

Supporting Information

Pushing the Limits of Single Chain Compaction Analysis by Observing Specific Size Reductions via High Resolution Mass Spectrometry

Tobias Nitsche^{a,b}, Stephen J. Blanksby^{a,c}, James P. Blinco^{a,b,*} and Christopher Barner-Kowollik^{a,b,d,*}

a. Centre for Materials Science, Queensland University of Technology, 2 George Street, Brisbane, QLD 4000, Australia

b. School of Chemistry and Physics, Queensland University of Technology, 2 George Street, Brisbane, QLD 4000, Australia.

c. Central Analytical Research Facility, Institute for Future Environments, Queensland University of Technology, 2 George Street, Brisbane, QLD 4000, Australia.

d. Macromolecular Architectures, Institut für Technische Chemie und Polymerchemie, Karlsruhe Institute of Technology, Engesserstrasse 18, 76131 Karlsruhe.

Contents

1. Materials	2
2. Characterization Methods and Instrumentation.....	2
3. Experimental Section	3
4. Additional SEC curves.....	8
4. Hydrodynamic radius (R_H) calibration.....	11
5. SEC-ESI-MS Analysis	12
6. XIC Separation	23
6. References	30

1. Materials

(1-Bromoethyl) benzene (97%), copper powder (99%), 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO, 98%), *N,N,N',N'',N''*-pentamethyldiethylenetriamine (PMDETA, 99%), styrene (>99%), 1-butanethiol (99%), 1,2-dichloroethane (anhydrous, 99.8%), tin(IV) chloride (98%), magnesium sulfate (anhydrous) and chloroform-*d*₁ were purchased from *Sigma Aldrich*. Chloromethylstyrene (CMS, technical grade, 90%), tetrahydrofuran (THF, HPLC grade), acetonitrile, methanol and *n,n*-Dimethylformamide (DMF) were purchased from *Thermo Fisher Scientific*. Sodium hydroxide was purchased from *Chem-Supply*.

All materials were reagent grade and used as received, unless stated otherwise. Styrene was de-inhibited by passing over a column of activated basic alumina (*Ajax*) directly prior to use. CMS was dissolved in diethyl ether, washed three times with 0.5% aqueous NaOH solution and dried over sodium sulfate. The residual solvent was removed under reduced pressure and the remaining CMS was distilled under vacuum at 95 °C.

2. Characterization Methods and Instrumentation

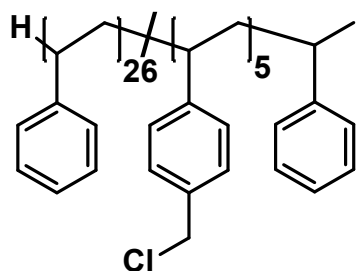
Size exclusion chromatography-electrospray ionization mass spectrometry (SEC-ESI MS). Spectra were recorded on a Q Exactive Biopharma (Orbitrap) mass spectrometer (*Thermo Fisher Scientific*, Bremen, Germany) equipped with an HESI II electrospray ionization probe. The instrument was calibrated in the *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 auxiliary 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 1-4 mg mL⁻¹ was injected into the SEC system.

Nuclear magnetic resonance (NMR) spectroscopy. ^1H NMR -spectra were recorded on a *Bruker* System 600 Ascend LH, equipped with an BBO-Probe (5 mm) with z-gradient (^1H : 600.13 MHz). Resonances are reported in parts per million (ppm) relative to tetramethylsilane (TMS). The δ -scale was normalized relative to the solvent signal of CHCl_3 .

3. Experimental Section

2,2,6,6-Tetramethyl-1-(1-phenylethoxy)piperidine

The synthesis was adapted from the literature.²



Poly(styrene-co-chloromethylstyrene) (P(S-co-CMS)) (P1)

150 mg 2,2,6,6-Tetramethyl-1-(1-phenylethoxy)piperidine (0.57 mmol, 1.00 eq.) and 9.3 mg TEMPO (0.06 mmol, 0.10 eq.) were dissolved in a mixture of 3.94 mL styrene (3.59 g, 34.4 mmol, 60.0 eq.) and 0.81 mL chloromethylstyrene (0.87 g, 5.74 mmol, 10.0 eq.). The reaction mixture was degassed via four freeze-thaw cycles. The reaction was carried out for 6.5 h at 125 °C. The crude mixture was diluted with THF and precipitated twice dropwise into 1 L methanol. The

precipitate was collected by filtration and dried at 35 °C under vacuum. 1.20 g of the precipitate (0.34 mmol, 1.00 eq) were dissolved in 90 mL DMF and degassed by bubbling the solution with a stream of argon for 15 mins. 0.37 mL butanethiol (0.31 g, 3.43 mmol, 10.0 eq.) were added and the solution was heated to 120 °C for 1.5 h. The solvent was removed under reduced pressure, the residual was dissolved in 5 mL THF and precipitated twice into 350 mL ice-cold methanol. The polymer **P1** was filtered and dried at 35 °C under vacuum.

^1H NMR (CDCl_3 , 600 MHz) δ = 7.61 – 5.99 (m, a), 4.79 – 4.30 (s, b), 2.50-0.64 (m, c).

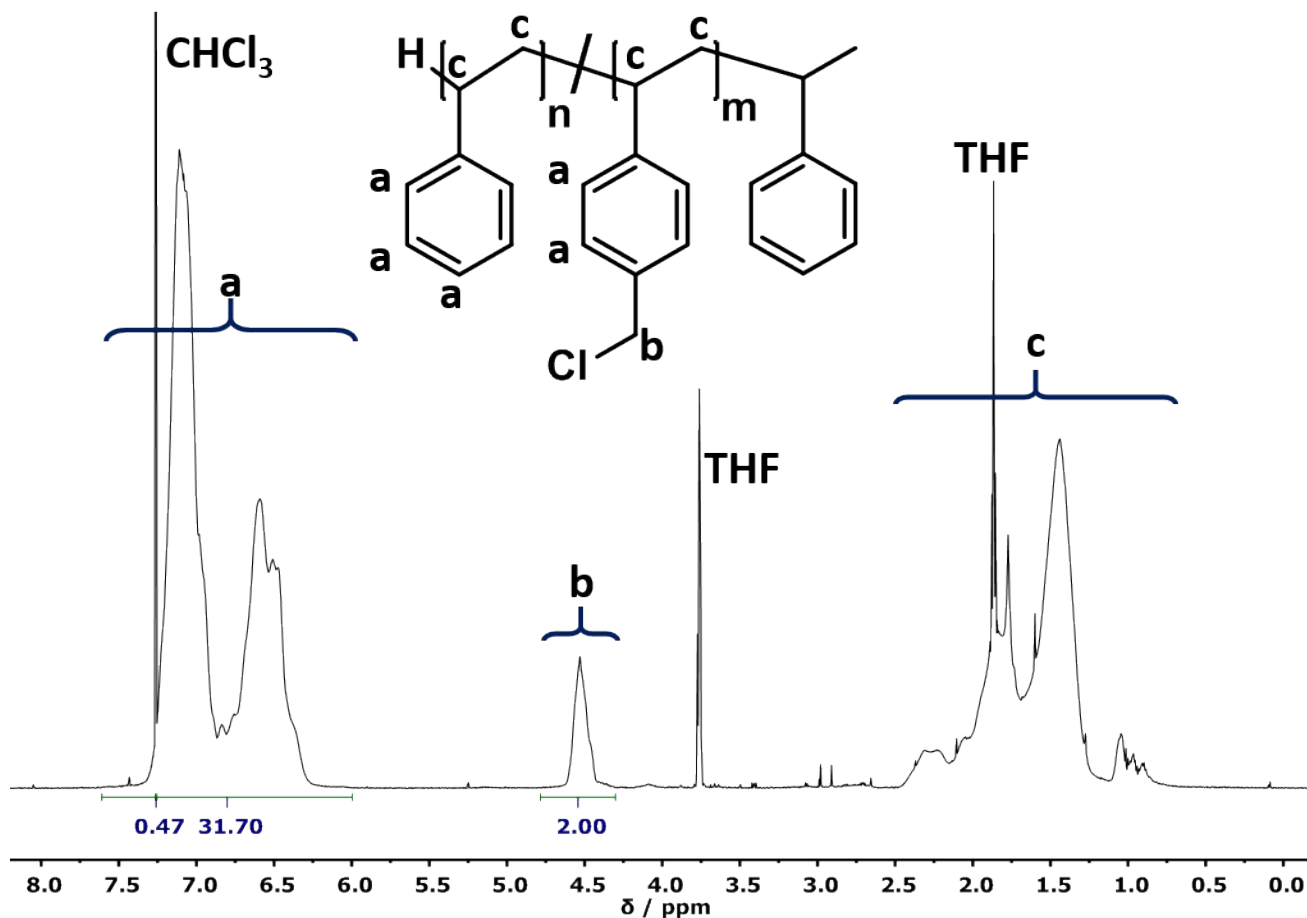


Figure S1. ^1H NMR of P(S-co-CMS) P1 in chloroform- d_1 .

The ratio of styrene to CMS can be readily determined from the intensity of the proton CMS signals in α -position to the chloride (b) in relation to the aromatic proton signals of both monomers (a). If the small influence of the end group is ignored, the ratio of styrene (n) to CMS (m) can be determined as:

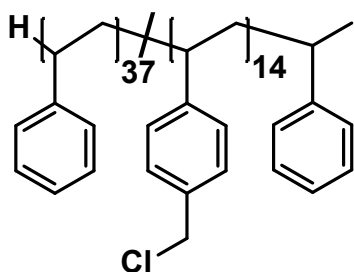
$$31.70 - 0.47 = a = 5n + 4m \text{ with } m = \frac{b}{2} = 1$$

$$\text{CMS ratio [\%]} = \frac{m}{n + m} * 100 = 15.5\%$$

To simplify the calculation the CH_2 integral (b) was set to 2. The integrals do not represent the number of monomers incorporated in the polymer chain, but only describe the relative abundance.

Poly(styrene-co-chloromethylstyrene) (P(S-co-CMS)) (P2)

153 mg 2,2,6,6-Tetramethyl-1-(1-phenylethoxy)piperidine (0.58 mmol, 1.00 eq.) and 9.1 mg TEMPO (0.06 mmol, 0.10 eq.) were dissolved in a mixture of 3.94 mL



styrene (3.59 g, 34.4 mmol, 60.0 eq.) and 1.61 mL chloromethylstyrene (1.74 g, 5.74 mmol, 20.0 eq.). The reaction mixture was degassed via four freeze-thaw cycles. The reaction was carried out for 2.5 h at 125 °C. The crude mixture was diluted with THF and precipitated twice dropwise into 1 L methanol. The precipitate was collected by filtration and dried at 35 °C under vacuum. 1.20 g of the precipitate (0.20 mmol, 1.00 eq) were dissolved in 90 mL DMF and degassed by bubbling the solution with a stream of argon for 15 mins. 0.21 mL butanethiol (0.18 g, 1.97 mmol, 10.0 eq.) were added and the solution was heated to 120 °C for 1.5 h. The solvent was removed under reduced pressure, the residual was dissolved in 5 mL THF and precipitated twice into 350 mL ice-cold methanol. The polymer **P1** was filtered and dried at 35 °C under vacuum.

$^1\text{H NMR}$ (CDCl_3 , 600 MHz) δ = 7.61 – 5.99 (m, a), 4.79 – 4.30 (s, b), 2.50-0.64 (m, c).

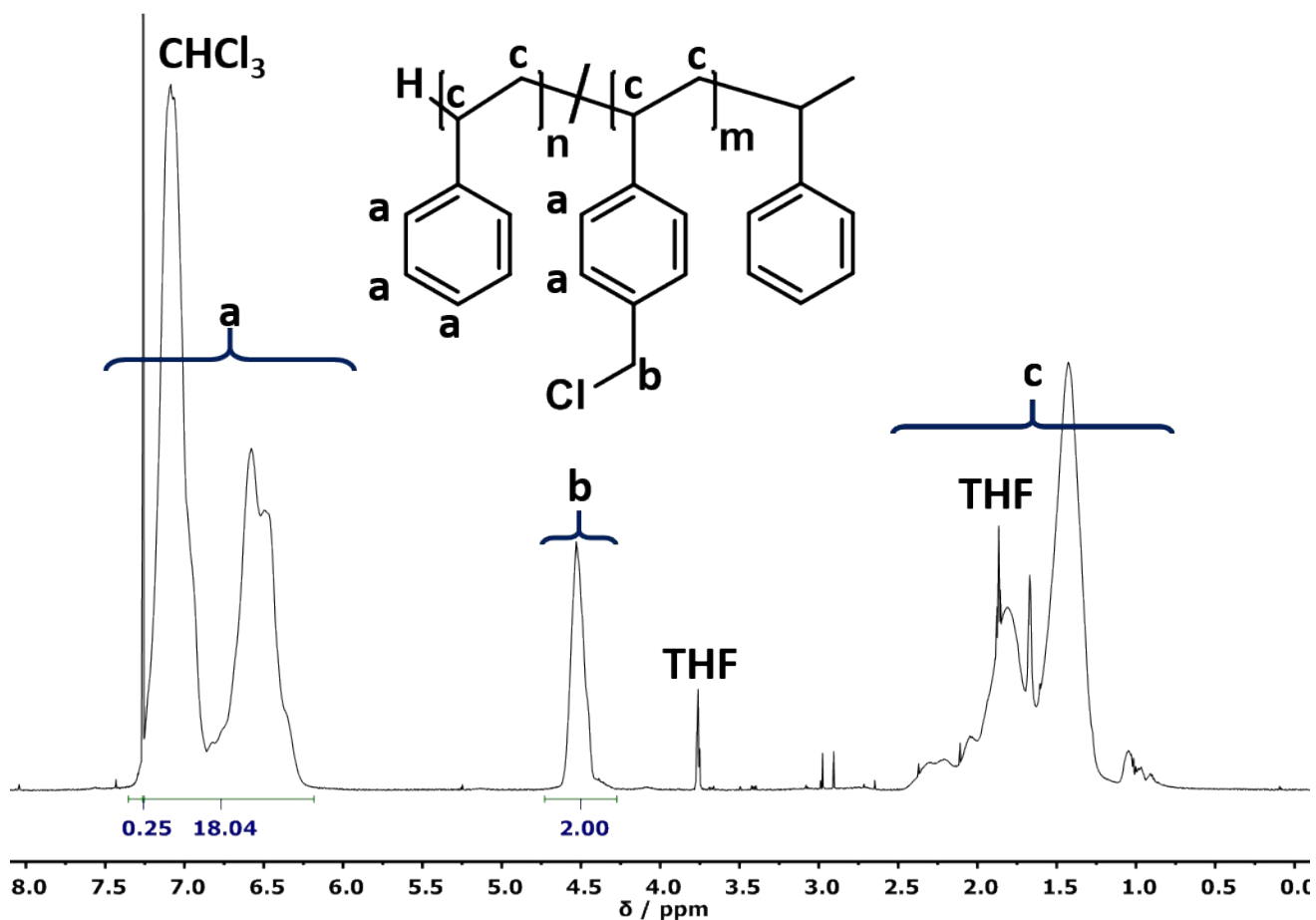


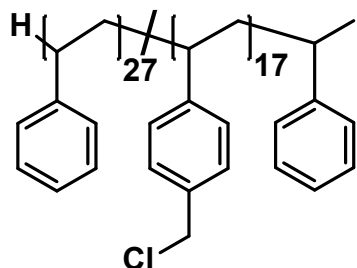
Figure S2. $^1\text{H NMR}$ of **P(S-co-CMS) P2** in chloroform- d_1 .

