

Supporting Information

Polyselenoureas via Multicomponent Polymerizations using Elemental Selenium as Monomer

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Materials

Dichloromethane (DCM, 99.8% extra dry, Acros), N, N'-dimethylformamide (DMF, 99.8%, anhydrous, Sigma-Aldrich), diethyl ether (99.8% extra dry, Acros), 1,3-diaminopentane (Dytek EP, 98%, Sigma-Aldrich), 1,5-diamino-2-methylpentane (99%, Sigma-Aldrich), 4, 7, 10-trioxa-1, 13-tridecanediamine (97% Sigma-Aldrich), hexamethylenediamine (98% Sigma-Aldrich), selenium (powder, -100 mesh, >99.5% trace metals basis, Sigma-Aldrich)

Characterization

¹H NMR spectroscopy was performed on a Bruker Avance 600 MHz NMR spectrometer. Samples were prepared at 10-20 mg mL⁻¹ concentration in CDCl₃ or DMSO-d₆. ¹H-spectra of small molecules were recorded at 16 scans with 1 s d1 time. Polymer spectra were recorded at 128 scans and 1 s d1-time.

2D Diffusion ordered spectroscopy (DOSY) experiments based on ¹H NMR were performed in DMSO-d₆ at 295.0 K on a Bruker 400 UltraShield spectrometer equipped with a Quattro Nucleus Probe (QNP) with an operating frequency of 400 MHz (¹H). 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

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

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

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

$$D_h = \frac{k_b * T}{3 * \pi * \eta * D}$$

Where k_B is the Boltzmann constant, T the temperature and η the solvent viscosity (DMSO: 1.99 mPa*s).¹

A set of narrowly distributed PMMA samples (10 kDa, 21 kDa, 45 kDa, and 90 kDa respectively, $\bar{D} < 1.10$) was employed for DOSY in order to obtain a standard calibration for the determination of molecule weights. The empirically derived power law $D_h = K M_n^\alpha$ correlates the molecular weight M_n to the hydrodynamic diameter D_h , where K is a polymer specific constant and α describes the shape of the particle. Therefore, the hydrodynamic diameter was plotted vs the molecular weight in a double logarithmic plot and fitted by linear regression, where a represents $\log(D_h)$ and b represents α . The molecular weight of the polymers reported were calculated according to these parameters.

Electrospray ionisation mass spectrometry (ESI-MS) were performed via positive ion mass spectra which were acquired using a chip-based nano-electrospray ionization (nESI) source (TriVersa NanoMate, Advion, Ithaca, NY) coupled to an Orbitrap Elite mass spectrometer (Thermo Fisher Scientific, Bremen, Germany). A clean, conductive pipette tip in the TriVersa NanoMate collected 10 μ L of sample from a 96-well plate and delivered it to the mass spectrometer via the nESI chip (nozzle diameter 4.1 μ m). A spray voltage of 1.4 kV and delivery gas pressure of 0.5 psi (N_2) was applied to the chip. The S-lens RF level in the source region of the mass spectrometer was set to 65-70%, and the transfer capillary temperature set at 200 °C. In order to minimize sample carryover, a new pipette tip and chip nozzle were used for each sample. Presented mass spectra represent the average of at least 50 scans, acquired at a mass resolution of 120,000 (at m/z 400). MS/MS spectra of $[M+nH]^{n+}$ ions were acquired using a normalized collision energy of 20 – 25%. Mass-to-charge ratios of precursor ions and product ions were within 3 ppm of their predicted values based on the proposed structures. Although polyselenoureas are readily soluble in polar aprotic solvents such as DMF, DMSO, and DMAc, these solvents do not give rise to stable spray conditions in ESI-MS analysis. To overcome this challenge, the polymers were dissolved at approximately 0.1 M in DMF solution. Next, 50 μ L of this solution was added to 1.5 mL of a 2/1 mixture of acetonitrile/DCM. The solution became slightly hazy, and in some instances, polymeric material precipitated from solution. The samples were left standing for 5 min. and the supernatant was subjected to ESI-MS analysis.

X-ray photoelectron spectroscopy (XPS) samples were prepared by spin coating 10 μ L of an approximately 40 mg/mL solution of the polymers were spin-coated onto glass slides. XPS analysis was performed with a Kratos Axis ULTRA XPS incorporating a 165 mm hemi-spherical electron energy analyser. The incident radiation was monochromatic Al X-rays (1486.6 eV) at 225W (15 kV, 15 mA). Survey (wide) scans were taken at analysing pass energy of 160 eV and multiplex (narrow) higher resolution scans at 20 eV. Survey scans were carried out over 13600-0 eV binding energy range with 1.0 eV steps and a dwell time of 100 ms. Narrow higher resolution scans were run with 0.2 eV steps and 250 ms dwell time. Base pressure in the analysis chamber was $1.0 \cdot 10^9$ Torr during sample analysis $1.0 \cdot 10^8$ Torr. The experimental data were analysed using the software Avantage.

Infrared (IR) spectroscopy was recorded on a Nicolet iS50 from Thermo Scientific with a scan number of 64 and a diamond reference. The sample was measured from 400-4000 cm^{-1} . The analysis and assignments of the spectra were done with the software OMNIC.

Syntheses

General synthetic procedure for diisocyanide monomer

The procedure was adapted from literature.² A solution of 1,5-diamino-2-methylpentane (10.0 g, 86.1 mmol) in ethyl formate (158 g, 172 mL, 2.02 mol) was refluxed overnight. The reaction mixture was concentrated in vacuo. The resulting formamide was dissolved in 175 mL dichloromethane without additional purification and diisopropylamine (87.1 g, 121 mL, 861 mmol) was added. The mixture was cooled to 0 °C and phosphoryl chloride (36.9 g, 22.5 mL, 241 mmol) was added dropwise at such a rate that the reaction temperature remained below 0 °C. The mixture was stirred for 2 hours. The reaction mixture was poured into 500 mL ice-water containing 100 g potassium carbonate maintaining the reaction temperature below 25 °C. The resulting emulsion was stirred for 1 hour at ambient temperature. The organic layer was separated, the aqueous layer extracted three times with 50 mL dichloromethane and the combined organic layers were dried with potassium carbonate. Purification by column chromatography (hexane/ethyl acetate 5:1) and concentration in vacuo yielded 8.44 grams of 1,5-diisocyano-2-methylpentane as a yellow oil at 72.0% yield. MS: $[M+Na]^+$ $C_8H_{12}N_2$ m/z theoretical = 159.0893, experimental = 159.0894

