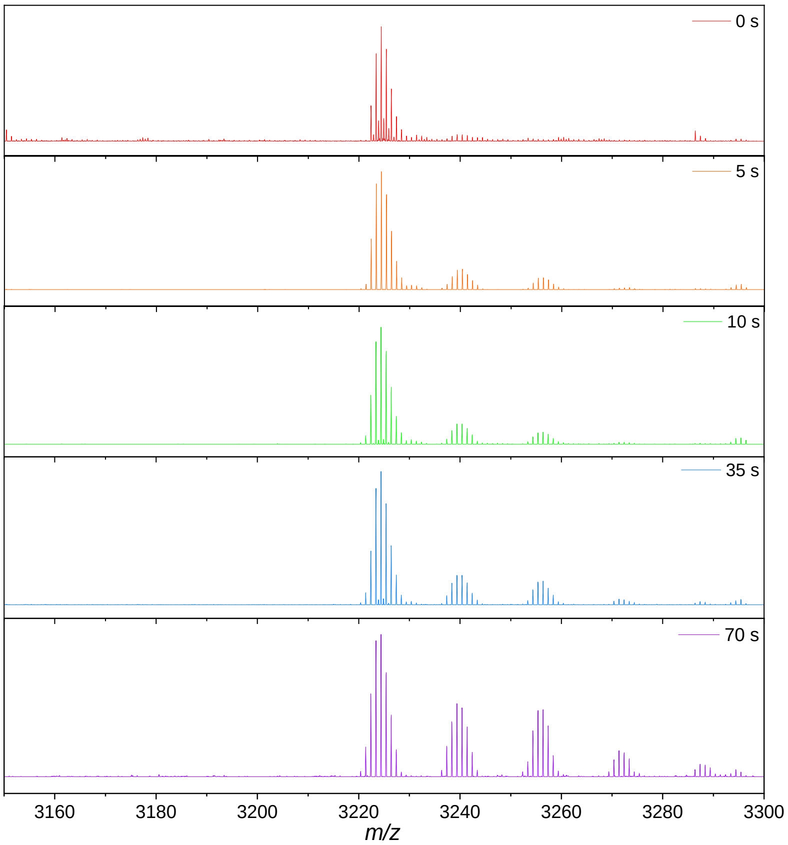
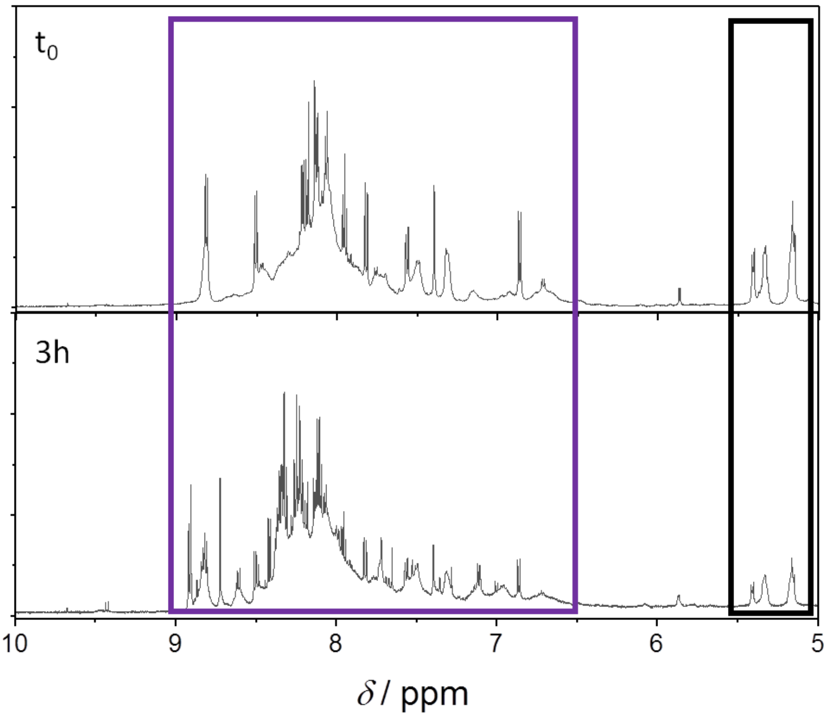


Figure S6: Mass spectra of the different oligomers obtained over different irradiation times. **a)** Overview of m/z = 1000-3300 for the different irradiation times. **b-e)** Single ion monitoring spectra centred at the nominal mass of each species with a range of m/z ± 50. **f)** Single ion monitoring spectra centred around m/z = 3224.