The ratio of styrene to CMS can be readily determined from the intensity of the proton CMS signals in α -position to the chloride (b) in relation to the aromatic proton signals of both monomers (a). If the small influence of the end group is ignored, the ratio of styrene (n) to CMS (m) can be determined as:

$$18.04 - 0.25 = a = 5n + 4m \text{ with } m = \frac{b}{2} = 1$$

$$CMS \text{ ratio } [\%] = \frac{m}{n + m} * 100 = 26.6\%$$

To simplify the calculation, the CH₂ integral (b) was set to 2. The integrals do not represent the number of monomers incorporated in the polymer chain, but only describe the relative abundance.



Poly(styrene-*co*-chloromethylstyrene) (P(S-*co*-CMS)) (P3)

400 mg 2,2,6,6-Tetramethyl-1-(1-phenylethoxy)piperidine (1.53 mmol, 1.00 eq.) and 5.2 mg TEMPO (0.03 mmol, 0.02 eq.) were dissolved in a mixture of 7.01 mL styrene (6.37 g, 61.2 mmol, 40.0 eq.) and 4.3 mL chloromethylstyrene (4.66 g, 30.6 mmol, 20.0 eq.). The reaction mixture was degassed via four freeze-thaw cycles. The reaction was carried out for 2.5 h at 120 °C. The crude mixture was diluted with THF and precipitated twice dropwise into 1 L methanol. The

precipitate was collected by filtration and dried at 35 °C under vacuum. 0.50 g of the precipitate (0.09 mmol, 1.00 eq) were dissolved in 90 mL DMF and degassed by bubbling the solution with a stream of argon for 15 mins. 0.21 mL dodecanethiol (0.18 g, 0.88 mmol, 10.0 eq.) were added and the solution was heated to 120 °C for 3 h. The solvent was removed under reduced pressure, the residual was dissolved in 5 mL THF and precipitated twice into 350 mL ice-cold methanol. The polymer **P1** was filtered and dried at 35 °C under vacuum.

¹H NMR (CDCl₃, 600 MHz) δ = 7.61 – 5.99 (m, a), 4.79 – 4.30 (s, b), 2.50-0.64 (m, c).

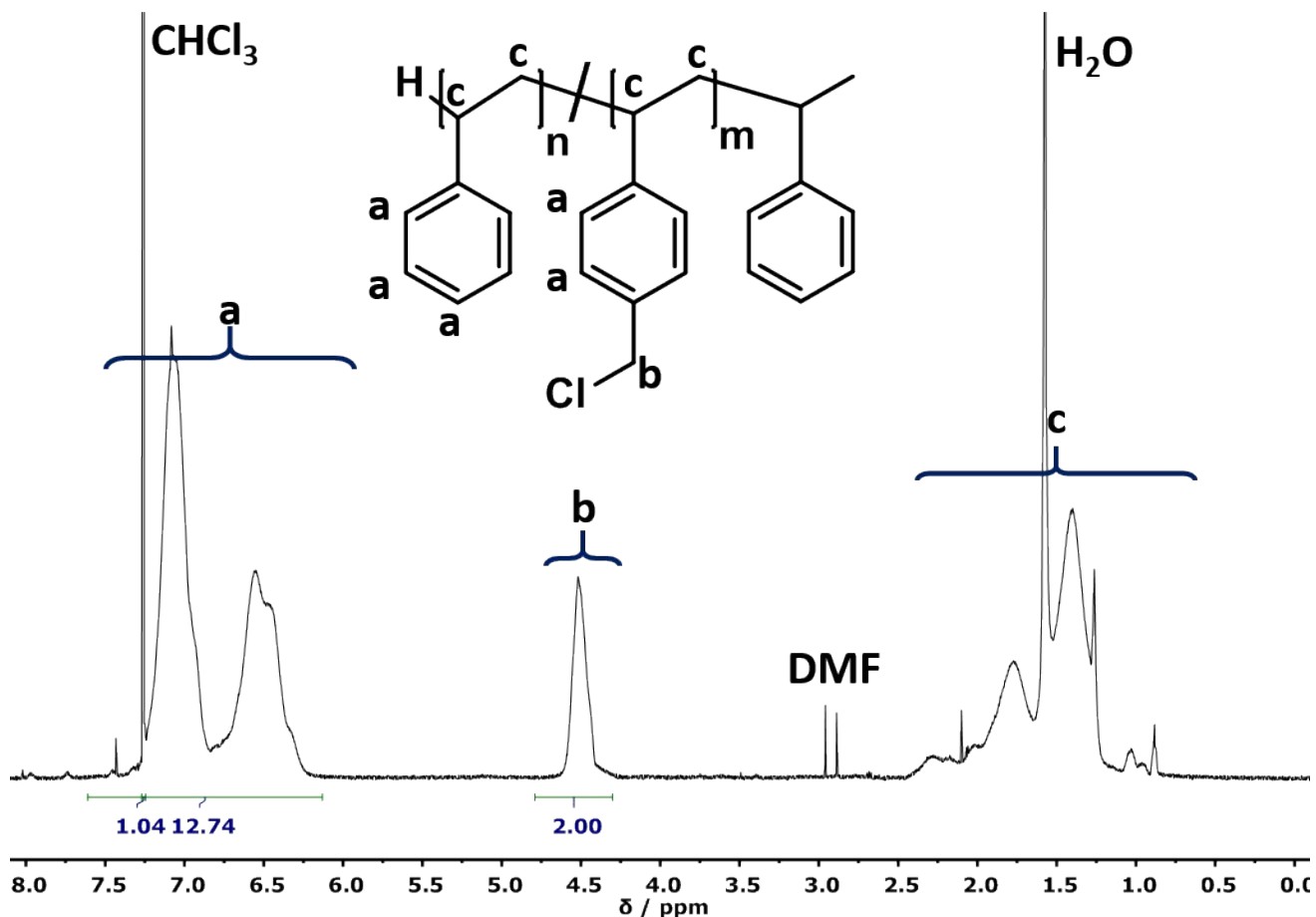


Figure S3. ^1H NMR of P(S-co-CMS) P3 in chloroform- d_1 .

The ratio of styrene to CMS can be readily determined from the intensity of the proton CMS signals in α -position to the chloride (b) in relation to the aromatic proton signals of both monomers (a). If the small influence of the end group is ignored, the ratio of styrene (n) to CMS (m) can be determined as:

$$12.74 - 1.04 = a = 5n + 4m \quad \text{with} \quad m = \frac{b}{2} = 1$$

$$\text{CMS ratio [\%]} = \frac{m}{n + m} * 100 = 39.4\%$$

To simplify the calculation, the CH_2 integral (b) was set to 2. The integrals do not represent the number of monomers incorporated in the polymer chain, but only describe the relative abundance.

SCNP Synthesis via Friedel-Crafts Alkylation (SCNP1-3)

Sample	$M_{\text{SEC, PS cal.}}$ [g mol ⁻¹]	Functionalization degree	n Polymer [mmol]	n SnCl ₄ [mmol]	m SnCl ₄ [mg]	V SnCl ₄ [mL]
SCNP1	P1 3500	15%	4.10×10^{-3}	0.357	93	0.042
SCNP2	P2 6100	27%	7.14×10^{-3}	0.574	150	0.067
SCNP3	P3 5400	39%	4.63×10^{-3}	0.833	217	0.098

25 mg of the precursor polymers **P1-P3** were dissolved in 100 mL dry Dichloroethane (DCE). Subsequently, 10 eq. (relative to CMS groups) tin(IV) chloride were diluted to a concentration of 0.01 mL SnCl₄ per mL dry DCE. The polymer solution was stirred, heated to 80 °C and the diluted catalyst solution was added via syringe pump over 6 h. After the reaction time, the heating was removed and the solution was stirred overnight. To remove the residual catalyst the reaction solution was washed five times with 1M NaOH solution, dried over MgSO₄ and dried under reduced pressure. The residual solid was dissolved in THF and filtered before injection into the SEC-ESI-MS.

4. Additional SEC curves

To ensure the reproducibility of the compaction reactions, they were carried out several times. The following SEC curves show the same overall size reduction for all precursor polymer samples **P1-3**.

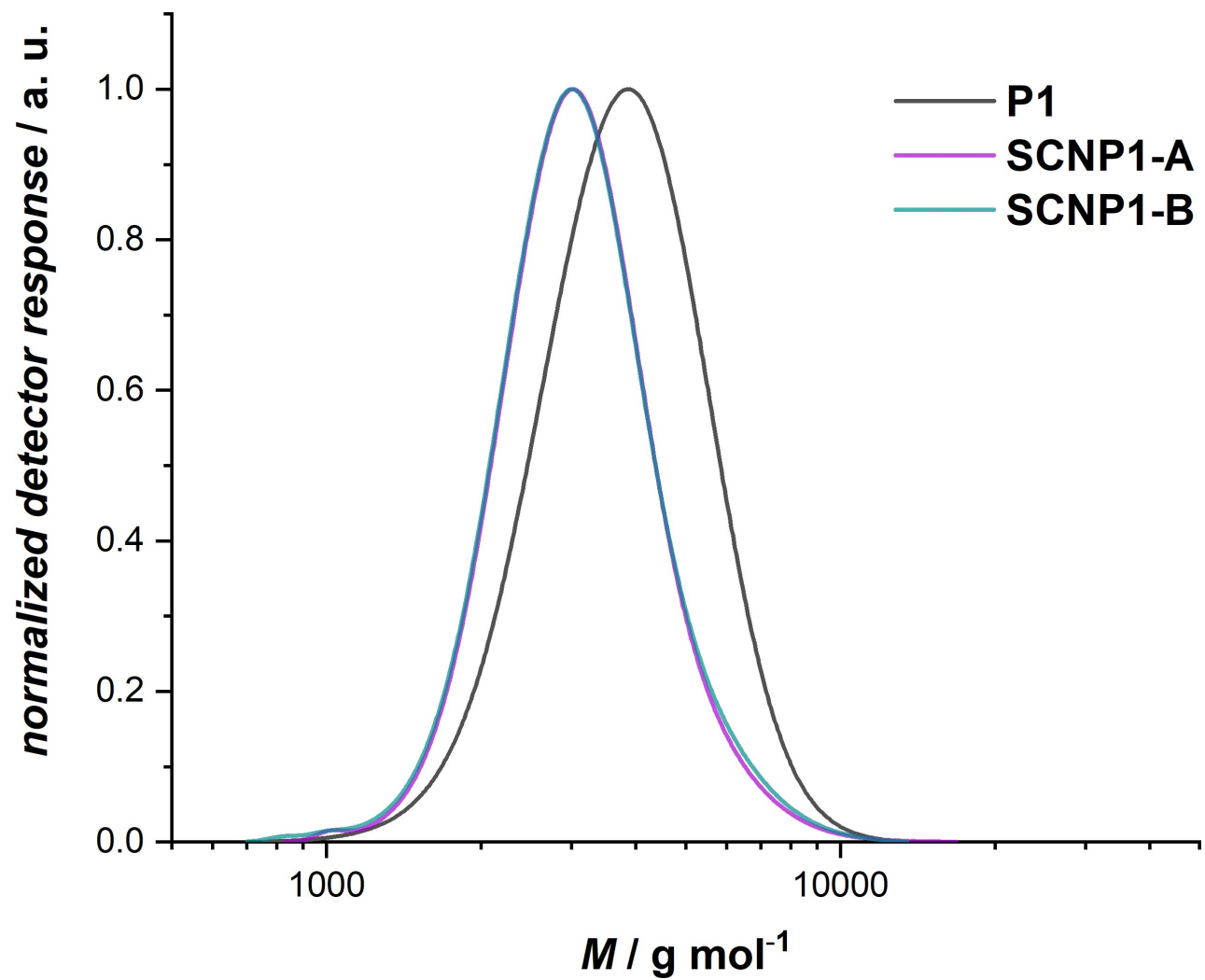


Figure S4. SEC curves of different compaction reactions of the precursor polymer P1 resulting in a near identical size reduction.