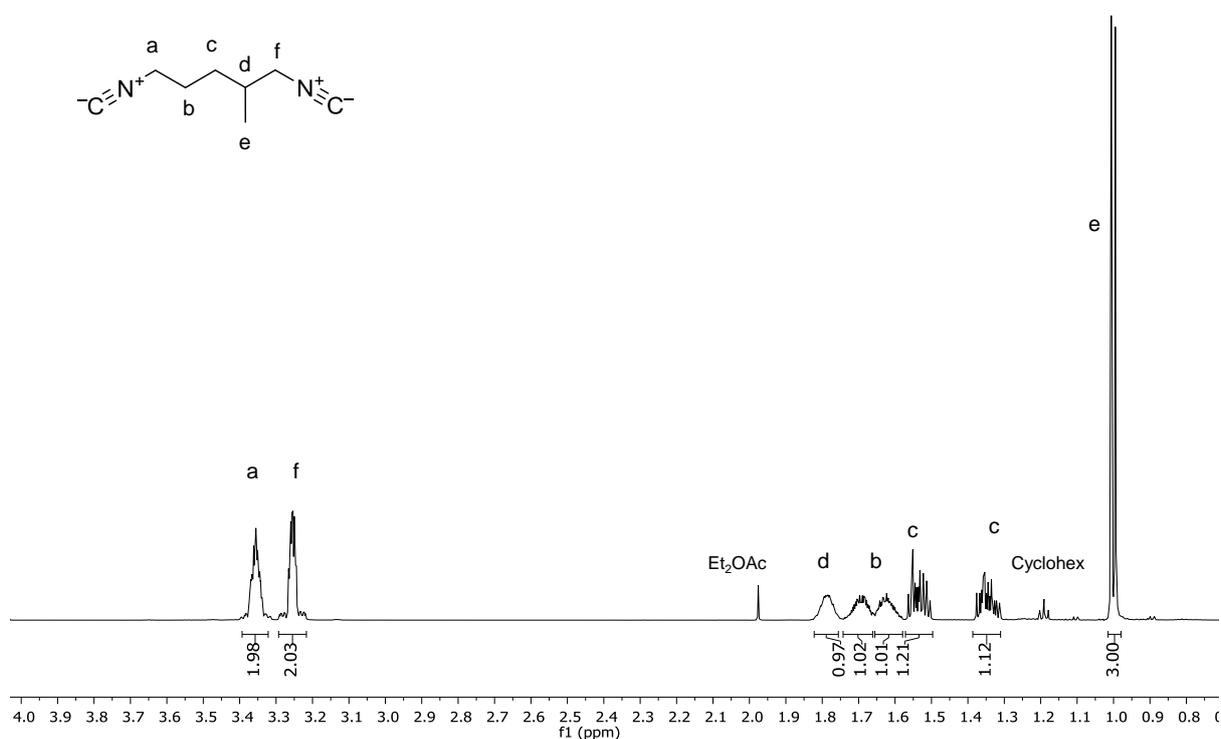


Figure S1 Proton NMR of 1,5-diisocyano-2-methylpentane. CDCl₃ as solvent

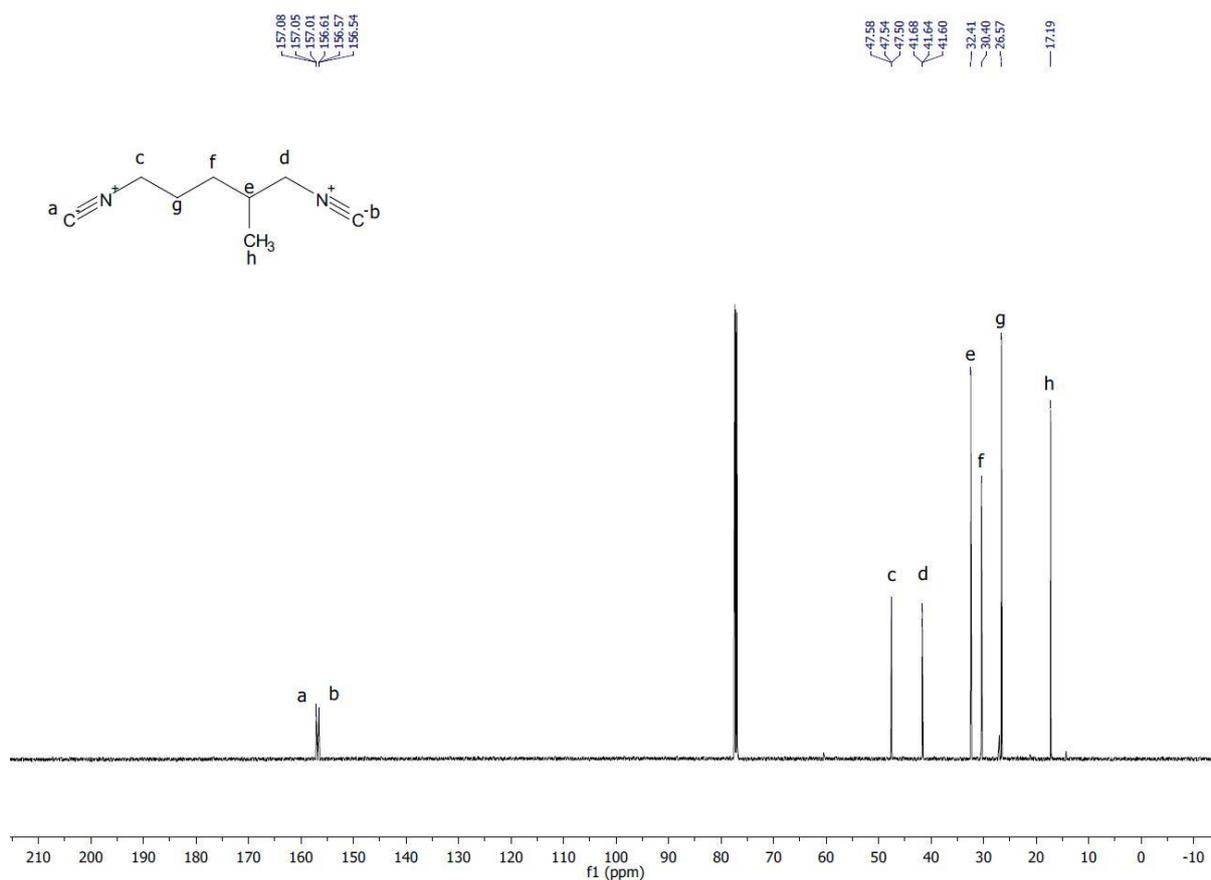


Figure S2 ¹³C NMR of 1,5-diisocyanato-2-methylpentane. DMSO-*d*₆ as solvent.

General procedure for optimized multicomponent polymerization

To a 10 mL scintillation vial was added 87.4 mg (1.10 mmol, 2.05 eq.) of black elemental selenium, 75 mg (0.54 mmol, 1 eq.) of 1,6-diisocyanohexane, 119.6 mg (0.54 mmol, 1 eq.) of 4,7,10-trioxa-1, 13-tridecanediamine and 0.3 mL of dichloromethane. The plastic lid for the scintillation vial was attached and the solution was magnetically stirred overnight. After stirring overnight, most of the black elemental selenium was no longer visible and the solution was extremely viscous. The reaction mixture was diluted with 2 mL of dimethylformamide and subsequently filtered over fritted filter paper (to remove any residual elemental selenium left in the reaction mixture) directly into ice cold diethyl ether (Note: Some polymers were precipitated into methanol, however, in our hands, we found diethyl ether to be the superior precipitating solvent), yielding 256 mg of an off white, pasty elastic solid at 91% yield.

^1H NMR

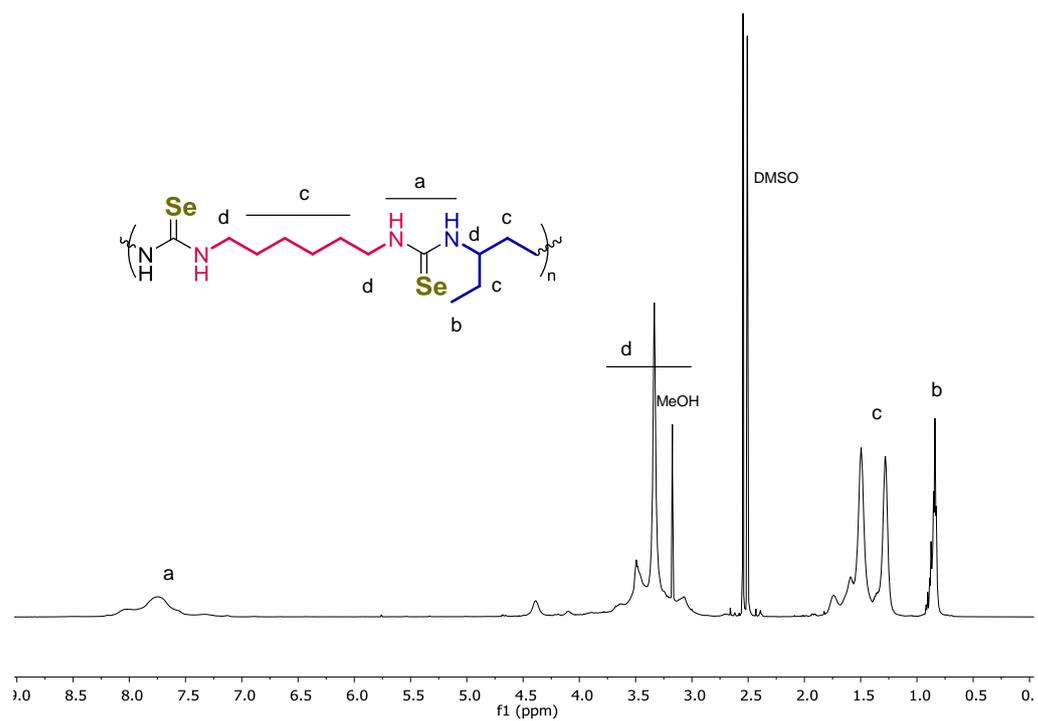


Figure S3 Proton NMR of P1. DMSO- d_6 as solvent.

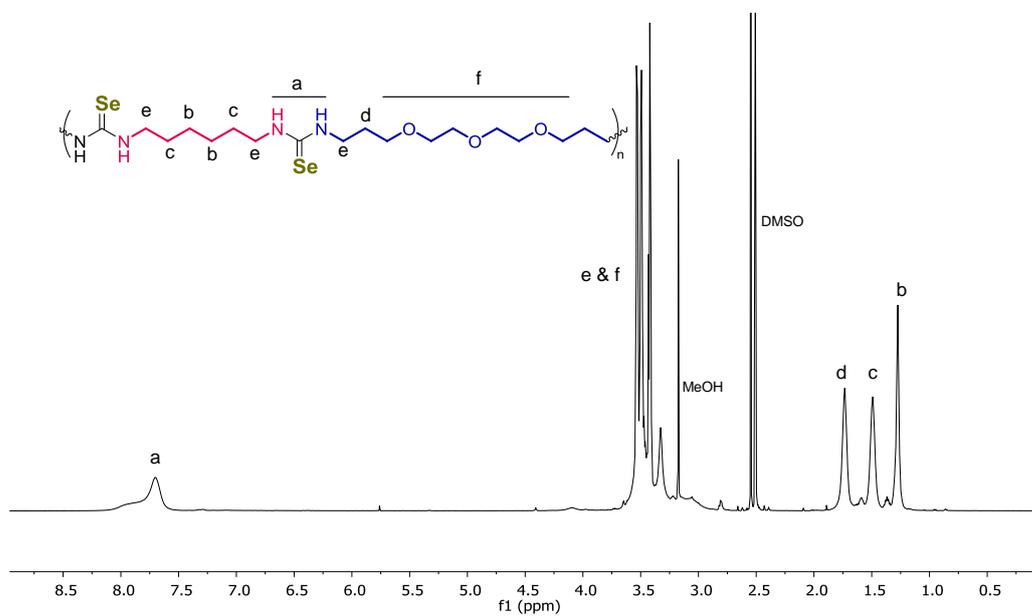


Figure S4 Proton NMR of P2. DMSO- d_6 as solvent.

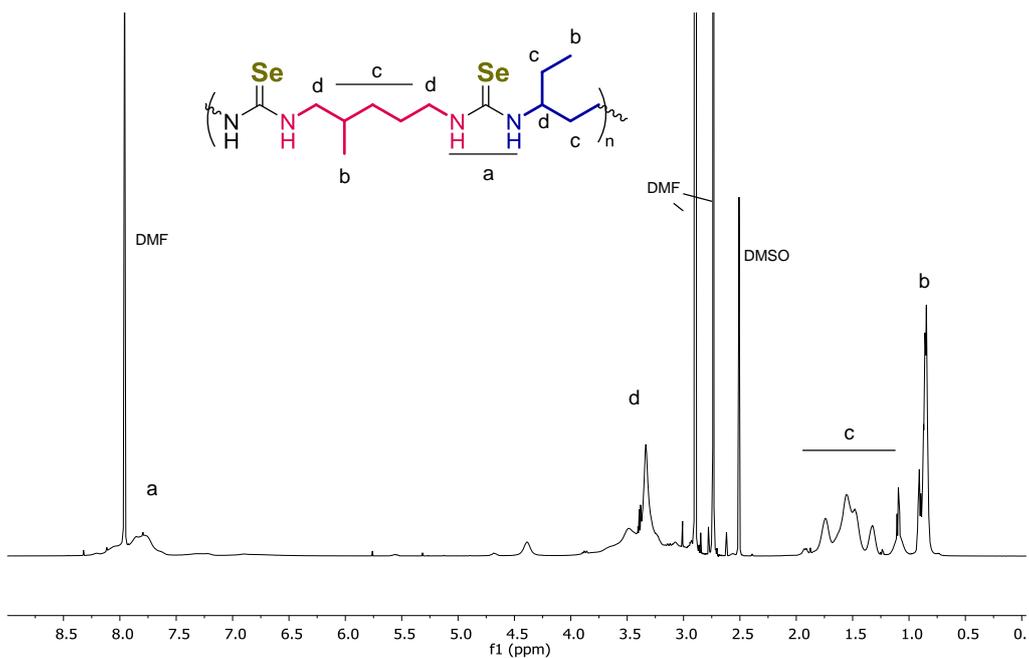


Figure S5 Proton NMR of P3. DMSO- d_6 as solvent.