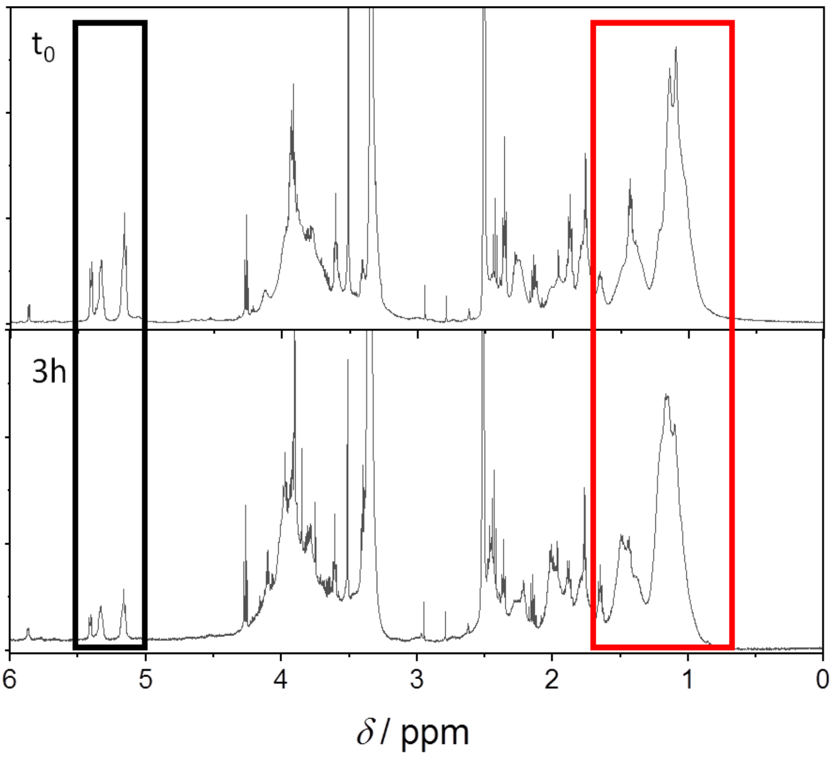
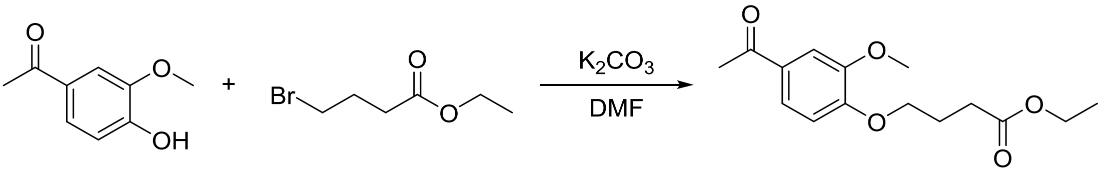


Figure S7: ^{1}H-NMR spectra (dmso-d_6, 600 MHz) of the polymer before (t_0) and after (3 h) irradiation with UV-B light. The signal intensity of the protons corresponding to the cyclobutane ring of the PC-dimer (black) reduces relative compared to the resonances associated with the aromatic protons (purple) and the aliphatic protons in the backbone (red).

Synthesis of bisPC

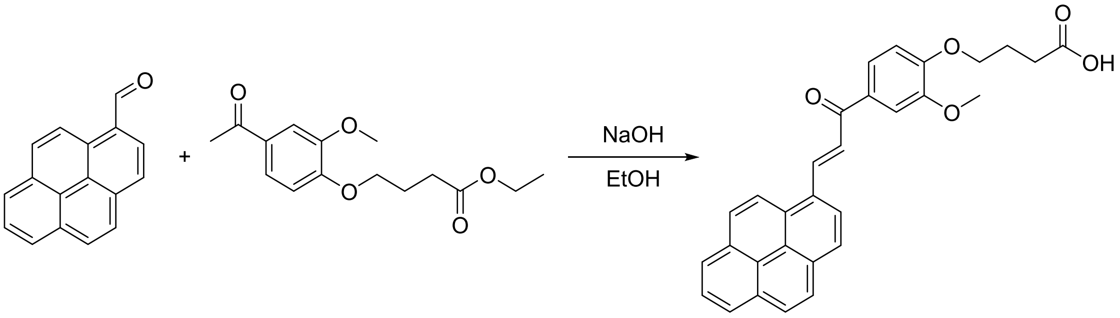
Ethyl 4-(4-acetyl-2-methoxyphenoxy)butanoate **(1)**



The synthesis of ethyl 4-(4-acetyl-2-methoxyphenoxy)butanoate was based on a published procedure.[1] Acetovanillone (16.6 g, 99.9 mmol, 1eq) and ethyl 4-bromobutyrate (23.4 g, 0.120 mol, 1.2 eq) were dissolved in 50 mL dimethylformamide. 30.4 g potassium carbonate (0.220 mol, 2.2 eq) was added in portions. After stirring overnight at ambient temperature under an inert atmosphere, the suspension was gently poured in 800 mL ice-cold water. The product was filtered, dried overnight in a vacuum oven (40°C) and used without further purification.