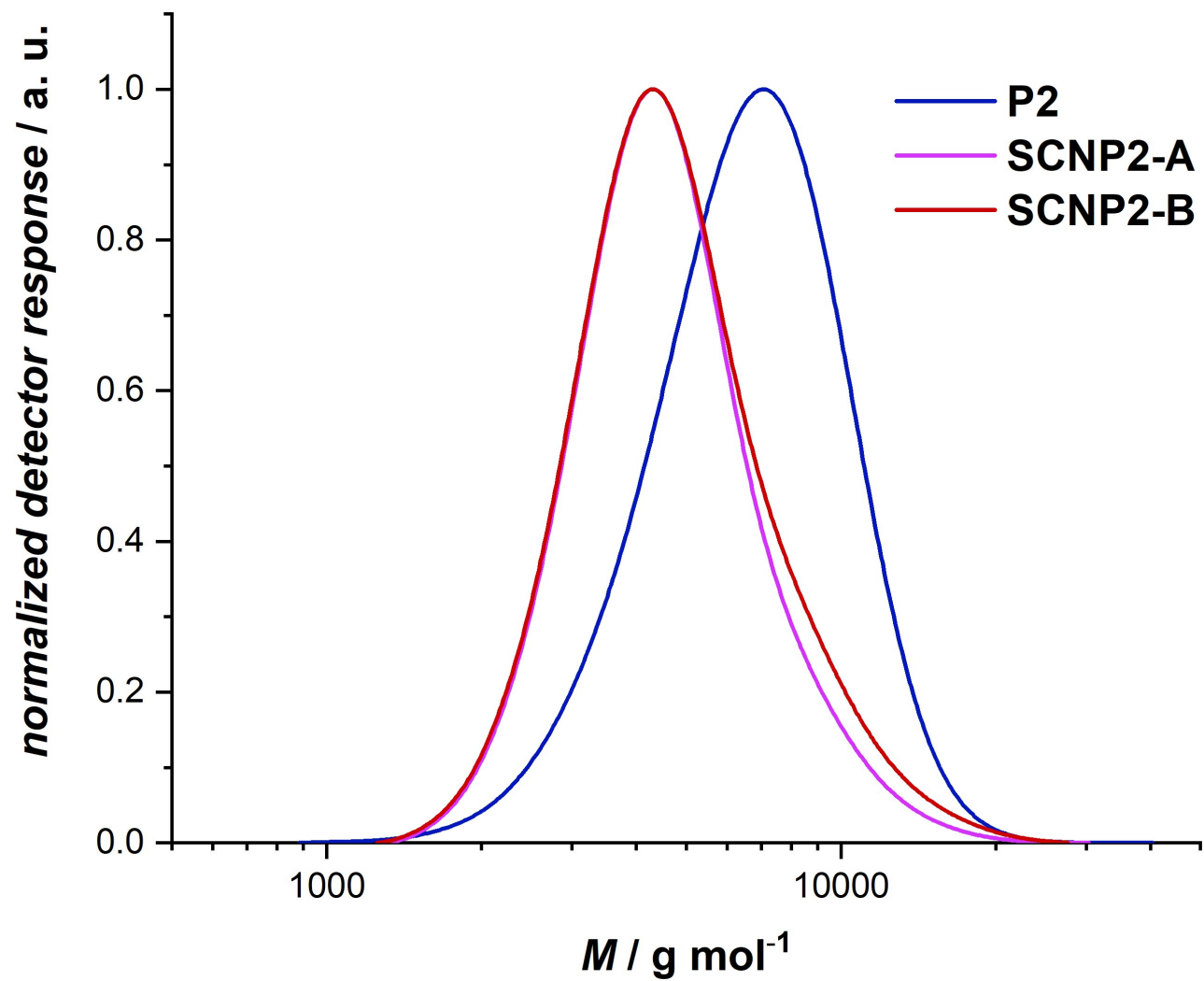


Figure S5. SEC curves of different compaction reactions of the precursor polymer P2 resulting in a near identical size reduction.

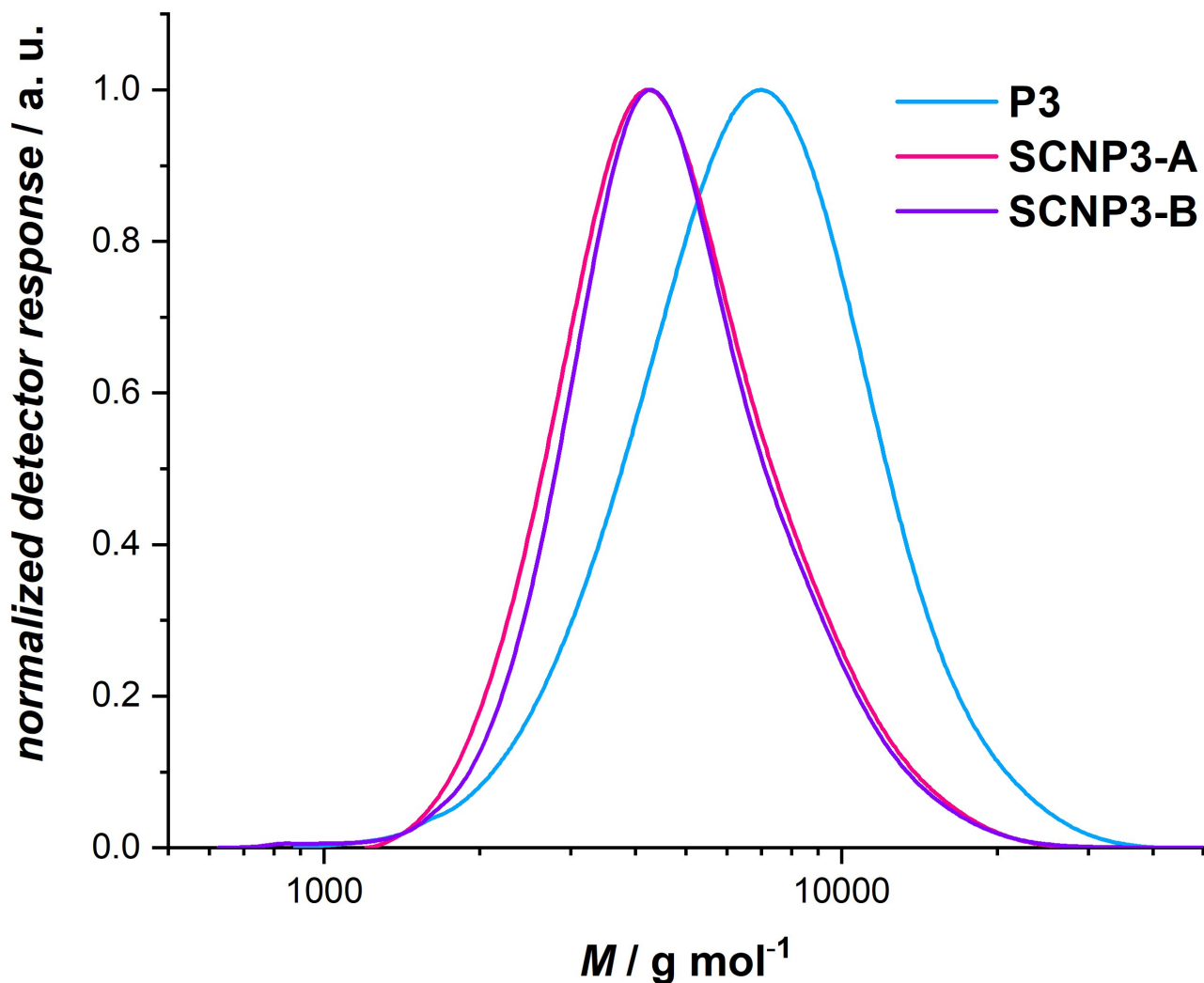


Figure S6. SEC curves of different compaction reactions of the precursor polymer **P1** resulting in a near identical size reduction.

4. Hydrodynamic radius (R_H) calibration

Our previous research showed relatively low variation between the hydrodynamic radius calibration utilizing Mark-Houwink-Sakurada (MHS) values and experimental values determined via diffusion ordered spectroscopy.³ Therefore, we utilized the specific MHS values for short polystyrene polymers in THF at 30 °C ($K = 0.17 \text{ ml g}^{-1}$, $\alpha = 0.428$) to establish a R_H calibration.

$$\log R_H = 14.26311 - 2.17823 * x + 0.11688 * x^2 - 0.0022 * x^3$$

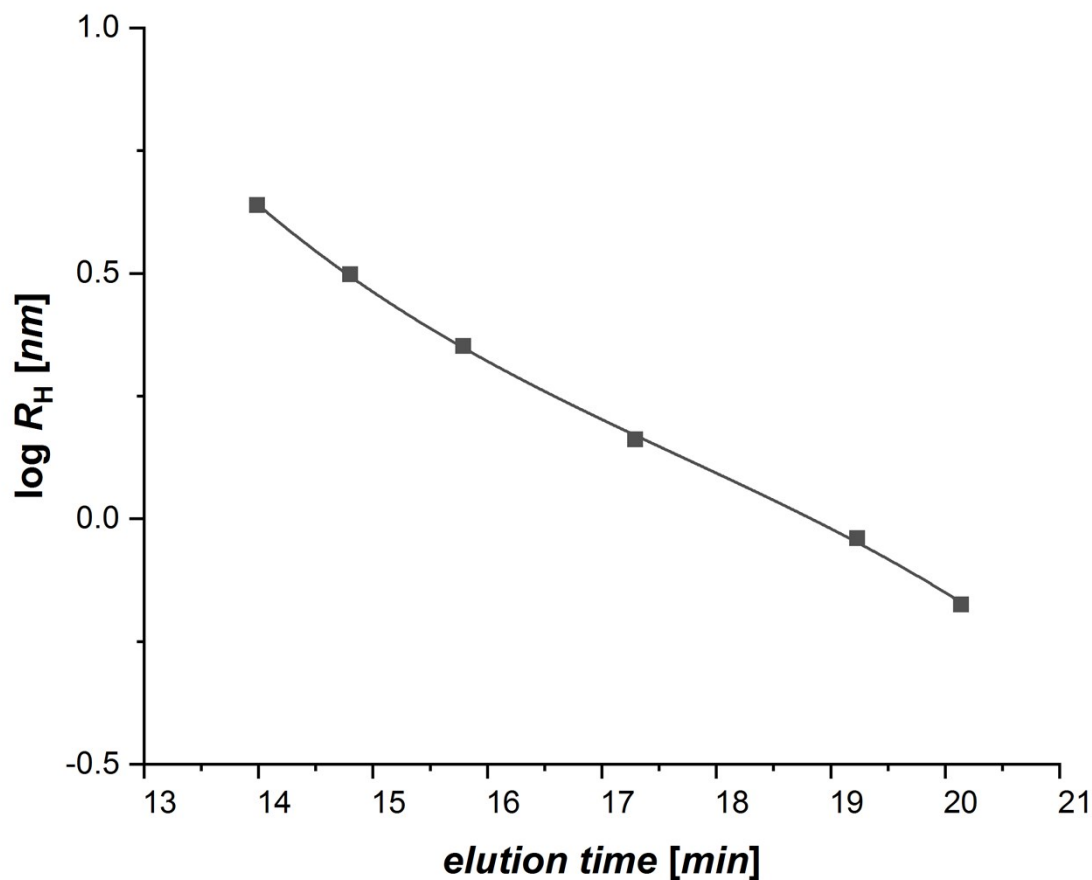
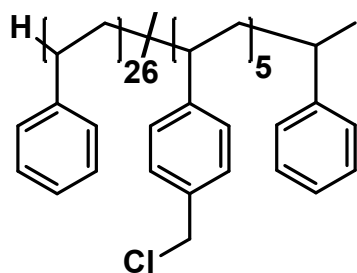


Figure S7. Hydrodynamic radius calibration of the SEC coupled to the MS setup utilizing defined single polystyrene standards ($M_p = 682\text{-}34800$).

5. SEC-ESI-MS Analysis

Precursor polymer P(S-co-CMS) P1.



The mass spectrum of the precursor polymer **P1** at the retention time t_1 (17.5 – 18.0 min) including the simulation is shown in Figure S8. The full list of signal assignments is summarized in Table S1. All signals carry the same end groups and are ionized via iodide attachment. The table shows the different polymer compositions depending on the number of incorporated styrene and chloromethylstyrene (CMS) monomers. The relative intensities utilized in the simulation (0-1) as well as the theoretical and measured molecular weight for the most abundant isotope

combination are given. The absolute deviation from the theoretical mass value of the most abundant isotopic peak, as well as the deviation in ppm are given.

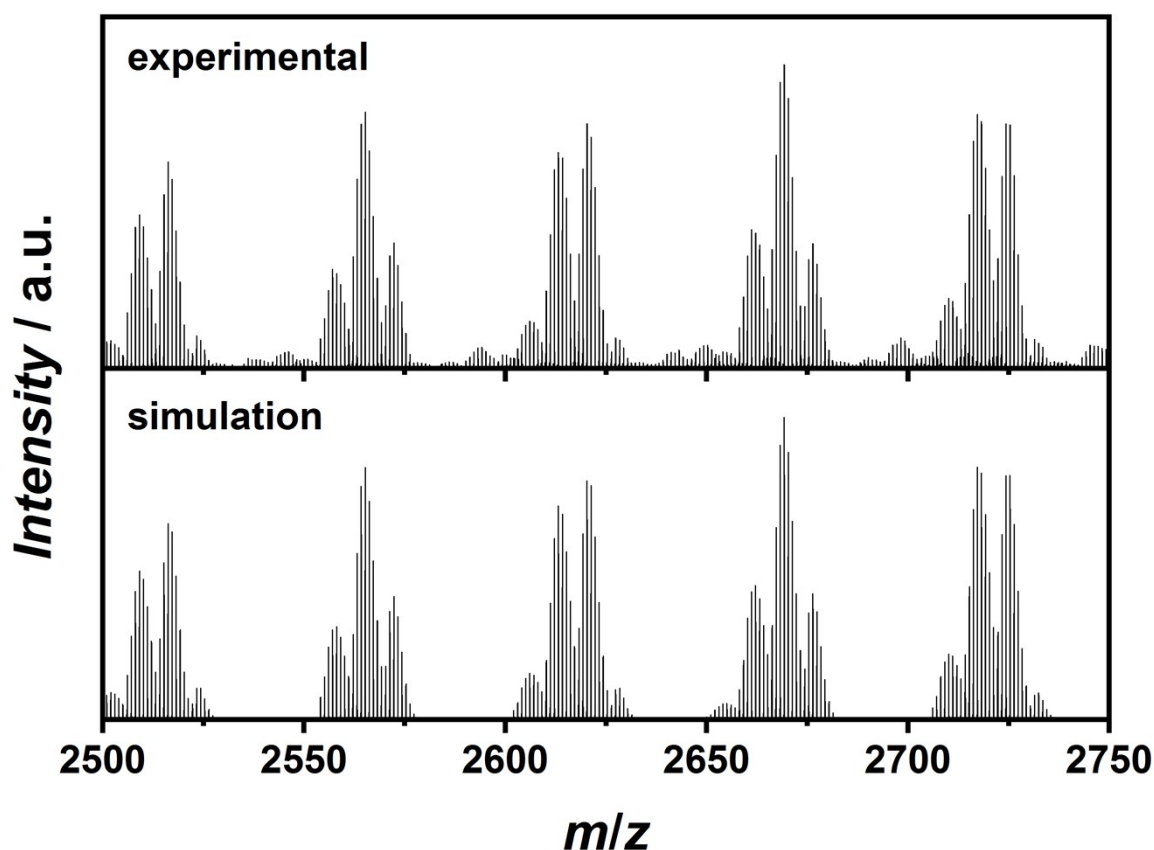


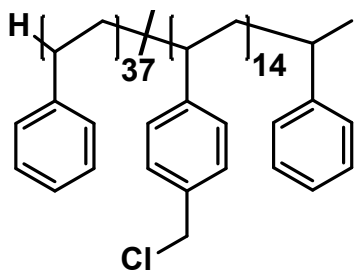
Figure S8. MS spectrum of the summation of all signals of precursor polymer **P1** between the retention time of 17.5 – 18.0 min.

