Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

for

High Resolution Mass Spectrometric Access to Nitroxide Containing Polymers

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Table of Contents

Materials

4-Carboxy-2,2,6,6-tetramethylpiperidine 1-oxyl (4-carboxy-TEMPO, >97%, TCI), anisole (99%, Acros), chloroform-d_1 ($CDCl_3$, 99.8%, EURISO-TOP), copper (II) bromide (99% Sigma-Aldrich), copper(II) sulfate pentahydrate (98%, Acros), dichloromethane (dry) (DCM, 99.8%, extra dry, over molecular sieve, stabilized, Acros), *N*,*N*'-dicyclohexylcarbodiimide (DCC, 99%, Acros), dimethylaminopyridine (DMAP, ≥99%, Sigma-Aldrich), dimethylsulfoxide-d_6 (DMSO-d_6, 99.8%, EURISO-TOP), *N*,*N*-dimethylformamide (DMF, 99%, extra pure, Acros), neutral Aluminum oxide (Acros), potassium carbonate (≥99%, Alfa Aesar), sodium sulfate (≥99%, Roth), sodium ascorbate (98%, VWR), sodium azide (99%, Acros), tin (II) ethylhexanoate (92.5-100%, Sigma-Aldrich), tris[2-(dimethylamino)ethyl]amine (Me_6TREN, >98%, TCI). Styrene (>99.5%, Sigma-Aldrich) was passed over a column of basic alumina (Acros) and 4-(chloromethyl)styrene (>90%, TCI) was distilled before usage and stored at -20 °C. Tetrahydrofuran (THF), dichloromethane (DCM), ethyl acetate and methanol were purchased as analytical grade solvents (VWR) and used as received.

Instrumentation

Nuclear Magnetic Resonance Spectroscopy (NMR)

^{1}H NMR measurements were performed on a Bruker Ascend 400 MHz spectrometer. s (singlet), bs (broad singlet). d(duplet), t (triplet), m (multiplet) serve as abbreviations for the multiplicity of the signals. The coupling constants (J) are reported in Hertz [Hz]. NMR spectra of synthesized compounds are enclosed in the appendix.

The mole fraction of CMS and styrene was calculated according to literature.[1]

Electron Paramagnetic Resonance Spectroscopy (EPR)

Electron paramagnetic resonance (EPR) spectroscopy was performed on a Magnettech MiniScope MS400 spectrometer. All samples were recorded in chloroform at 23 °C. A TEMPO calibration curve was employed for quantitative EPR measurements.

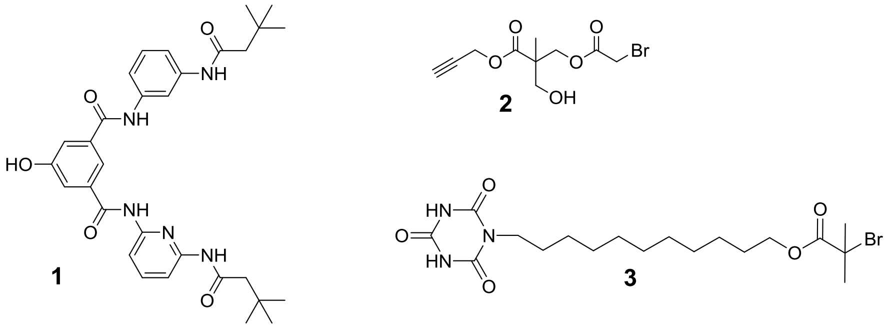
Size Exclusion Chromatography (SEC)

SEC was performed to obtain the molecular weight distribution of synthesized polymers. The employed system was a Agilent Series 1200 running on tetrahydrofuran (THF, HPLC grade) featuring an autosampler, a PLgel Mixed C guard column (50 × 7.5 mm), followed by three PLgel Mixed C linear columns (300 × 7.5 mm, 5µm bead-size), a and a differential refractive index (RI) detector. The device was run at 35 °C with a flow rate of 1 mL·min^{-1}. The calibration was carried out with linear poly(styrene) standards ranging from 160 to $6 \cdot 10^{6}$ g·mol^{-1}. The injected samples were dissolved in THF (2 mg·mL^{-1}).

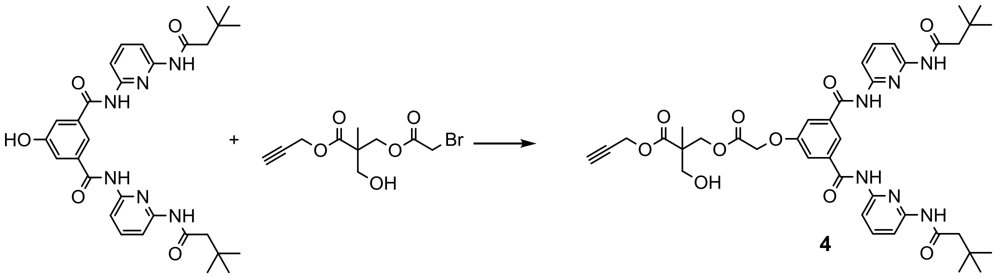
Electrospray Ionization Mass Spectrometry (ESI MS)

Mass spectra were recorded on a Q Exactive (Orbitrap) mass spectrometer (Thermo Fisher Scientific, San Jose, CA, USA) equipped with a HESI II probe. All spectra were recorded in negative ion mode, using DCM/MeOH (doped with 0.1% NaCl) (3:1, v/v) in a concentration of 0.5 mg·mL^{-1} as solvent. The Fourier-Transform resolution was set to 140 000, employing three microscans during an acquisition time between 3 and 6 min, measuring with a capillary temperature of 320 °C. The aux gas flow was set to (dimensionless) 0.00, the sheath gas to 10.00, and the spare gas to 0.00. The flow rate was set to 5 µL·min^{-1}. The spray voltage was set to 3.6 keV for the PS-*co*-CMS (9.3%), 3.9 keV for PS-*co*-TEMPO (11.3%), 3.3 keV for PS-*co*-CMS (15.3%), 3.3 keV for PS-*co*-TEMPO (16.3%), 2.8 keV for PS-*co*-CMS (35.7%), 3.0 keV PS-*co*-TEMPO (27.8%), 4.3 keV for PS-*co*-CMS (34.9%), 3.7 keV for PS-*co*-TEMPO (29.1%) and 3.2 keV for the CA-PS-HW/TEMPO polymer.

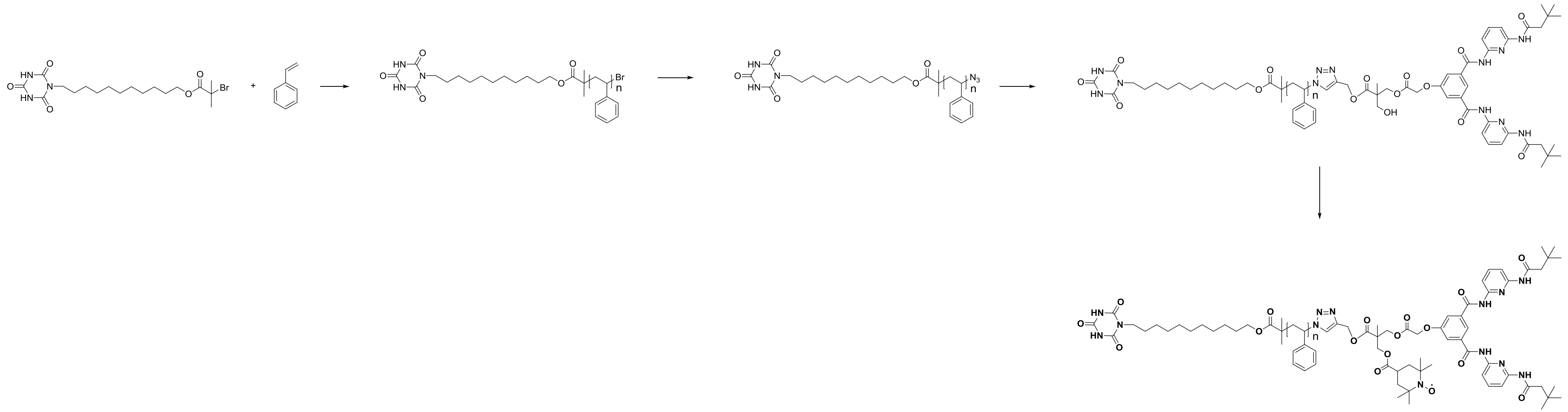
Overview Schemes



Scheme S1. Structures of compounds used in the current study.



Scheme S2. Structure of the small molecule compound synthesized in the current study.

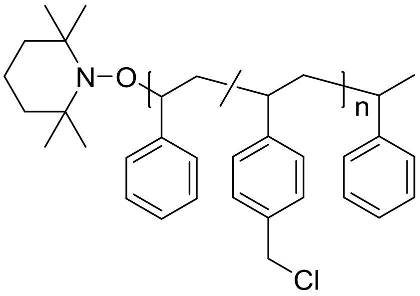


Scheme S3. Reaction sequence for the CA-PS-HW/TEMPO polymer **P5**.

Synthesis

Prop-2-yn-1-yl 3-(2-bromoacetoxy)-2-(hydroxymethyl)-2-methylpropanoate,[2] N^1,N^3-Bis(6-(3,3-dimethylbutanamido)pyridin-2-yl)-5-hydroxyisophthalamide,[3] 11-(2,4,6-trioxo-1,3,5-triazinan-1-yl)undecyl 2-bromo-2-methylpropanoate[4] were synthesized according to literature procedures.

General Procedure for the Synthesis of PS-*co*-CMS

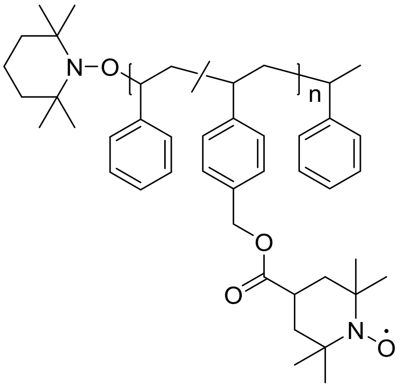


Styrene (2.25 mL, 19.6 mmol, 95.0 eq.), 4-(chloromethyl)styrene (0.31 mL, 2.18 mmol, 5.0 eq.) and 2,2,6,6-tetramethyl-1-(1-phenylethoxy)piperidine (57.0 mg, 0.218 mmol, 1.00 eq.) were placed into a flame-dried Schlenk flask and deoxygenated by four consecutive freeze–pump–thaw cycles. Subsequently, the reaction mixture was placed into an oil bath tempered at 125 °C. After 2 h the polymerization was stopped by cooling the flask with liquid nitrogen and opening it to the atmosphere. The crude product was diluted with THF (20 mL) and precipitated twice into cold methanol (200 mL). The polymer was afforded as a white powder by filtration and dried under high vacuum.

For **P2** the styrene (4-chloromethyl) styrene ratio was adjusted to 90:10. For the polymer **P3** the styrene (4-chloromethyl) styrene ratio was adjusted to 70:30 and the reaction time reduced to 0.5 h in bulk. For the polymer **P4** the styrene (4-chloromethyl) styrene ratio was adjusted to 70:30 and the reaction time reduced to 1 h.

^{1}H NMR (400 MHz, $CDCl_3$) δ / ppm = 7.09 – 6.50 (aromatic protons of PS and initiator), 4.52 (bs, 2H, CH_2Cl), 2.33 – 0.93 (m, aliphatic protons of PS and initiator).

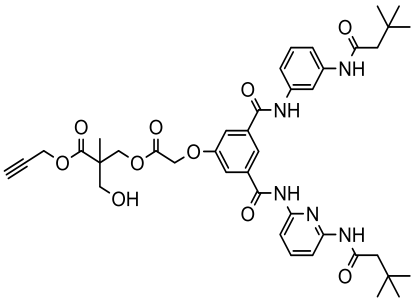
General Procedure for the Synthesis of PS-*co*-CMS/TEMPO



The PS-*co*-CMS polymer (200 mg, 0.414 mmol CMS, 1.00 eq.), K_2CO_3 (286 mg, 2.07 mmol, 5.00 eq.) and 4-carboxy-TEMPO (165 mg, 0.83 mmol, 2.00 eq.) were dissolved in DMF (10 mL). The mixture was stirred at 50 °C for 3 d. Subsequently, the mixture was diluted with ethyl acetate and washed three times with brine. The organic phase was dried over Na_2SO_4 and filtered. The solvent was removed under reduced pressure. The crude product was diluted with THF (10 mL) and precipitated twice into cold methanol (200 mL). After drying overnight under high vacuum, the product was obtained as an orange solid.

