Supporting Information

Mapping the Compaction of Discrete Polymer Chains by Size-Exclusion Chromatography Coupled to High Resolution Mass Spectrometry

Tobias Nitsche[1], Jan Steinkoenig[4], Kevin De Bruycker[1], Fabian R. Bloesser[1], Stephen J. Blanksby[3], James P. Blinco[1,*] and Christopher Barner-Kowollik[1,2,*]

1. School of Chemistry, Physics and Mechanical Engineering, Queensland University of Technology (QUT), 2 George Street, Brisbane, QLD 4000, Australia.

2. Macromolecular Architectures, Institut für Technische Chemie und Polymerchemie, Karlsruhe Institute of Technology (KIT), Engesserstrasse 18, 76131 Karlsruhe.

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

4. Department of Organic and Macromolecular Chemistry, Polymer Chemistry Research group, Center of Macromolecular Chemistry (CMaC), Ghent University, Krijgslaan 281 S4bis, 9000 Ghent, Belgium

Contents

1. Materials

(1-Bromoethyl) benzene (97%), copper powder (99%), *p*-anisidine (>99%), *p*-toluenesulfonylhydrazide (97%), 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO, 98%), *N*,*N*,*N*',*N*'',*N*''-pentamethyldiethylenetriamine (PMDETA, 99%), pyridine, styrene (>99%), mono-methyl fumarate (97%) and chloroform-d_1 were purchased from *Sigma Aldrich*. Caesium carbonate (Cs_2CO_3, 99.5%), chloromethyl styrene (CMS, technical grade, 90%), 4-formylbenzoic acid (98%), hydrochloric acid (32%) and sodium nitrite were purchased from *Thermo Fisher Scientific*. Acetonitrile (ACN), dichloromethane (DCM), dimethylformamide (DMF), diethyl ether, ethanol and methanol were purchased from *Thermo Fisher Scientific*.

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 Plus (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 microflow HPLC syringe pump (Teledyne ISCO, Model 100DM). A 100 µL aliquot of a polymer solution with a concentration of 2-6 mg mL^{-1} was injected into the SEC system.

Nuclear magnetic resonance (NMR) spectroscopy. ^{1}H NMR -spectra were recorded on a *Bruker* System 600 Ascend LH, equipped with an BBO-Probe (5 mm) with z-gradient (^{1}H: 600.13 MHz). The δ-scale was normalized relative to the solvent signal of $CHCl_3$.

DOSY experiments based on ^{1}H NMR were performed in THF-d_8 at 303.0 K on a Bruker 400 UltraShield spectrometer equipped with a Quattro Nucleus Probe (QNP) with an operating frequency of 400 MHz (^{1}H).

UV-Vis spectroscopy. UV-Vis spectra were recorded on a *Shimadzu* UV-2700 spectrophotometer equipped with a CPS-100 electronic temperature control cell positioner. Samples were prepared in tetrahydrofuran with a concentration of 0.0175 mg mL^{-1} and measured in *BrandTech* disposable UV cuvettes at room temperature.

Photoreactor. The samples were irradiated in a *Luzchem* LZC-4V photoreactor using LZC-UVB lamps, emitting at 300 nm with a peak maximum at 313 nm. Four lamps were installed for side irradiation. The internal chamber was ventilated to maintain ambient temperature during the entire experiment. The samples were stirred employing the built-in LZC-D recessed magnetic stirrer.

3. Experimental Section

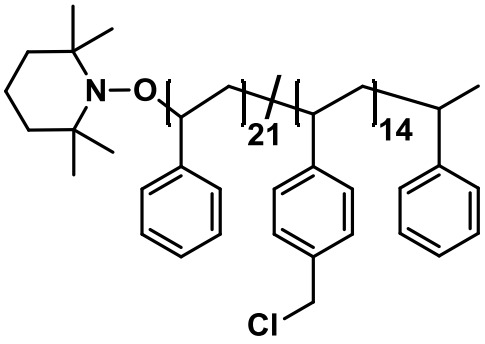
2,2,6,6-Tetramethyl-1-(1-phenylethoxy)piperidine

The synthesis was adapted from the literature.[2]

4-(2-(4-methoxyphenyl)-2H-tetrazol-5-yl) benzoic acid (TET-COOH)

The synthesis was adapted from the literature.[2]

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



164 mg 2,2,6,6-Tetramethyl-1-(1-phenylethoxy)piperidine (0.628 mmol, 1.00 eq.) and 9.8 mg TEMPO (0.0628 mmol, 0.10 eq.) were dissolved in a mixture of 4.30 mL styrene (3.92g, 37.7 mmol, 60.0 eq.) and 2.63 mL chloromethyl styrene (2.85 g, 18.9 mmol, 30.0 eq.). The reaction mixture was degassed via four freeze-thaw cycles. The reaction was carried out for 6 hours at 125 °C. The crude mixture was diluted with THF and precipitated dropwise into 1 L methanol. The precipitate was collected by filtration and dried at 35 °C under vacuum.

^{1}H NMR ($CDCl_3$, 600 MHz) δ = 7.33 − 6.20 (m, a), 4.72 − 4.26 (s, b), 2.45-0.80 (m, c).

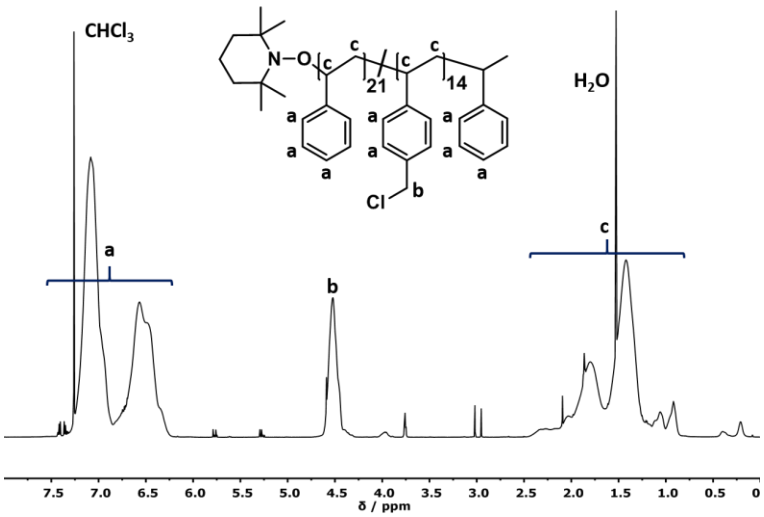
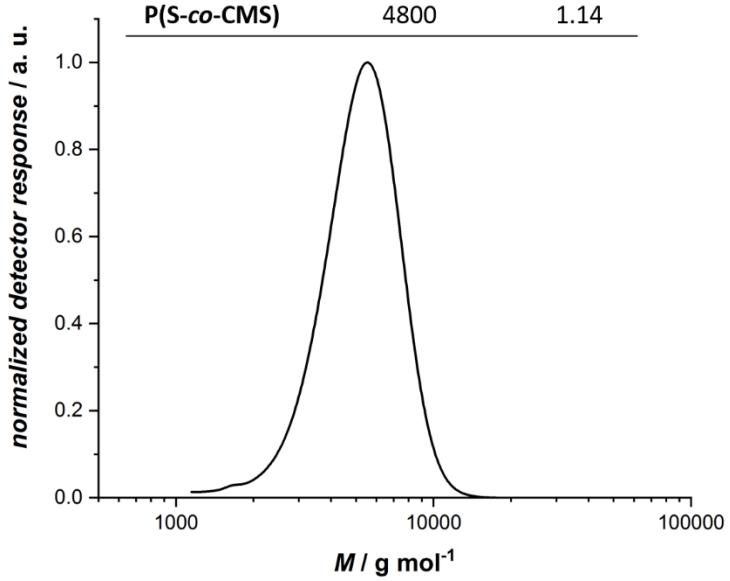


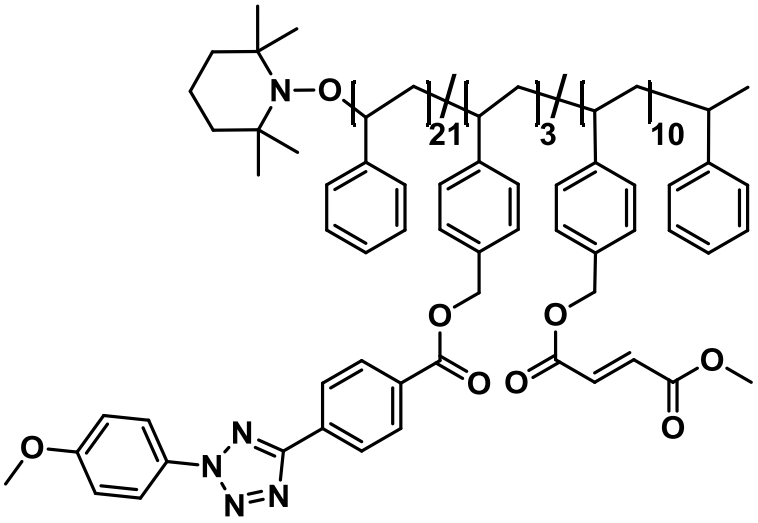
Figure S1. ^{1}H NMR of **P(S-*stat*-CMS)** in chloroform-d_1.

	M_n / g mol^{-1} (SEC, PS cal.)	$Đ$ (SEC)
P(S-*co*-CMS)	4800	1.14



FigureS2: SEC trace of **P(S-*co*-CMS)** in THF using PS calibration.

Poly(styrene-*co*-TET-*co*-FU) (Precursor)



500 mg **P(S-*co*-CMS)** (M_n = 4800, $Đ$ = 1.14) (0.104 mmol, 1.00 eq), 617.7 mg Cs_2CO_3 (1.896 mmol, 1.3 eq. relative to CMS) and 129.6 mg **TET-COOH** (0.0383 mmol, 0.30 eq relative to CMS groups) were dissolved in 20 mL dry DMF. The reaction mixture was stirred in the dark for 24 hours. 142.3 mg mono-methylfumarate (1.094 mmol, 0.75 eq relative to CMS) were added and the reaction mixture was stirred in the dark for another 24 hours before crudely removing the solvent under reduced pressure. The crude reaction mixture was diluted with DCM and undissolved salts were filtered off. The solution was washed three times with water and brine. The organic phase was dried over magnesium sulphate and the solvent was removed under reduced pressure. The polymer was dissolved in THF and precipitated into cold methanol.

^{1}H NMR ($CDCl_3$, 600 MHz) δ = 8.31 – 7.91 (m, a), 7.28 – 6.10 (m, b-d), 5.37-5.14 (s, e), 5.14-4.88 (s, f), 4.58-4.24 (s, g), 3.85-3.75 (s, h), 3.75-3.61 (s, i), 2.40-0.63 (m, j).