Yield: 27.6 g (98%, white solid).
Bruto formula: $C_{15}H_{20}O_5$.
MW.: 280.32 g/mol.
LC-MS (m/z for $[M+H]^+$): calculated: 281.1384, found: 281.1388.
^{1}H-NMR (600 MHz, DMSO-d$_6$): δ (ppm) = 1.18 (t, 3H, O-CH$_2$-C*H*$_3$), 1.99 (quint., 2H, CH$_2$-C*H*$_2$-CH$_2$), 2.46 (t, 2H, C*H*$_2$-CO), 2.52 (s, 3H, C*H*$_3$-CO), 3.82 (s, 3H, C*H*$_3$-O), 4.06 (m, 4H, 2 x C*H*$_2$-O), 7.05 (d, 1H, O-C-C*H*-CH), 7.44 (d, 1H, C-C*H*-C), 7.60 (dd, 1H, O-C-CH-C*H*).

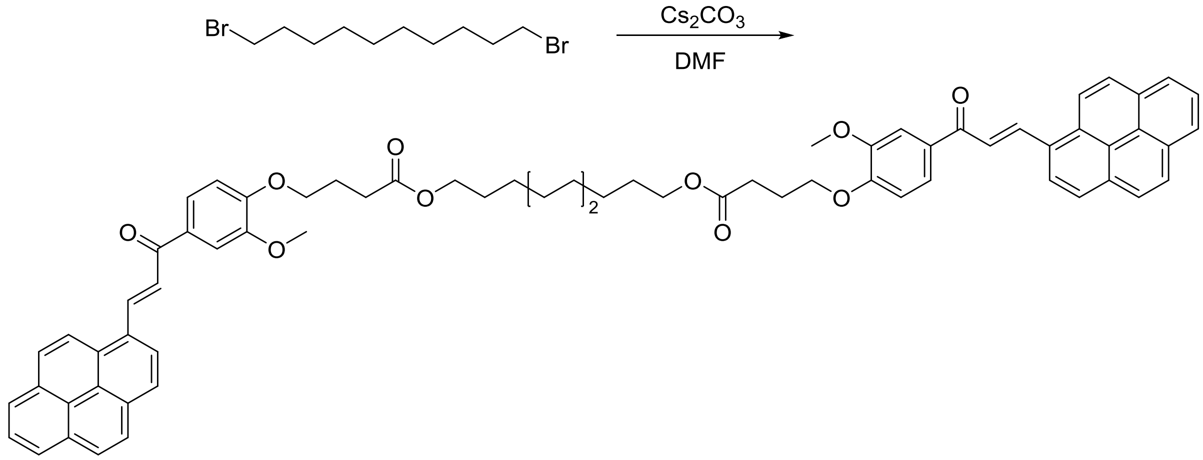
(E)-4-(2-Methoxy-4-(3-(pyren-1-yl)acryloyl)phenoxy)butanoic acid **(2 – PC-COOH)**



The synthesis of PC-COOH was adapted from a published procedure.[2] 1-Pyrenecarboxaldehyde (5.00 g, 21.7 mmol, 1 eq) and ethyl 4-(4-acetyl-2-methoxyphenoxy)butanoate (6.09 g, 21.7 mmol, 1 eq) were weighed in a 250 mL flask. 60 mL ethanol and 18 mL 3M aqueous sodium hydroxide solution were sequentially added. The resulting suspension was stirred overnight in the dark at ambient temperature under an inert atmosphere. Next, the mixture was poured in 1200 mL ice-cold water to which 10 mL concentrated aqueous hydrochloric acid was added. The flask was rinsed with a minimal amount of ethanol. The target compound was filtered, washed with water and dried in a vacuum oven overnight (40°C).