^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ / ppm = 7.12 – 6.63 (aromatic protons of PS and initiator), 5.15 (bs, 2H, CH_2-OCO), 2.33 – 0.96 (m, aliphatic protons of PS, initiator and carboxy TEMPO).

Synthesis of prop-2-yn-1-yl 3-(2-(3-((3-(3,3-dimethylbutanamido)phenyl)carbamoyl)-5-((6-(3,3-dimethylbutanamido)pyridin-2-yl)carbamoyl)phenoxy)acetoxy)-2-(hydroxymethyl)-2-methylpropanoate (4)



1 (1.00 g, 1.79 mmol) and **2** (0.524 g, 1.79 mmol) were each dissolved in dry DMF (5 mL). The solutions were combined and subsequently K_2CO_3 (0.562 g, 3.57 mmol) was added. The reaction mixture was stirred at ambient temperature for 3 d at rt. DCM (200 mL) was added and the solution was washed with water (50 mL). The organic phase was isolated and dried over Na_2SO_4. The solvent was removed under reduced pressure. The crude product was purified via column chromatography using ethyl acetate/dichloromethane as eluent (gradient from 1:10 to 1:1). The product was obtained as a white solid (0.82 g, 1.06 mmol, 59%).

^{1}H NMR (400 MHz, DMSO-d_6, 298 K) δ / ppm = 10.49 (s, 2H, NH^{a}), 10.01 (s, 2H, NH^{b}), 8.18 (s, 1H, CH^{c}), 7.93 – 7.69 (m, 8H, CH^{d}), 5.01 (s, 2H, CH_2^{e}), 4.69 (d, ^{4}J = 2.4 Hz, 2H, CH_2^{f}), 4.28 (dd, ^{1}J = 41.4 Hz,^{2}J = 10.8 Hz, 2H, CH_2^{g}), 3.53–3.52 (m, 3H, C$H_2^{h,k}$), 2.31 (s, 4H, CH_2^{l}), 1.10 (s, 3H. CH_3^{m}), 1.02 (s, 18H, CH_3^{n}).

^{13}C NMR (101 MHz, $CDCl_3$) δ / ppm = 174.8, 171.0, 168.5, 164.1, 158.4, 149.9, 149.5, 141.2, 136.2, 120.0, 117.0, 110.2, 109.8, 77.4, 76.0, 66.9, 65.2, 64.9, 60.5, 53.3, 51.4, 49.2, 31.5, 30.0, 21.2, 18.4, 14.3.

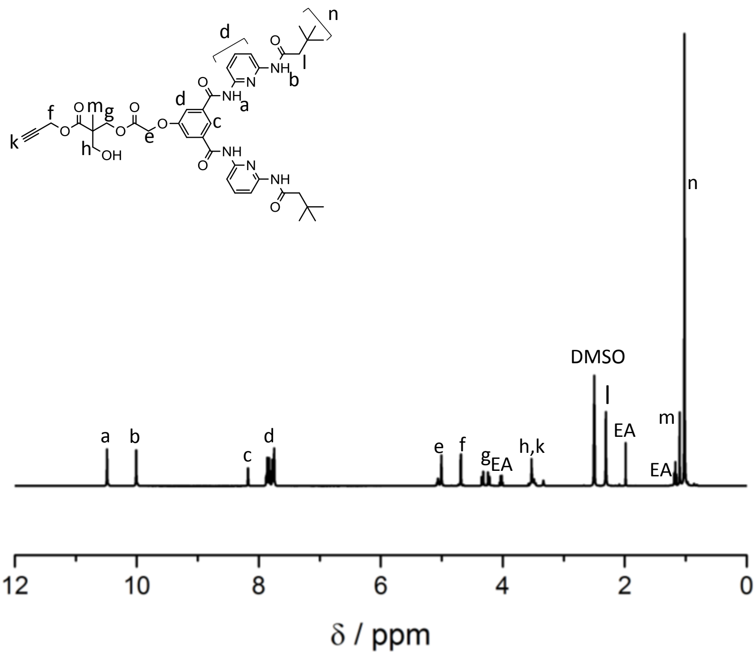
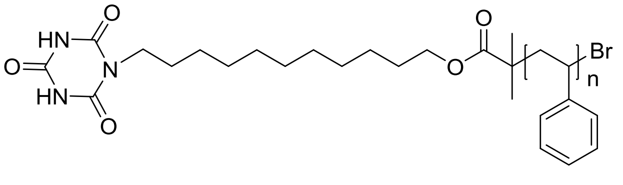


Figure S1. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298K) prop-2-yn-1-yl 3-(2-(3-((3-(3,3-dimethylbutanamido)-phenyl)carbamoyl)-5-((6-(3,3-dimethylbutanamido)pyridin-2-yl)carbamoyl)phenoxy)ace-toxy)-2-(hydroxymethyl)-2-methylpropanoate (4).

Synthesis of CA-PS-Br

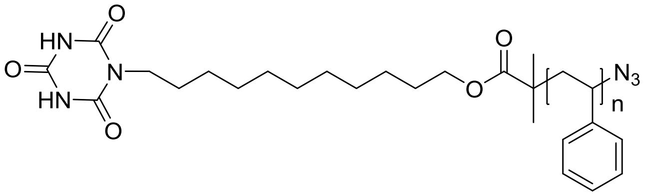


Styrene (6.00 mL, 52.0 mmol, 200 eq.), Cu(II)Br_2 (5.90 mg, 0.026 mmol, 0.1 eq.), and Me_6TREN (7.00 µL, 0.026 mmol, 0.1 eq.) were dissolved in anisole (5 mL) in a flame-dried Schlenk flask and subsequently purged with argon for 30 min. **3** (98.7 mg, 0.26 mmol, 1.00 eq.) and tin(II) 2-ethylhexanoat (53.0 mg, 0.130 mmol, 0.5 eq.) were each dissolved in anisole (1.5 mL) in separate round-bottom flasks and purged with argon for 10 min. The initiator and reducing agent were transferred to the reaction flask *via* a cannula. The reaction mixture was subsequently placed into an oil bath tempered at 90 °C for 24 h. After polymerisation, the flask was cooled to ambient temperature in a water bath and opened to the atmosphere. The copper catalyst was removed by passing the solution over a short column of neutral alumina oxide. The solvent was evaporated and the crude polymer dissolved in THF and precipitated twice into cold methanol (200 mL). The polymer was dried overnight under high vacuum and isolated as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ / ppm = 7.69 (2H of cyanuric acid), 7.41 – 6.09 (5H, Ar*H* of PS), 4.43 – 4.38 (1H, C*H*-Br), 3.76 (2H, $\mathrm{C}\mathit{H}_2$-O), 3.57 (2H, $\mathrm{C}\mathit{H}_2$-N), 1.88– 1.27 (aliphatic protons of PS).

M_n = 4400 g mol^{-1}, Đ = 1.08.

Synthesis of CA-PS-N_3

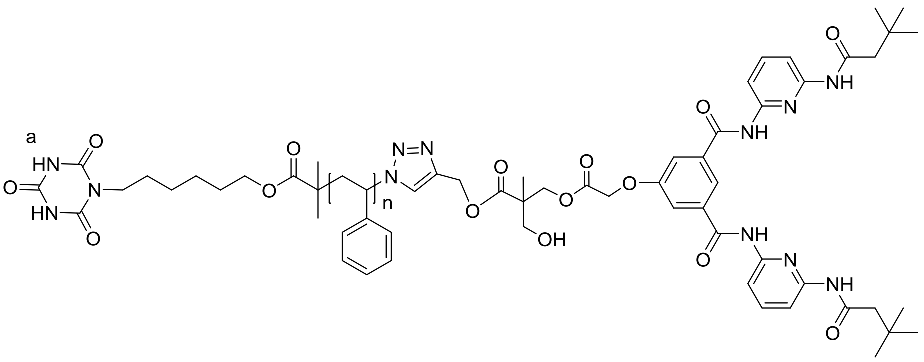


CA-PS-Br (2.50 g, 0.10 mmol, 1.0 eq.) was dissolved in DMF (10 mL) and NaN_3 (0.65 g, 1.00 mmol, 10 eq.) was added. The mixture was stirred for 3 d at ambient temperature. The reaction mixture was diluted with ethyl acetate and washed with distilled water. The organic phase was dried over Na_2SO_4 and the solvent was removed under reduced pressure. The residue was diluted with THF and precipitated into cold MeOH (200 mL). The polymer was dried overnight under high vacuum and isolated as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ / ppm = 7.87 (2H of cyanuric acid), 7.10 – 6.38 (5H, Ar*H* of PS), 3.94 (1H, C*H*-N_3), 3.82 (2H, $\mathrm{CH_2C}\mathit{H}_2$-N), 3.56 (2H, $\mathrm{CH_2C}\mathit{H}_2$-OCO), 1.88– 1.27 (aliphatic protons of PS).

M_n = 4400 g mol^{-1}, Đ = 1.07.

Synthesis of CA-PS-HW/OH

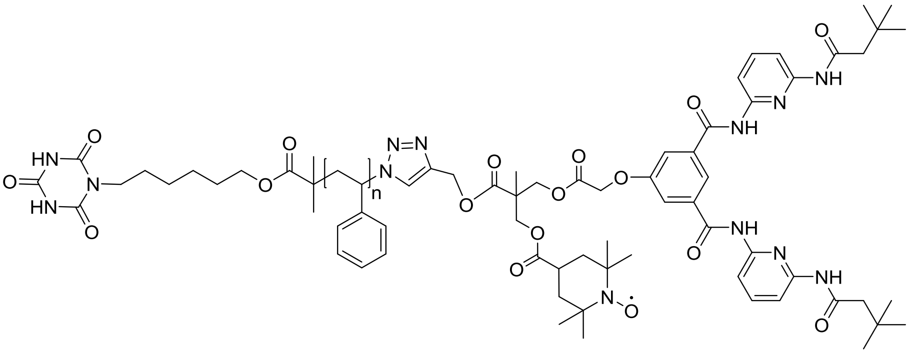


CA-PS-N_3 (400 mg, 17.3 µmol. 1.00 eq), **4** (20.1 mg, 0.03 mmol, 1.50 eq.), $CuSO_4 \times 5H_2O$ (9.00mg, 0.03 mmol, 2.00 eq.), sodium ascorbate (7 mg, 0.03 mmol, 2.00 eq.) were dissolved in dry DMF (10 mL) and stirred for 24 h at room temperature. Subsequently, the solids were filtered off, the solution was diluted with DCM and extracted with 5% EDTA solution. The organic phase was separated and dried over Na_2SO_4, concentrated and precipitated into cold MeOH (200 mL). The polymer was dried under high vacuum. The product was obtained as a white solid.

^{1}H NMR (400 MHz, CD_2Cl_2) δ / ppm = 12.71 (2H, NH^a), 9.92 – 9.49 (4H, N$H^{b,c}$), 8.24 – 7.67 (9H, CH^d), 7.41 – 6.09 (5H, ArH of PS), 5.18 – 5.07 (3H, CH^e, CH_2^f), 4.69 (2H, CH_2^g), 4.36 (2H, CH_2^h), 3.94 (2H, CH_2^i), 3.61 (2H, CH_2^k), 1.84-1.22 (aliphatic protons of PS), 1.11 (18H, CH_3^m).

$M_n = 5500$ g mol^{-1}, $Đ = 1.06$.

Synthesis of CA-PS-HW/TEMPO (P5)



Dry DCM (20 mL) was purged with argon in a flame dried Schlenk-flask for 15 minutes. CA-PS-HW/OH (150 mg, 5.80 μmol, 1.00 eq.), 4-carboxy-TEMPO (10.0 mg, 0.05 mmol, 10.0 eq.) and DMAP (3.60 mg, 0.03 mmol, 5.00 eq.) were dissolved in dry DCM (6 mL) in a flake dried Schlenk-flask. DCC (12.0 mg, 0.06 mmol, 10.0 eq.) dissolved in dry DCM (2 mL) was added rapidly through a septum. The mixture was stirred at ambient temperature and protected from light for 72 h. The solids were filtered off and the solvent was removed under vacuum. The residue was diluted with DCM and precipitated into cold MeOH (80 mL). The polymer was dried under high vacuum yielding an orange solid.