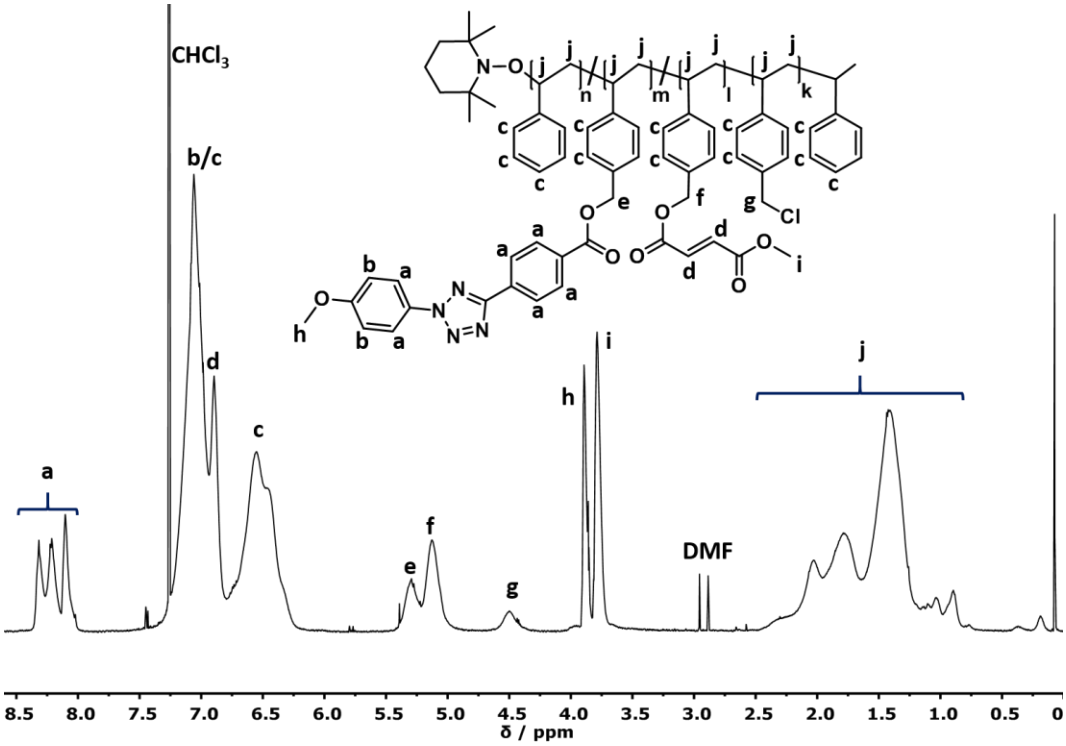


Figure S3. ^{1}H NMR of **P(S-*stat*-TET-*stat*-FU)** in chloroform-d_1.

	M_n / g mol^{-1} (SEC, PS cal.)	$Đ$ (SEC)
P(S-*co*-TET-*co*-FU)	7100	1.26

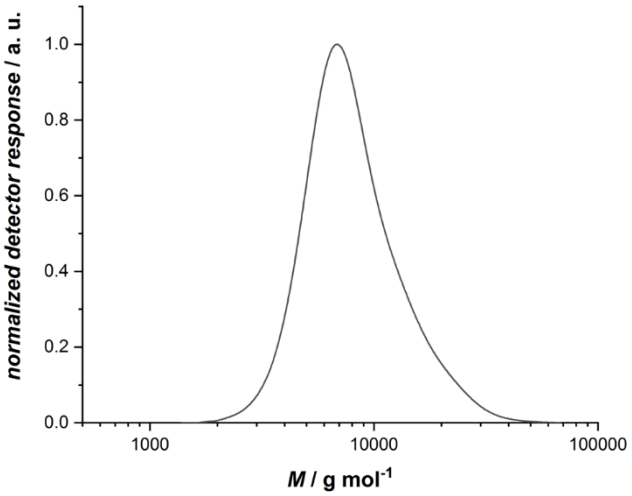


Figure S4. : SEC trace of **P(S-*stat*-TET-*stat*-FU)** in THF using PS calibration.

Compaction of the precursor copolymer to form the SCNP

For the compaction reaction, 7.0 mg of the precursor polymer **P(S-*stat*-TET-*stat*-FU**) were dissolved in 400 mL of freshly distilled dichloromethane. The reaction mixture was degassed by bubbling filtered argon through the solution for 45 minutes. Subsequently, the reaction solution was irradiated for two minutes in a *Luzchem* LZC-4V photoreactor using 2 LZC-UVB lamps, emitting at 300 nm with a peak maximum at 313 nm. The solution was dried under reduced pressure in the absence of light and re-dissolved in HPLC grade THF without further purification for the subsequent SEC or SEC-ESI-MS analysis.

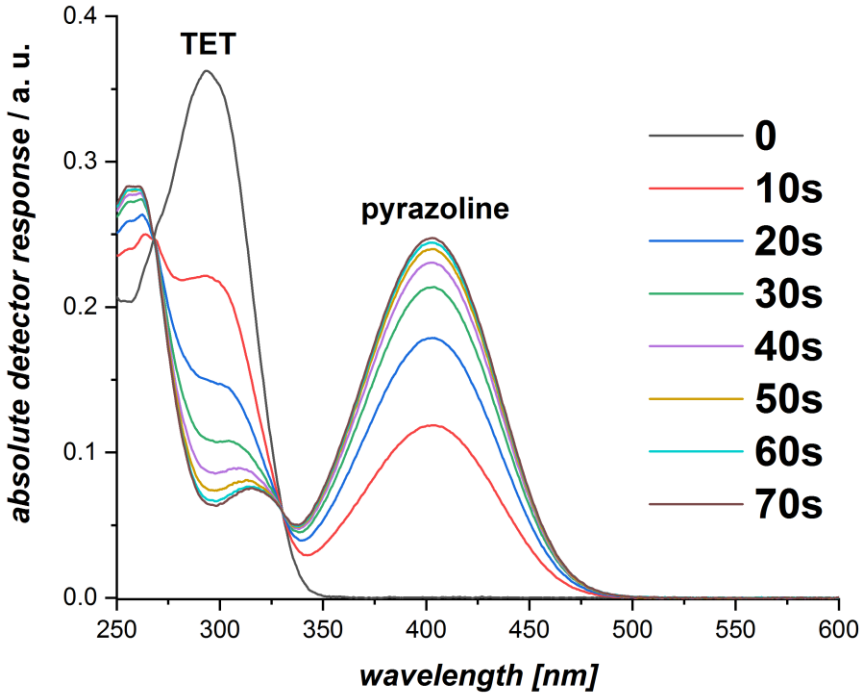


Figure S5. UV-Vis traces of the kinetic investigation of the compaction reaction of **P(S-*stat*-TET-*stat*-FU)** showing the reduction of the tetrazole signal (λ_{max} = 295 nm) and the increase in pyrazoline signal (λ_{max} = 403 nm) reaching a steady value after 70 seconds.

4. DOSY Measurements

DOSY experiments based on ^{1}H NMR were performed in THF-d_8 at 303.0 K on a Bruker 400 UltraShield spectrometer equipped with a Quattro Nucleus Probe (QNP) with an operating frequency of 400 MHz (^{1}H). A sequence with longitudinal eddy current delay (LED) using bipolar gradients was used in order to compensate eddy currents. Bipolar gradient δ and a diffusion delay Δ were determined separately for each sample. Gradient strength was linearly incremented from 2% at 0.96 G to 95% at 45.7 G in 64 steps. The obtained data was processed with TopSpin 3.5 and Dynamics Center 2.5.3.

After Fourier transform of the 1D spectra, the signal decay along the gradients *G* was fitted to

$$f(G) = I_0 \cdot e^{-D*G^2*\gamma^2*\delta^2*\left(\Delta-\frac{\delta}{3}\right)} \cdot 10^4$$

with the gyromagnetic ratio *γ* and the full signal intensity I_0.

Hydrodynamic diameters d_H were calculated from the Stokes-Einstein equation:

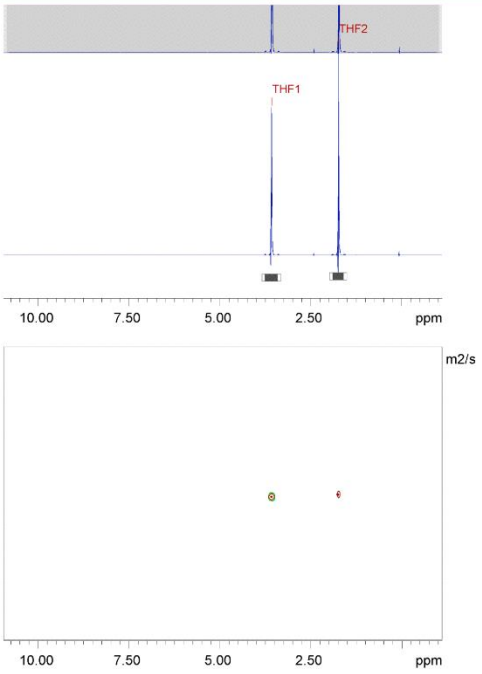
$$d_H = \frac{k_B \cdot T}{3 \cdot \pi \cdot \eta \cdot D}$$

Where k_B is the Boltzmann constant, T the temperature and η the solvent viscosity (THF: 0.456 mPa s).[3]

In addition, a correction of the solvent viscosity was carried out to consider the influence of the dissolved polymers. For this approach, the hydrodynamic radius of pure THF was determined. The corrected solvent viscosity η' can then be determined simply by rearranging the Stokes-Einstein equation and applying the measured Diffusion coefficient of the THF signal at δ = 3.58.

$$\eta' = \frac{k_B \cdot T}{6 \cdot \pi \cdot R_{THF} \cdot D}$$

The raw data of the measurements of single PS standards from a mass range of M_p = 682 – 34800 g mol^{-1}, as well as the measurement of pure THF are shown in Figure S6-12.