Yield: 9.91 g (98%, yellow solid).
Bruto formula: $C_{30}H_{24}O_5$.
MW.: 464.52 g/mol.
LC-MS (m/z for $[M+H]^+$): calculated: 465.1697, found: 465.1701.
^{1}H-NMR (600 MHz, DMSO-d_6): δ (ppm) = 2.00 (quint., 2H, CH_2-$C\mathit{H}_2$-CH_2), 2.42 (t, 2H, $C\mathit{H}_2$-CO), 3.91 (s, 3H, $C\mathit{H}_3$-O), 4.13 (t, 2H, $C\mathit{H}_2$-O), 7.15 (d, 1H, O-C=C*H*-CH), 7.72 (d, 1H, C=C*H*-C), 8.00 (dd, 1H, O-C=CH-C*H*), 8.12 (t, 1H, Ar-*H*), 8.23-8.30 (m, 3H, 2 x Ar-*H* + CO-C*H*), 8.33-8.40 (m, 4H, Ar-*H*), 8.62 (d, 1H, Ar-*H*), 8.83 (d, 1H, CO-CH=CH-C-C*H*), 8.85 (d, 1H, CO-CH=C*H*).

decane-1,10-diyl bis(4-(2-methoxy-4-((E)-3-(pyren-1-yl)acryloyl)phenoxy)butanoate) **(3 – bisPC)**

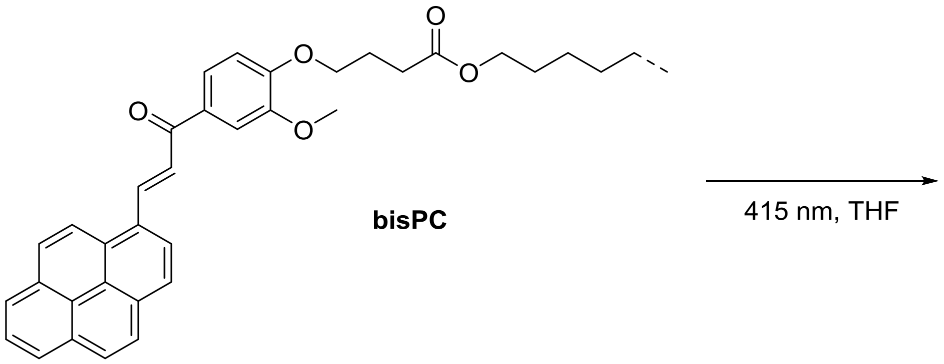


A mixture of 1,10-dibromodecane (0.22 g, 1.00 eq), PC-COOH (1.00 g, 3.00 eq) and caesium carbonate (0.94 g, 4.00 eq) in 60 mL dimethylformamide (250 mL amber round bottom flask) was prepared and mixed vigorously overnight at 50˚C. The mixture was filtered and the residue was washed with dichloromethane (100 mL). The organic filtrate was washed with 5% hydrochloric acid, saturated sodium bicarbonate and brine. The collected organic phase was dried over magnesium sulfate. The solvent was removed *in vacuo* afterwards.

Yield: 0.71 g (91%, yellow powder).
Bruto formula: $C_{70}H_{66}O_{10}$.
MW.: 1067.29 g/mol.
^{1}H-NMR (600 MHz, DMSO-d_6): δ (ppm) = 8.88 – 8.80 (m, 4H, *Ar* + CO-CH=C*H*), 8.63 (d, *J* = 9.4 Hz, 2H, *Ar*), 8.42 – 8.34 (m, 8H, *Ar*), 8.32 – 8.23 (m, 6H, *Ar*), 8.13 (t, *J* = 7.6 Hz, 2H, *Ar*), 8.01 (dd, *J* = 8.5, 2.1 Hz, 2H, O-C=CH-C*H*), 7.73 (d, *J* = 2.0 Hz, 2H, *Ar*), 7.16 (d, *J* = 8.5 Hz, 2H, *Ar*), 4.10 (t, *J* = 6.4 Hz, 4H, CH-O-$C\mathit{H}_2$-CH_2), 3.97 (t, *J* = 6.6 Hz, 4H, CO-O-$C\mathit{H}_2$-CH_2); 3.89 (s, 6H, $C\mathit{H}_3$-O), 2.45 (t, 4H, CO-$C\mathit{H}_2$-CH_2), 2.00 (p, *J* = 7.1 Hz, 4H, CO-CH_2-$C\mathit{H}_2$), 1.49 (p, *J* = 7.1 Hz, 4H, CO-O-CH_2-$C\mathit{H}_2$), 1.15-1.27 (b, 12H, $C\mathit{H}_2$-$C\mathit{H}_2$-$C\mathit{H}_2$-$C\mathit{H}_2$-$C\mathit{H}_2$-$C\mathit{H}_2$).