$M_n = 5600$ g mol^{-1}, $Đ = 1.05$.

No NMR assignment possible due to line broadening.

NMR Spectra of the synthesized polymers P1-P5 and P1’-P4’

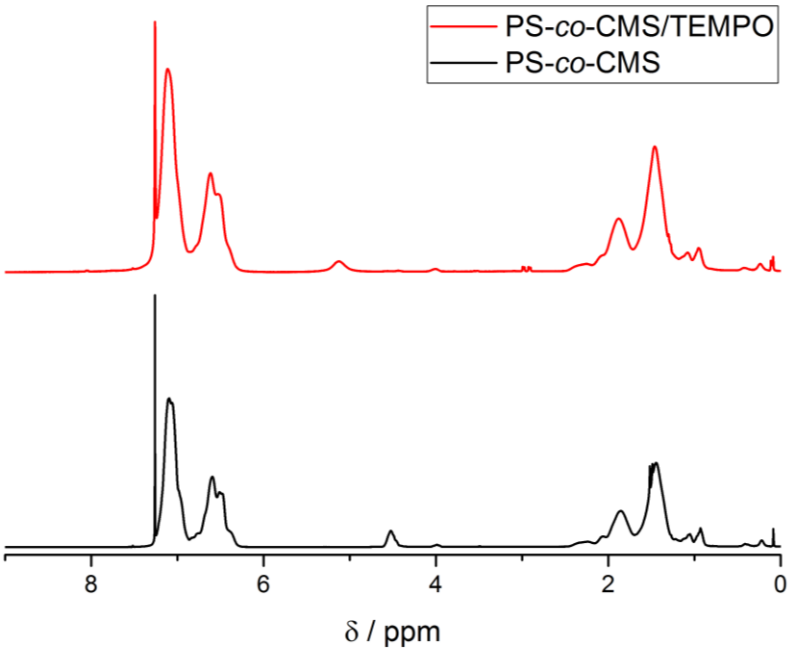


Figure S2. ^{1}H NMR spectra (400 MHz, $CDCl_3$, 298 K) of the polymers **P1** (black curve) and **P1’** (red curve).

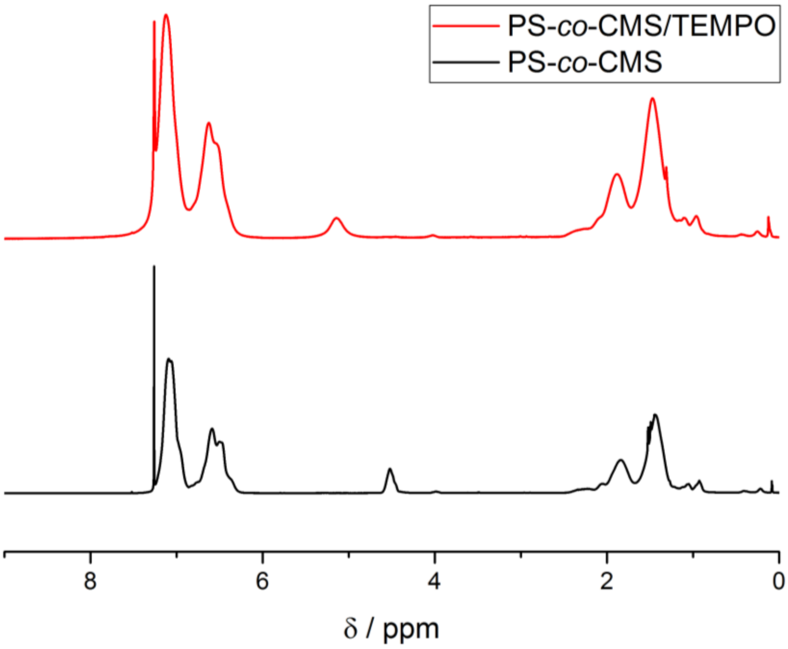


Figure S3. ^{1}H NMR spectra (400 MHz, $CDCl_3$, 298 K) of the polymers **P2** (black curve) and **P2’** (red curve).

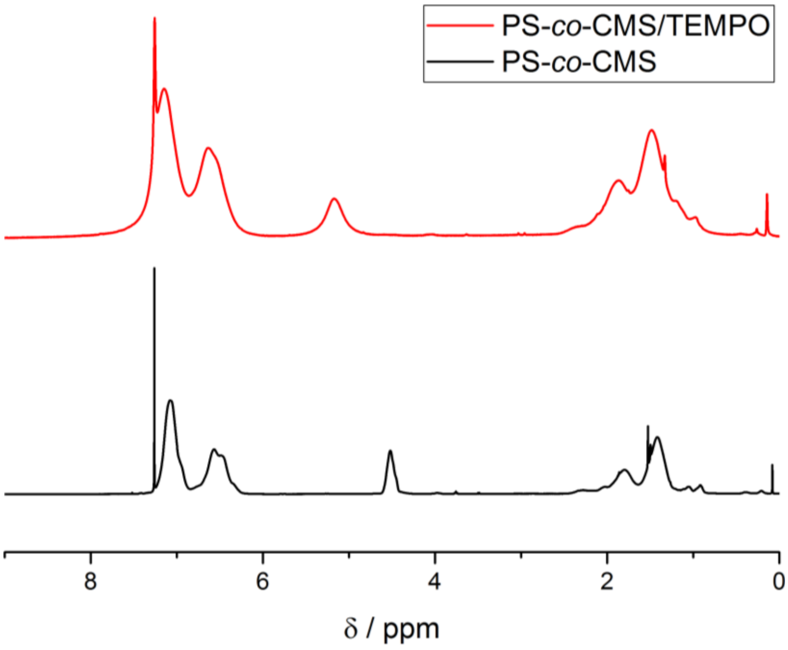


Figure S4. ^{1}H NMR spectra (400 MHz, $CDCl_3$, 298 K) of the polymers **P3** (black curve) and **P3'** (red curve).

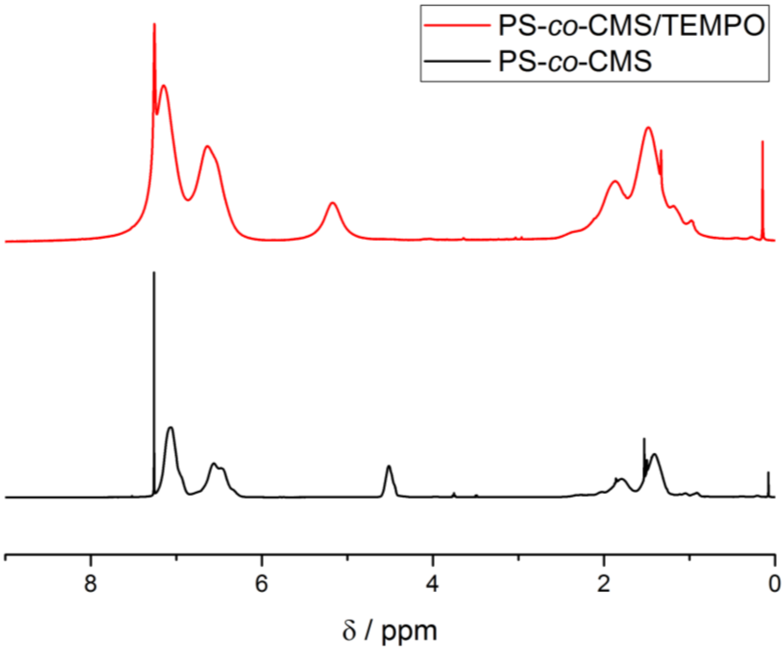


Figure S5. ^{1}H NMR spectra (400 MHz, $CDCl_3$, 298 K) of the polymers **P4** (black curve) and **P4'** (red curve).

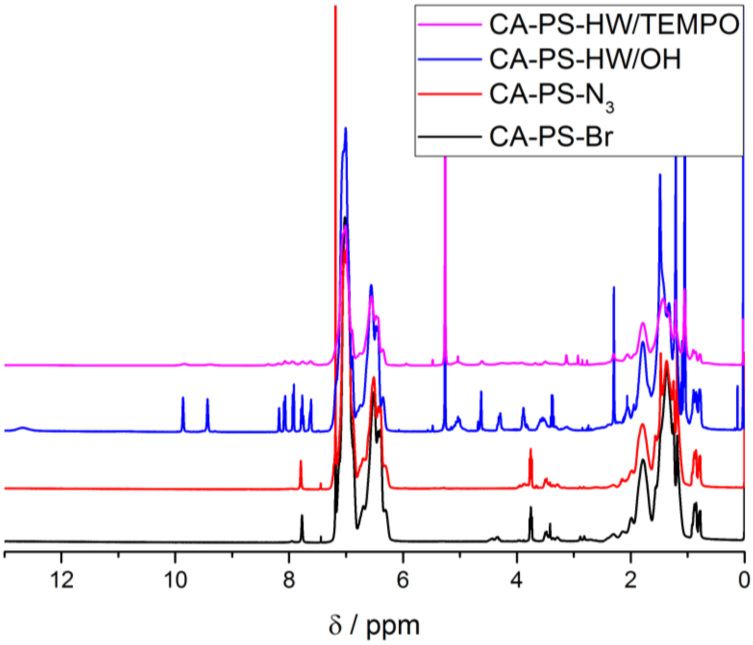


Figure S6. ^{1}H NMR spectra (400 MHz, $CDCl_3$, 298 K) of the polymers CA-PS-Br (black curve), CA-PS-N_3 (red curve), CA-PS-HW/OH (blue curve) and CA-PS-HW/TEMPO **P5** (pink curve).

SEC traces of the synthesized polymers

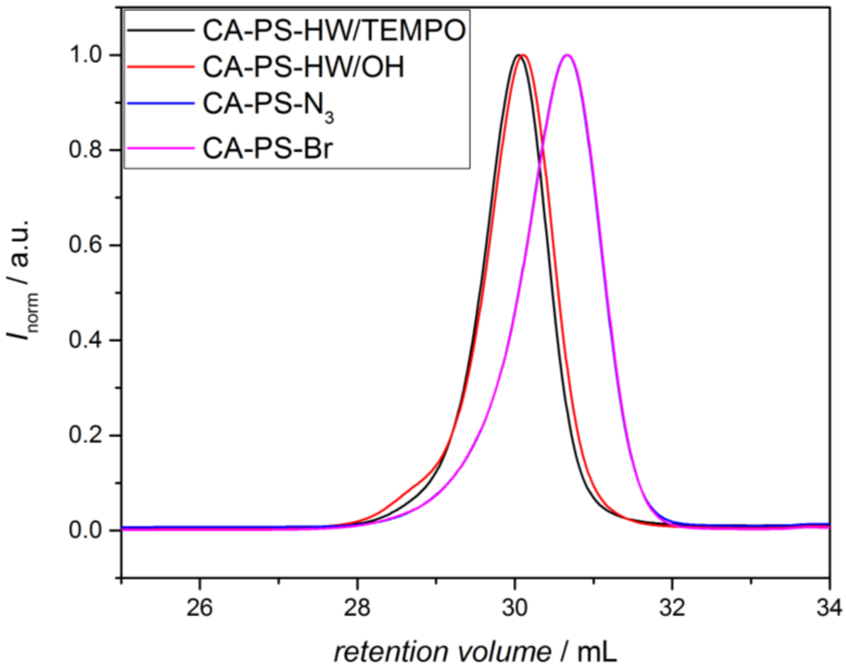


Figure S7. SEC chromatograms of CA-PS-Br (pink curve), CA-PS-N$_3$ (blue curve), CA-PS-HW/OH (red curve) and CA-PS-HW/TEMPO **P5** (black curve) using THF as eluent, calibrated with PS standards. The average molecular weights and *Đ* can be found in Table 1 for **P5** and in the experimental section of the Supporting Information for the polymer precursors.