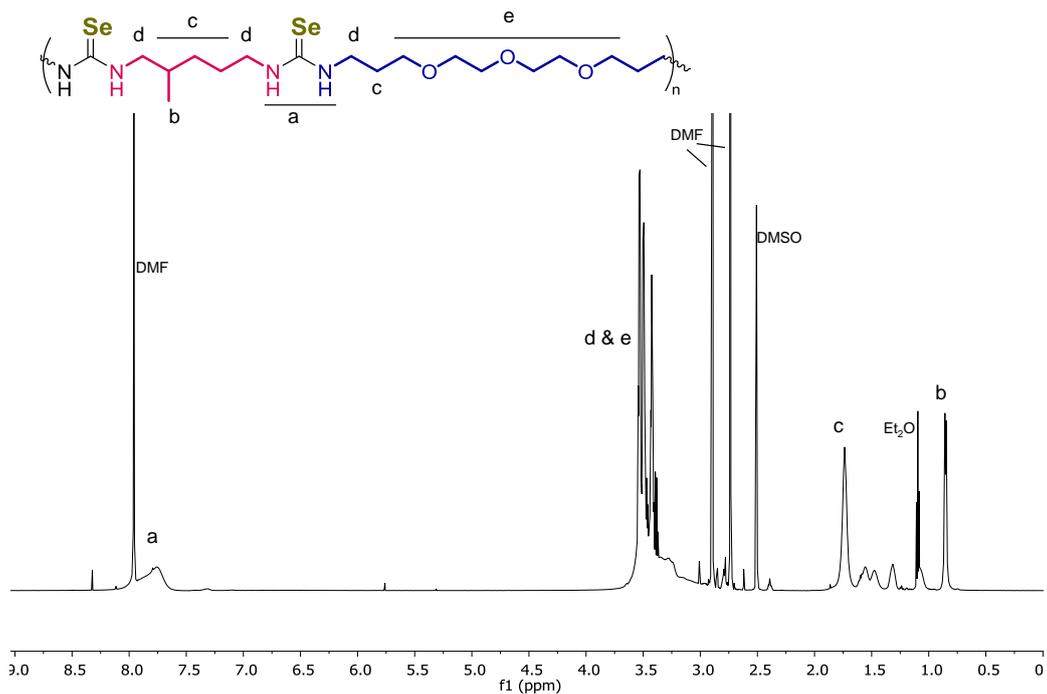


Figure S6 Proton NMR of P4. DMSO- d_6 as solvent.

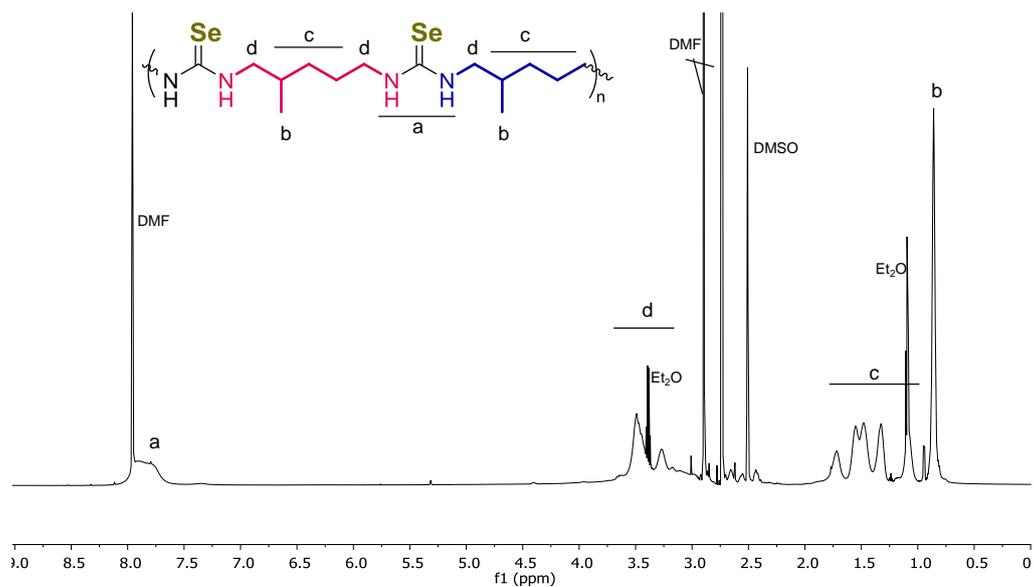


Figure S7 Proton NMR of P5. DMSO- d_6 as solvent.

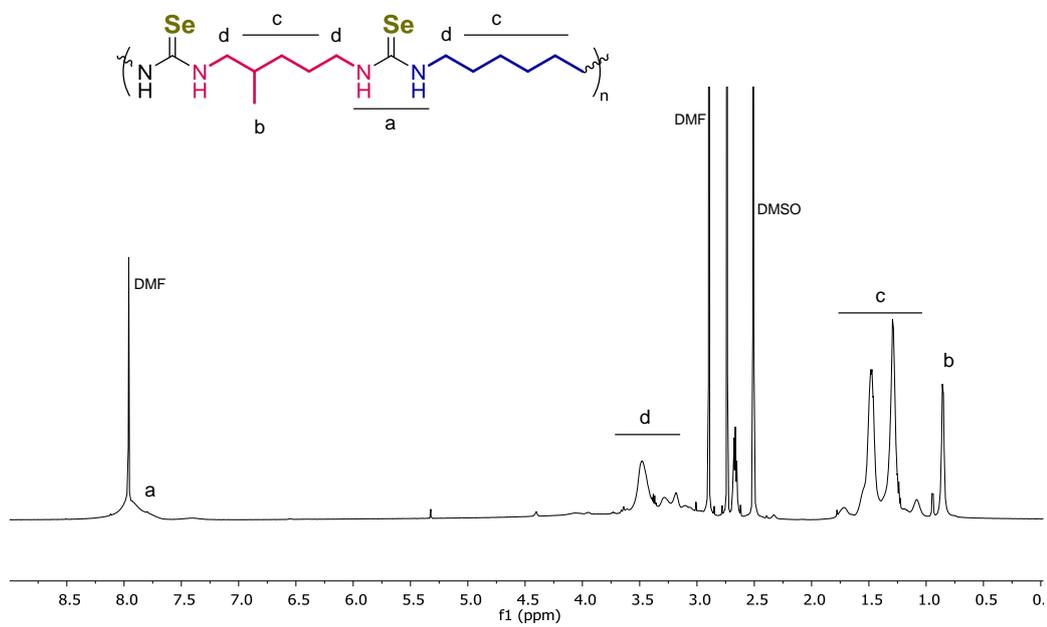


Figure S8 Proton NMR of P6. DMSO- d_6 as solvent.

2D DOSY NMR

Table S1 DOSY analysis of **P1-P6** with diffusion coefficient (D_0), hydrodynamic radius (R_0), and hydrodynamic diameter (D_H).
^a Number average molecular weight based on a PMMA double log 2D DOSY calibration

Polymer	D_0 ($\text{m}^2 \text{s}^{-1}$) 10^{11}	R_0 (m) 10^9	D_H (nm)	M_n (kDa) ^a
P1	1.35	8.09	14.36	99.3
P2	2.43	4.48	8.97	32.4
P3	5.83	1.88	3.75	6.19
P4	2.63	4.14	8.28	27.8
P5	5.55	1.96	3.93	6.74
P6	5.86	1.94	3.88	6.59

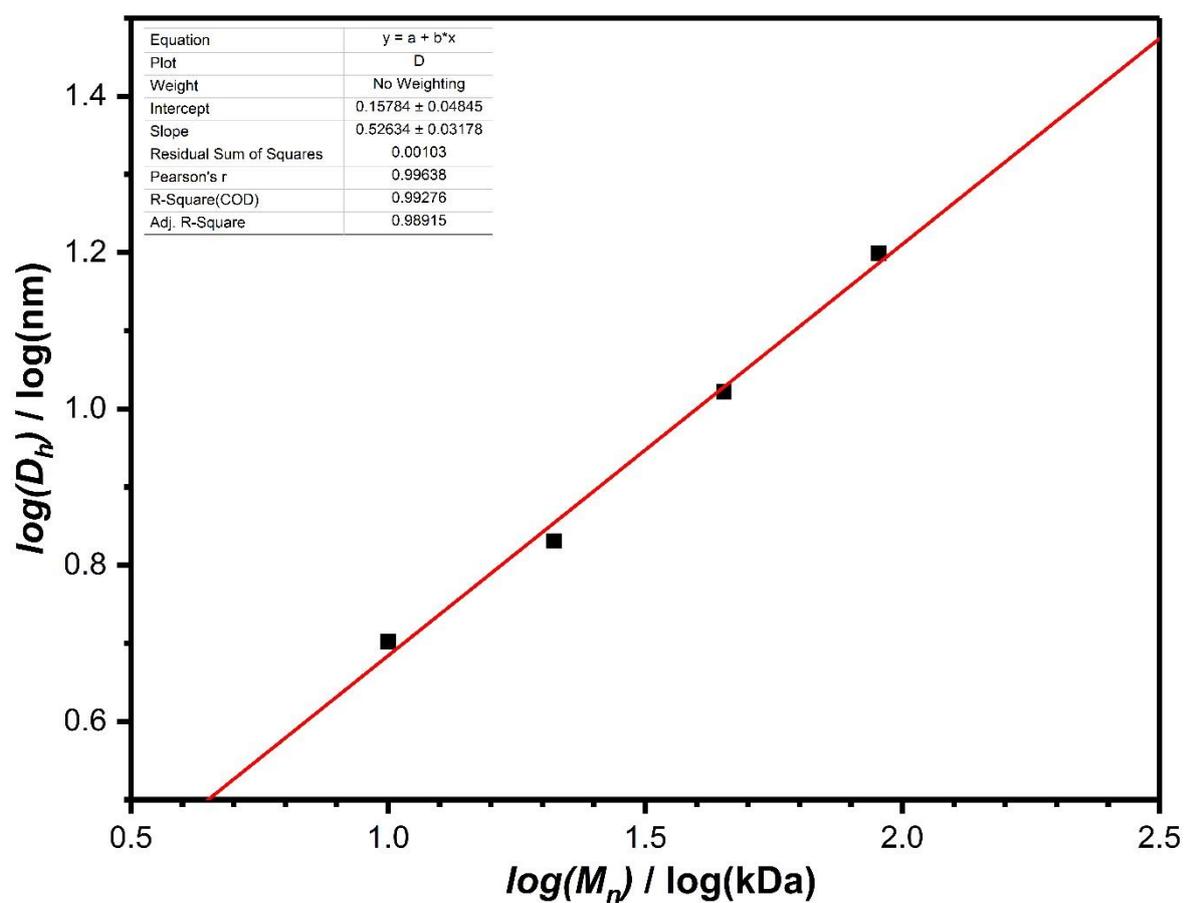


Figure S9 Double log 2D DOSY NMR molecular weight calibration curve using PMMA standards in DMSO- d_6 at 295 K.