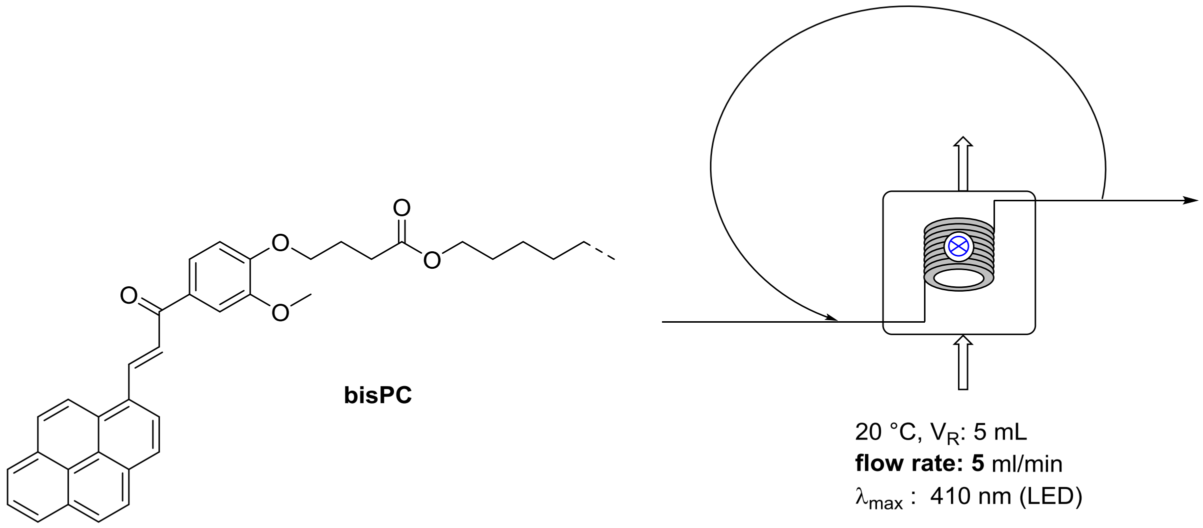
Photopolymerisation of bisPC

In small batch



A degassed solution/dispersion of **x** mg bisPC in THF (1 mL) was prepared and irradiated with a 3W 415 nm LED overnight (1 mL vial, distance to LED +/- 5 cm). The obtained polymer mixture **poly(bisPC)$_x$** was analysed via size exclusion chromatography.

In looped continuous flow



A degassed solution of 200 mg bisPC in THF (20 mL) was prepared and irradiated with a 410 nm LED (Vapourtec photoflow UV-150 module) overnight in a continuous looped setup. The flow rate was set at 5 mL min^{-1}. A 5 mL flow coil was employed.

Depolymerisation of poly(bisPC)

In small batch

A degassed solution of **x** mg **poly(bisPC)$_{\mathbf{x}}$** in THF (1 mL) was irradiated with UV-B light (Luzchem photoreactor, 1 lamp, 1 mL vial, distance to lamp +/- 5 cm).

Time dependent depolymerisation

Degassed solutions of **poly(bisPC)$_{\mathbf{100\_dialysed}}$** (product obtained after dialysis against THF, 10 kDa MWCO) in THF (1 mg mL^{-1}, 1 mL volume) were irradiated with UV-B light (Luzchem photoreactor, 1 lamp, 1 mL vial, distance to lamp +/- 5 cm) for 10 minutes, 30 minutes, 1 hour and 3 hours (Figure S4).

Repolymerisation of bisPC/oligo(bisPC)

After irradiation with UV-B light, the samples were re-irradiated with a 3 W 415 nm LED overnight (1 mL vials, distance to LED +/- 5 cm).

Photoflow – ESI -MS

Poly(bisPC)$_{100}$ (100 mg) dissolved in THF (5 mL) was dialysed against THF to remove smaller oligomer fractions (Spectrum^{TM} RC dialysis membrane, pre-wetted, 10 kDa MWCO). Afterwards a solution was prepared of 0.05 mg mL^{-1} **poly(bisPC)$_{100\_dialysed}$** in THF as a starting mixture for the flow-MS setup. A second solution of 14 µg mL^{-1} sodium trifluoroacetate in methanol was prepared. The polymer solution and dopant solution were connected to pump A and B with flow speed 0.350 mL min^{-1} and 0.150 mL min^{-1}, respectively. A back pressure regulator was used to tune the flow rate ratio (99:1) of the waste stream to the mass spectrometer inlet. A UV-B lamp was installed adjacent to a short fragment of tubing to control the irradiation time.