MS Data

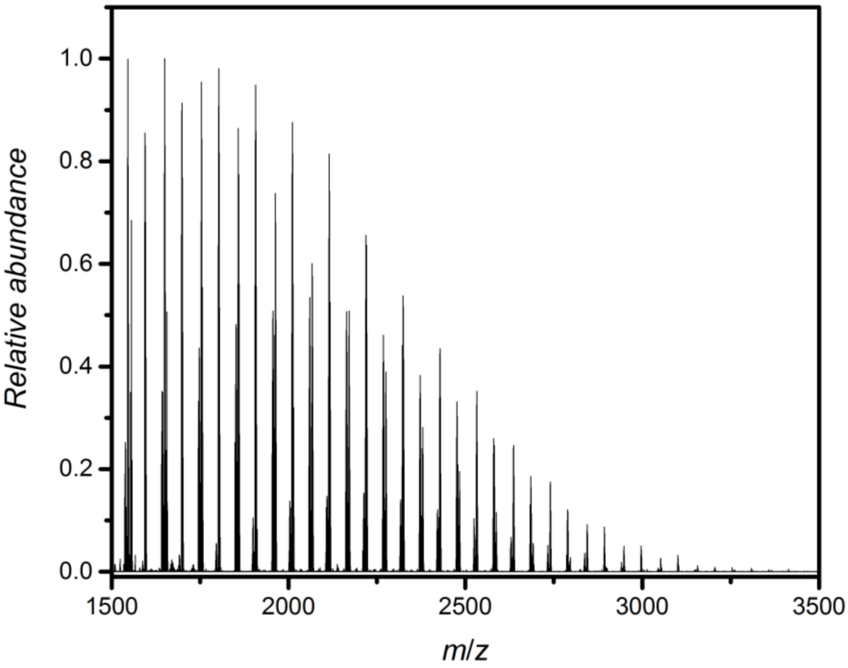


Figure S8. Overview ESI mass spectrum of **P1** recorded from *m*/*z* 1500 to 3500 recorded in negative ion mode.

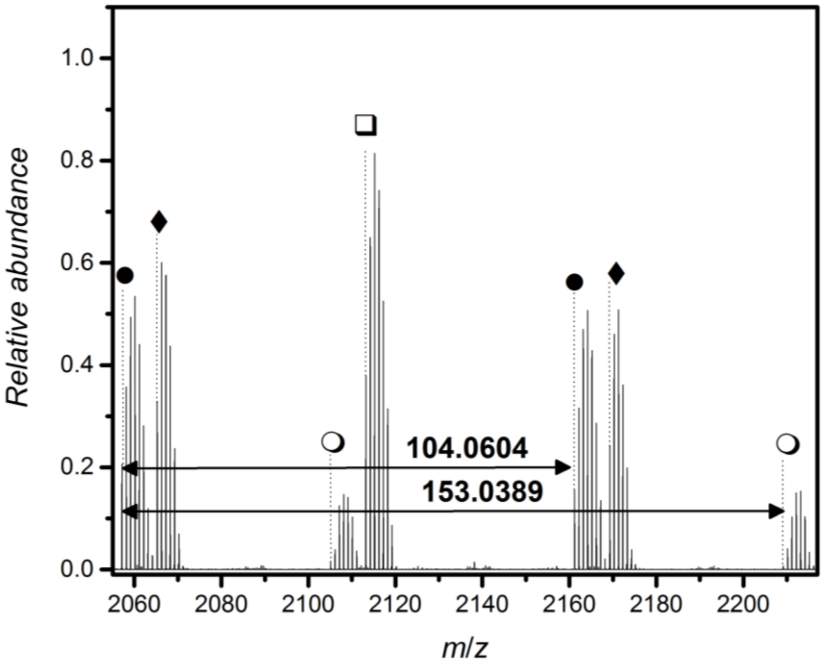
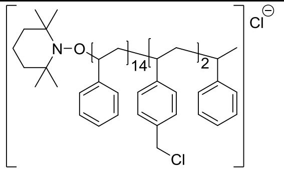
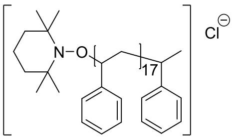
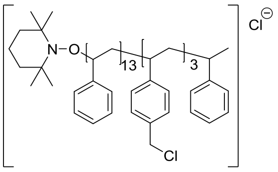
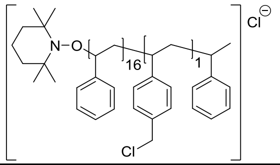


Figure S9. Expanded region of the ESI mass spectrum of **P1** recorded from *m*/*z* 2055 to 2217 recorded in negative ion mode.

Table S1 Peak assignment of the ESI Orbitrap mass spectrum of **P1** showing the labels (corresponding to the species in ***Figure S9***, the resolution (obtained by the Xcalibur software), the experimental *m*/*z* and theoretical *m*/*z* values, Δ*m*/*z,* their calculated double bond equivalents (DBE) and the proposed chemical structures.

Label	**Resolution**	***m*/*z*(exp)**	***m*/*z*(theo)**	**Δ*m*/*z***	**DBE**	**Structure**
●	48000	2057.1311	2057.1336	0.0025	68.5	
♦	46000	2065.2404	2065.2429	0.0025	72.5	
❍	49000	2105.1054	2105.1103	0.0049	68.5	
❑	47000	2113.2169	2113.2195	0.0027	72.5	

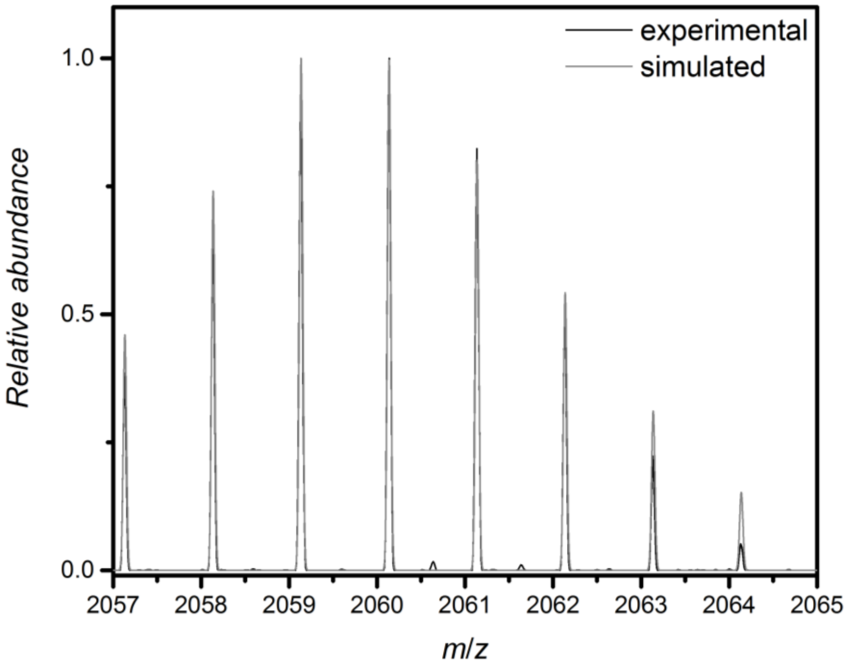


Figure S10. Isotopic simulation of a selected peak at *m*/*z* 2057 of **P1 (●)** comparing the experiment (black line) with the simulation (grey line).

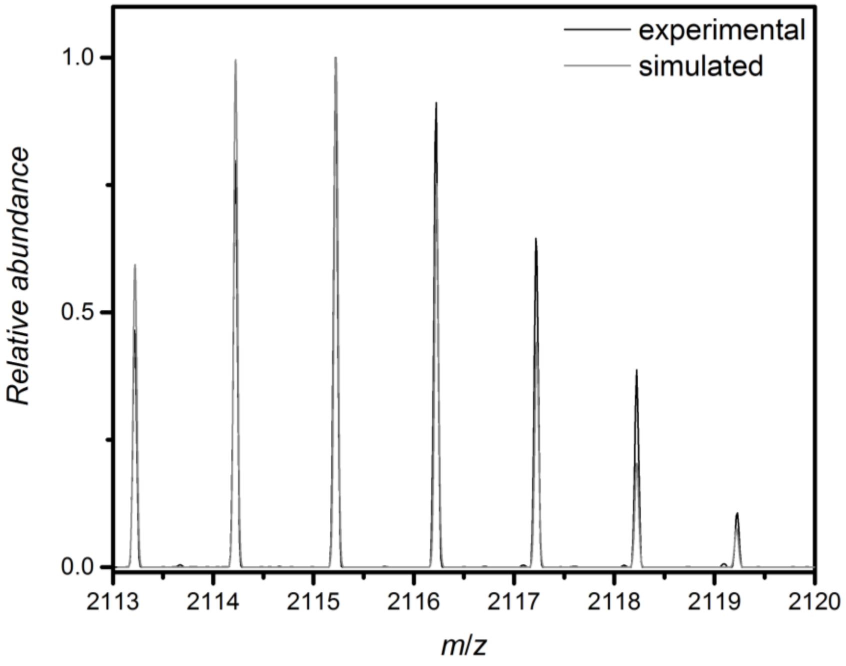


Figure S11. Isotopic simulation of a selected peak at *m*/*z* 2113 of **P1** (❑) comparing the experiment (black line) with the simulation (grey line).

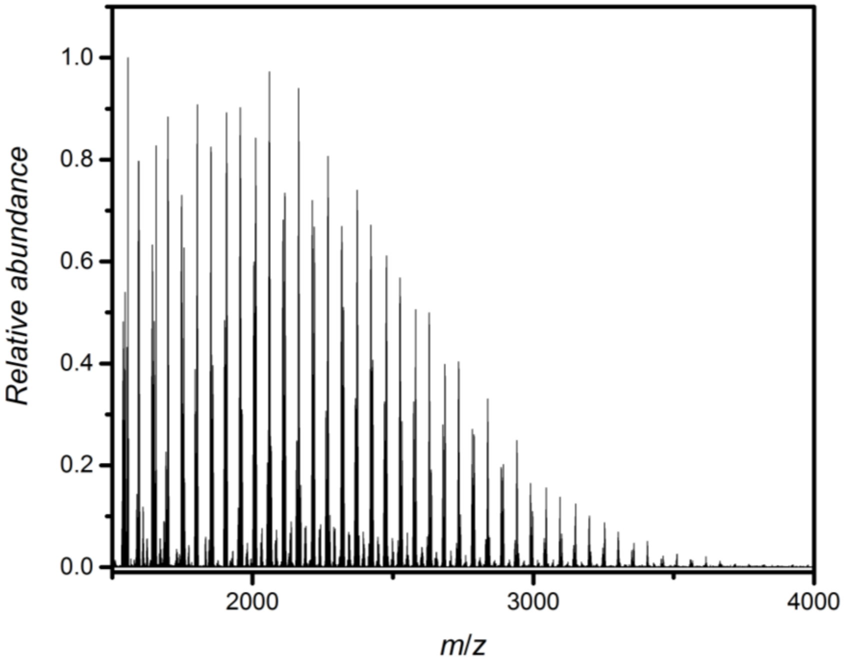


Figure S12. Overview ESI mass spectrum of **P2** recorded from *m*/*z* 1500 to 4000 measured in negative ion mode.