Fitted function:	f (x) = Io * exp (-D * x^2 * gamma^2 * littleDelta^2 (bigDelta-littleDelta/3)* $10^{\wedge}4$
used gamma:	26752 rad/(s*Gauss)
used little delta:	0.0010000 s
used big delta:	0.099900 s
used gradient strength:	variable
Random error estimation of data:	RMS per spectrum (or trace/plane)
Systematic error estimation of data:	worst case per peak scenario
Fit parameter Error estimation method:	from fit using arbitray y uncertainties
Confidence level:	95%
Used peaks:	peaks from C:/other projects/SEC Dh calibration/THF/5/pdata/1/peaklist1D.xml
Used integrals:	area integral
Used Gradient strength:	all values (including replicates) used

Peak name	F2 [ppm]	Io	error	D [m2/s]	error
THF1	3.580	1.64e+10	1.434e+08	2.97e-09	5.865e-11
THF2	1.744	1.81e+10	1.586e+08	2.94e-09	5.814e-11

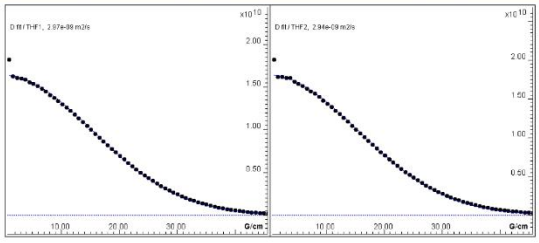
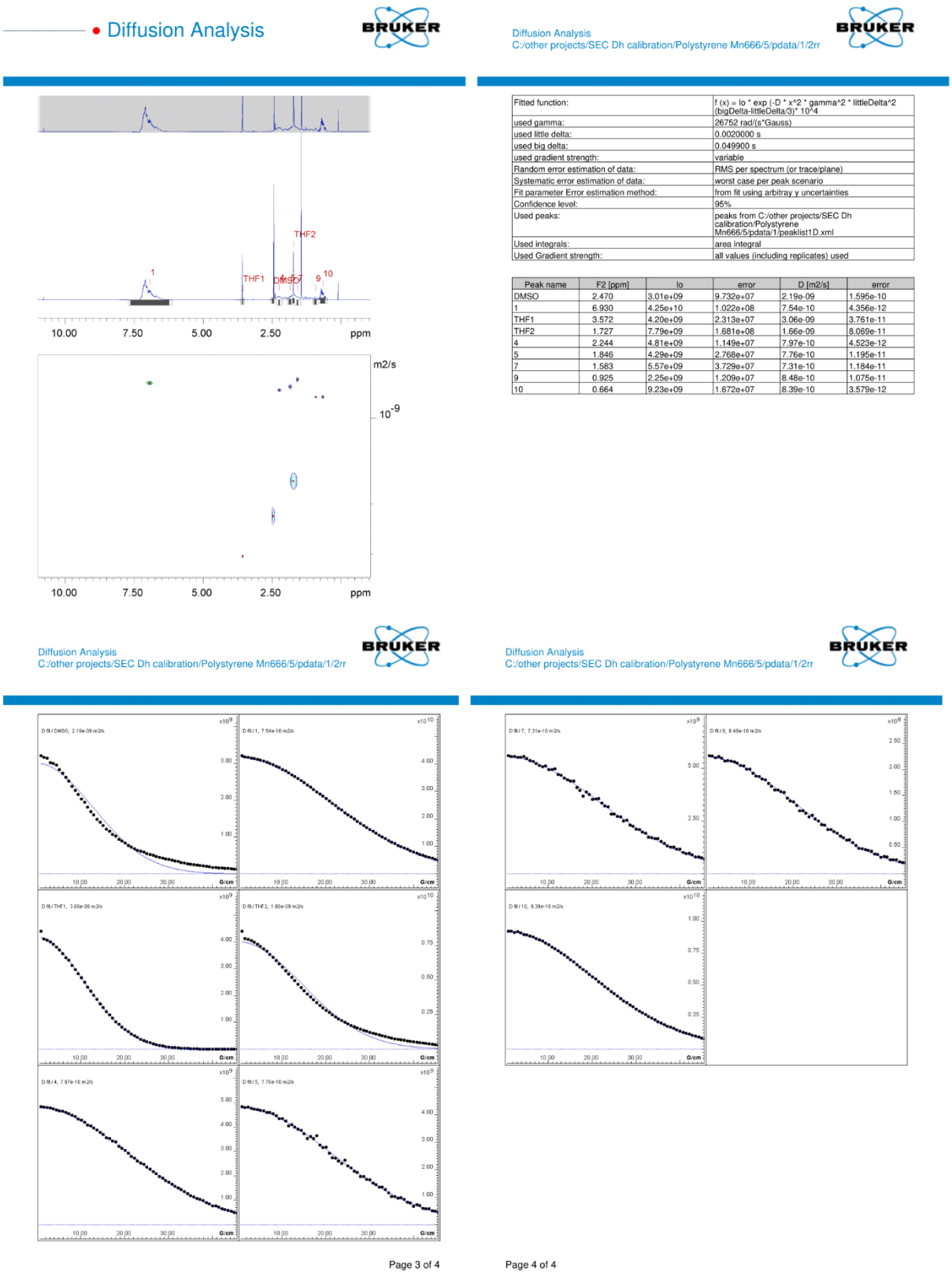


Figure S6. DOSY NMR Diffusion analysis of pure THF-d_8.



Fitted function:	f (x) = Io * exp (-D * x^2 * gamma^2 * littleDelta^2 (bigDelta-littleDelta/3)* 10^4
used gamma:	26752 rad/(s*Gauss)
used little delta:	0.0020000 s
used big delta:	0.049900 s
used gradient strength:	variable
Random error estimation of data:	RMS per spectrum (or trace/plane)
Systematic error estimation of data:	worst case per peak scenario
Fit parameter Error estimation method:	from fit using arbitray y uncertainties
Confidence level:	95%
Used peaks:	peaks from C:/other projects/SEC Dh calibration/Polystyrene Mn666/5/pdata/1/peaklist1D.xml
Used integrals:	area integral
Used Gradient strength:	all values (including replicates) used

Peak name	F2 [ppm]	Io	error	D [m2/s]	error
DMSO	2.470	3.01e+09	9.732e+07	2.19e-09	1.595e-10
1	6.930	4.25e+10	1.022e+08	7.54e-10	4.356e-12
THF1	3.572	4.20e+09	2.313e+07	3.06e-09	3.761e-11
THF2	1.727	7.79e+09	1.681e+08	1.66e-09	8.069e-11
4	2.244	4.81e+09	1.149e+07	7.97e-10	4.523e-12
5	1.846	4.29e+09	2.768e+07	7.76e-10	1.195e-11
7	1.583	5.57e+09	3.729e+07	7.31e-10	1.184e-11
9	0.925	2.25e+09	1.209e+07	8.48e-10	1.075e-11
10	0.664	9.23e+09	1.672e+07	8.39e-10	3.579e-12

Figure S7. DOSY NMR Diffusion analysis of PS1 sample (Mp = 682 g mol^{-1}).

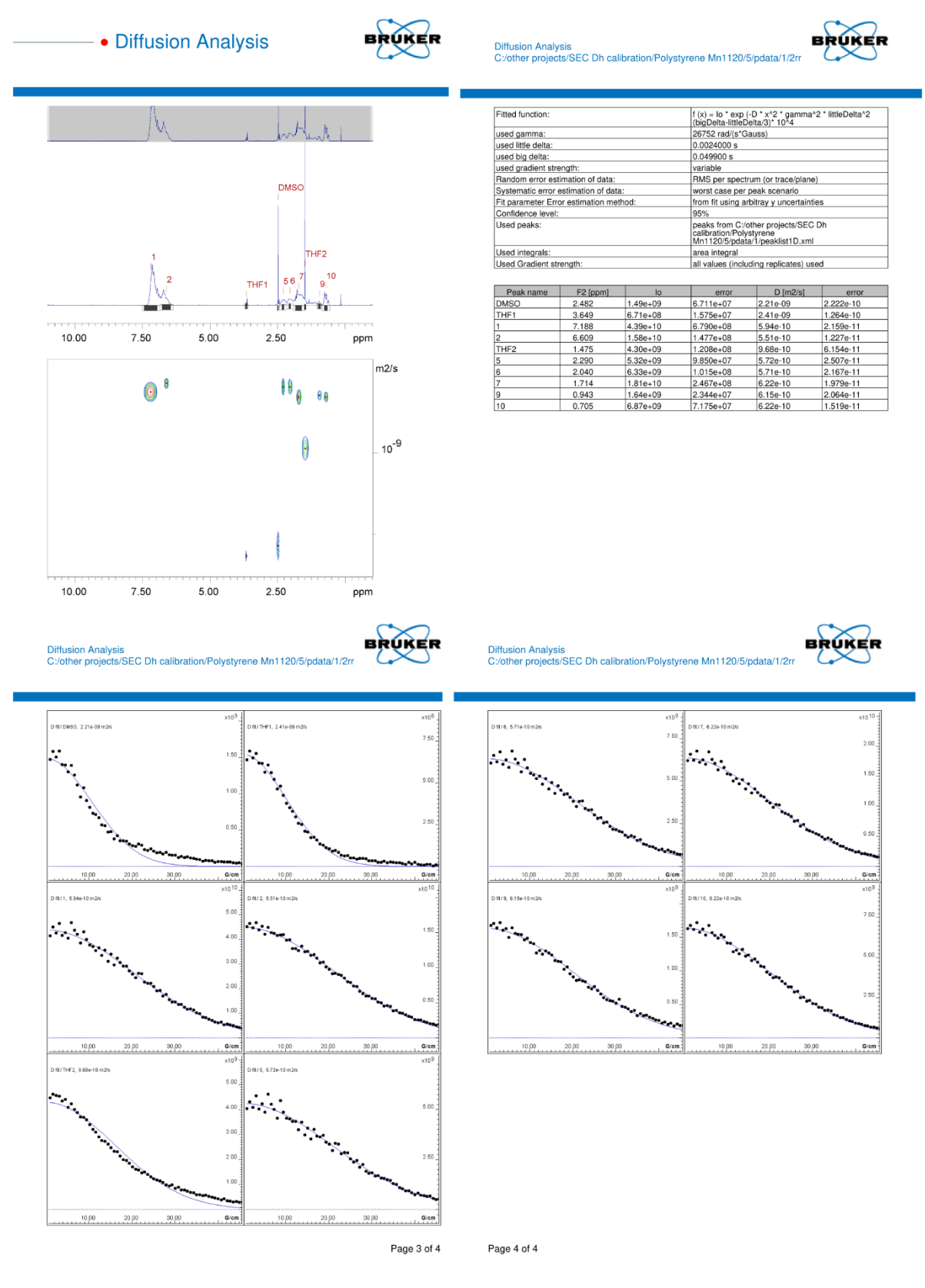


Figure S8. DOSY NMR Diffusion analysis of PS2 sample (Mp = 1306 g mol^{-1}).