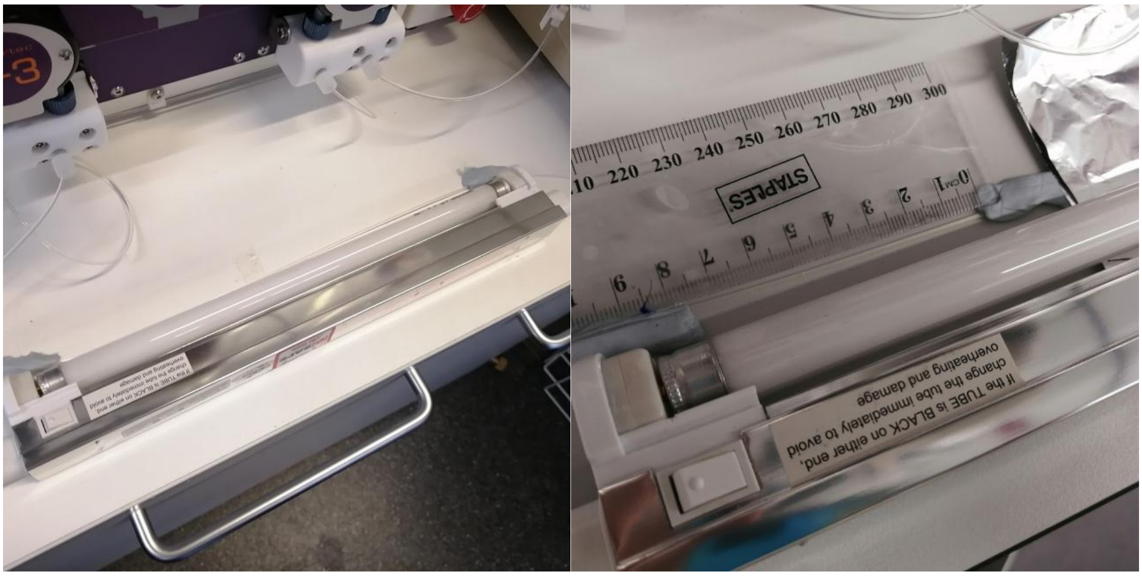


Figure S8: Photos of the photoflow setup connected to the mass spectrometer. The irradiation time was altered by changing the length of the tubing subject the UV-B light. At a flow rate of 0.35 mL min^{-1} with 1mm internal diameter tubing, 3.7 cm, 7.5 cm, 26.5 cm and 53.0 cm of the tubing was irradiated with the UV-B lamp to achieve an irradiation time of 5, 10, 35 and 70 seconds, respectively.

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 3.6 kV, a dimensionless sheath gas and a dimensionless auxiliary gas flow rate of 10 and 0 were applied, respectively. The capillary temperature and was set to 320 °C, the S-lens RF level was set to 150, and the auxiliary gas heater temperature was set to 125 °C. A Collision-induced dissociation (CID) voltage of 150 eV was applied and 100 scans were recorded and averaged for each measurement.

Characterisation and Instruments

NMR

^{1}H-NMR-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). Resonances are reported in parts per million (ppm) relative to tetramethylsilane (TMS). The δ-scale was calibrated to the respective solvent signal of DMSO for ^{1}H spectra. The annotation of the signals is based on HSQC-, COSY- and DEPT-experiments.

LC-MS

LC-MS measurements were performed on an UltiMate 3000 UHPLC System (Dionex, Sunnyvale, CA, USA) consisting of a pump (LPG 3400SZ), autosampler (WPS 3000TSL) and a temperature controlled column compartment (TCC 3000). Separation was performed on a C18 HPLC column (Phenomenex Luna 5µm, 100 Å, 250 × 2.0 mm) operating at 40 °C. Water (containing 5 mmol L^{-1} ammonium acetate) and acetonitrile were used as eluents. A gradient of acetonitrile:water 5:95 to 100:0 (v/v) in 7 min at a flow rate of 0.40 mL min^{-1} was applied. The flow was split in a 9:1 ratio, where 90 % of the eluent was directed through a DAD UV-detector (VWD 3400, Dionex) and 10 % was infused into the electrospray source. Spectra were recorded on an LTQ Orbitrap Elite mass spectrometer (Thermo Fisher Scientific, San Jose, CA, USA) equipped with a HESI II probe. The instrument was calibrated in the m/z range 74-1822 using premixed calibration solutions (Thermo Scientific). A constant spray voltage of 3.5 kV, a dimensionless sheath gas and a dimensionless auxiliary gas flow rate of 5 and 2 were applied, respectively. The capillary temperature and was set to 300 °C, the S-lens RF level was set to 68, and the aux gas heater temperature was set to 100 °C.

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 and 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.[§] 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.

[§] Gruendling, T.; Guilhaus, M.; Barner-Kowollik, C. *Macromolecules* **2009**, *42*, 6366.

SEC (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 (8x150 mm 5 µm Precolumn, 8x300 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(styrene) (Mn: 266 g mol^{-1} to 2.52x106 g mol^{-1}) and poly(methyl methacrylate) (Mn: 202 g mol^{-1} to 2.2x106 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).