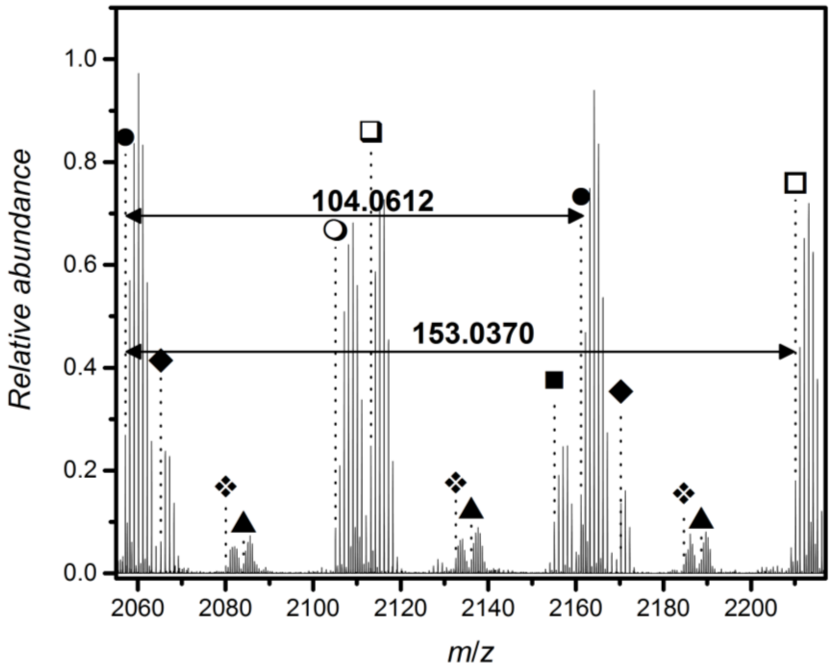
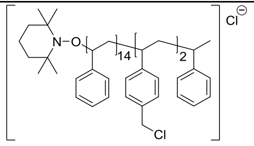
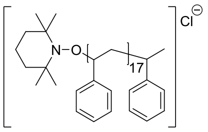
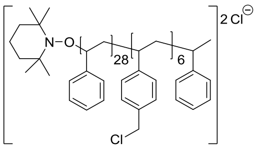
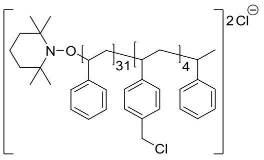
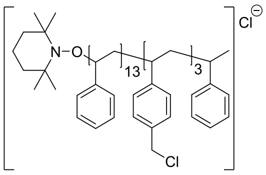
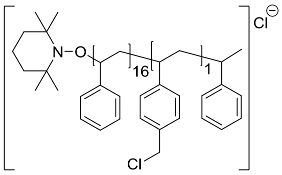
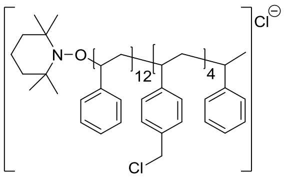
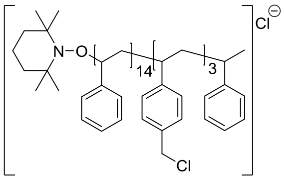


Figure S13. Expanded region of the ESI mass spectrum of **P2** recorded from *m*/*z* 2055 to 2217 measured in negative ion mode.

Table S2 Peak assignment of the ESI Orbitrap mass spectrum of **P2** showing the labels (corresponding to the species in ***Figure S13***, the resolution (obtained by the Xcalibur software), the experimental *m*/*z* and theoretical *m*/*z* values, Δ*m*/*z*, the calculated DBE and the proposed chemical structures.

Label	**Resolution**	***m*/*z*(exp)**	***m*/*z*(theo)**	**Δ*m*/*z***	**DBE**	**Structure**
●	52000	2057.1330	2057.1336	0.0006	68.5	
♦	46000	2065.2403	2065.2429	0.0026	62.5	
❖	50000	2080.0675	2080.0704	0.0029	140.5	
▲	47000	2084.1261	2084.1255	0.0006	144.5	

❍	49000	2105.1072	2105.1103	0.0031	68.5	
❑	49000	2113.2167	2113.2195	0.0028	72.5	
■	48000	2155.0838	2155.0884	0.0046	68.5	
□	47000	2209.1688	2209.1729	0.0041	72.5	

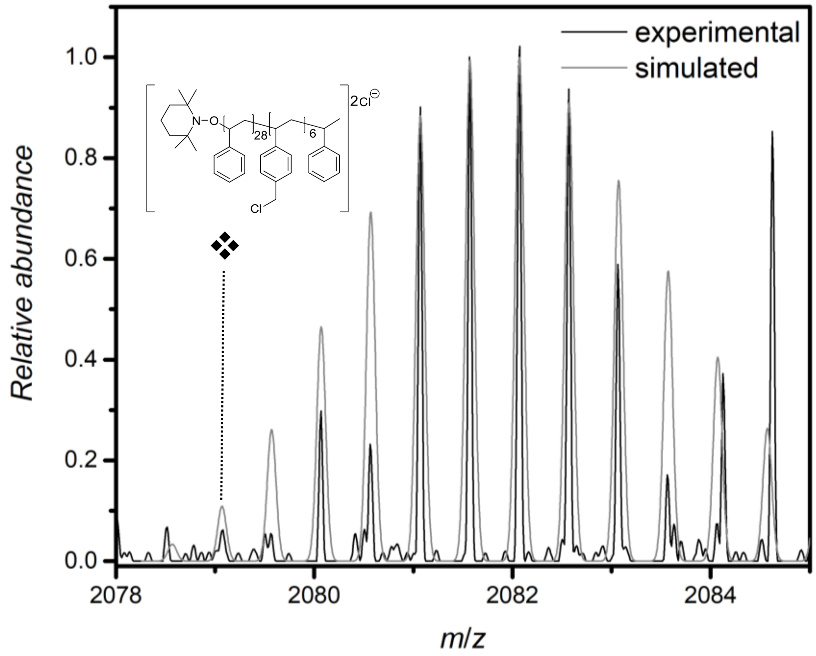


Figure S14. Isotopic simulation of a selected peak at *m*/*z* 2079 of **P2** (❖) comparing the experiment (black line) with the simulation (grey line) with a resolution of 47000.

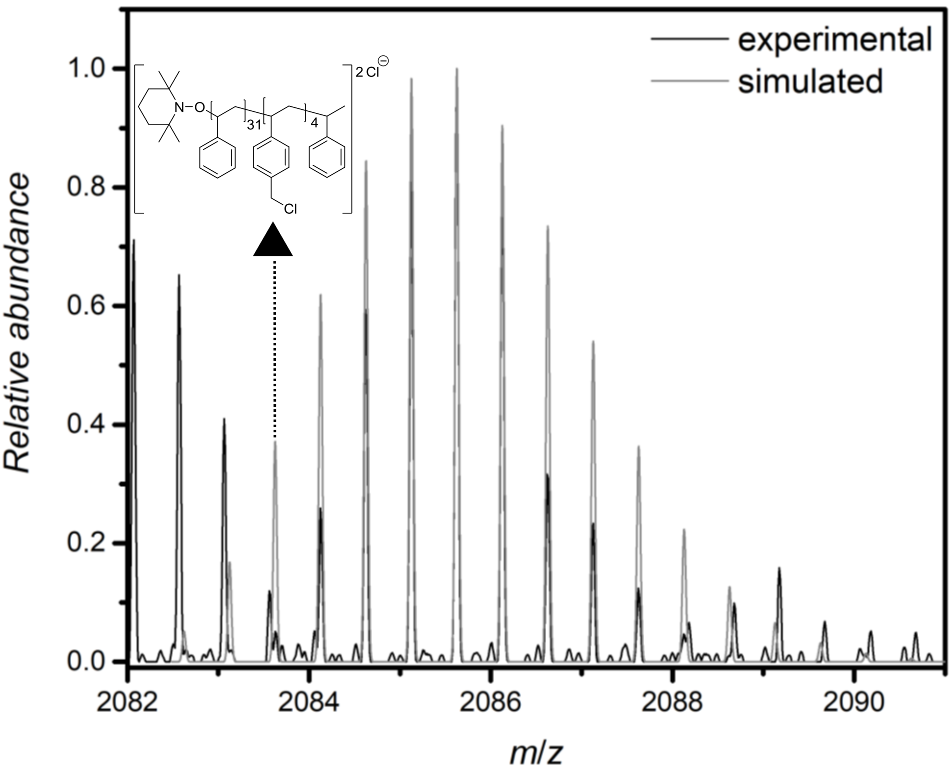


Figure S15. Isotopic simulation of a selected peak at *m*/*z* 2084 of **P2** (▲) comparing the experiment (black line) with the simulation (grey line) with a resolution of 47000.

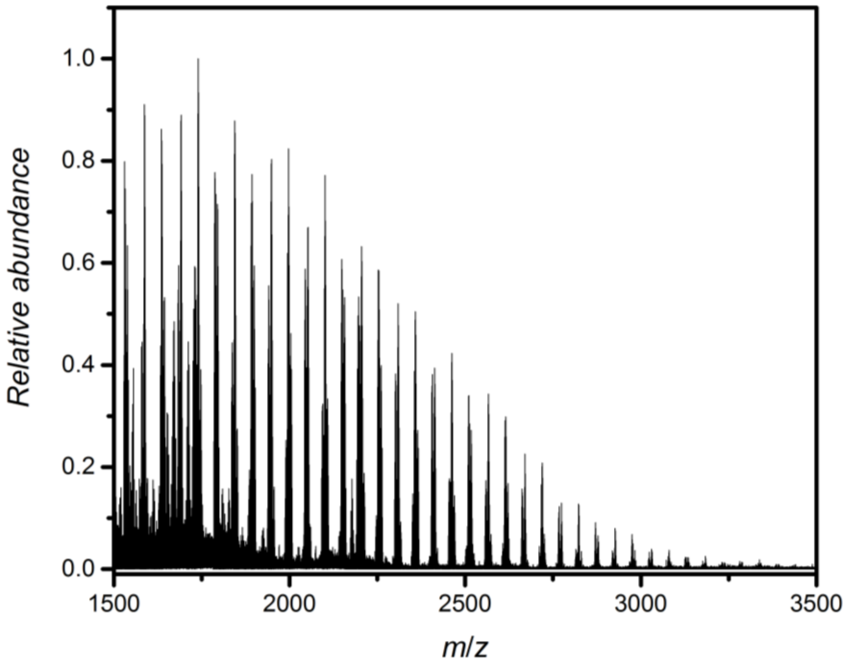


Figure S16. Overview ESI mass spectrum of **P3** recorded from *m*/*z* 1500 to 3500 measured in negative ion mode.

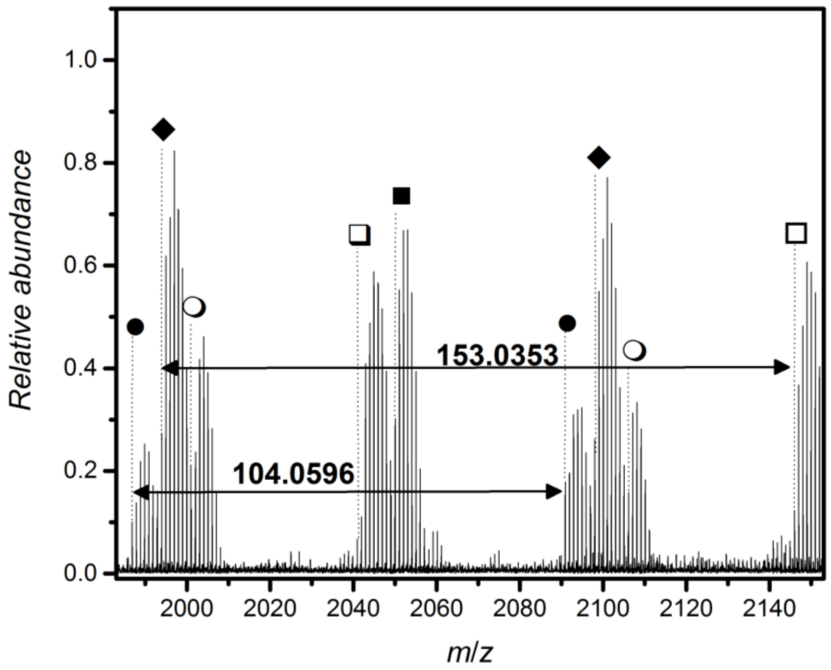
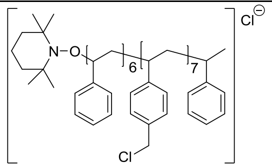
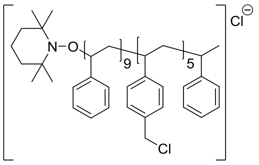
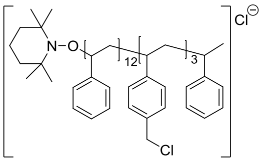
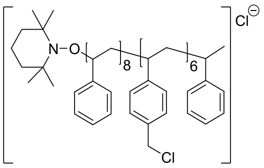
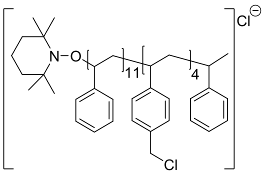
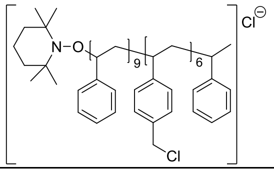


Figure S17. Expanded region of the ESI mass spectrum of **P3** recorded from *m*/*z* 1983 to 2153 measured in negative mode (refer to Table S3 for peak assignments).