Table S1. Complete list of all MS signals shown in Figure S8 of the precursor polymer **P1** in the mass region m/z 2500-2750 at the retention time 17.5-18.0 min, the masses and deviations are determined from the most abundant isotopic peak.

Composition Styrene / CMS	Elemental composition	abundance (sim)	m/z (theo.)	m/z (exp.)	Deviation (abs)	Deviation (ppm)
[13, 6]	H168C166Cl6I1	0.11	2502.0344	2502.0356	0.0011	0.4590
[16, 4]	H174C172Cl4I1	0.53	2509.1454	2509.1473	0.0019	0.7585
[19, 2]	H180C178Cl2I1	0.59	2516.2555	2516.2578	0.0024	0.9383
[22, 0]	H186C184I1	0.07	2523.3638	2523.3646	0.0008	0.3164
[15, 5]	H175C173Cl5I1	0.36	2558.1213	2558.1230	0.0017	0.6615
[18, 3]	H181C179Cl3I1	0.83	2565.2321	2565.2336	0.0014	0.5647
[21, 1]	H187C185Cl1I1	0.32	2572.3425	2572.3434	0.0008	0.3263
[14, 6]	H176C174Cl6I1	0.19	2606.0973	2606.0979	0.0006	0.2325
[17, 4]	H182C180Cl4I1	0.77	2613.2082	2613.2086	0.0004	0.1432
[20, 2]	H188C186Cl2I1	0.73	2620.3182	2620.3194	0.0012	0.4563

Composition Styrene / CMS	Elemental composition	abundance (sim)	<i>m/z</i> (theo.)	<i>m/z</i> (exp.)	Deviation (abs)	Deviation (ppm)
[23, 0]	H194C192I1	0.07	2628.4298	2628.4308	0.0010	0.3859
[13, 7]	H177C175Cl7I1	0.07	2654.0735	2654.0715	-0.0020	0.7574
[16, 5]	H183C181Cl5I1	0.52	2662.1842	2662.1843	0.0001	0.0472
[19, 3]	H189C187Cl3I1	1.00	2669.2949	2669.2949	-0.0001	0.0208
[22, 1]	H195C193Cl1I1	0.33	2676.4052	2676.4052	-0.0000	0.0029
[15, 6]	H184C182Cl6I1	0.27	2710.1602	2710.1592	-0.0010	0.3629
[18, 4]	H190C188Cl4I1	0.92	2717.2710	2717.2702	-0.0008	0.3021
[21, 2]	H196C194Cl2I1	0.76	2725.3820	2725.3812	-0.0008	0.3074
[24, 0]	H202C200I1	0.06	2732.4924	2732.4896	-0.0028	1.0290

Precursor polymer P(S-co-CMS) P2.



The mass spectrum of the precursor polymer **P2** at the retention time t_1 (17.5 – 18.0 min) including the simulation is shown in Figure S9. The full list of signal assignments is summarized in Table S2. All signals carry the same end groups and are ionized via iodide attachment. The table shows the different polymer compositions depending on the number of incorporated styrene and chloromethylstyrene (CMS) monomers. The relative intensities utilized in the simulation (0-1) as well as the theoretical and measured molecular weight for the most abundant isotope combination are given. The absolute deviation from the theoretical mass value of the most abundant isotopic peak, as well as the deviation in ppm are given.

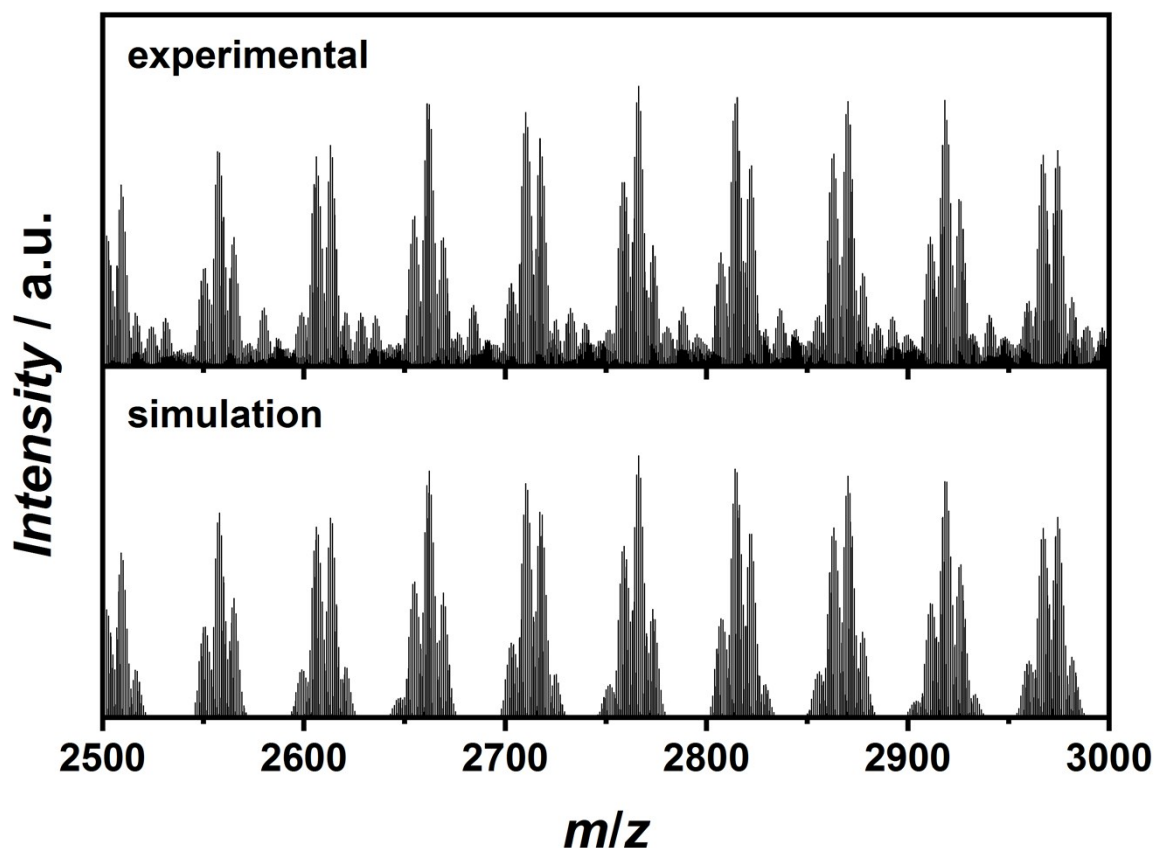


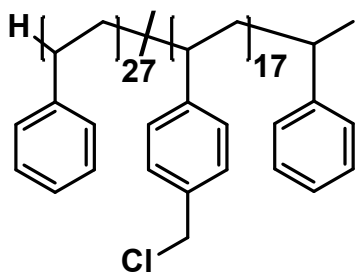
Figure S9. MS spectrum of the summation of all signals of precursor polymer **P2** between the retention time of 17.5 – 18.0 min.

Table S2. Complete list of all MS signals shown in Figure S9 of the precursor polymer **P2** in the mass region m/z 2500-3000 at the retention time 17.5-18.0 min, the masses and deviations are determined from the most abundant isotopic peak.

Composition Styrene / CMS	Elemental composition	abundance (sim)	m/z (theo.)	m/z (exp.)	Deviation (abs)	Deviation (ppm)
[13, 6]	H168C166Cl6I1	0.42	2502.0344	2502.0445	0.0101	4.1
[16, 4]	H174C172Cl4I1	0.57	2509.1454	2509.1549	0.0095	3.8
[19, 2]	H180C178Cl2I1	0.14	2516.2555	2516.2649	0.0094	3.7
[12, 7]	H169C167Cl7I1	0.38	2550.0106	2550.0192	0.0086	3.4
[15, 5]	H175C173Cl5I1	0.76	2558.1213	2558.1309	0.0096	3.7
[18, 3]	H181C179Cl3I1	0.38	2565.2321	2565.2415	0.0094	3.7
[11, 8]	H170C168Cl8I1	0.21	2598.9867	2598.9955	0.0088	3.4
[14, 6]	H176C174Cl6I1	0.75	2606.0973	2606.1061	0.0088	3.4
[17, 4]	H182C180Cl4I1	0.70	2613.2082	2613.2171	0.0089	3.4
[20, 2]	H188C186Cl2I1	0.15	2620.3182	2620.3273	0.0091	3.5
[10, 9]	H171C169Cl9I1	0.09	2647.9623	2647.9689	0.0066	2.5
[13, 7]	H177C175Cl7I1	0.57	2654.0735	2654.0810	0.0075	2.8
[16, 5]	H183C181Cl5I1	0.92	2662.1842	2662.1935	0.0093	3.5
[19, 3]	H189C187Cl3I1	0.40	2669.2949	2669.3040	0.0091	3.4

Composition Styrene / CMS	Elemental composition	abundance (sim)	<i>m/z</i> (theo.)	<i>m/z</i> (exp.)	Deviation (abs)	Deviation (ppm)
[12, 8]	H178C176Cl8I1	0.33	2704.0490	2704.0553	0.0063	2.3
[15, 6]	H184C182Cl6I1	0.93	2710.1602	2710.1686	0.0084	3.1
[18, 4]	H190C188Cl4I1	0.73	2717.2710	2717.2791	0.0081	3.0
[21, 2]	H196C194Cl2I1	0.13	2725.3820	2725.3933	0.0113	4.1
[11, 9]	H179C177Cl9I1	0.15	2752.0252	2752.0305	0.0053	1.9
[14, 7]	H185C183Cl7I1	0.72	2759.1365	2759.1438	0.0073	2.6
[17, 5]	H191C189Cl5I1	0.98	2766.2471	2766.2555	0.0084	3.1
[20, 3]	H197C195Cl3I1	0.35	2773.3577	2773.3659	0.0082	2.9
[13, 8]	H186C184Cl8I1	0.44	2808.1119	2808.1172	0.0053	1.9
[16, 6]	H192C190Cl6I1	1.00	2814.2231	2814.2298	0.0067	2.4
[19, 4]	H198C196Cl4I1	0.66	2822.3341	2822.3427	0.0086	3.1
[22, 2]	H204C202Cl2I1	0.10	2829.4448	2829.4577	0.0129	4.5
[12, 9]	H187C185Cl9I1	0.21	2856.0881	2856.0913	0.0032	1.1
[15, 7]	H193C191Cl7I1	0.80	2863.1994	2863.2049	0.0055	1.9
[18, 5]	H199C197Cl5I1	0.91	2870.3099	2870.3174	0.0075	2.6
[21, 3]	H205C203Cl3I1	0.28	2877.4205	2877.4300	0.0095	3.3
[11, 10]	H188C186Cl10I1	0.08	2904.0644	2904.0625	0.0019	0.6
[14, 8]	H194C192Cl8I1	0.51	2911.1756	2911.1805	0.0049	1.7
[17, 6]	H200C198Cl6I1	0.96	2918.2860	2918.2921	0.0061	2.1
[20, 4]	H206C204Cl4I1	0.55	2926.3969	2926.4051	0.0082	2.8
[23, 2]	H212C210Cl2I1	0.07	2933.5076	2933.5191	0.0115	3.9
[13, 9]	H195C193Cl9I1	0.26	2960.1510	2960.1526	0.0016	0.5
[16, 7]	H201C199Cl7I1	0.80	2967.2622	2967.2673	0.0051	1.7
[19, 5]	H207C205Cl5I1	0.76	2974.3728	2974.3798	0.007	2.4
[22, 3]	H213C211Cl3I1	0.20	2981.4833	2981.4941	0.0108	3.6

Precursor polymer P(S-co-CMS) P3.



The mass spectrum of the precursor polymer **P1** at the retention time t_r (17.5 – 18.0 min) including the simulation is shown in Figure S10. The full list of signal assignments is summarized in Table S3. All signals carry the same end groups and are ionized via iodide attachment. The table shows the different polymer compositions depending on the number of incorporated styrene and chloromethylstyrene (CMS) monomers. The relative intensities utilized in the simulation (0-1) as well as the theoretical and measured molecular weight for the most abundant isotope combination are given. The absolute deviation from the theoretical mass value of the most abundant isotopic peak, as well as the deviation in ppm are given.