Vapourtec E2 Flow Reactors and UV-150 Module

Photoreactions under flow conditions were performed using a *Vapourtec* E-series platform (peristaltic pumps) in combination the UV-150 module and the VSD006 cooling module. The module consists of a temperature controlled irradiation chamber, a transparent fluorinated ethylene polymer (FEP) reactor coil (1.3 mm inner diameter, 0.15 mm wall thickness, 5 mL PN: 50-1287) and a LED assembly (390 to 420 nm, peak 410 nm, total power output of 18 W, PN: 50-1444). The temperature is controlled employing pre-cooled nitrogen (heat exchange in the cooling module).

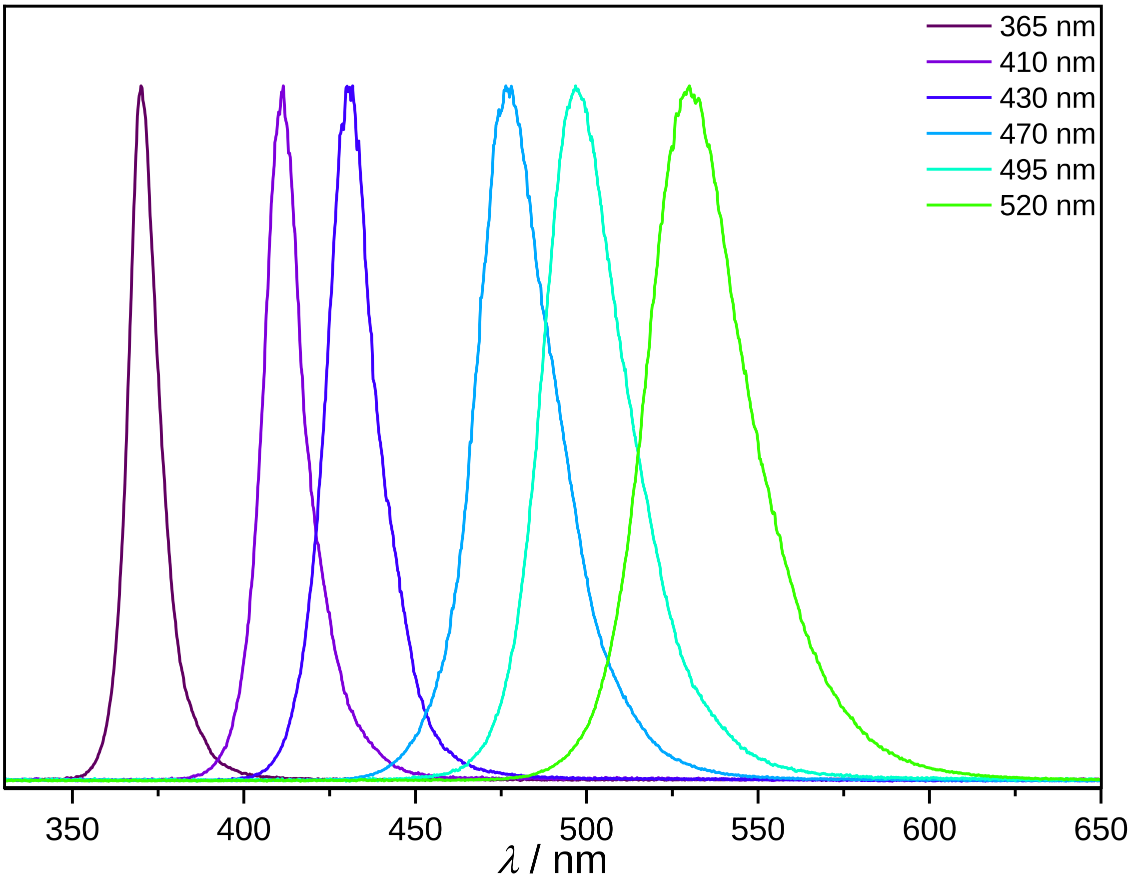


Figure S9: Emission spectra of the Vapourtec LEDs.

Luzchem Photoreactor

The samples were irradiated in a *Luzchem* LZC-4V photoreactor using UV-B lamps (LZC-UVB), emitting at 313 nm. 1 lamps was installed for side irradiation; distance to sample +/- 5 cm. The internal chamber was ventilated to maintain ambient temperature during the entire experiment.