Table S3 Peak assignments of the ESI Orbitrap mass spectrum of **P3** showing the labels (corresponding to the species in ***Figure S17***), the resolution (obtained by the Xcalibur software), the experimental *m*/*z* and theoretical *m*/*z* values, Δ*m*/*z*, the calculated DBE and the proposed chemical structures.

Label	**Resolution**	***m*/*z*(exp)**	***m*/*z*(theo)**	**Δ*m*/*z***	**DBE**	**Structure**
●	47000	1985.8391	1985.8326	0.0065	56.5	
♦	51000	1992.9441	1992.9385	0.0056	60.5	
❍	51000	2002.0572	2002.0506	0.0065	64.5	
❑	50000	2040.9210	2040.9151	0.0059	60.5	
■	49000	2050.0337	2050.0278	0.0059	64.5	
☐	49000	2145.9854	2145.9811	0.0043	64.5	

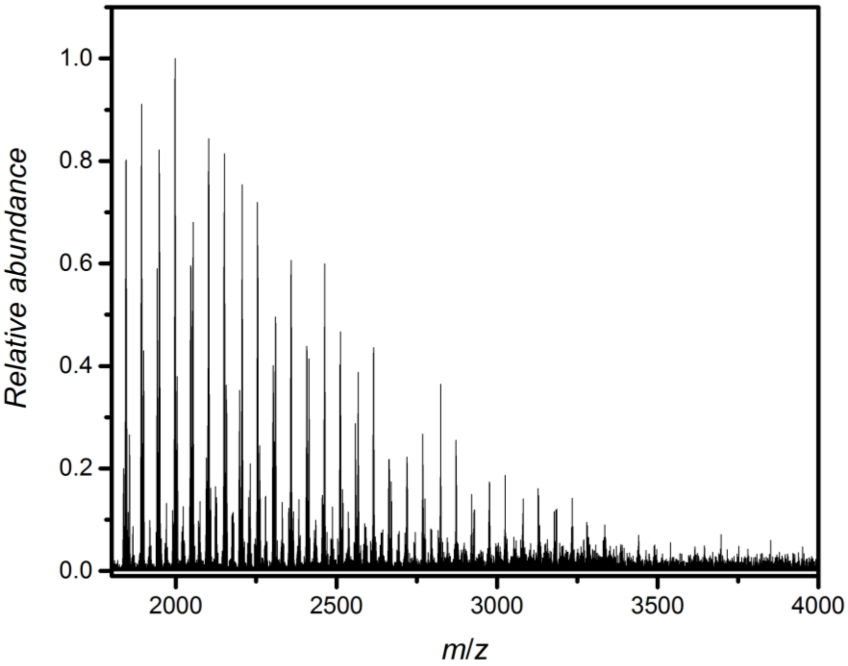


Figure S18. Overview ESI mass spectrum of **P4** recorded from *m*/*z* 1800 to 4000 measured in negative ion mode.

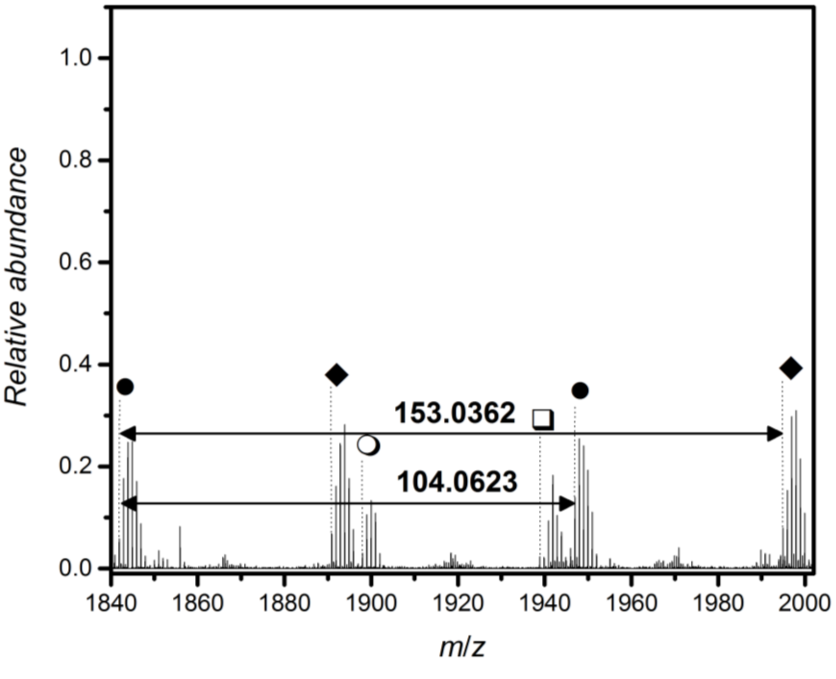


Figure S19. Expanded region of the ESI mass spectrum of **P4** recorded from *m*/*z* 1840 to 2010 measured in negative ion mode.

Table S4 Peak assignment of the ESI Orbitrap mass spectrum of **P4** showing the labels (corresponding to the species in ***Figure S19***), the resolution (obtained by the Xcalibur software), the experimental *m*/*z* and theoretical *m*/*z* values, Δ*m*/*z*, the calculated DBE and the proposed chemical structures.

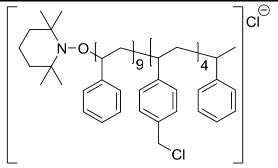
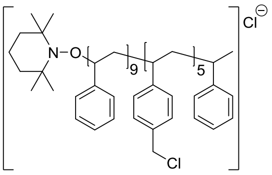
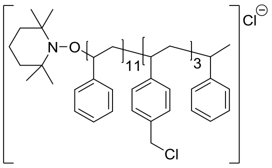
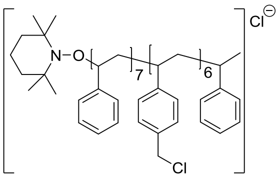
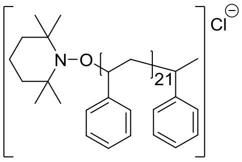
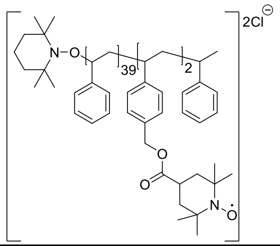
Label	**Resolution**	***m*/*z*(exp)**	***m*/*z*(theo)**	**Δ*m*/*z***	**DBE**	**Structure**
●	51000	1840.9000	1840.8992	0.0008	56.5	
♦	49000	1994.9400	1994.9390	0.0010	60.5	
❍	50000	1897.9888	1897.9885	0.0003	60.5	
❑	44000	1938.8505	1938.8525	0.0020	56.5	

Table S5 Peak assignment of the SEC-ESI Orbitrap mass spectrum of **P1'** showing the labels (corresponding to the species in ***Figure 2 and 3***), the resolution (obtained by the Xcalibur software), the experimental *m*/*z* and theoretical *m*/*z* values, Δ*m*/*z* and the proposed chemical structures.

Label	Resolution	*m*/*z*(exp)	*m*/*z*(theo)	Δ*m*/*z*	Structure
●	43000	2841.4822	2481.4933	0.0110	
♦	44000	2511.4804	2511.4877	0.0073	

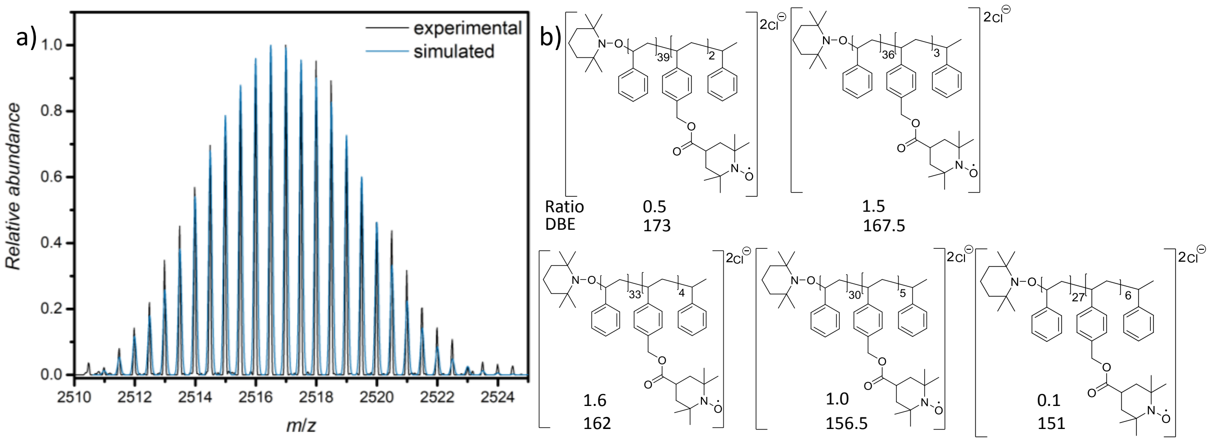


Figure S20. a) Isotopic simulation of a selected doubly charged pattern from *m*/*z* 2510 to 2525 of **P1'** (♦) comparing the experiment (black line) with the simulation (grey line) with a resolution of 43000. b) Identified structures and their ratio within the pattern as well as the DBE.

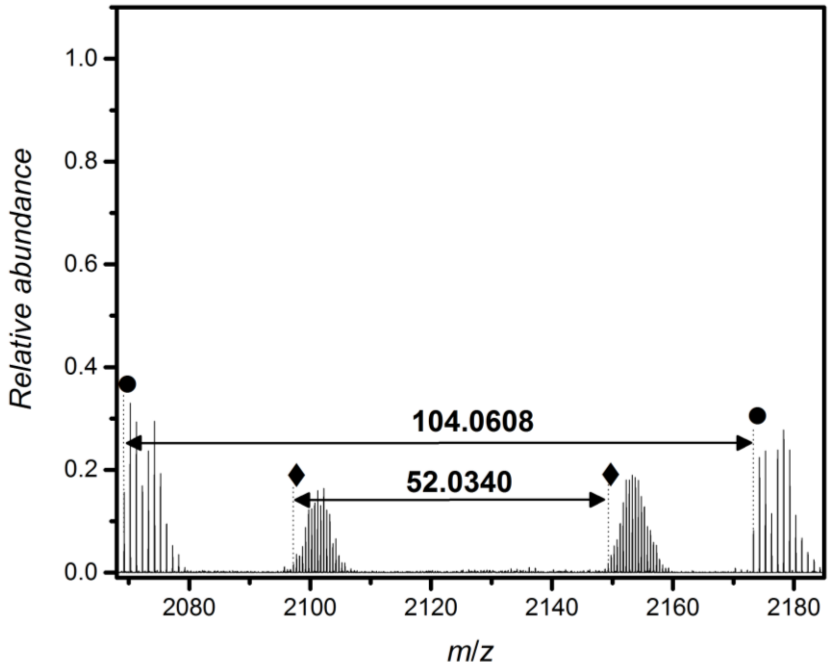
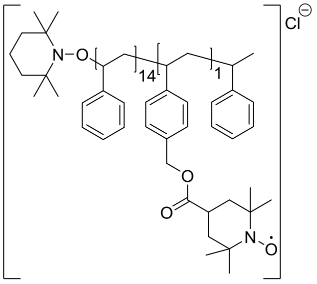
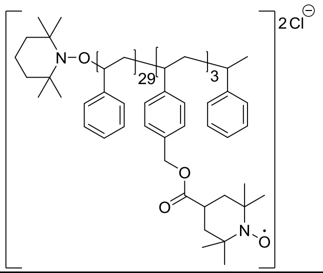


Figure S21. Expanded region of the ESI mass spectrum of **P2’** recorded from *m*/*z* 2068 to 2185 measured in negative mode.