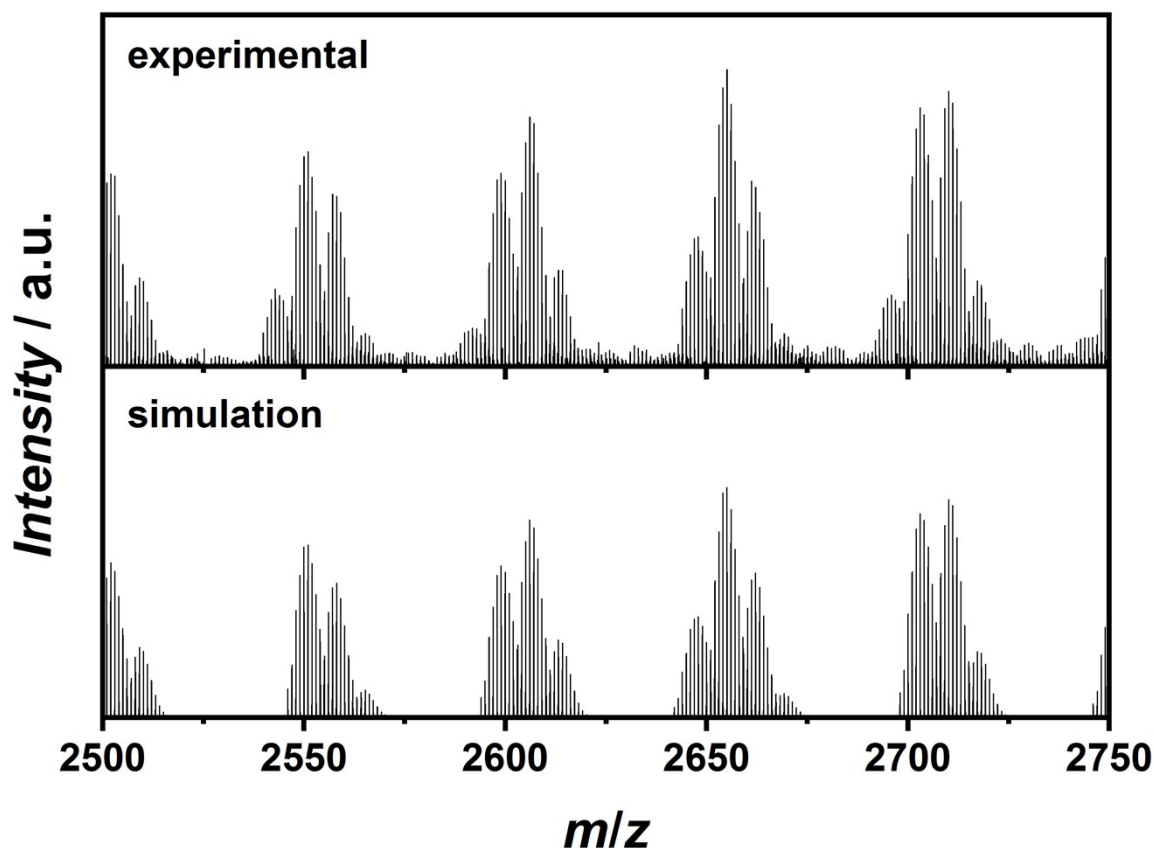


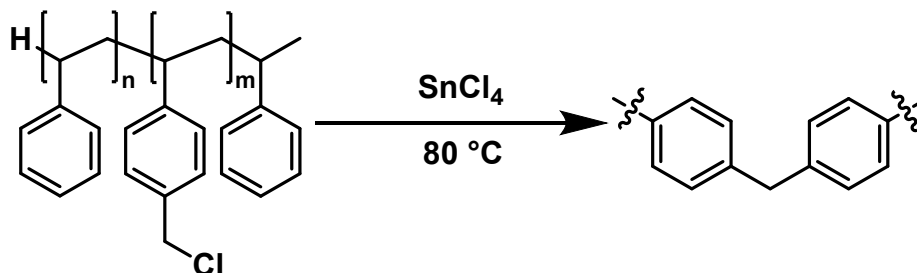
Figure S10. MS spectrum of the summation of all signals of precursor polymer **P3** between the retention time of 17.5 – 18.0 min.

Table S3. Complete list of all MS signals shown in Figure S10 of the precursor polymer **P3** in the mass region m/z 2500-2750 at the retention time 17.5-18.0 min, the masses and deviations are determined from the most abundant isotopic peak.

Composition Styrene / CMS	Elemental composition	abundance (sim)	m/z (theo.)	m/z (exp.)	Deviation (abs)	Deviation (ppm)
[13, 6]	H168C166Cl6I1	0.63	2502.0344	2502.0403	0.0059	2.34
[16, 4]	H174C172Cl4I1	0.25	2509.1454	2509.1494	0.0040	1.62
[12, 7]	H169C167Cl7I1	0.75	2550.0106	2550.0159	0.0053	2.11
[15, 5]	H175C173Cl5I1	0.52	2558.1213	2558.1263	0.0050	1.95
[18, 3]	H181C179Cl3I1	0.09	2565.2321	2565.2357	0.0036	1.39
[11, 8]	H170C168Cl8I1	0.69	2598.9867	2598.9911	0.0044	1.68
[14, 6]	H176C174Cl6I1	0.81	2606.0973	2606.1022	0.0049	1.88
[17, 4]	H182C180Cl4I1	0.28	2613.2082	2613.2109	0.0027	1.05
[10, 9]	H171C169Cl9I1	0.48	2647.9623	2647.9667	0.0044	1.66
[13, 7]	H177C175Cl7I1	1.00	2654.0735	2654.0779	0.0044	1.66
[16, 5]	H183C181Cl5I1	0.56	2662.1842	2662.1880	0.0038	1.44
[19, 3]	H189C187Cl3I1	0.08	2669.2949	2669.2992	0.0043	1.61
[12, 8]	H178C176Cl8I1	0.93	2704.0490	2704.0533	0.0043	1.59
[15, 6]	H184C182Cl6I1	0.90	2710.1602	2710.1639	0.0037	1.36

Composition Styrene / CMS	Elemental composition	abundance (sim)	<i>m/z</i> (theo.)	<i>m/z</i> (exp.)	Deviation (abs)	Deviation (ppm)
[18, 4]	H190C188Cl4I1	0.24	2717.2710	2717.2729	0.0019	0.71
[11, 9]	H179C177Cl9I1	0.69	2752.0252	2752.0275	0.0023	0.84

SCNP formation



The collapse reaction was carried out as described in Section 3. The full list of signal assignments are summarized in Table S4-S6. All signals carry the same end groups and are ionized via iodide attachment. The table shows the different polymer compositions depending on the number of incorporated styrene, residual CMS and formed intramolecular crosslinks. The relative intensities utilized in the simulation (0-1) as well as the theoretical and measured molecular weight for the most abundant isotope combination are given. The absolute deviation from the theoretical mass value of the most abundant isotopic peak, as well as the deviation in ppm are given.

Table S4. Complete list of all MS signals shown in Figure S11 of **SCNP1** in the mass region *m/z* 2500-2750 at the retention time 17.8-18.8 min, the masses and deviations are determined from the most abundant isotopic peak.

Composition Styrene /residual CMS/ compaction points	Elemental composition	abundance (sim)	<i>m/z</i> (theo.)	<i>m/z</i> (exp.)	Deviation (abs)	Deviation (ppm)
[17, 1, 3]	H179C180Cl1I1	0.55	2504.2799	2504.2826	-0.0027	1.08
[16, 1, 4]	H179C181Cl1I1	0.23	2516.2799	2516.2826	-0.0027	1.09
[22, 0, 0]	H186C184I1	0.21	2523.3638	2523.3650	-0.0012	0.47
[18, 2, 1]	H180C179Cl2I1	0.16	2528.2555	2528.2552	0.0003	0.12
[21, 0, 1]	H186C185I1	0.71	2536.3672	2536.3685	-0.0013	0.52
[17, 2, 2]	H180C180Cl2I1	0.28	2540.2555	2540.2561	-0.0006	0.24
[20, 0, 2]	H186C186I1	1	2548.3672	2548.3688	-0.0016	0.65
[16, 2, 3]	H180C181Cl2I1	0.22	2552.2555	2552.2564	-0.0008	0.33
[19, 0, 3]	H186C187I1	0.74	2560.3672	2560.3689	-0.0017	0.66
[15, 2, 4]	H180C182Cl2I1	0.08	2564.2556	2564.2576	-0.0020	0.78
[18, 0, 4]	H187C185Cl1I1	0.45	2572.3672	2572.3684	-0.0013	0.49
[20, 1, 1]	H186C188I1	0.29	2584.3426	2584.3414	0.0011	0.43
[19, 1, 2]	H187C186Cl1I1	0.38	2596.3426	2596.3432	-0.0007	0.25
[18, 1, 3]	H187C187Cl1I1	0.63	2608.3426	2608.3439	-0.0013	0.50
[17, 1, 4]	H187C188Cl1I1	0.54	2620.3426	2620.3427	-0.0001	0.03
[23, 0, 0]	H187C189Cl1I1	0.25	2628.4298	2628.4278	0.0020	0.75

Composition Styrene /residual CMS/ compaction points	Elemental composition	abundance (sim)	<i>m/z</i> (theo.)	<i>m/z</i> (exp.)	Deviation (abs)	Deviation (ppm)
[19, 2, 1]	H194C192I1	0.13	2632.3183	2632.3166	0.0016	0.62
[22, 0, 1]	H188C187Cl2I1	0.13	2640.4298	2640.4293	0.0005	0.19
[18, 2, 2]	H194C193I1	0.51	2644.3183	2644.3169	0.0014	0.53
[21, 0, 2]	H188C188Cl2I1	0.24	2652.4298	2652.4299	-0.0002	0.06
[17, 2, 3]	H194C194I1	0.8	2657.3193	2657.3184	0.0009	0.33
[20, 0, 3]	H188C189Cl2I1	0.22	2664.4298	2664.4300	-0.0002	0.09
[16, 2, 4]	H194C195I1	0.66	2669.3193	2669.3165	0.0028	1.03
[19, 0, 4]	H188C190Cl2I1	0.11	2676.4298	2676.4284	0.0014	0.52
[21, 1, 1]	H195C193Cl1I1	0.42	2688.4053	2688.4032	0.0020	0.76
[20, 1, 2]	H194C196I1	0.31	2700.4053	2700.4041	0.0011	0.42
[19, 1, 3]	H195C194Cl1I1	0.28	2712.4053	2712.4044	0.0008	0.30
[18, 1, 4]	H195C195Cl1I1	0.5	2724.4053	2724.4041	0.0012	0.45
[24, 0, 0]	H195C196Cl1I1	0.49	2732.4924	2732.4896	0.0027	1.01
[23, 0, 1]	H195C197Cl1I1	0.25	2744.4924	2744.4897	0.0026	0.96
[19, 2, 2]	H202C200I1	0.08	2749.3821	2749.3784	0.0037	1.34

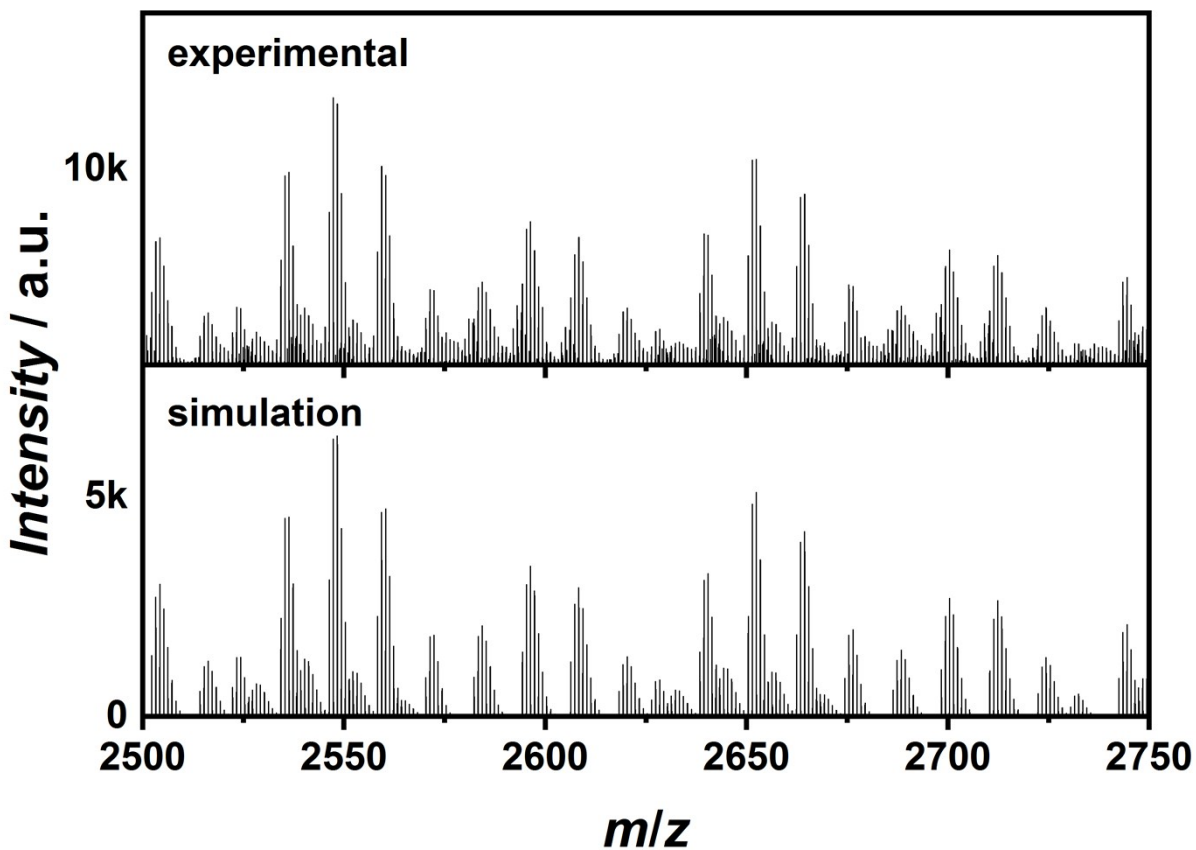


Figure S11. Comparison between the measured and simulated spectra of SCNP1 at retention time 17.8-18.8 min.

Table S5. Complete list of all MS signals shown in Figure S12 of **SCNP2** in the mass region m/z 2500-2750 at the retention time 17.8-18.8 min, the masses and deviations are determined from the most abundant isotopic peak.