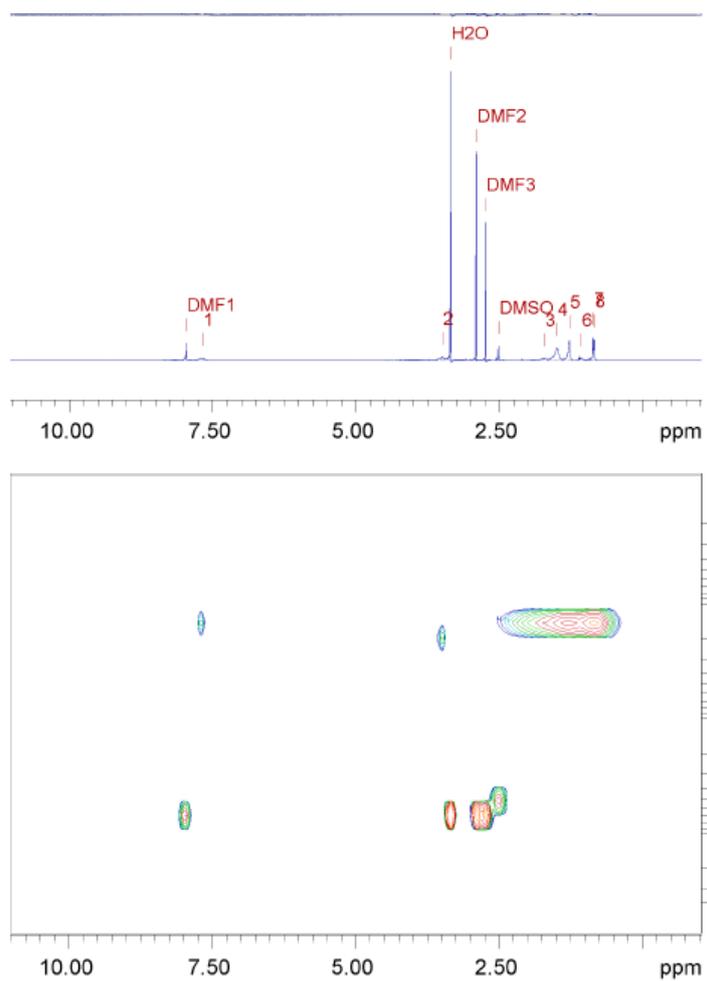


Figure S10 2D DOSY of **P1**. DMSO-*d*₆ as solvent.

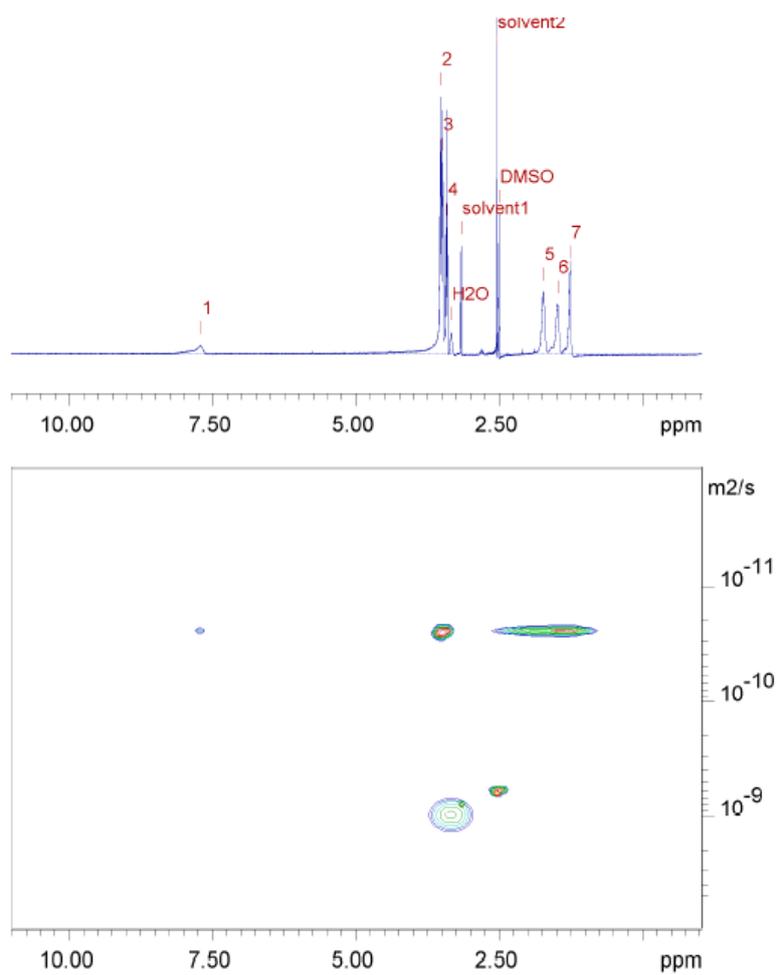


Figure S11 2D DOSY of P2. DMSO-*d*₆ as solvent.

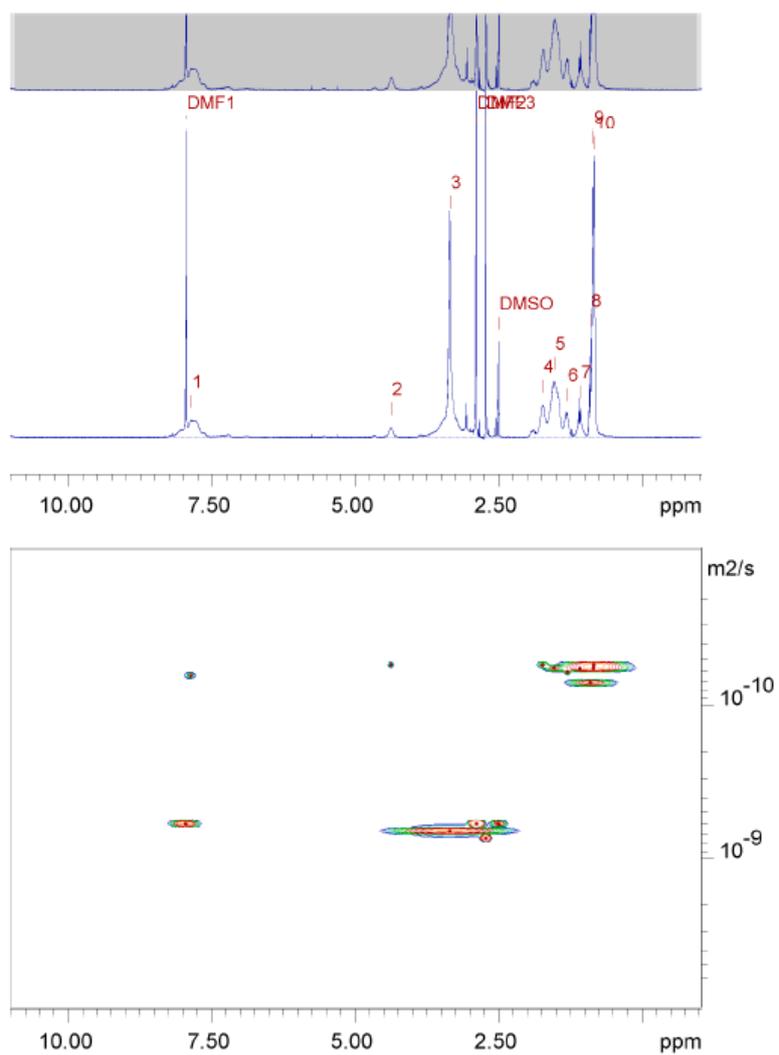


Figure S12 2D DOSY of P3. DMSO-*d*₆ as solvent.

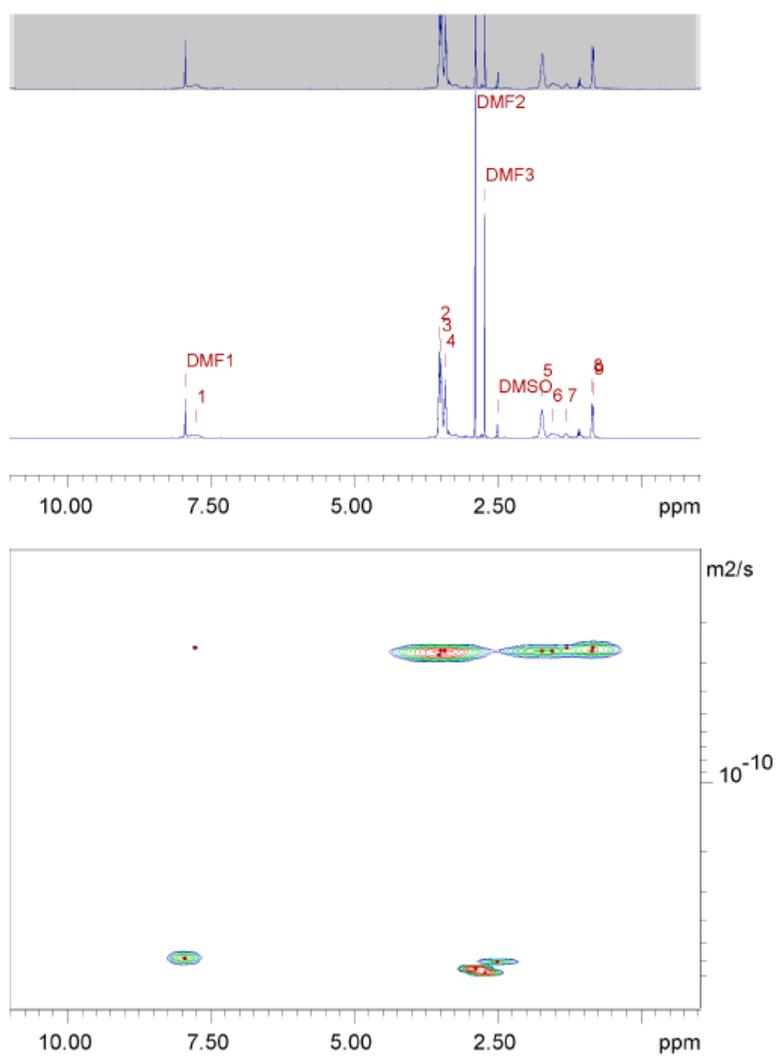


Figure S13 2D DOSY of P4. DMSO-*d*₆ as solvent.