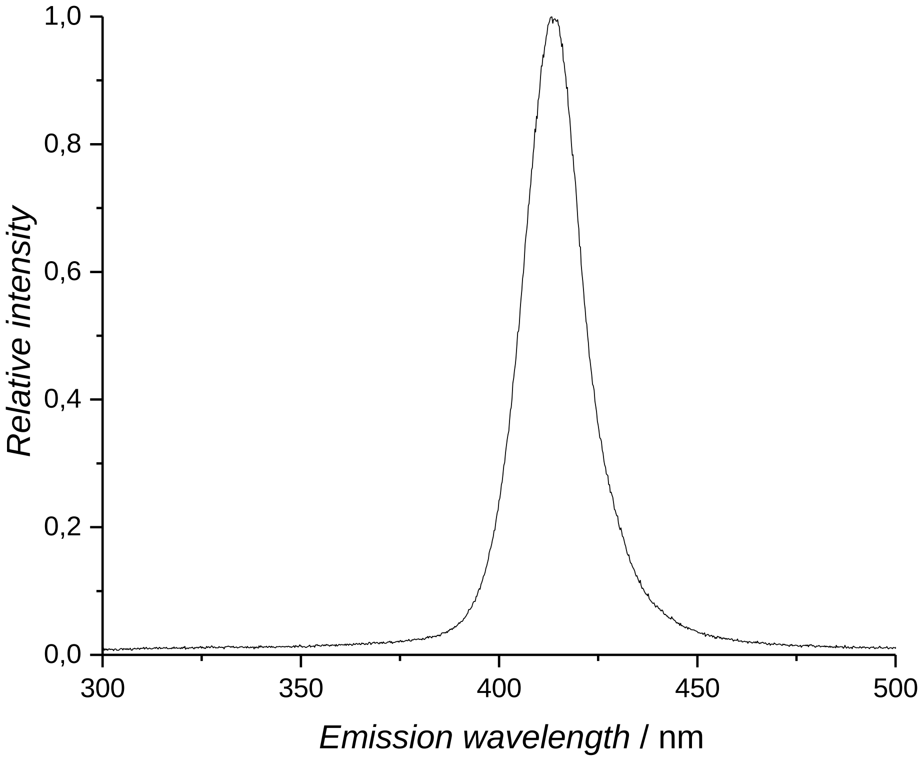


Figure S10: Emission spectrum of the LED, wavelength around 415 nm.

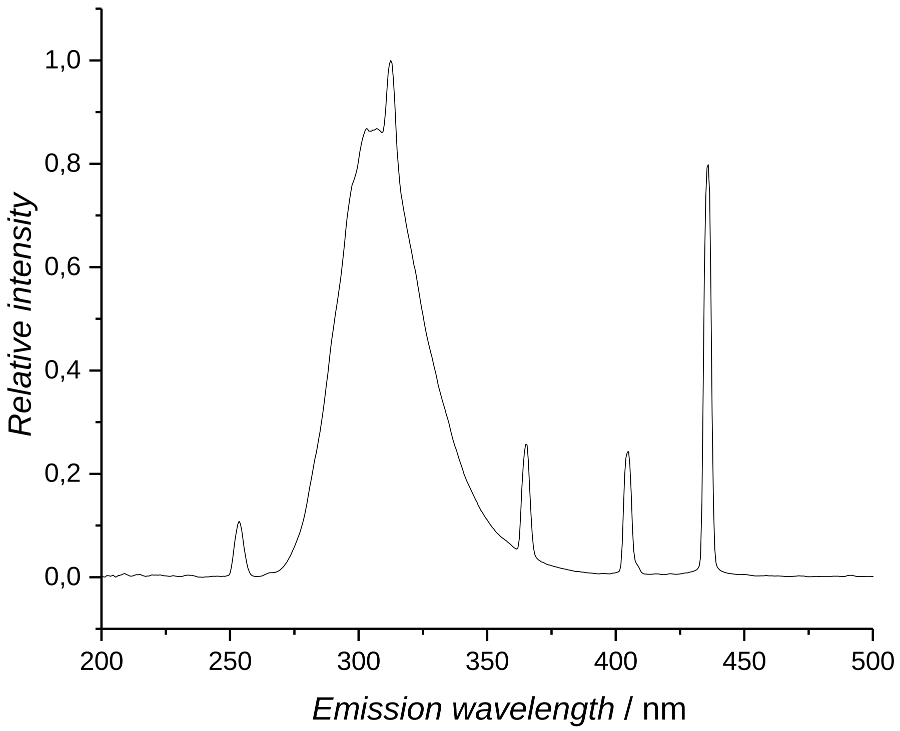


Figure S11: Emission spectrum of the UV-B light in the photoreactor setup.

References

[1] K. S. Anseth, A. M. Kasko, Photodegradable groups for tunable polymeric materials, *US8343710B1*, **2013**.

[2] Q. Feng, M. Wang, B. Dong, J. He, C. Xu, *Crystal Growth & Design* **2013**, *13*, 4418-4427.