Table S6 Peak assignment of the ESI Orbitrap mass spectrum of **P2’** showing the labels (corresponding to the species in ***Figure S21***), the resolution (obtained by the Xcalibur software), the experimental *m*/*z* and theoretical *m*/*z* values, Δ*m*/*z* and the proposed chemical structures.

Label	**Resolution**	***m*/*z*(exp)**	***m*/*z*(theo)**	**Δ*m*/*z***	**Structure**
●	48000	2069.2441	2069.2463	0.0022	
♦	45000	2148.7670	2148.7686	0.0016	

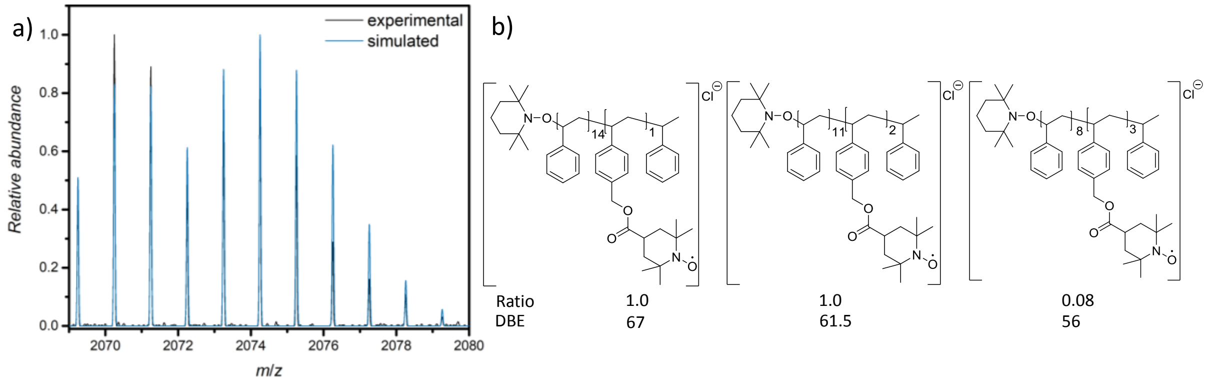


Figure S22. a) Isotopic simulation of a selected single charged pattern from *m/z* 2069 to 2079 of **P2’** (●) comparing the experiment (black line) with the simulation (grey line) with a resolution of 49000. b) Identified structures and their ratio within the pattern as well as the DBE.

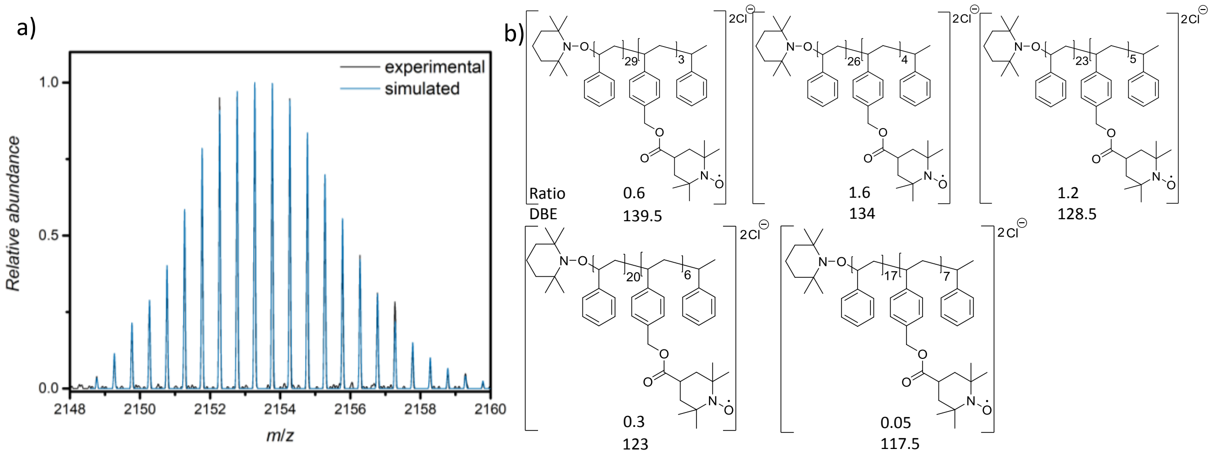


Figure S23. a) Isotopic simulation of a selected double charged pattern from *m/z* 2149 to 2159 of **P2’** (♦) comparing the experiment (black line) with the simulation (grey line) with a resolution of 47000. b) Identified structures and their ratio within the pattern as well as the DBE.

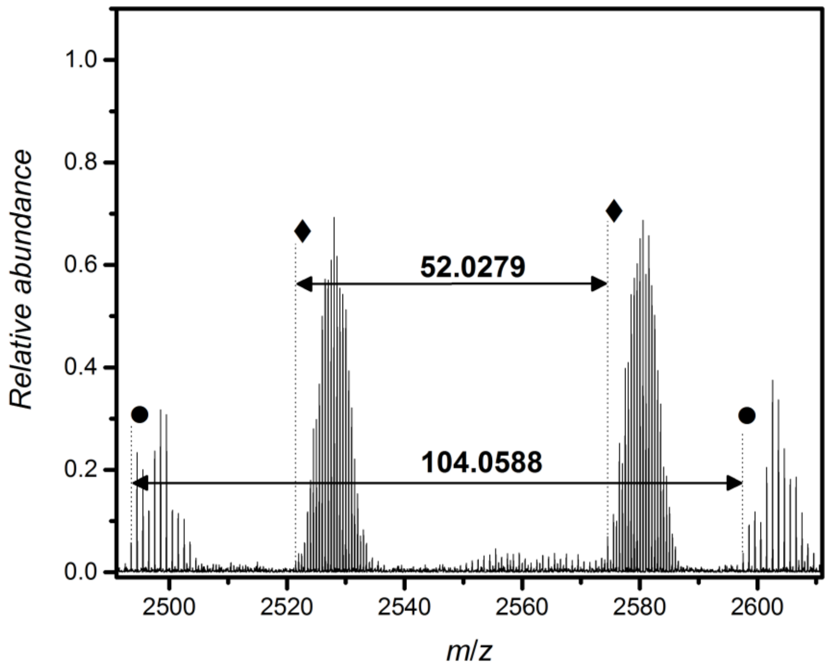
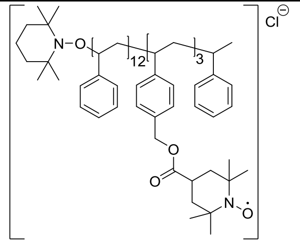
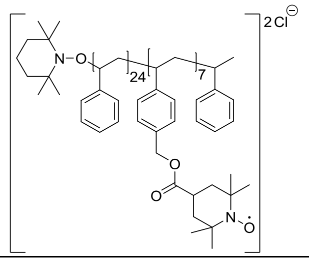


Figure S24. Expanded region of the ESI mass spectrum of **P3’** recorded from *m*/*z* 2491 to 2611 measured in negative mode.

Table S7 Peak assignment of the ESI Orbitrap mass spectrum of **P3’** showing the labels (corresponding to the species in ***Figure S24***), the resolution (obtained by the Xcalibur software), the experimental *m*/*z* and theoretical *m*/*z* values, Δ*m*/*z* and the proposed chemical structures.

Label	**Resolution**	***m*/*z*(exp)**	***m*/*z*(theo)**	**Δ*m*/*z***	**Structure**
●	42000	2493.4995	2493.5037	0.0042	
♦	39000	2521.9906	2521.9976	0.0070	

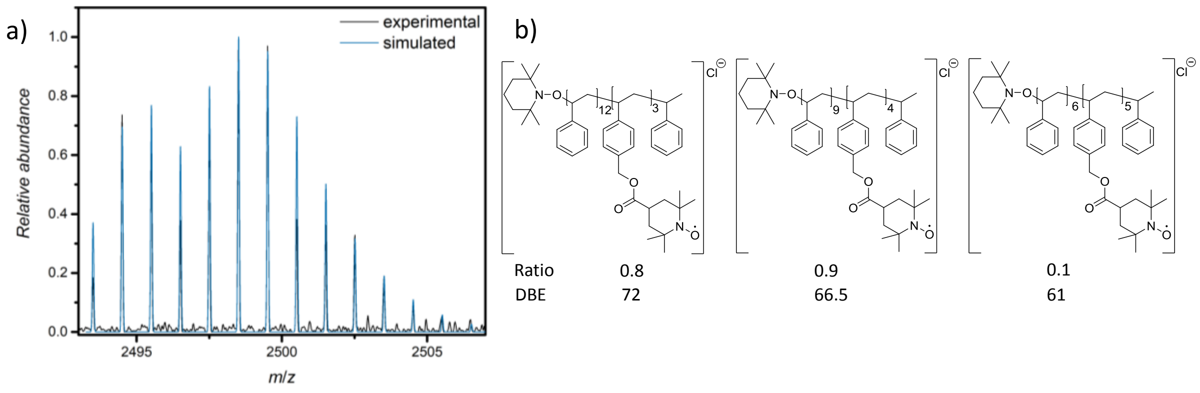


Figure S25. a) Isotopic simulation of a selected single charged pattern from *m/z* 2491 to 2504 of **P3'** comparing the experiment (black line) with the simulation (grey line) with a resolution of 43000. b) Identified structures and their ratio within the pattern as well as the DBE.

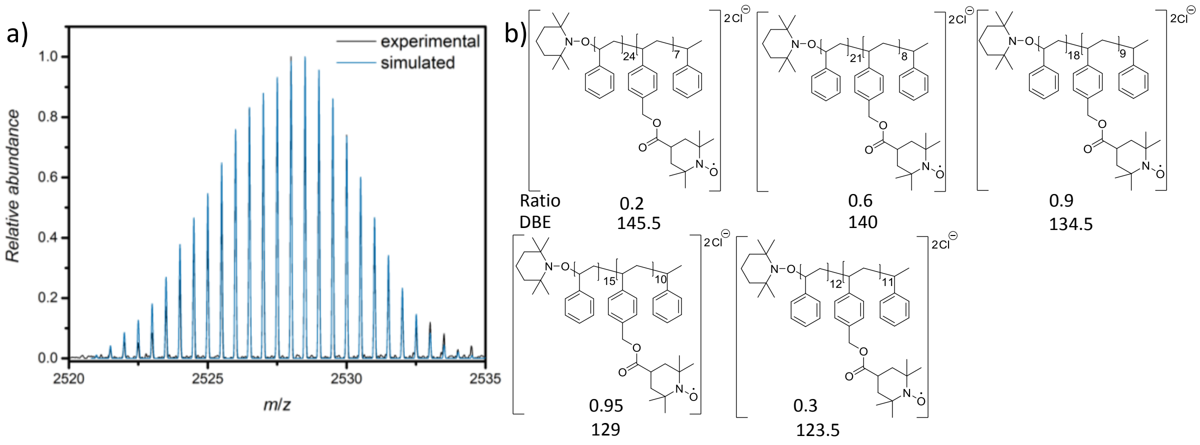


Figure S26. a) Isotopic simulation of a selected double charged pattern from *m/z* 2521 to 2533 of **P3'** comparing the experiment (black line) with the simulation (grey line) with a resolution of 43000. b) Identified structures and their ratio within the pattern as well as the DBE.