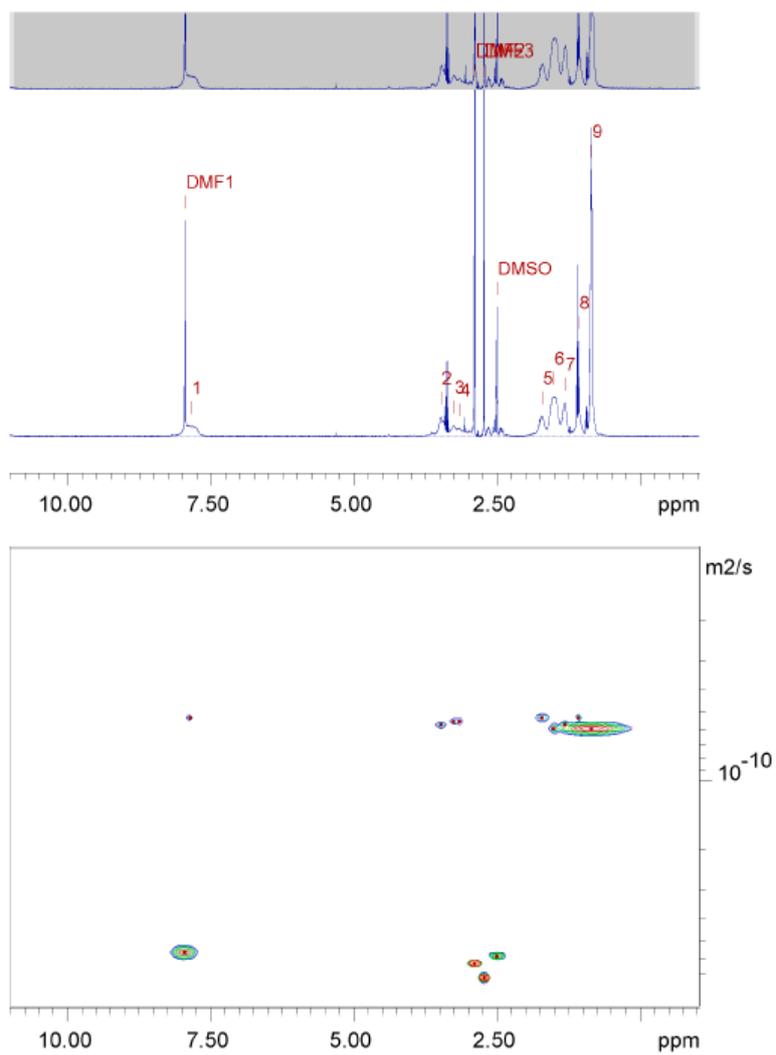


Figure S14 2D DOSY of P5. DMSO-*d*₆ as solvent.

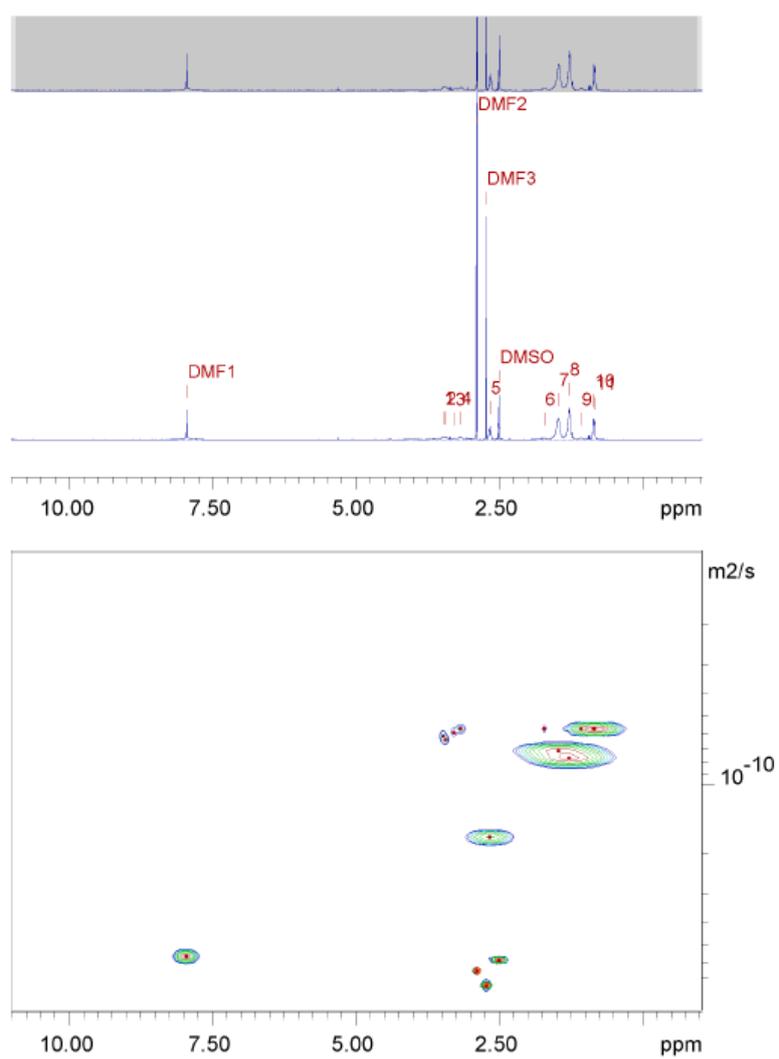


Figure S15 2D DOSY of P6. DMSO-*d*₆ as solvent.

ESI-MS

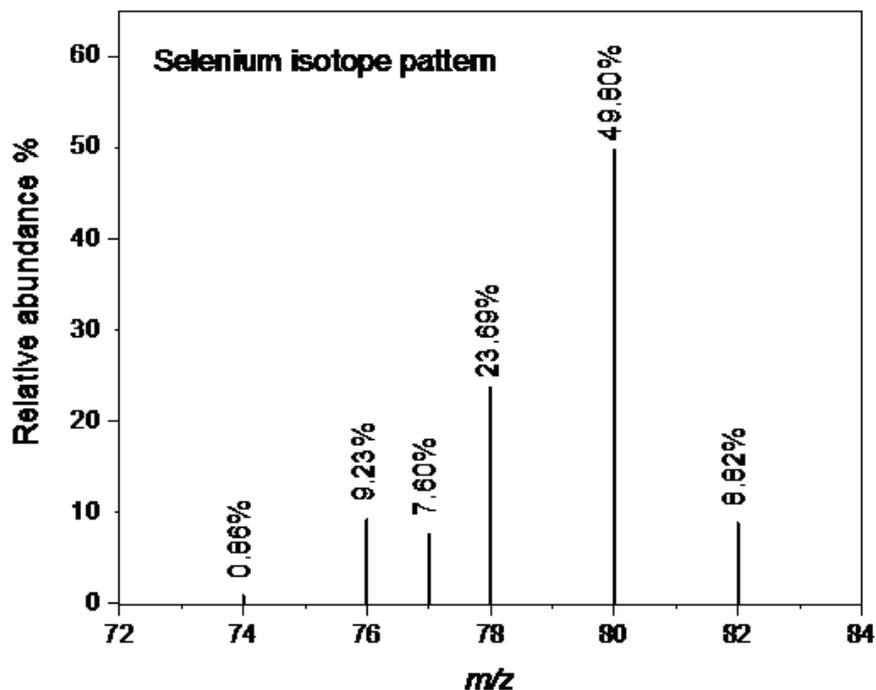


Figure S16 Isotopic pattern of naturally abundant selenium isotopes

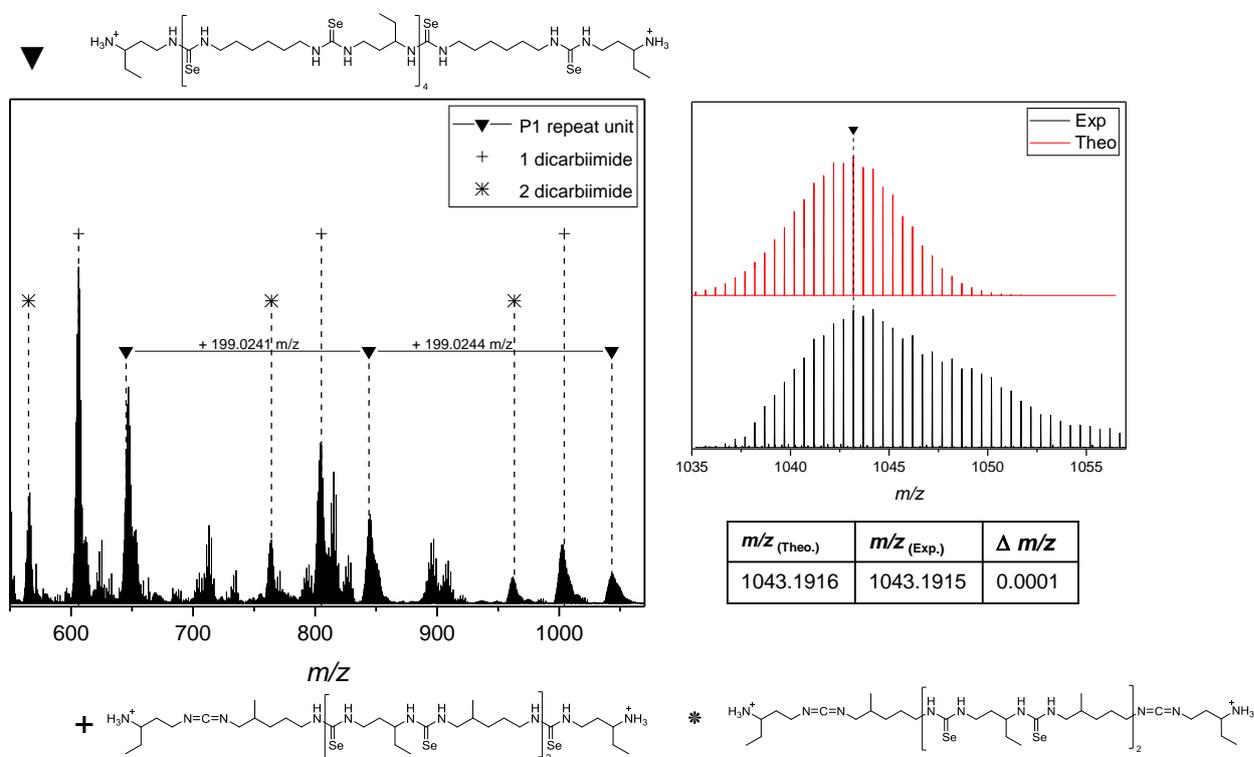


Figure S17 ESI-MS of P1 demonstrating 3 repeat units. Single and double losses of selenium to form carbodiimides are labelled appropriately. Resolution is 120,000