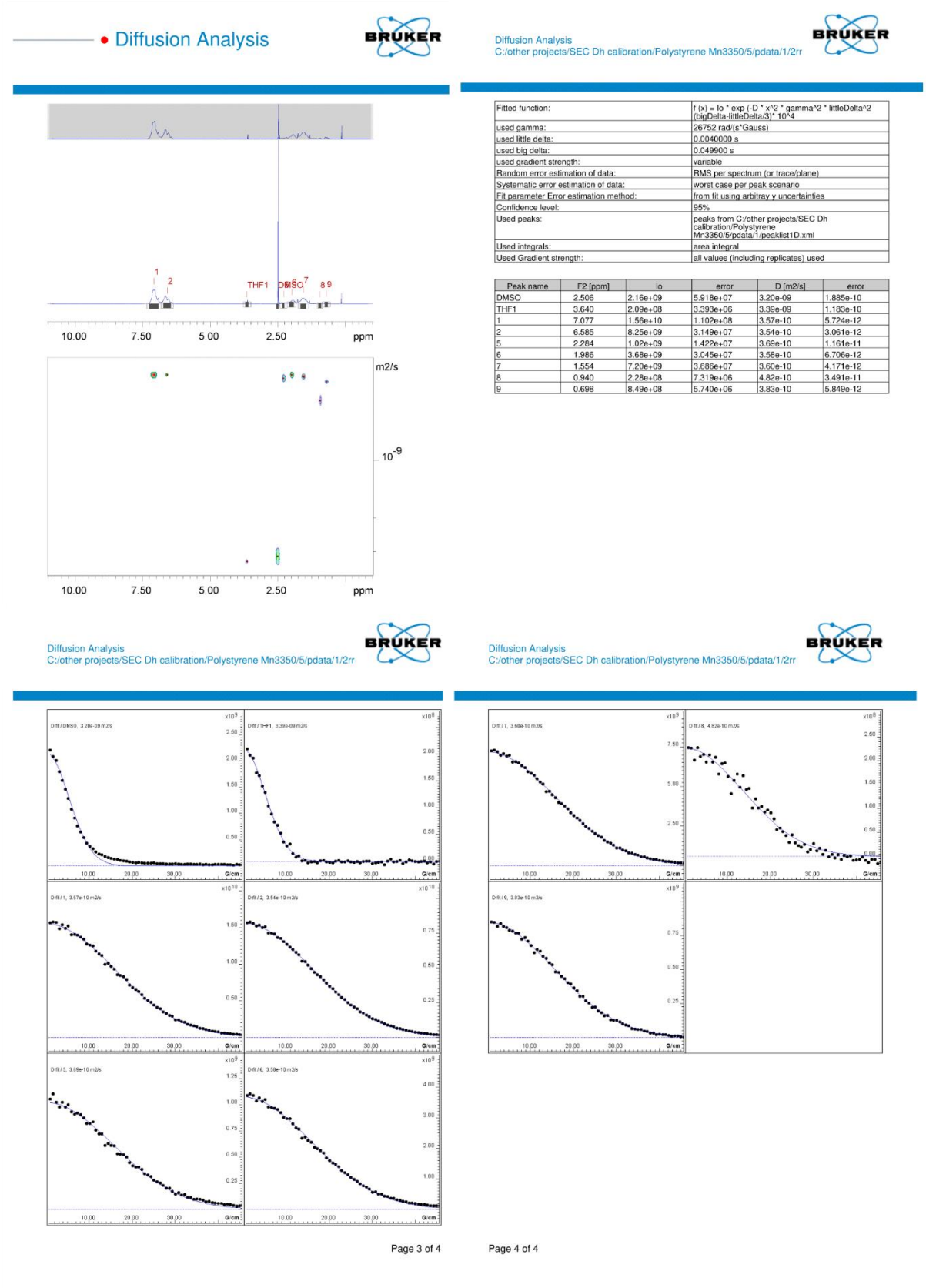


Figure S9. DOSY NMR Diffusion analysis of PS3 sample (Mp = 3500 g mol^{-1}).

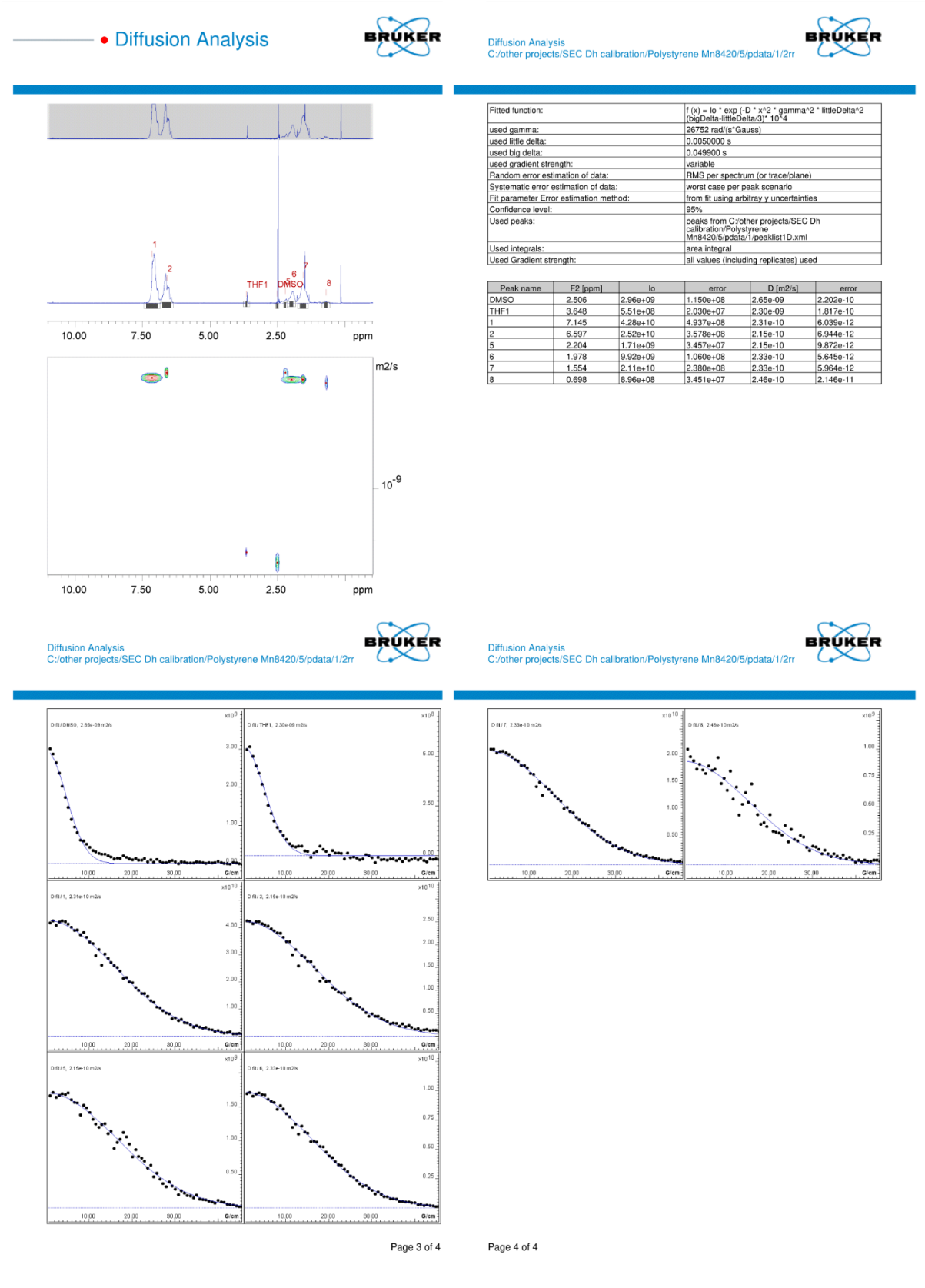
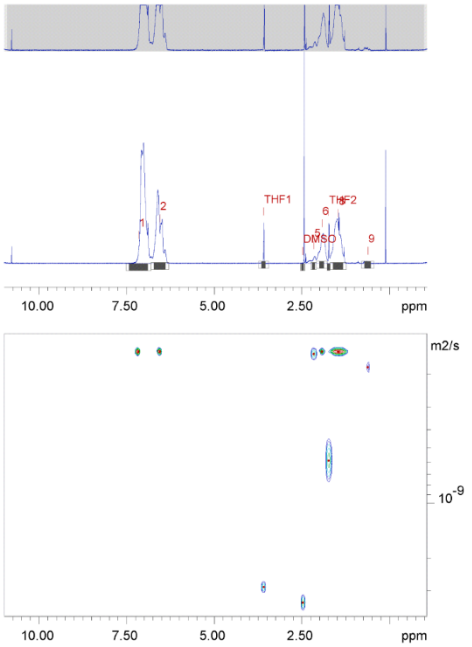
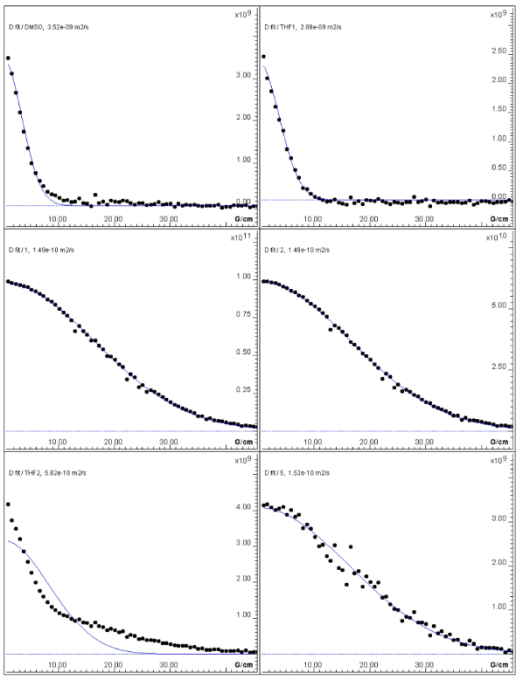


Figure S10. DOSY NMR Diffusion analysis of PS4 sample (Mp = 8680 g mol^{-1}).



Fitted function:	f (x) = Io * exp (-D * x^2 * gamma^2 * littleDelta^2 (bigDelta-littleDelta/3)* 10^{-4}
used gamma:	26752 rad/(s*Gauss)
used little delta:	0.0060000 s
used big delta:	0.049900 s
used gradient strength:	variable
Random error estimation of data:	RMS per spectrum (or trace/plane)
Systematic error estimation of data:	worst case per peak scenario
Fit parameter Error estimation method:	from fit using arbitray y uncertainties
Confidence level:	95%
Used peaks:	peaks from C:/other projects/SEC Dh calibration/Polystyrene Mn16900/10/pdata/1/peaklist1D.xml
Used integrals:	area integral
Used Gradient strength:	all values (including replicates) used

Peak name	F2 [ppm]	Io	error	D [m2/s]	error
DMSO	2.474	3.49e+09	1.159e+08	3.52e-09	2.410e-10
THF1	3.592	2.38e+09	6.263e+07	2.89e-09	1.586e-10
1	7.160	9.83e+10	7.379e+08	1.49e-10	2.540e-12
2	6.550	6.14e+10	4.754e+08	1.49e-10	2.610e-12
THF2	1.737	3.17e+09	2.859e+08	5.82e-10	1.159e-10
5	2.161	3.33e+09	7.972e+07	1.53e-10	8.301e-12
6	1.927	2.33e+10	1.847e+08	1.50e-10	2.692e-12
8	1.463	4.83e+10	3.892e+08	1.52e-10	2.779e-12
9	0.618	9.71e+08	3.475e+07	1.81e-10	1.461e-11



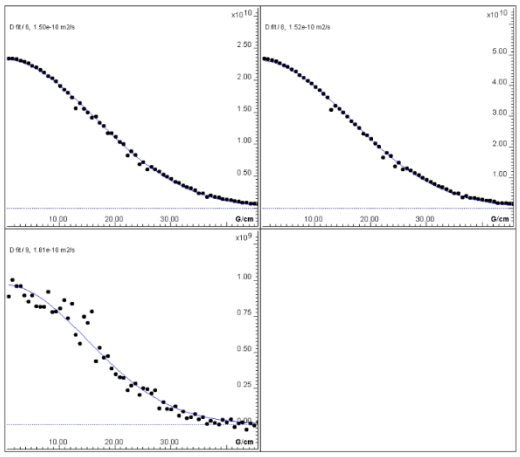
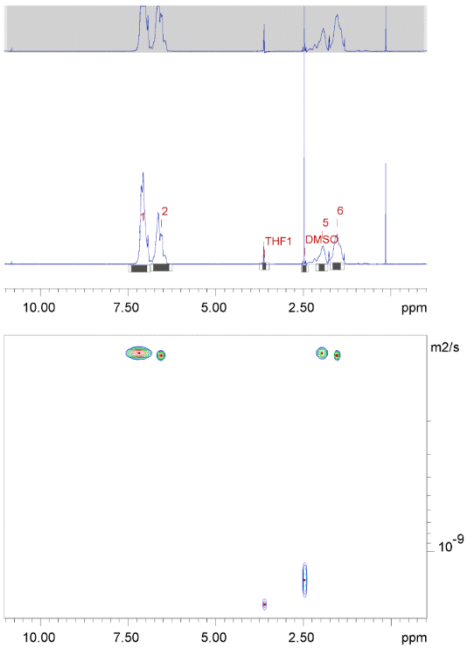


Figure S11. DOSY NMR Diffusion analysis of PS5 sample (*Mp* = 17600 g mol^{-1}).