Composition Styrene /residual CMS/ compaction points	Elemental composition	abundance (sim)	m/z (theo.)	m/z (exp.)	Deviation (abs)	Deviation (ppm)
[17, 1, 3]	H179C180Cl1I1	1	2504.2799	2504.2853	0.0054	2.17
[13, 3, 4]	H173C175Cl3I1	0.227909	2509.1694	2509.1718	0.0024	0.96
[16, 1, 4]	H179C181Cl1I1	0.911576	2516.2799	2516.2867	0.0068	2.71
[15, 1, 5]	H179C182Cl1I1	0.44078	2528.2799	2528.2868	0.0069	2.72
[21, 0, 1]	H186C185I1	0.211738	2536.3672	2536.3708	0.0036	1.41
[17, 2, 2]	H180C180Cl2I1	0.272036	2540.2555	2540.2595	0.0040	1.57
[20, 0, 2]	H186C186I1	0.578281	2548.3672	2548.3706	0.0035	1.36
[16, 2, 3]	H180C181Cl2I1	0.596591	2552.2555	2552.2599	0.0044	1.72
[19, 0, 3]	H186C187I1	0.9216	2560.3672	2560.3713	0.0041	1.59
[15, 2, 4]	H180C182Cl2I1	0.5686	2564.2556	2564.2593	0.0038	1.46
[18, 0, 4]	H186C188I1	0.842646	2572.3672	2572.3721	0.0049	1.89
[14, 2, 5]	H180C183Cl2I1	0.273885	2576.2556	2576.2601	0.0046	1.77
[17, 0, 5]	H186C189I1	0.443212	2584.3672	2584.3729	0.0057	2.21
[19, 1, 2]	H187C187Cl1I1	0.459916	2596.3426	2596.3453	0.0027	1.04
[15, 3, 3]	H181C182Cl3I1	0.233856	2601.2322	2601.2332	0.0010	0.38
[18, 1, 3]	H187C188Cl1I1	0.892225	2608.3426	2608.3455	0.0030	1.13
[14, 3, 4]	H181C183Cl3I1	0.257432	2613.2322	2613.2333	0.0011	0.42
[17, 1, 4]	H187C189Cl1I1	0.916217	2620.3426	2620.3458	0.0032	1.22
[13, 3, 5]	H181C184Cl3I1	0.118043	2625.2323	2625.2345	0.0022	0.85
[16, 1, 5]	H187C190Cl1I1	0.54435	2632.3426	2632.3476	0.0050	1.90
[22, 0, 1]	H194C193I1	0.13651	2640.4298	2640.4316	0.0018	0.69
[21, 0, 2]	H194C194I1	0.408085	2652.4298	2652.4319	0.0021	0.80
[17, 2, 3]	H188C189Cl2I1	0.522883	2657.3193	2657.3215	0.0022	0.84
[20, 0, 3]	H194C195I1	0.749057	2664.4298	2664.4323	0.0025	0.93
[16, 2, 4]	H188C190Cl2I1	0.634848	2669.3193	2669.3200	0.0007	0.28
[19, 0, 4]	H194C196I1	0.781461	2676.4298	2676.4325	0.0027	1.02
[15, 2, 5]	H188C191Cl2I1	0.353929	2681.3193	2681.3214	0.0021	0.78
[18, 0, 5]	H194C197I1	0.476747	2688.4298	2688.4322	0.0024	0.90
[20, 1, 2]	H195C195Cl1I1	0.343561	2700.4053	2700.4122	0.0070	2.59
[16, 3, 3]	H189C190Cl3I1	0.225032	2705.2950	2705.2952	0.0002	0.07
[19, 1, 3]	H195C196Cl1I1	0.685432	2712.4053	2712.4067	0.0014	0.52
[15, 3, 4]	H189C191Cl3I1	0.240012	2717.2950	2717.2944	-0.0006	0.23
[18, 1, 4]	H195C197Cl1I1	0.81889	2724.4053	2724.4071	0.0018	0.66
[14, 3, 5]	H189C192Cl3I1	0.152534	2729.2951	2729.2959	0.0008	0.31
[17, 1, 5]	H195C198Cl1I1	0.577006	2736.4053	2736.4079	0.0026	0.94
[16, 1, 6]	H195C199Cl1I1	0.219182	2748.4053	2748.4015	-0.0038	1.40

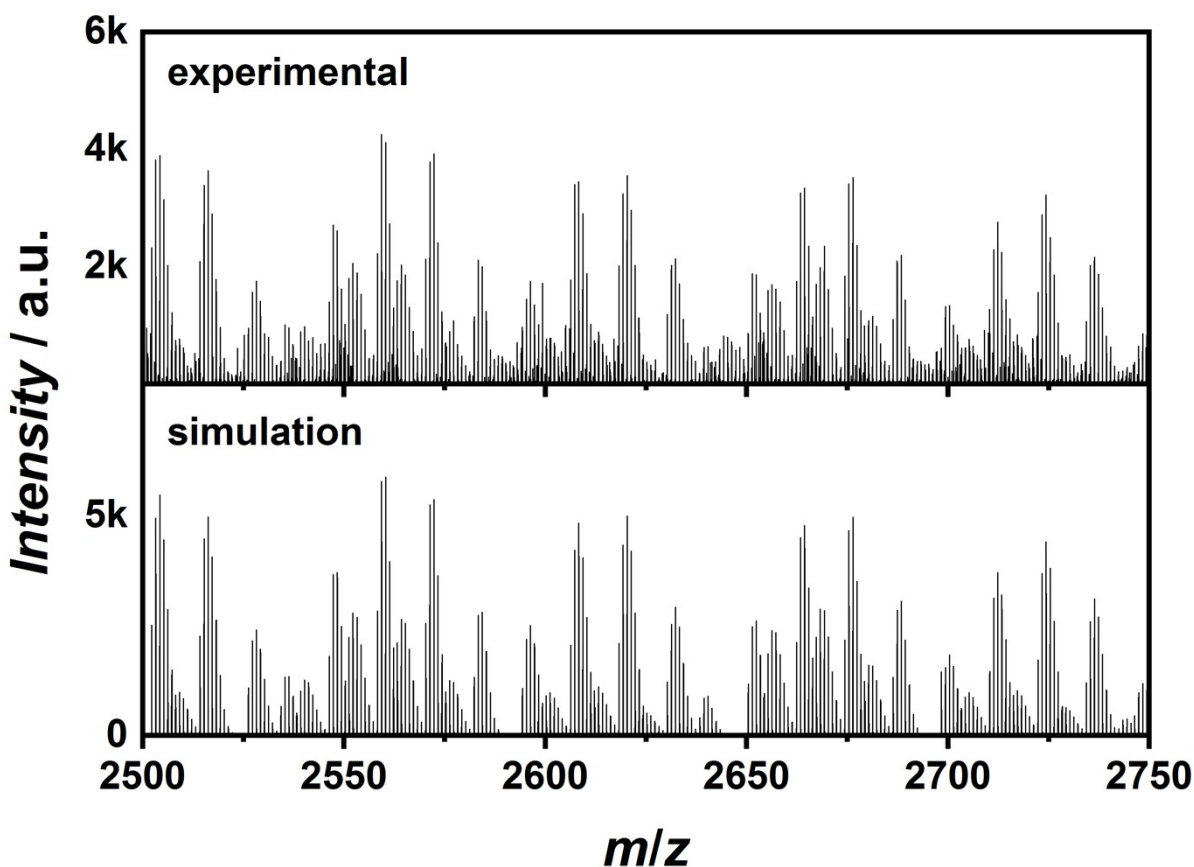


Figure S12. Comparison between the measured and simulated spectra of **SCNP2** at retention time 17.8-18.8 min.

Table S6. Complete list of all MS signals shown in Figure S13 of **SCNP3** in the mass region m/z 2500-2750 at the retention time 17.8-18.8 min, the masses and deviations are determined from the most abundant isotopic peak.

Composition Styrene /residual CMS/ compaction points	Elemental composition	abundance (sim)	m/z (theo.)	m/z (exp.)	Deviation (abs)	Deviation (ppm)
[10, 5, 4]	H167C169Cl5I1	0.31	2502.0585	2502.0599	0.0014	0.53
[17, 1, 3]	H179C180Cl1I1	0.56	2504.2799	2504.2832	0.0033	1.33
[13, 3, 4]	H173C175Cl3I1	0.94	2509.1694	2509.1727	0.0033	1.30
[16, 1, 4]	H179C181Cl1I1	0.78	2516.2799	2516.2840	0.0041	1.64
[12, 3, 5]	H173C176Cl3I1	0.56	2521.1694	2521.1727	0.0032	1.28
[15, 1, 5]	H179C182Cl1I1	0.62	2528.2799	2528.2845	0.0046	1.84
[13, 4, 3]	H174C175Cl4I1	0.46	2545.1455	2545.1481	0.0026	1.04
[20, 0, 2]	H186C186I1	0.06	2548.3672	2548.3680	0.0009	0.34
[16, 2, 3]	H180C181Cl2I1	0.61	2552.2555	2552.2577	0.0021	0.83
[12, 4, 4]	H174C176Cl4I1	0.65	2557.1455	2557.1472	0.0017	0.65
[19, 0, 3]	H186C187I1	0.21	2560.3672	2560.3694	0.0022	0.87
[15, 2, 4]	H180C182Cl2I1	1.00	2564.2556	2564.2586	0.0031	1.20

Composition Styrene /residual CMS/ compaction points	Elemental composition	abundance (sim)	m/z (theo.)	m/z (exp.)	Deviation (abs)	Deviation (ppm)
[11, 4, 5]	H174C177C14I1	0.36	2569.1455	2569.1456	0.0001	0.03
[18, 0, 4]	H186C188I1	0.29	2572.3672	2572.3686	0.0014	0.55
[14, 2, 5]	H180C183C12I1	0.78	2576.2556	2576.2590	0.0034	1.34
[17, 0, 5]	H186C189I1	0.25	2584.3672	2584.3692	0.0020	0.79
[12, 5, 3]	H175C176C15I1	0.23	2594.1214	2594.1212	-0.0002	0.06
[15, 3, 3]	H181C182C13I1	0.52	2601.2322	2601.2349	0.0027	1.03
[11, 5, 4]	H175C177C15I1	0.34	2606.1214	2606.1220	0.0005	0.20
[18, 1, 3]	H187C188C11I1	0.40	2608.3426	2608.3448	0.0022	0.86
[14, 3, 4]	H181C183C13I1	0.89	2613.2322	2613.2339	0.0016	0.62
[17, 1, 4]	H187C189C11I1	0.67	2620.3426	2620.3448	0.0022	0.83
[13, 3, 5]	H181C184C13I1	0.67	2625.2323	2625.2342	0.0019	0.73
[16, 1, 5]	H187C190C11I1	0.63	2632.3426	2632.3448	0.0022	0.82
[15, 1, 6]	H187C191C11I1	0.25	2644.3426	2644.3431	0.0005	0.18
[17, 2, 3]	H188C189C12I1	0.49	2657.3193	2657.3207	0.0014	0.52
[13, 4, 4]	H182C184C14I1	0.59	2661.2083	2661.2062	-0.0021	0.78
[20, 0, 3]	H194C195I1	0.11	2664.4298	2664.4310	0.0012	0.45
[16, 2, 4]	H188C190C12I1	0.88	2669.3193	2669.3188	-0.0005	0.17
[12, 4, 5]	H182C185C14I1	0.47	2673.2083	2673.2074	-0.0009	0.32
[19, 0, 4]	H194C196I1	0.23	2676.4298	2676.4299	0.0001	0.04
[15, 2, 5]	H188C191C12I1	0.78	2681.3193	2681.3205	0.0012	0.46
[18, 0, 5]	H194C197I1	0.20	2688.4298	2688.4302	0.0004	0.16
[14, 2, 6]	H188C192C12I1	0.36	2693.3193	2693.3194	0.0001	0.03
[16, 3, 3]	H189C190C13I1	0.35	2705.2950	2705.2961	0.0010	0.39
[12, 5, 4]	H183C185C15I1	0.30	2710.1843	2710.1834	-0.0009	0.34
[19, 1, 3]	H195C196C11I1	0.22	2712.4053	2712.4063	0.0010	0.38
[15, 3, 4]	H189C191C13I1	0.70	2717.2950	2717.2960	0.0009	0.34
[18, 1, 4]	H195C197C11I1	0.51	2724.4053	2724.4049	-0.0004	0.13
[14, 3, 5]	H189C192C13I1	0.70	2729.2951	2729.2969	0.0019	0.68
[17, 1, 5]	H195C198C11I1	0.53	2736.4053	2736.4055	0.0002	0.06
[13, 3, 6]	H189C193C13I1	0.31	2741.2951	2741.2958	0.0007	0.27
[16, 1, 6]	H195C199C11I1	0.31	2748.4053	2748.4021	-0.0032	1.15

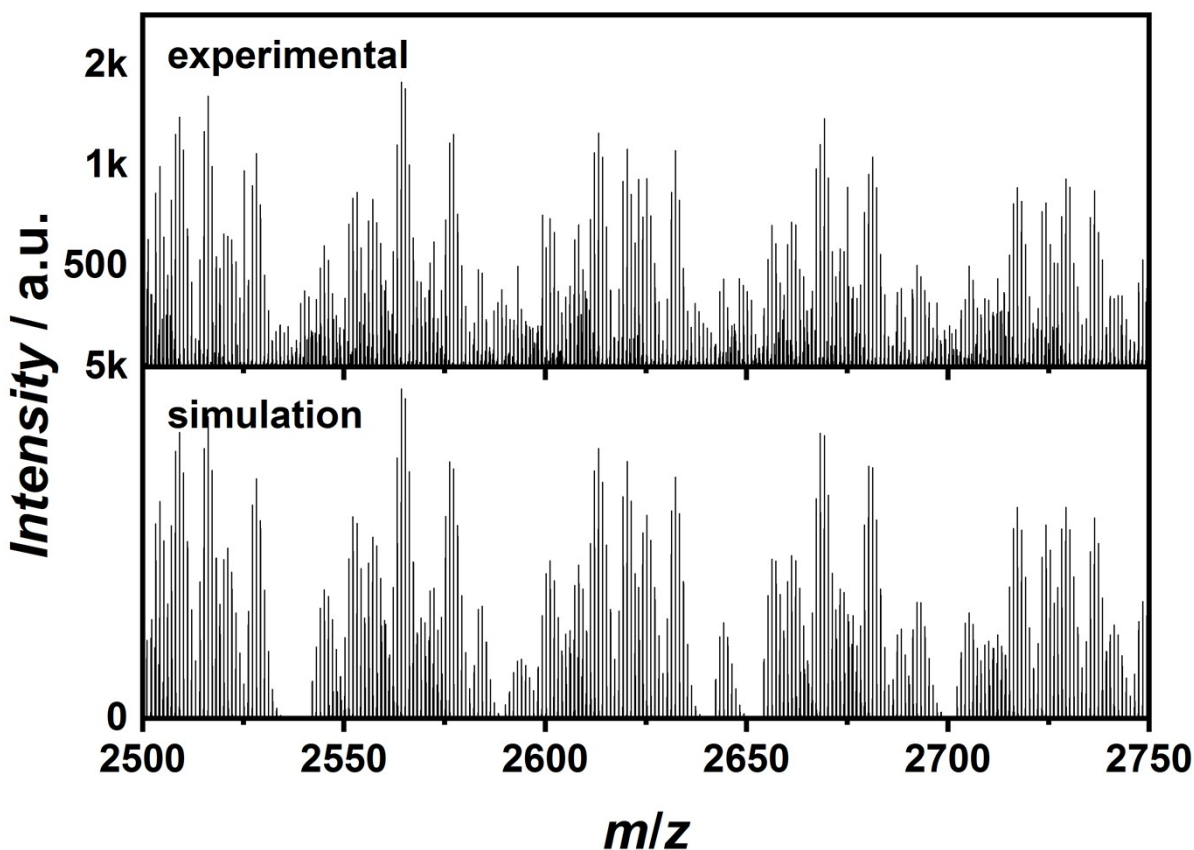


Figure S13. Comparison between the measured and simulated spectra of **SCNP3** at retention time 17.8-18.8 min.