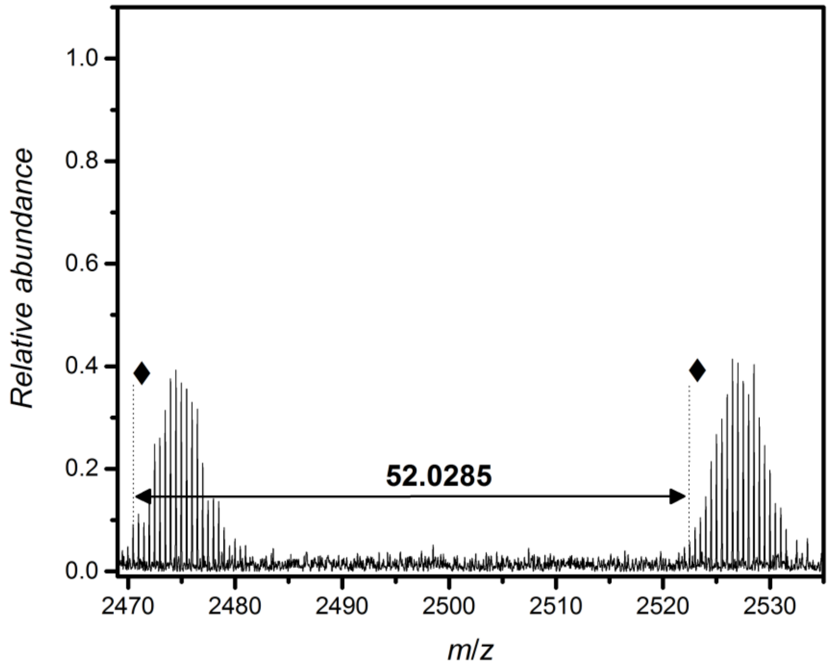
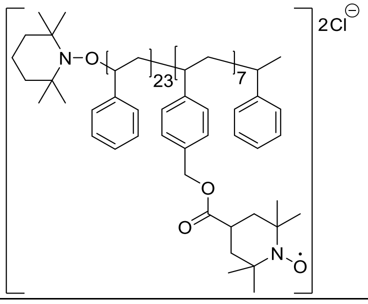


Figure S27. Expanded region of the ESI mass spectrum of **P4’** recorded from *m*/*z* 2469 to 2535 measured in negative mode.

Table S8 Peak assignment of the ESI Orbitrap mass spectrum of **P4’** showing the labels (corresponding to the species in ***Figure S27***), the resolution (obtained by the Xcalibur software), the experimental *m*/*z* and theoretical *m*/*z* values, Δ*m*/*z* and the proposed chemical structures.

Label	**Resolution**	***m*/*z*(exp)**	***m*/*z*(theo)**	**Δ*m*/*z***	**Structure**
●	33000	2469.4577	2469.4650	0.0073	

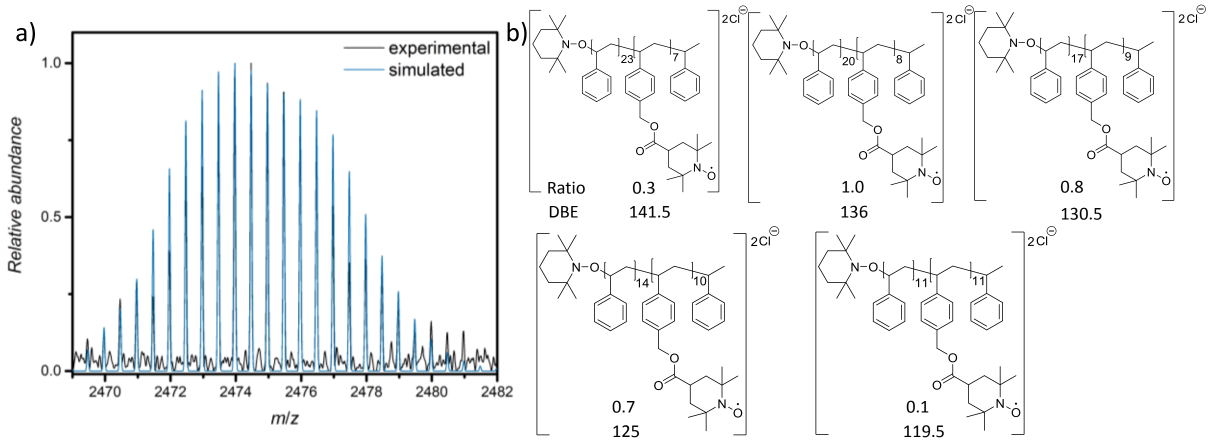


Figure S28. a) Isotopic simulation of a selected double charged pattern from *m*/*z* 2470 to 2480 of **P4'** comparing the experiment (black line) with the simulation (grey line) with a resolution of 42000. b) Identified structures and their ratio within the pattern as well as the DBE.

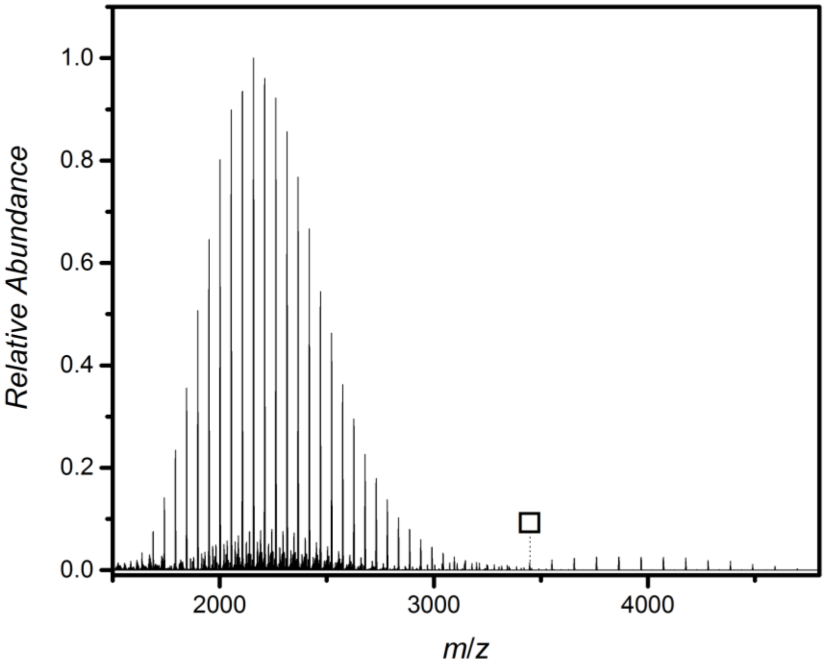


Figure S29. Overview ESI mass spectrum of **P5** recorded from *m*/*z* 1500 to 4800 measured in negative mode.

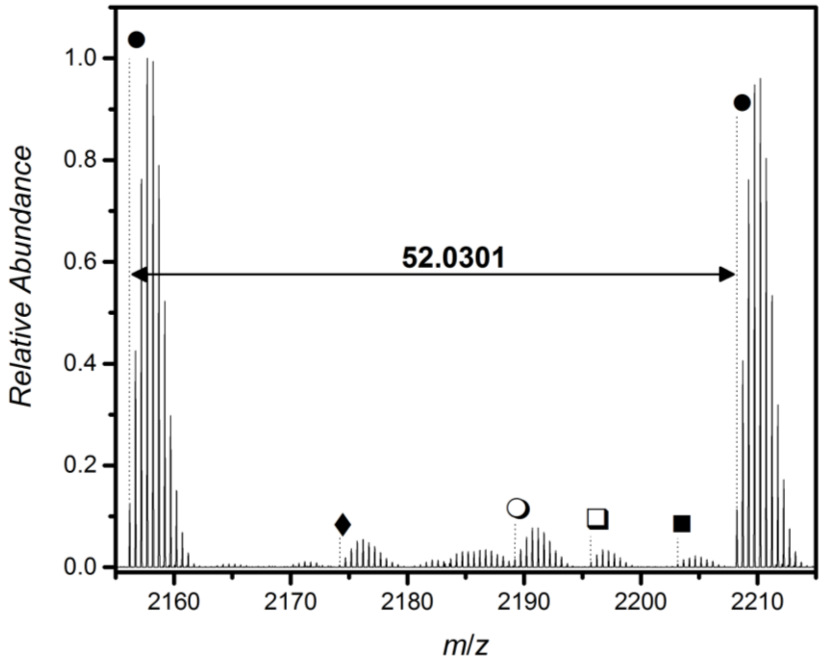
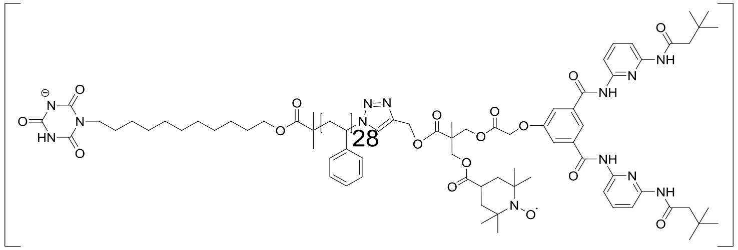
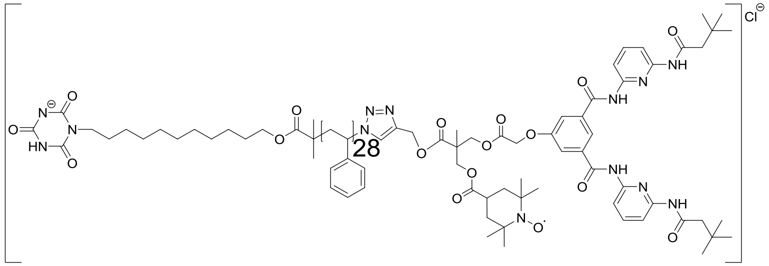
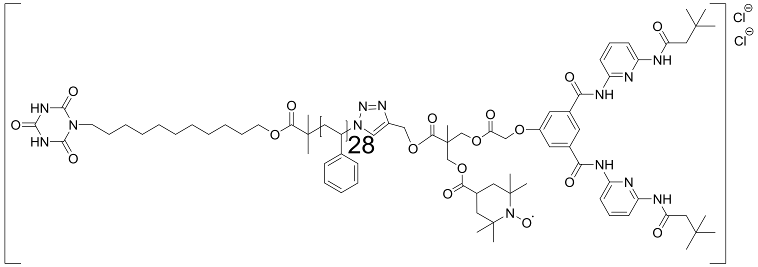
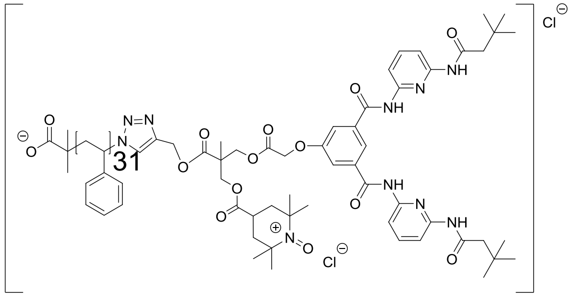
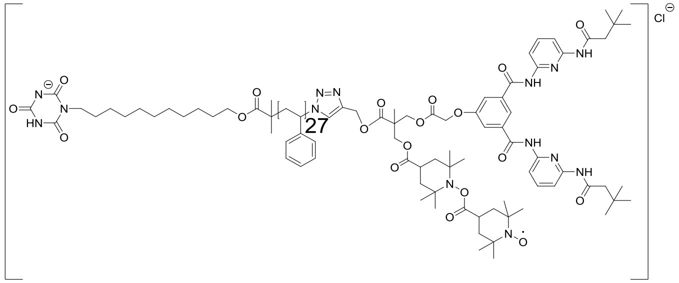
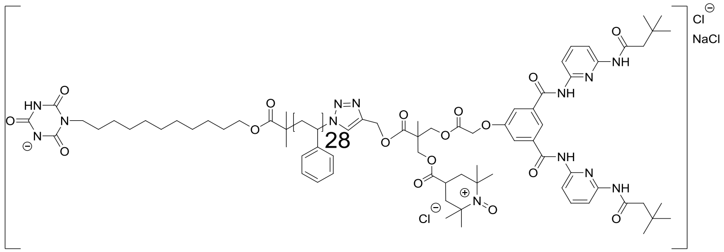


Figure S30. Expanded region of the ESI mass spectrum of **P5** recorded from *m*/*z* 2155 to 2215 measured in negative mode.

Table S9 Peak assignment of the ESI Orbitrap mass spectrum of **P5** showing the labels (corresponding to the species in ***Figure S29 and S30***), the resolution (obtained by the Xcalibur software), the experimental *m*/*z* and theoretical *m*/*z* values, Δ*m*/*z* and the proposed chemical structures.

Label	Resolution	***m*/*z*(exp)**	***m*/*z*(theo)**	**Δ*m*/*z***	DBE	Structure
□	35000	4278.3730	4278.4379	0.0649	141	
●	45000	2156.2037	2156.2020	0.0017	140.5	
◆	42000	2174.1942	2174.1903	0.0039	139.5	

❍	43000	2189.2056	2189.1934	0.0122	148	
❑	45000	2195.7291	2195.7337	0.0046	138.5	
■	42000	2203.1659	2203.1674	0.0015	140	

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