Fitted function:	f (x) = Io * exp (-D * x^2 * gamma^2 * littleDelta^2 (bigDelta-littleDelta/3)* 10^4
used gamma:	26752 rad/(s*Gauss)
used little delta:	0.0080000 s
used big delta:	0.049900 s
used gradient strength:	variable
Random error estimation of data:	RMS per spectrum (or trace/plane)
Systematic error estimation of data:	worst case per peak scenario
Fit parameter Error estimation method:	from fit using arbitray y uncertainties
Confidence level:	95%
Used peaks:	peaks from C:/other projects/SEC Dh calibration/Polystyrene Mn32700/5/pdata/1/peaklist1D.xml
Used integrals:	area integral
Used Gradient strength:	all values (including replicates) used

Peak name	F2 [ppm]	Io	error	D [m2/s]	error
DMSO	2.462	3.22e+09	2.752e+08	1.40e-09	2.527e-10
THF1	3.604	1.53e+09	6.601e+07	1.94e-09	1.730e-10
1	7.179	8.71e+10	1.259e+09	8.56e-11	2.807e-12
2	6.550	5.39e+10	6.684e+08	8.83e-11	2.482e-12
5	1.967	1.93e+10	3.227e+08	8.67e-11	3.291e-12
6	1.542	3.96e+10	5.212e+08	8.80e-11	2.628e-12

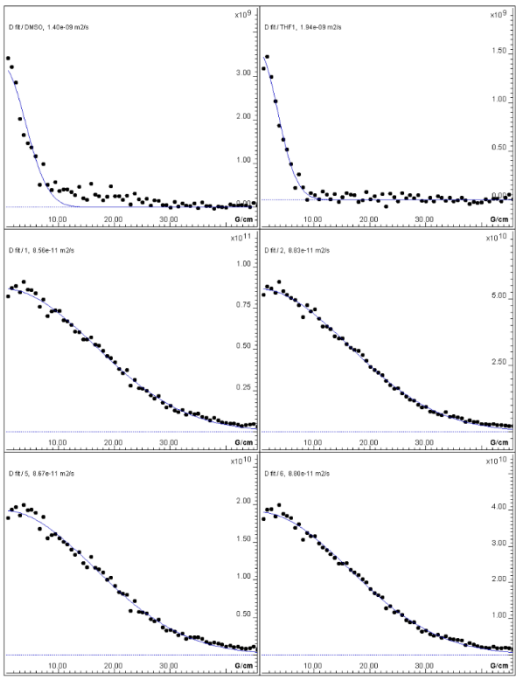
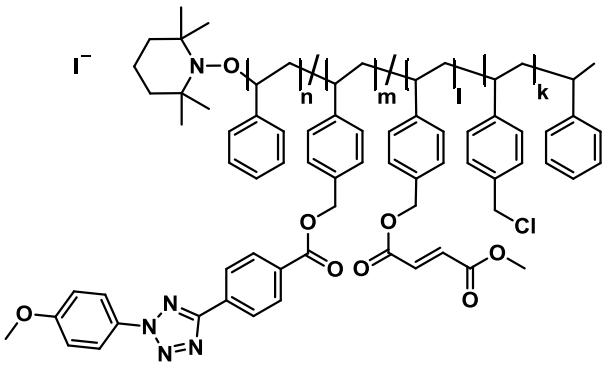


Figure S12. DOSY NMR Diffusion analysis of PS5 sample (*M*p = 34800 g mol^{-1}).

5. SEC-ESI-MS Analysis

Precursor polymer P(S-*stat*-TET-*stat*-FU).



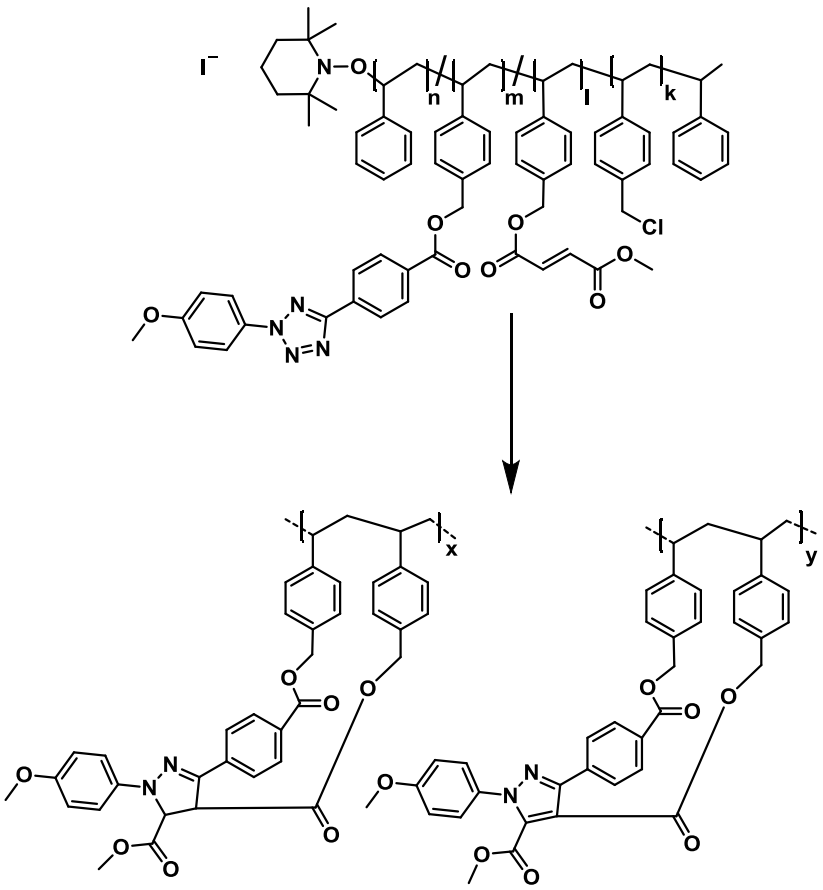
The mass spectrum of the precursor polymer at the retention time t_1 (18.0 - 18.3 min) including the simulation is shown in Figure 3. The full list of signal assignments is summarized in Table S1. All signals carry the same end groups and are ionized via iodide attachment. The table shows the different polymer compositions depending on the number of each incorporated monomer. 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 S1. Complete analysis of all MS signals shown in Figure 3 of the main paper. The region shows approximately one styrene repeating unit of **P(S-*stat*-TET-*stat*-FU)** (*m/z* 2579-2700) at the retention time t_1 (18.0-18.3 min), the masses and deviations are determined from the most abundant isotopic peak.

Composition (St(n)/TET(m)/FU(l)/CMS(k))	Elemental composition	abundance (sim)	*m/z* (theo.)	*m/z* (exp.)	*Deviation* (abs)	*Deviation* (ppm)
10/1/3/0	C163H169IN5O16	1	2580.1648	2580.1760	0.0112	4.3
14/0/3/0	C171H181INO13	0.7	2585.2611	2585.2784	0.0173	6.7
7/2/2/1	C158H160ClIN9O15	0.13	2587.0826	2587.0922	0.0096	3.7
11/1/2/1	C166H172ClIN5O12	0.48	2591.1773	2591.1877	0.0104	4.0
7/0/6/0	C157H167INO25	0.03	2594.0860	2594.0973	0.0113	4.4
15/0/2/1	C174H184ClINO9	0.35	2595.2738	2595.2911	0.0173	6.7
7/3/1/0	C159H157IN13O14	0.2	2600.1056	2600.1113	0.0057	2.2
11/2/1/0	C167H169IN9O11	0.5	2604.1992	2604.2105	0.0113	4.3
15/1/1/0	C175H181IN5O8	0.35	2608.2994	2608.3143	0.0149	5.7
5/1/4/2	C155H161Cl2IN5O20	0.05	2611.0200	2611.0252	0.0052	2.0
9/0/4/2	C163H173N1O17Cl2I	0.16	2615.1111	2615.1300	0.0189	7.2
8/1/4/0	C161H167IN5O20	0.45	2618.1288	2618.1381	0.0093	3.6
16/1/0/1	C178H184ClIN5O4	0.15	2619.3140	2619.3251	0.0111	4.2
12/0/4/0	C169H179INO17	0.5	2622.2257	2622.2382	0.0125	4.8
9/1/3/1	C164H170ClIN5O16	0.4	2629.1432	2629.1547	0.0115	4.4
13/0/3/1	C172H182ClINO13	0.43	2633.2402	2633.2516	0.0114	4.3
6/2/2/2	C159H161Cl2IN9O15	0.07	2635.0577	2635.0623	0.0046	1.7
5/3/2/0	C157H155IN13O18	0.03	2638.0695	2638.0693	0.0002	0.1
10/1/2/2	C167H173Cl2IN5O12	0.1	2639.1598	2639.1655	0.0057	2.2
9/2/2/0	C165H167IN9O15	0.65	2642.1665	2642.1747	0.0082	3.1
13/1/2/0	C173H179IN5O12	0.8	2646.2634	2646.2758	0.0124	4.7
6/3/1/1	C160H158ClIN13O14	0.03	2649.0845	2649.0896	0.0051	1.9

Composition (St(n)/TET(m)/FU(l)/CMS(k))	Elemental composition	abundance (sim)	*m/z* (theo.)	*m/z* (exp.)	*Deviation* (abs)	*Deviation* (ppm)
17/0/2/0	C181H191INO9	0.19	2650.3592	2650.3807	0.0215	8.1
10/2/1/1	C168H170ClIN9O11	0.19	2653.1799	2653.1911	0.0112	4.2
6/1/5/0	C159H165IN5O24	0.1	2656.0937	2656.0966	0.0029	1.1
14/1/1/1	C176H182ClIN5O8	0.3	2657.2736	2657.2919	0.0183	6.9
10/0/5/0	C167H177INO21	0.28	2660.1884	2660.2002	0.0118	4.4
10/3/0/0	C169H167IN13O10	0.10	2666.2043	2666.2143	0.0100	3.8
7/1/4/1	C162H168ClIN5O20	0.20	2667.1057	2667.1159	0.0102	3.8
11/0/4/1	C170H180ClIN1O17	0.38	2671.2024	2671.2192	0.0168	6.3
14/2/0/0	C177H179IN9O7	0.08	2670.3063	2670.3112	0.0049	1.8
18/1/0/0	C185H191IN5O4	0.04	2675.3961	2675.4062	0.0101	3.8
8/1/3/2	C165H171Cl2IN5O16	0.20	2676.1131	2676.1265	0.0134	5.0
7/2/3/0	C163H165IN9O19	0.25	2680.1284	2680.1341	0.0057	2.1
11/1/3/0	C171H177IN5O16	1	2684.2249	2684.2378	0.0129	4.8
15/0/3/0	C179H189INO13	0.6	2688.3203	2688.3422	0.0219	8.1
8/2/2/1	C166H168ClIN9O15	0.22	2691.1450	2691.1539	0.0089	3.3
12/1/2/1	C174H180ClIN5O12	0.6	2695.2382	2695.2549	0.0167	6.2

SCNP formation



The mass analysis of the SCNP was carried out at different retention times. The MS spectra of the full region are shown in Figure S12. The colorized peaks are highlighted in Figure S12 and Table S2 to refer to the identical values in Figure 4. The full assignments of the SCNP are shown in Table S2 (t_1, 18.0-18.3 min) with the comparison to the simulation shown in Figure S13. The polymer compositions are given in the same format as the precursor in Table S1 with the addition of the number of expulsed nitrogen molecules (–x N_2). In addition, the formed pyrazoline adduct partially undergoes re-aromatization resulting in additional removal of one hydrogen molecule per re-aromatization step (–y H_2).