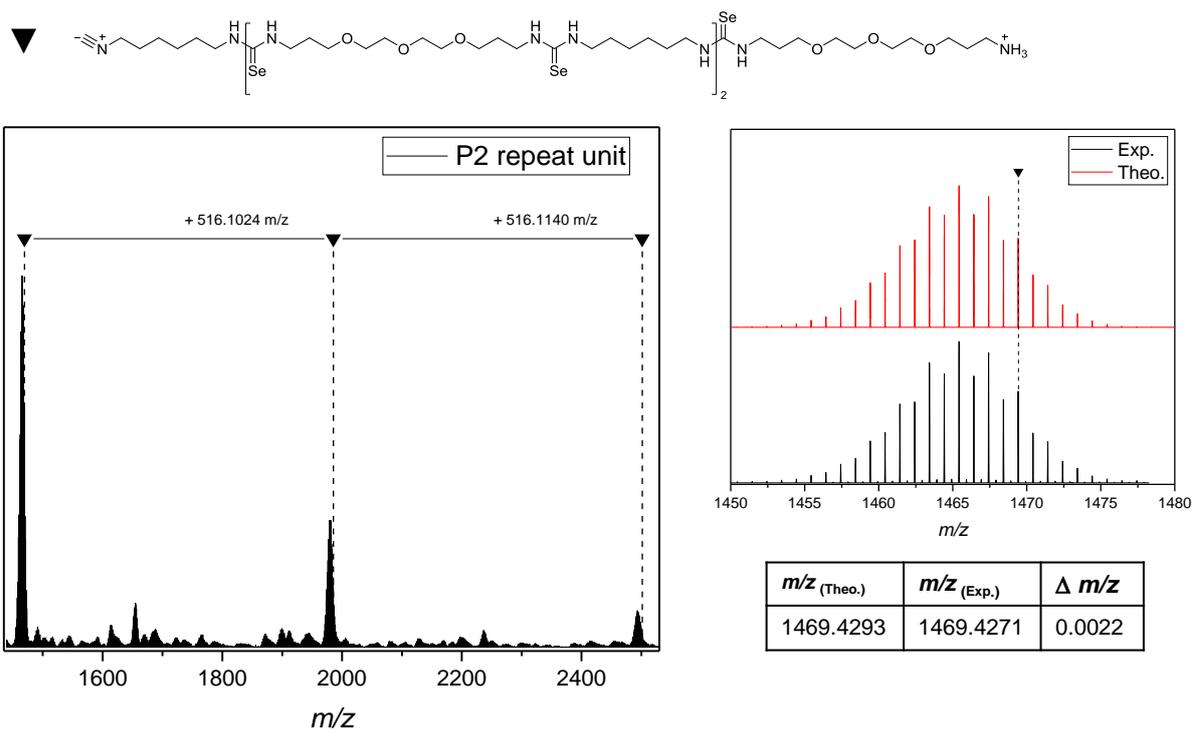


Figure S18 ESI-MS of **P2** demonstrating 3 repeat units. Resolution is 120,000

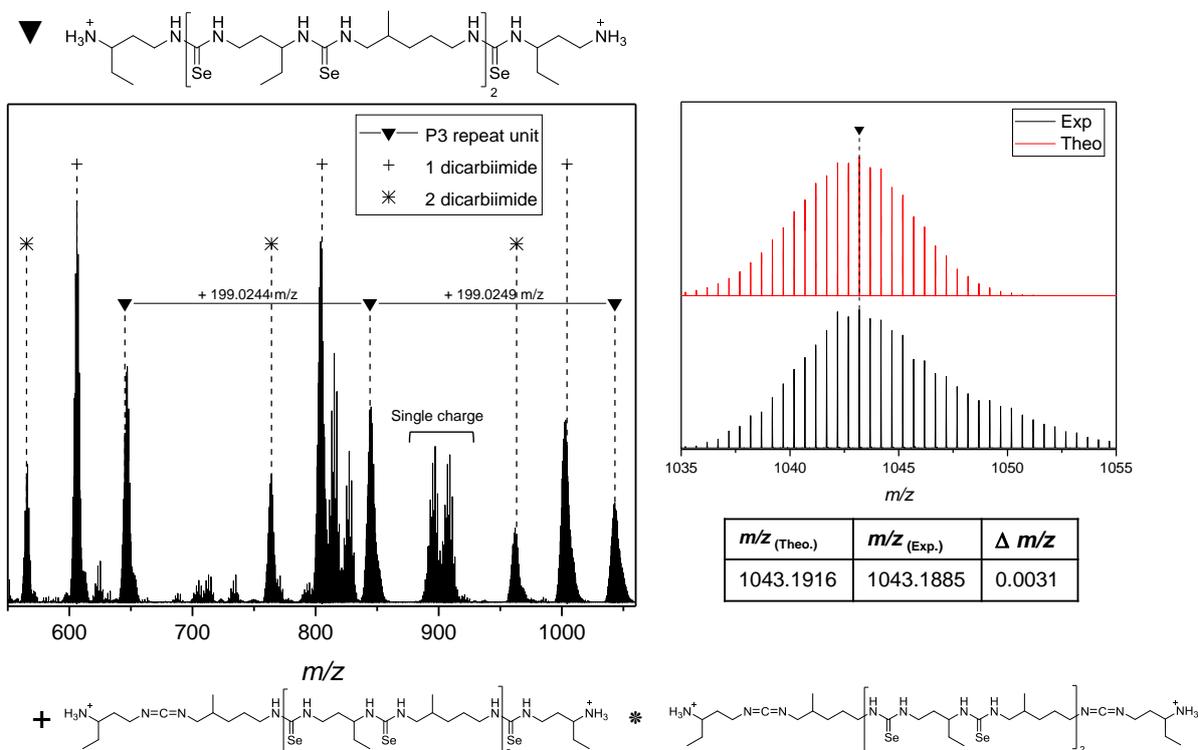


Figure S19 ESI-MS of **P3** demonstrating 3 repeat units. Single and double losses of selenium to form carbodiimides are labelled appropriately. Single charge region of main polymer is also labelled. Resolution is 120,000

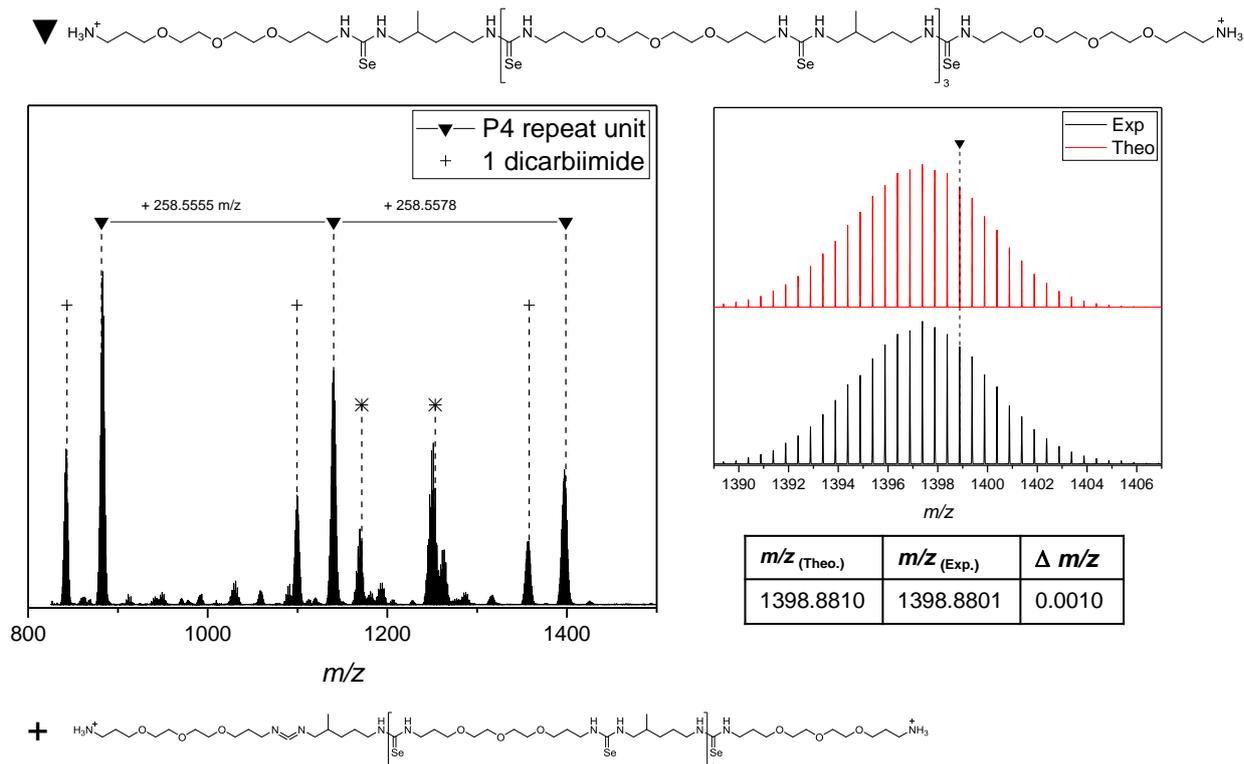


Figure S20 ESI-MS of P4 demonstrating 3 repeat units. Single and double losses of selenium to form carbodiimides are labelled appropriately. * indicates single charged species as well as single charge species with one loss of selenium. Resolution is 120,000

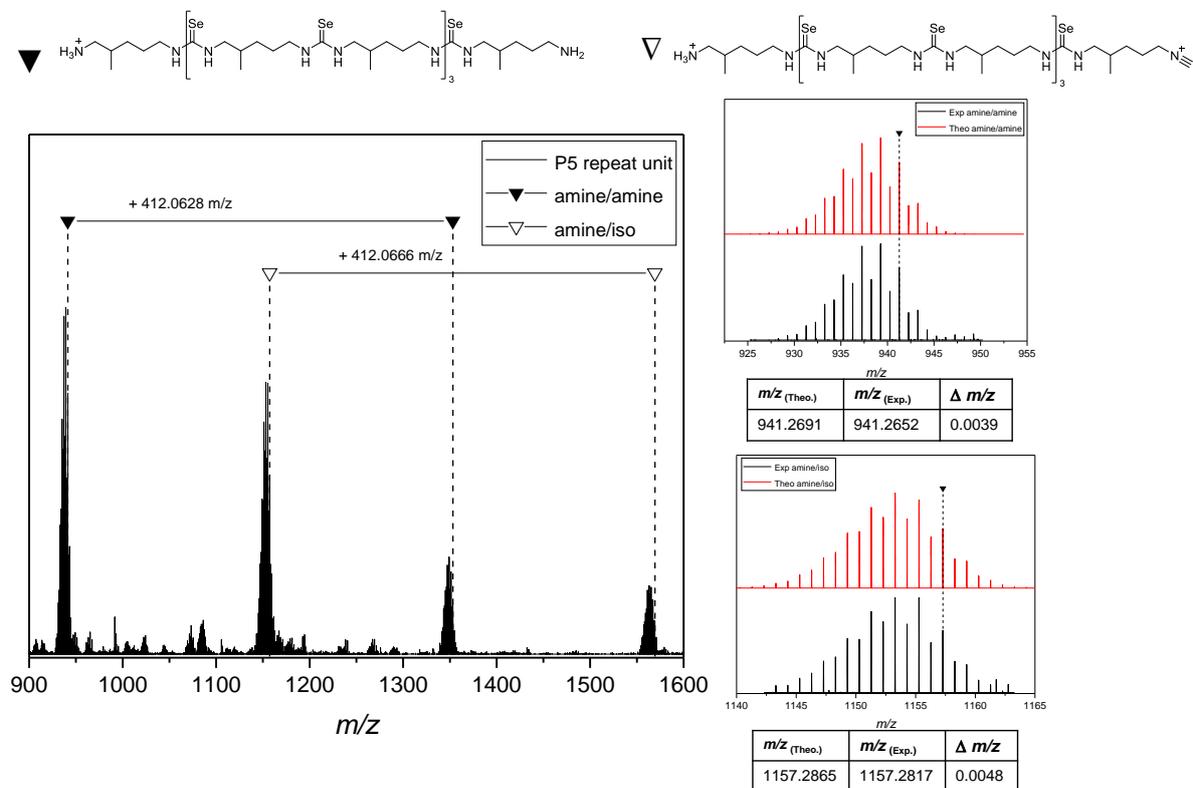


Figure S21 ESI-MS of P5 demonstrating 4 repeat units. Alternation between amine/amine and amine/isocyanide endgroups are clearly seen. Resolution is 120,000