6. XIC Separation

The raw data was fitted via an exponentially modified Gauss Fit (EMG):

$$f(x) = y_0 + (f_1 \times f_2)(x) = y_0 + \frac{A}{t_0} e^{\frac{1}{2} \left(\frac{w}{t_0}\right)^2 - \frac{x-x_c}{t_0}} \int_{-\infty}^z \frac{1}{\sqrt{2\pi}} e^{-\frac{y^2}{2}} dy$$

$$\text{where } f_1(x) = \frac{A}{t_0} e^{-\frac{x}{t_0}}, f_2(x) = \frac{1}{\sqrt{2\pi} w} e^{-\frac{(x-x_c)^2}{2w^2}}, z = \frac{x-x_c}{w} - \frac{w}{t_0}$$

The following Figure S14 shows the determined XICs between m/z 2500-2750 for **SCNP2**. Since mass signals with a low ion intensity give unreliable compaction values, only the shown XICs were utilized to determine the compaction values shown in Table S7-11. The polymer composition is indicated at the top of each spectrum show

the composition before the reaction (grey) and after the compaction including the number of styrene repeating units (n), the residual CMS repeating units (m) and the number of formed intramolecular crosslinks (l).

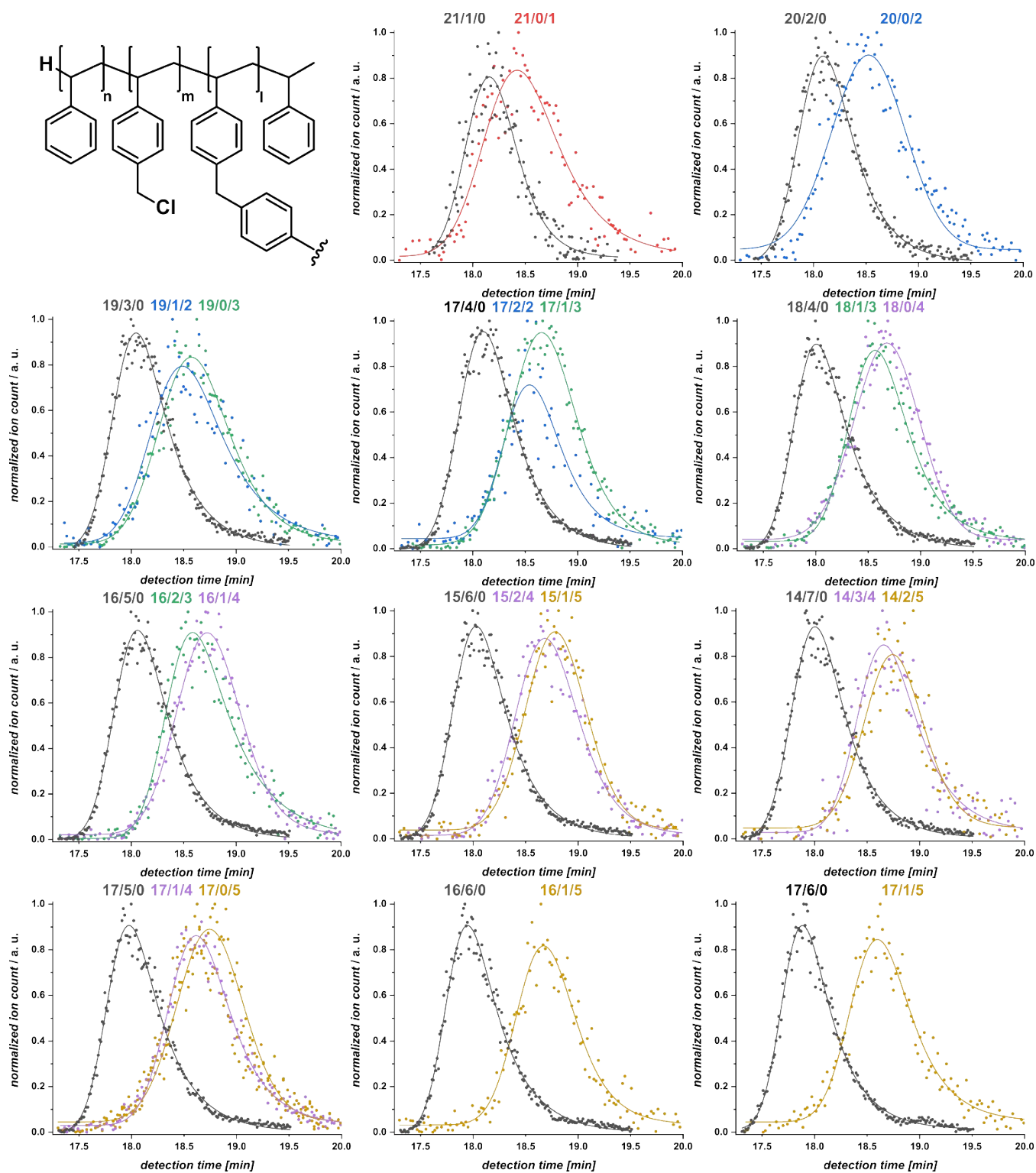


Figure S14. Extracted ion chromatograms for all strong mass signals between m/z 2500-2750 for SCNP2. The composition is given for each curve at the top as n/m/l with the respective repeating units: styrene (n), residual CMS (l) and formed intramolecular crosslinks (l).

Different sets of XICs were repeatedly measured to ensure the reproducibility of the data. The following Table S7-11 shows data from different measurements to determine hydrodynamic radii depending on the number of compaction steps. Figure S15 shows a comparison of XICs for m/z 2765.2225-2765.2725 (correlated to a precursor composition with 17 styrene and 5 CMS monomer units) determined from the different precursor samples **P1-P3**. The standard deviations between measured compaction values are given in Table S8.

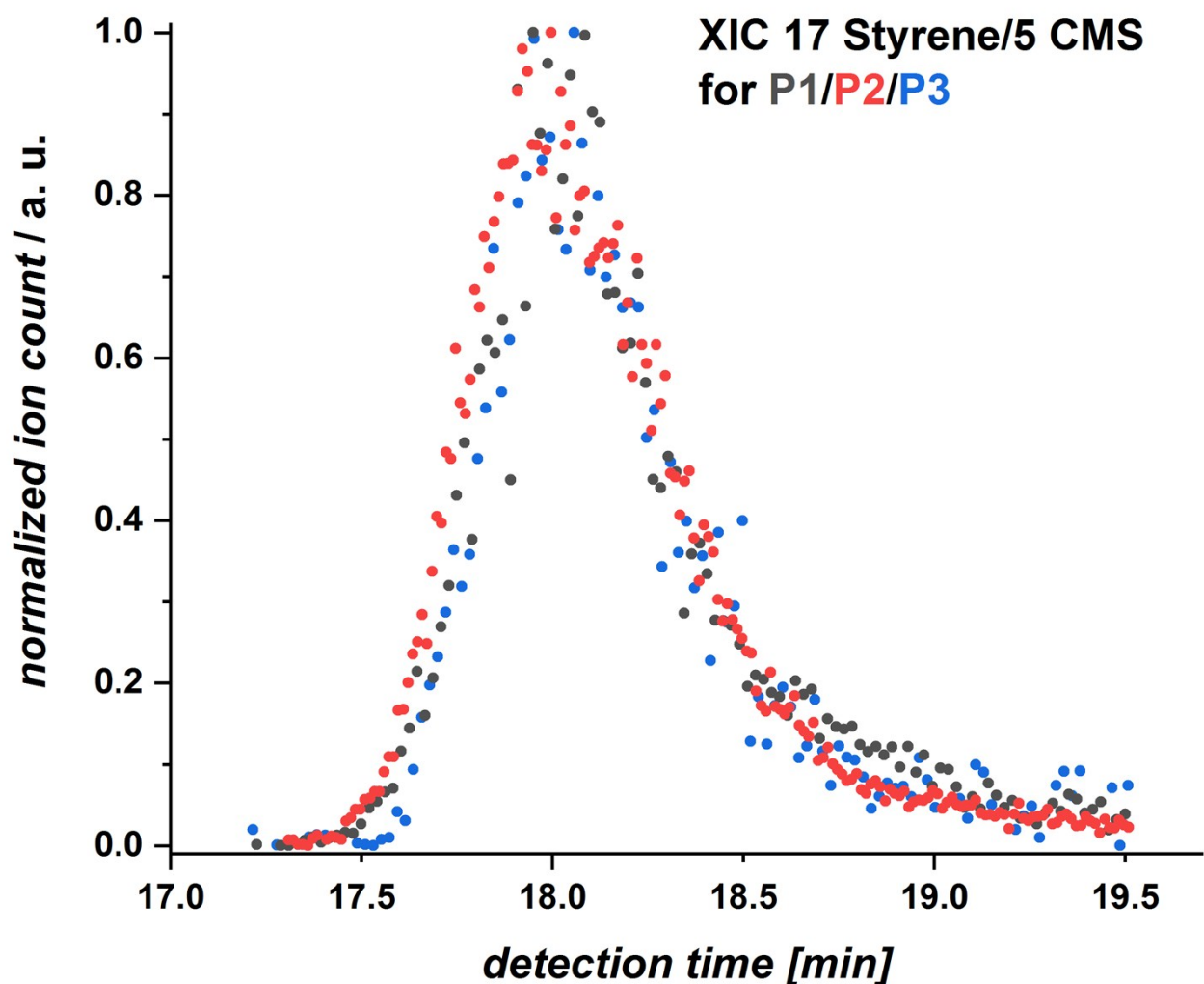


Figure S15. Comparison of XIC data from samples **P1-P3** for m/z 2765.2225-2765.2725 correlated to a precursor composition with 17 styrene and 5 CMS monomer units.

Determination of hydrodynamic radii and the size reduction depending on the number of compaction reactions

The hydrodynamic radii were determined with the calibration curve shown in Section 4. The resulting hydrodynamic radii for one dataset with retention time values that were averaged over 5 measurements (t_{AVG})

are shown in Table S7. The densities of the precursor compositions and the compacted chains were determined to compare them to the density of amorphous polystyrene (1.06 g cm^{-3}).

Table S7. Complete list of all XIC signals utilized to determine the change in hydrodynamic radii visualized in Figure 4. The values were determined over an retention time averaged over five measurements.

Composition Styrene /residual CMS/ compaction points	R_H precursor [%]	R_H SCNP [%]	R_H change [nm]	R_H change [%]	ρ precursor [g cm^{-3}]	ρ SCNP [g cm^{-3}]
21/0/1	1.19	1.13	0.06	5.32	0.60	0.70
20/0/2	1.21	1.10	0.11	9.20	0.58	0.75
19/0/3	1.23	1.07	0.15	12.37	0.57	0.82
19/1/2	1.23	1.09	0.14	11.09	0.57	0.79
18/0/4	1.24	1.05	0.19	15.15	0.57	0.88
18/1/3	1.24	1.08	0.16	12.90	0.57	0.82
17/0/5	1.25	1.03	0.21	17.20	0.56	0.93
17/1/4	1.25	1.06	0.19	15.23	0.56	0.88
16/1/5	1.26	1.05	0.21	16.72	0.56	0.91
18/0/3	1.20	1.05	0.14	12.06	0.59	0.83
17/0/4	1.21	1.03	0.18	14.60	0.58	0.88
17/2/2	1.21	1.08	0.13	11.04	0.58	0.81
17/1/3	1.21	1.05	0.16	13.16	0.58	0.85
16/0/5	1.22	1.02	0.20	16.63	0.58	0.93
16/2/3	1.22	1.06	0.16	12.88	0.58	0.84
16/1/4	1.22	1.03	0.19	15.39	0.58	0.90
15/2/4	1.23	1.05	0.19	15.14	0.57	0.89
15/1/5	1.23	1.02	0.21	17.41	0.57	0.95
14/2/5	1.24	1.03	0.21	16.66	0.57	0.92
14/3/4	1.24	1.06	0.18	14.89	0.57	0.88
17/1/5	1.28	1.07	0.21	16.47	0.55	0.89

Table S8. Complete list of all XIC signals utilized to determine the change in hydrodynamic radii visualized in Figure 4. The values were determined over five different measurements (SCNP A1-4, SCNP B1), as well as over an average retention time determined over all measurements (t_{AVG}). The standard deviation and relative standard (RSD) is given over the measurements excluding the values from the averaged retention time. The missing values were not determined either due to poor signal (SCNP B1) or they were outside the measured mass range (lower than m/z 2500 for SCNP A1-4).