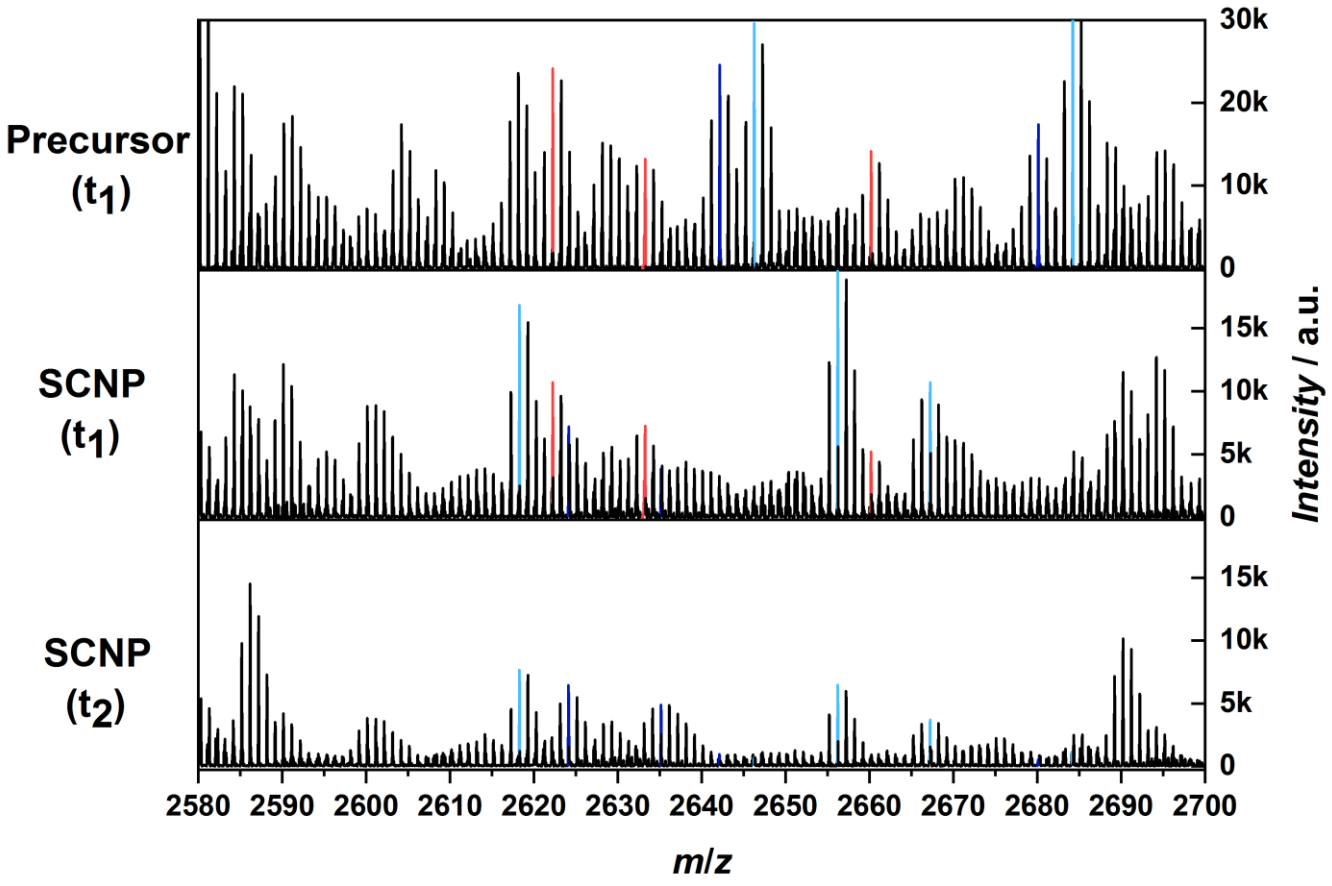


Figure S13. Representative mass spectra depicting a specific mass region (*m/z* 2580-2700) with the signals colored analogous to Figure 4: (A) Precursor polymer at the SEC retention time t_1 (18-18.3 min) (B) Compacted polymer at the same retention time t_1 (C) the same region at a higher SEC retention time t_2 (18.5-18.7 min).

Table S2. Complete analysis of all MS signals in the range of one styrene repeating unit after the compaction reaction of **P(S-*co*-TET-*co*-FU)** (2580-2700 *m/z*) at the retention time t_1 (18.0-18.3 min), the masses and deviations are determined from the smallest isotopic peak, in the case of very strong overlap and for very small intensities these values were not determined.

Composition (St(n)/TET(m)/FU(l)/CMS(k))	**Elemental composition**	***abun-dance* (sim)**	***m/z* (theo.)**	***m/z* (exp.)**	***Deviation* (abs)**	***Deviation* (ppm)**
10/1/3/0	C163H169IN5O16	0.13	2580.1642	2580.1659	0.0017	0.7
15/1/1/0 (−1 N_2, −1 H_2)	C175H179IN3O8	0.10	2578.2776	2578.2953	0.0177	6.9
15/1/1/0 (−1 N_2)	C175H181IN3O8	0.30	2580.2915	2580.2996	0.0081	3.1
14/0/3/0	C171H181INO13	0.6	2584.2638	2584.2685	0.0047	1.8
9/2/2/0 (−2 N_2, −1 H_2)	C165H165IN5O15	0.25	2584.1390	2584.1557	0.0167	6.5
9/2/2/0 (−2 N_2)	C165H167IN5O15	0.40	2586.1518	2586.1582	0.0064	2.5
8/1/4/0 (−1 N_2, −1 H_2)	C161H165IN3O20	0.25	2589.1244	2589.1256	0.0012	0.5
8/1/4/0 (−1 N_2)	C161H167IN3O20	0.50	2590.1237	2590.1289	0.0052	2.0
15/0/2/1	C174H184ClINO9	0.25	2595.2762	2595.2838	0.0076	2.9

Composition (St(n)/TET(m)/FU(l)/CMS(k))	Elemental composition	*abun-dance* (sim)	*m/z* (theo.)	*m/z* (exp.)	*Deviation* (abs)	*Deviation* (ppm)
9/1/3/1(−1 N_2, −1 H_2)	C164H168ClIN3O16	0.2	2599.1268	2599.1378	0.0110	4.2
9/1/3/1(−1 N_2)	C164H170ClIN3O16	0.4	2601.1345	2601.1430	0.0085	3.3
15/1/1/0	C175H181IN5O8	0.03	2608.2993	2608.2971	0.0022	0.8
10/1/2/2 (−1 N_2, −1 H_2)	C167H171N3O12Cl2I	0.05	2609.1390	2609.1408	0.0018	0.7
10/1/2/2 (−1 N_2)	C167H173N3O12Cl2I	0.12	2611.1455	2611.1523	0.0068	2.6
13/1/2/0 (−1 N_2, −1 H_2)	C173H177IN3O12	0.30	2617.2497	2617.2611	0.0114	4.4
13/1/2/0 (−1 N_2)	C173H179IN3O12	0.80	2619.2596	2619.2694	0.0098	3.7
12/0/4/0	C169H179INO17	0.50	2622.2319	2622.2325	0.0006	0.2
7/2/3/0 (−2 N_2, −1 H_2)	C163H163IN5O19	0.15	2622.1014	2622.1211	0.0197	7.5
7/2/3/0 (−2 N_2)	C163H165IN5O19	0.30	2624.1162	2624.1244	0.0082	3.1
14/1/1/1 (−1 N_2, −1 H_2)	C176H180ClIN3O8	0.10	2627.2594	2627.2725	0.0131	5.0
14/1/1/1 (−1 N_2)	C176H182ClIN3O8	0.24	2629.2689	2629.2786	0.0097	3.7
13/0/3/1	C172H182ClINO13	0.40	2633.2423	2633.2478	0.0055	2.1
8/2/2/1 (−2 N_2, −1 H_2)	C166H166N5O15Cl1I	0.10	2633.1214	2633.1312	0.0098	3.7
8/2/2/1(−2 N_2)	C166H168N5O15Cl1I	0.20	2635.1300	2635.1346	0.0046	1.7
7/1/4/1 (−1 N_2, −1 H_2)	C162H166N3O20ClI	0.08	2637.1074	2637.1259	0.0185	7.0
7/1/4/1 (−1 N_2)	C162H168N3O20ClI	0.25	2639.1024	2639.1121	0.0097	3.7
14/0/2/2	C175H185N1O9Cl2I	0.15	2643.2518	2643.2597	0.0079	3.0
13/1/2/0	C173H179IN5O12	0.08	2646.2600	2646.2612	0.0012	0.5
17/0/2/0	C181H191INO9	0.25	2651.3623	2651.3697	0.0074	2.8
11/1/3/0 (−1 N_2, −1 H_2)	C171H175IN3O16	0.40	2654.2056	2654.2224	0.0168	6.3
11/1/3/0 (−1 N_2)	C171H177IN3O16	0.80	2656.2191	2656.2286	0.0095	3.6
10/0/5/0	C167H177INO21	0.25	2660.2022	2660.1995	0.0027	1.0
12/1/2/1 (−1 N_2, −1 H_2)	C174H178ClIN3O12	0.15	2665.2259	2665.2369	0.0110	4.1
12/1/2/1(−1 N_2)	C174H180ClIN3O12	0.50	2667.2340	2667.2452	0.0112	4.2
11/0/4/1	C170H180ClINO17	0.25	2671.2121	2671.2172	0.0051	1.9
13/1/1/2(−1 N_2)	C177H183N3O8Cl2I1	0.10	2678.2453	2678.2377	0.0076	2.8
12/2/1/0 (−1 N_2)	C175H175N7O11I1	0.10	2677.2438	2677.2379	0.0059	2.2
12/0/3/2	C173H183N1O13Cl2I	0.15	2681.2273	2681.2333	0.0060	2.2
11/1/3/0	C171H177IN5O16	0.10	2684.2242	2684.2286	0.0044	1.6
16/1/1/0(−1 N_2)	C183H187N3O8I1	0.10	2683.3486	2683.3581	0.0095	3.5
16/1/1/0(−1 N_2)	C183H189N3O8I1	0.30	2685.3581	2685.3647	0.0066	2.5
15/0/3/0	C179H189INO13	0.40	2688.3282	2688.3314	0.0032	1.2
10/2/2/0 (−2 N_2, −1 H_2)	C173H173IN5O15	0.20	2688.2021	2688.2145	0.0124	4.6
10/2/2/0 (−2 N_2)	C173H175IN5O15	0.40	2690.2147	2690.2224	0.0077	2.9
9/1/4/0 (−1 N_2, −1 H_2)	C169H173N3O20I1	0.20	2693.1891	2693.1909	0.0018	0.7
9/1/4/0 (−1 N_2)	C169H175N3O20I1	0.50	2695.1890	2695.1937	0.0047	1.7
16/0/2/1	C182H192N1O9Cl1I1	0.20	2699.3388	2699.3448	0.0060	2.2