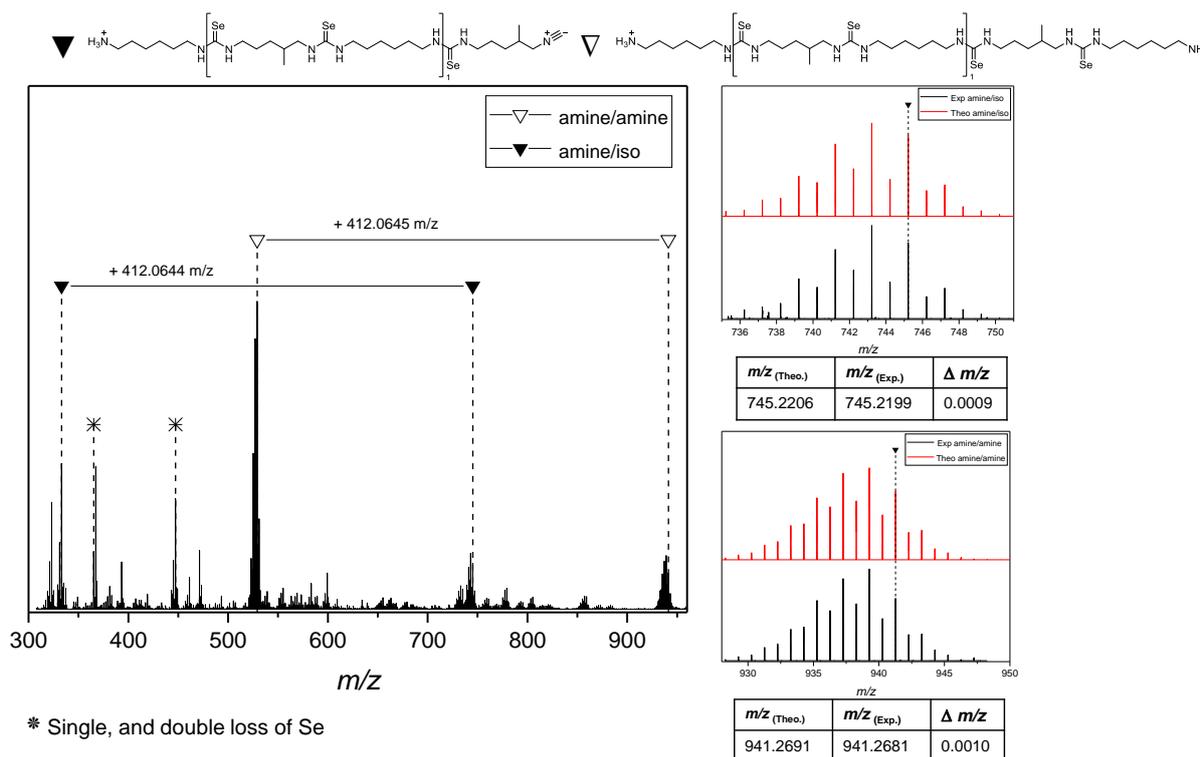
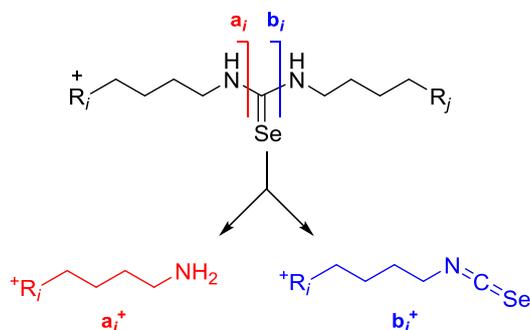


Figure S22 ESI-MS of P6 demonstrating 4 repeat units. Single and double losses of selenium to form carbodiimides are labelled appropriately. Alternation between amine/amine and amine/isocyanide endgroups are clearly seen. * Indicates a single and double loss of selenium (respectively) in relation to the amine/amine end group species. Resolution is 120,000

ESI-MS/MS



Scheme S1 Generalized mechanism to account for the formation of amine and isoselenocyanate product ions arising from collision-induced dissociation (CID) of $[M+nH]^{n+}$ ions generated by ESI-MS of polyselenourea oligomers.

Nomenclature is based on literature recommendations for synthetic polymer ion fragmentation by tandem mass spectrometry.³⁻⁴ Product ions retaining the charge on the α -terminus (R_i) are termed a_i^+ and b_i^+ , arising from cleavage of the first or second C-N bond of an oligomer containing i monomer units, respectively. Accurate mass measurements confirm that the elemental formula of each a_i^+ product ion is consistent with a primary amine, and each b_i product ion is an isoselenocyanate, indicating that intramolecular proton transfer occurs during fragmentation.

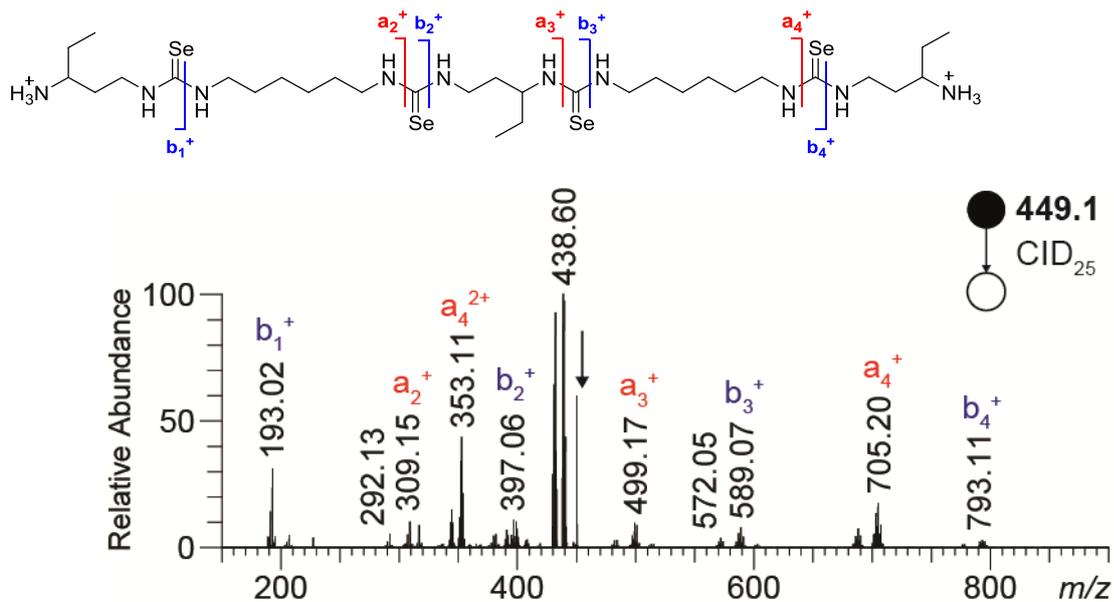


Figure S23 MS/MS spectrum acquired upon collisional activation (normalised collision energy = 25%) of the $[M+2H]^{2+}$ ion of **P1** containing 2.5 repeat units (m/z 449.1). Product ions are annotated using the nomenclature described in Scheme S1. Precursor ion is denoted by a downward arrow.

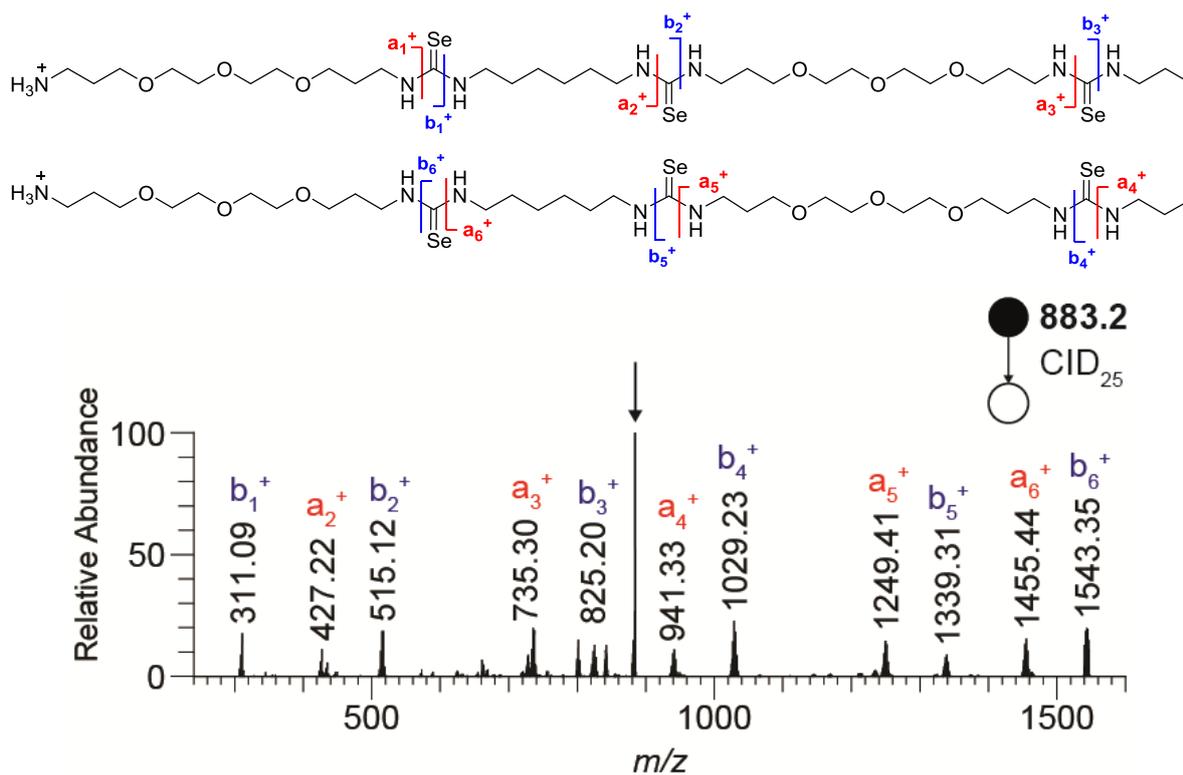


Figure S24 MS/MS spectrum acquired upon collisional activation (normalised collision energy = 25%) of the $[M+2H]^{2+}$ ion of **P2** containing 3.5 repeat units (m/z 883.3). Product ions are annotated using the nomenclature described in Scheme S1. Precursor ion is denoted by a downward arrow. Note the similarity to the equivalent MS/MS spectrum of isomeric **P4** ions (Figure 2, main text).