Composition Styrene /residual CMS/ compaction points	R_H change [%] SCNP A1	R_H change [%] SCNP A2	R_H change [%] SCNP A3	R_H change [%] SCNP A4	R_H change [%] SCNP B1	R_H change [%] t_{AVG}	standard deviation	RSD [%]
21/0/1	5.75	6.57	4.59	4.36	-	5.32	1.04	15.58
20/0/2	9.09	10.54	9.07	9.07	8.20	9.20	0.84	7.65
19/0/3	12.77	12.59	12.93	11.46	12.08	12.37	0.60	4.04

Composition Styrene /residual CMS/ compaction points	R_H change [%] SCNP A1	R_H change [%] SCNP A2	R_H change [%] SCNP A3	R_H change [%] SCNP A4	R_H change [%] SCNP B1	R_H change [%] t_{AVG}	standard deviation	RSD [%]
19/1/2	11.70	10.66	10.24	11.75	-	11.09	0.75	5.44
18/0/4	15.55	15.78	15.78	14.09	14.54	15.15	0.78	4.30
18/1/3	12.99	13.31	12.63	12.20	13.36	12.90	0.49	3.14
17/0/5	17.93	17.84	17.80	15.87	16.54	17.20	0.94	4.54
17/1/4	15.33	15.04	16.22	14.93	14.61	15.23	0.61	3.34
16/1/5	17.06	16.93	17.19	15.66	16.74	16.72	0.61	3.05
18/0/3	-	-	-	11.74	12.37	12.06	0.44	2.44
17/0/4	-	-	-	14.24	14.95	14.60	0.50	2.30
17/2/2	10.66	10.71	10.55	12.24	-	11.04	0.80	5.81
17/1/3	13.40	13.38	13.45	13.11	12.48	13.16	0.41	2.57
16/0/5	-	-	-	16.05	17.21	16.63	0.82	3.28
16/2/3	13.00	12.57	13.41	12.29	13.12	12.88	0.45	2.88
16/1/4	15.89	15.73	16.06	14.50	14.78	15.39	0.70	3.80
15/2/4	15.55	15.48	15.64	14.19	14.85	15.14	0.62	3.39
15/1/5	17.89	17.61	18.29	15.99	17.29	17.41	0.88	4.20
14/2/5	17.67	17.32	18.09	15.83	14.35	16.66	1.54	7.72
14/3/4	15.30	15.46	14.95	13.84	-	14.89	0.73	3.94
17/1/5	16.72	16.59	16.75	16.24	16.06	16.47	0.31	5.03

The resulting average compaction values for every number of compaction steps are shown in Table S9, as well as Figure 4.

Table S9. Average values for the change in hydrodynamic radii resulting from Table S8 including standard deviation, the data is visualized in Figure 4.

Number of compaction steps	average R_H change [%]	standard deviation
1	5.32	1.04
2	10.44	1.08
3	12.67	0.45
4	15.07	0.28
5	16.85	0.37

Hydrodynamic radii corrected for the difference in retention behavior caused by the change in mass

Since every compaction reaction causes a defined mass change ($\Delta m = 35.98$ amu), the change in retention behavior can be corrected depending on the number of compaction steps. Since the analysis was carried out in a small mass region (m/z 2500-2750), a linear dependence between retention time and molecular mass can be assumed and we determined a correction factor of 0.0262 min per compaction step. The resulting compaction values without influence of the mass shift are shown in Table S10-11 and Figure S16.

Table S10. Complete list of all mass-corrected XIC signals utilized to determine the change in hydrodynamic radii. The values were determined over five different measurements (SCNP A1-4, SCNP B1), as well as over an average retention time determined over all measurements (t_{AVG}). The standard deviation and relative standard (RSD) is given over the measurements excluding the values from the averaged retention time. The missing values were not determined either due to poor signal (SCNP B1) or they were outside the measured mass range (lower than m/z 2500 for SCNP A1-4).

Composition Styrene /residual CMS/ compaction points	R_H change [%] SCNP A1	R_H change [%] SCNP A2	R_H change [%] SCNP A3	R_H change [%] SCNP A4	R_H change [%] SCNP B1	R_H change [%] t_{AVG}	standard deviation	RSD [%]
21/0/1	5.13	5.95	3.95	3.72	-	4.69	1.04	17.79
20/0/2	7.89	9.35	7.86	7.86	6.98	7.99	0.86	8.92
19/0/3	11.03	10.84	11.19	9.69	10.33	10.62	0.61	4.80
19/1/2	10.53	9.48	9.05	10.58	-	9.91	0.76	6.17
18/0/4	13.30	13.53	13.53	11.80	12.26	12.88	0.80	5.19
18/1/3	11.26	11.58	10.89	10.45	11.63	11.16	0.50	3.71
17/0/5	15.19	15.10	15.05	13.06	13.75	14.43	0.97	5.59
17/1/4	13.08	12.78	13.99	12.67	12.34	12.97	0.63	4.03
16/1/5	14.29	14.15	14.42	12.85	13.96	13.94	0.63	3.78
18/0/3	-	-	-	9.97	10.61	10.29	0.45	2.92
17/0/4	-	-	-	11.94	12.67	12.31	0.52	2.80
17/2/2	9.48	9.52	9.36	11.07	-	9.86	0.81	6.59
17/1/3	11.67	11.64	11.71	11.37	10.72	11.43	0.41	3.02
16/0/5	-	-	-	13.23	14.43	13.83	0.84	4.07
16/2/3	11.26	10.82	11.68	10.54	11.39	11.14	0.45	3.40
16/1/4	13.64	13.48	13.82	12.22	12.50	13.13	0.72	4.57
15/2/4	13.29	13.22	13.38	11.89	12.58	12.87	0.63	4.10
15/1/5	15.14	14.85	15.55	13.17	14.51	14.65	0.91	5.17
14/2/5	14.91	14.55	15.34	13.01	11.48	13.87	1.59	9.59
14/3/4	13.05	13.21	12.68	11.54	-	12.62	0.75	4.77
17/1/5	15.46	13.81	13.97	13.45	13.26	13.69	0.87	5.19

The resulting average compaction values for every number of compaction steps are shown in Table S11, as well as Figure 4.

Table S11. Average values for the change in hydrodynamic radii resulting from Table S10 including standard deviation, the data is visualized in Figure S16.

Number of compaction steps	average R_H change [%]	standard deviation
1	4.691	1.04
2	9.253	1.09
3	10.927	0.46
4	12.798	0.29
5	14.066	0.38

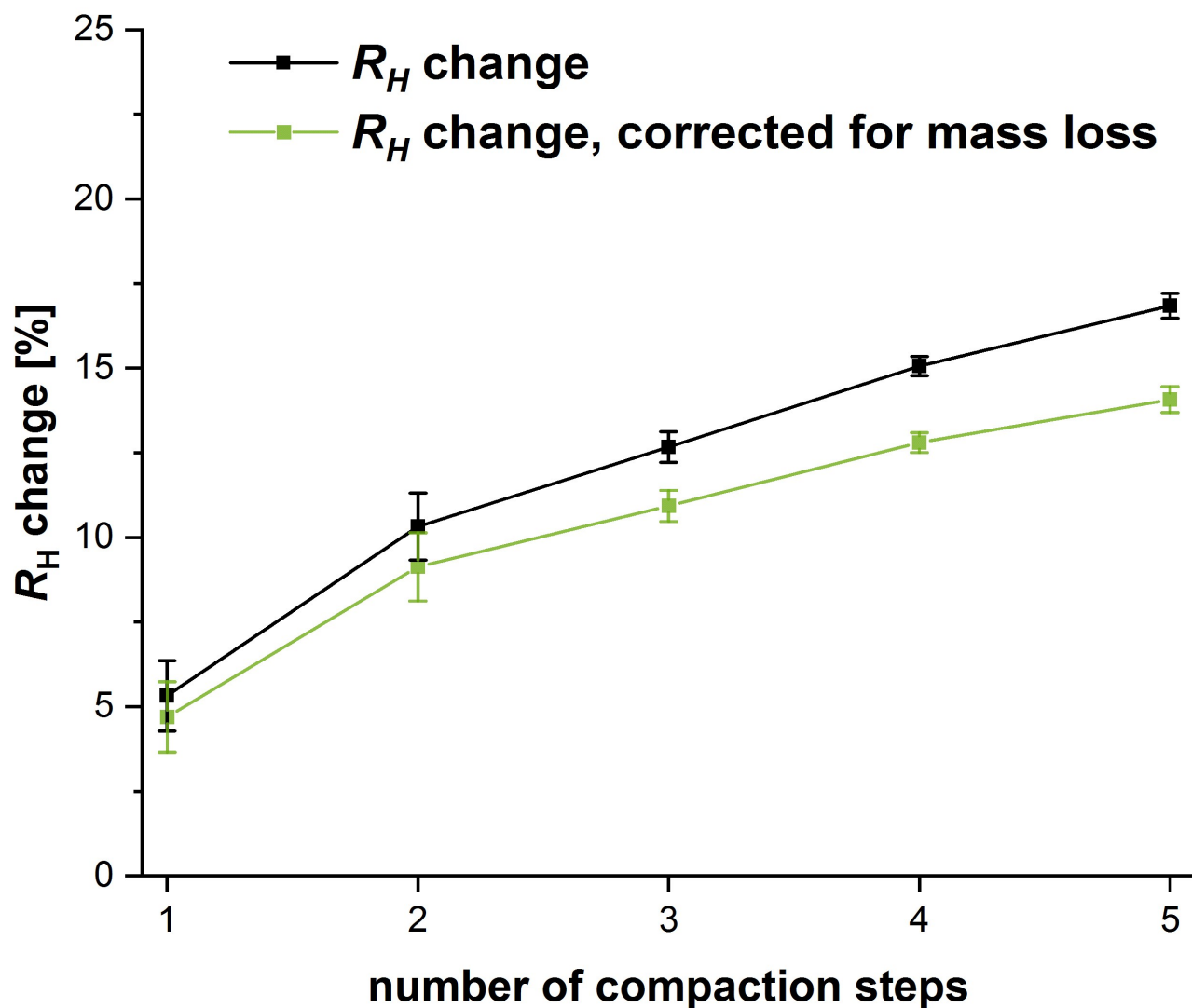


Figure S16. Reduction of the hydrodynamic radii depending on the number of compaction steps (black), as well as mass-corrected values only depicting the compaction shift without the influence of the mass change (green) with the standard deviation as error bars.

The determined compaction values were compared to our previous study determining the compaction of a polystyrene polymer with tetrazole and fumarate moieties, compacted via the nitril imine mediated tetrazole ene cycloaddition (NITEC).³ Overall, the compaction via Friedel-Crafts alkylation led to more densely compacted chains as visualized in Figure S16.

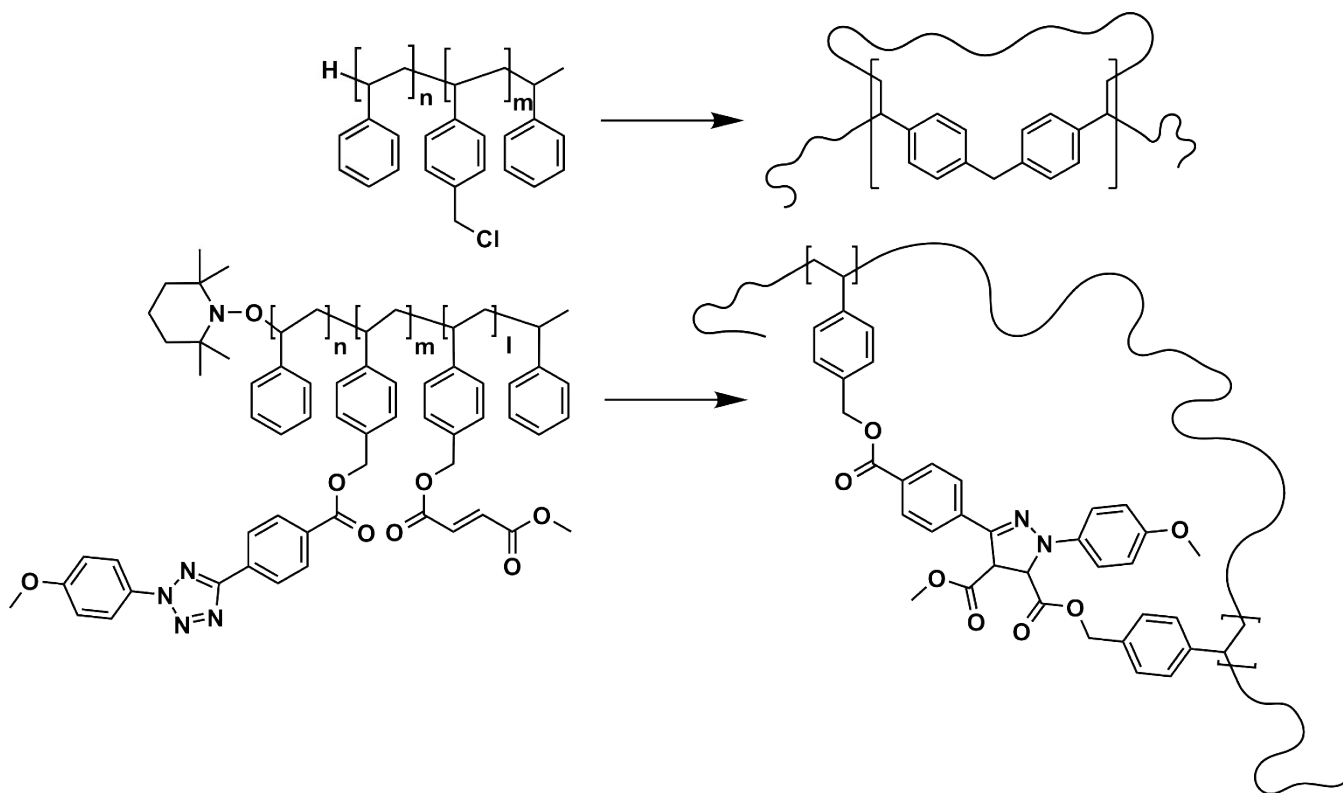


Figure S17. Comparison between formed bridging functionality in the SCNP formation via FC alkylation (top) and via NITEC reaction (bottom).

6. References

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