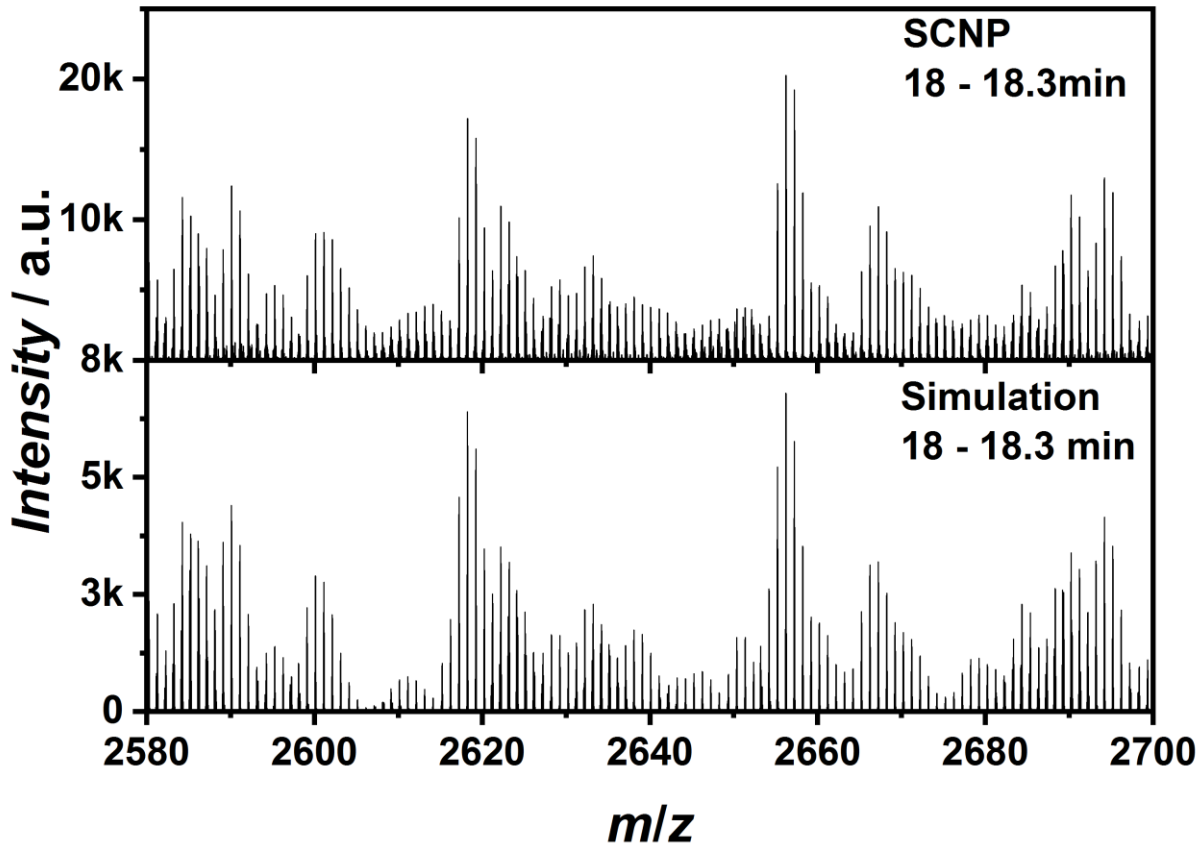


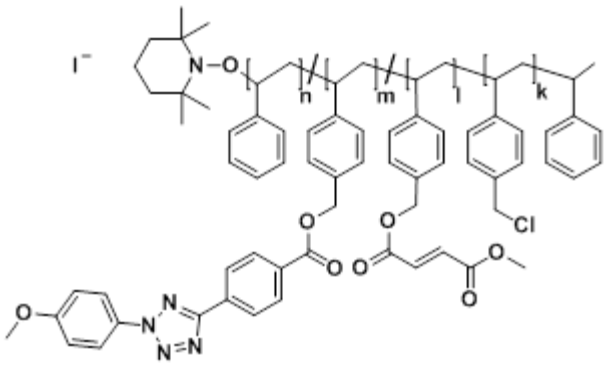
Figure S14. Comparison between the measured and simulated spectra of the SCNP at the retention time t_1

6. XIC Extraction

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

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

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



The following Figures S14-16 show all XICs for different numbers of tetrazole containing monomers incorporated. The fit and raw data points are colored depending on the sample with precursor species in dark grey and SCNP data depending on the number of expulsed nitrogen molecules (no nitrogen loss = red, 1 N_2 loss = light blue, 2 N_2 loss = dark blue, 3 N_2 loss = green). The composition is indicated at the top of each spectrum according to the shown structure as amount of n/m/l/k monomer units.

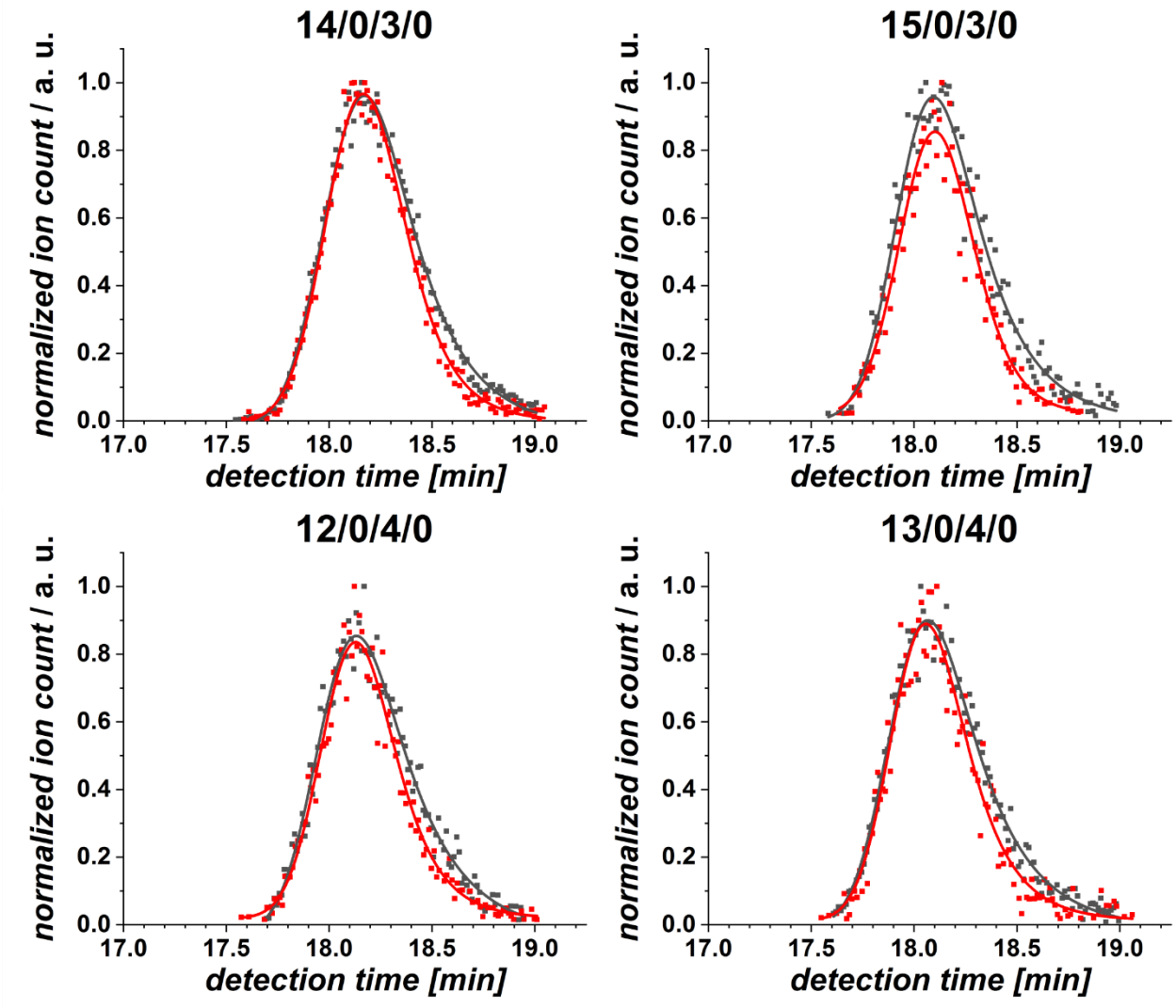


Figure S15. The fit and raw data points of polymer compositions with no tetrazole monomer. The plots were colored depending on the sample with precursor species in dark grey and SCNP data in red.

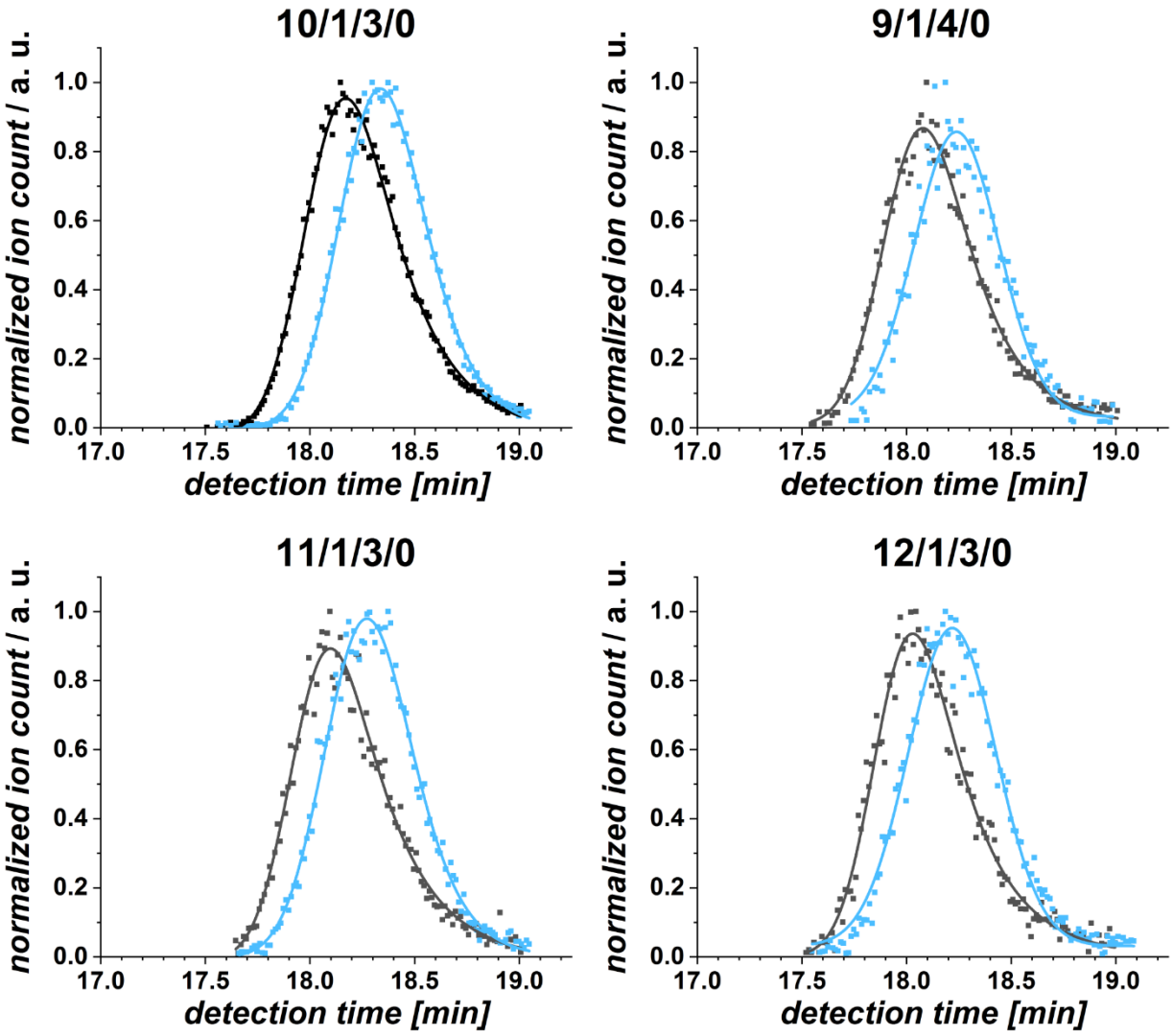


Figure S16. The fit and raw data points of polymer compositions with one tetrazole monomer. The plots were colored depending on the sample with precursor species in dark grey and SCNP data with one nitrogen loss in light blue.

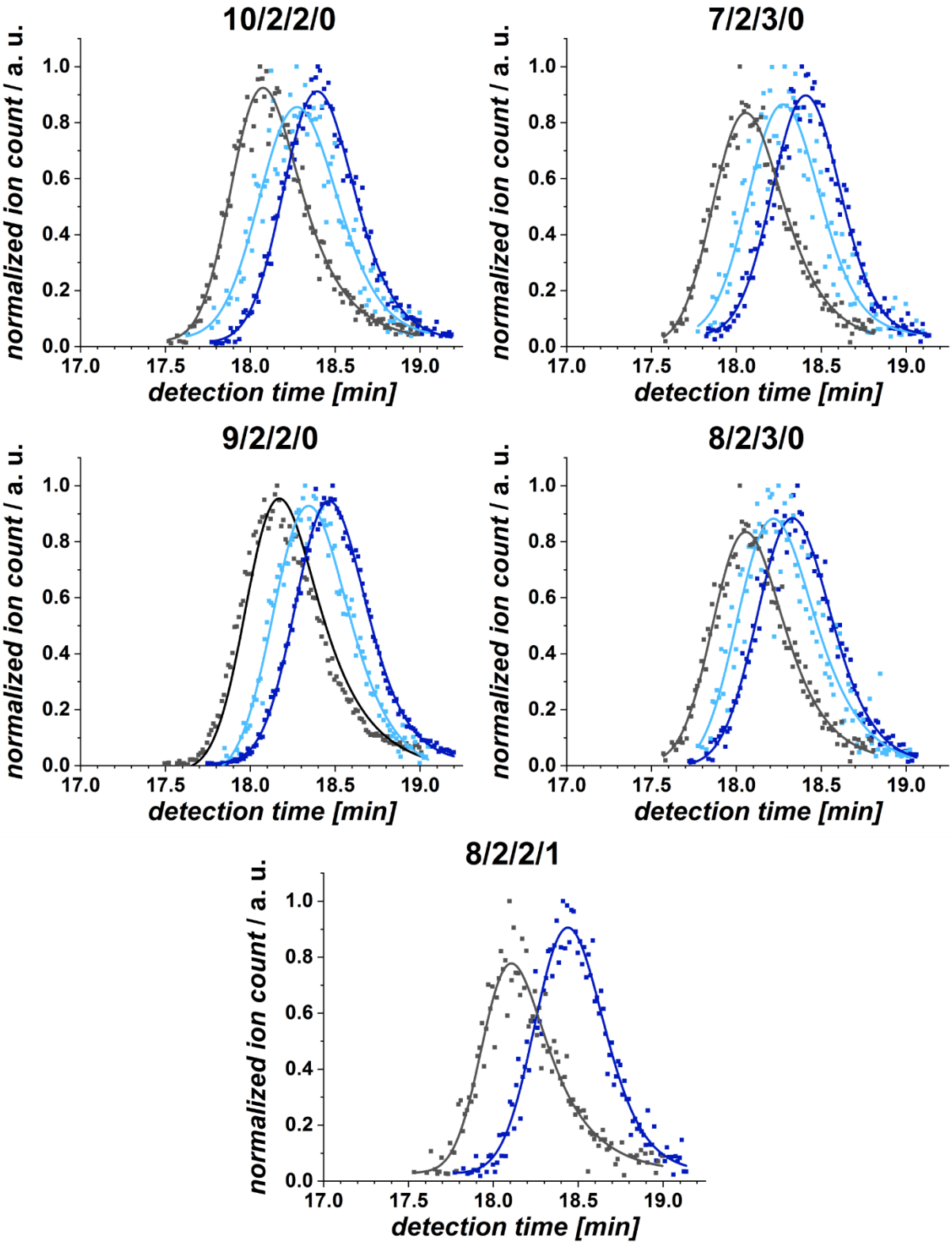


Figure S17. The fit and raw data points of polymer compositions with two tetrazole monomers. The plots were colored depending on the sample with precursor species in dark grey and SCNP data depending on the number of expulsed nitrogen molecules (1 N_2 loss = light blue, 2 N_2 loss = dark blue).

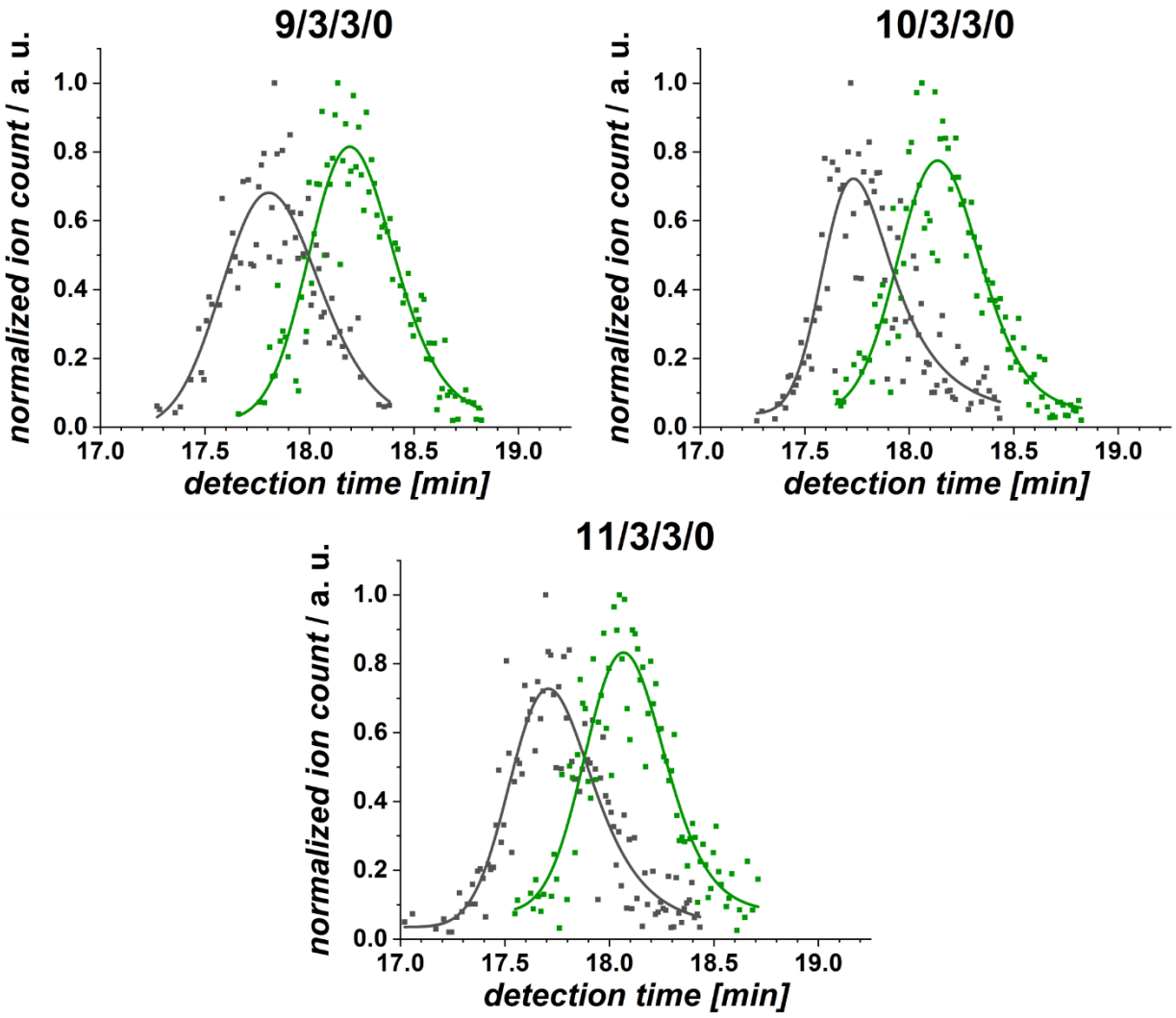


Figure S18. The fit and raw data points of polymer compositions with three tetrazole monomers. The plots were colored depending on the sample with precursor species in dark grey and SCNP data with three nitrogen losses in green.

6. References

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