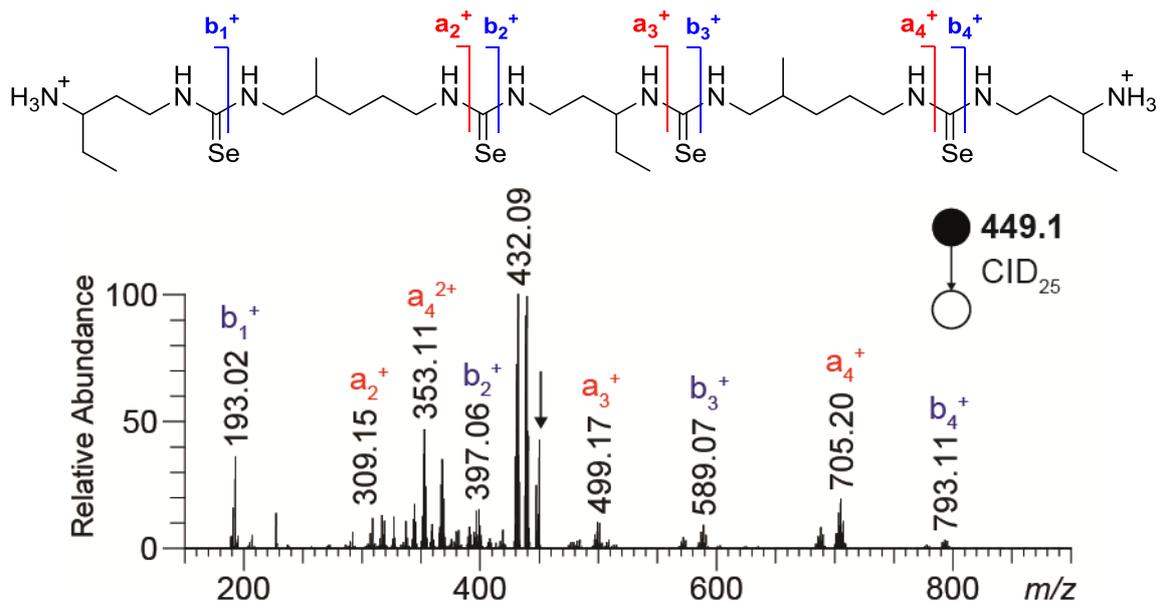


Figure S25 MS/MS spectrum acquired upon collisional activation (normalised collision energy = 25%) of the $[M+2H]^{2+}$ ion of **P3** containing 2.5 repeat units (m/z 449.1). Product ions are annotated using the nomenclature described in Scheme S1. Precursor ion is denoted by a downward arrow. Note the similarity to the equivalent MS/MS spectrum of isomeric **P1** ions (Figure S21).

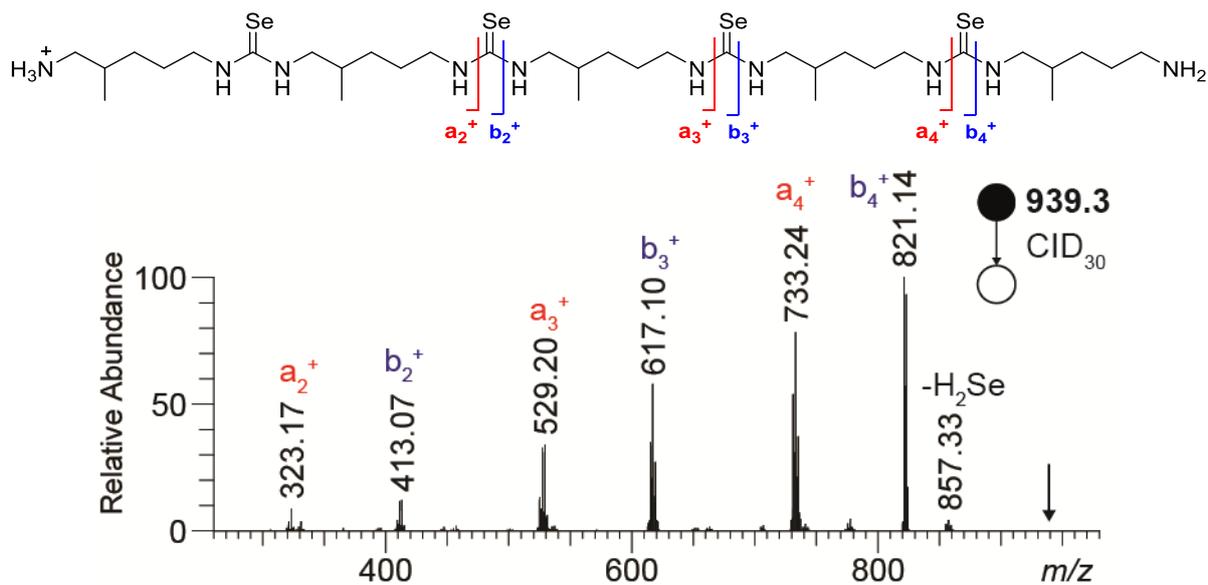


Figure S26 MS/MS spectrum acquired upon collisional activation (normalised collision energy = 30%) of the $[M+H]^+$ ion of **P5** containing 2.5 repeat units (m/z 939.3). Product ions are annotated using the nomenclature described in Scheme S1. Precursor ion is denoted by a downward arrow.

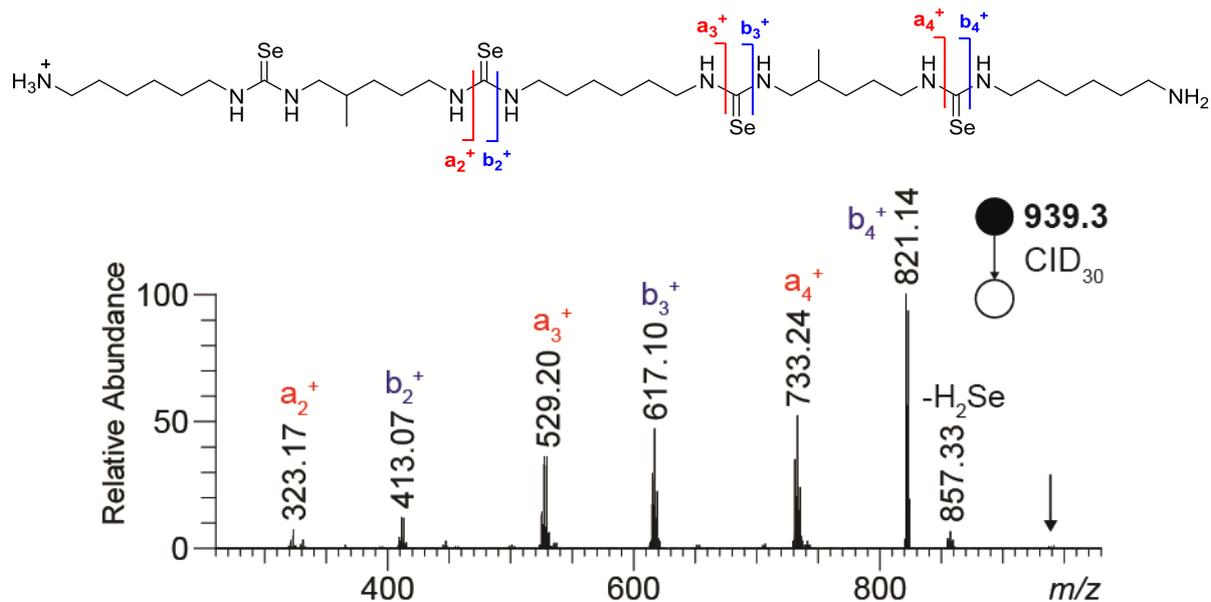


Figure S27 MS/MS spectrum acquired upon collisional activation (normalised collision energy = 30%) of the $[M+H]^+$ ion of **P6** containing 2.5 repeat units (m/z 939.3). Product ions are annotated using the nomenclature described in Scheme S1. Precursor ion is denoted by a downward arrow. Note the similarity to the equivalent MS/MS spectrum of isomeric **P5** ions (Figure S24).

IR

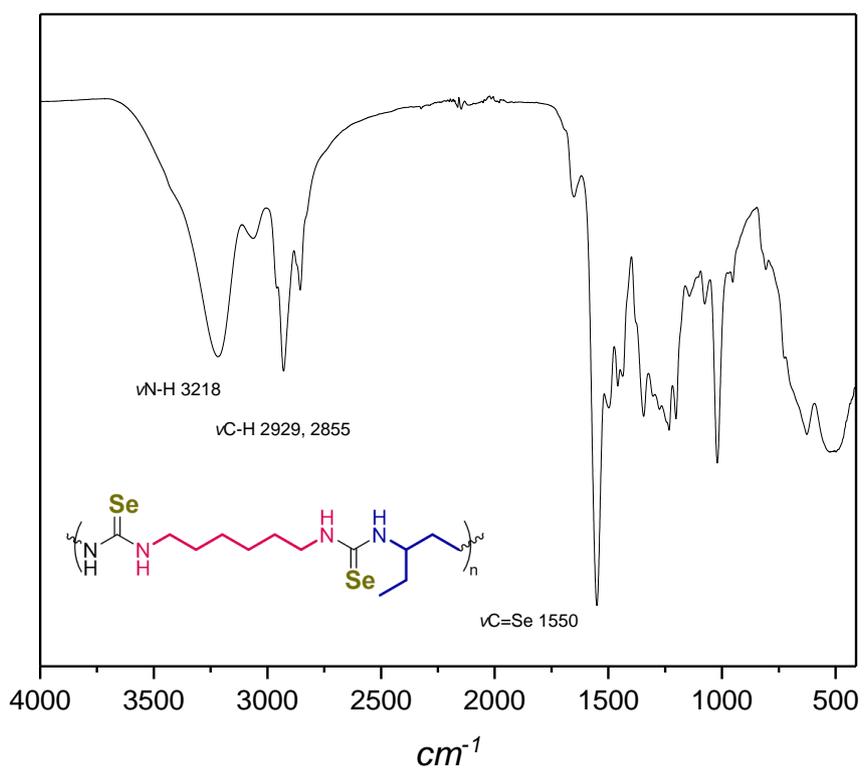


Figure S28 IR spectrum of P1

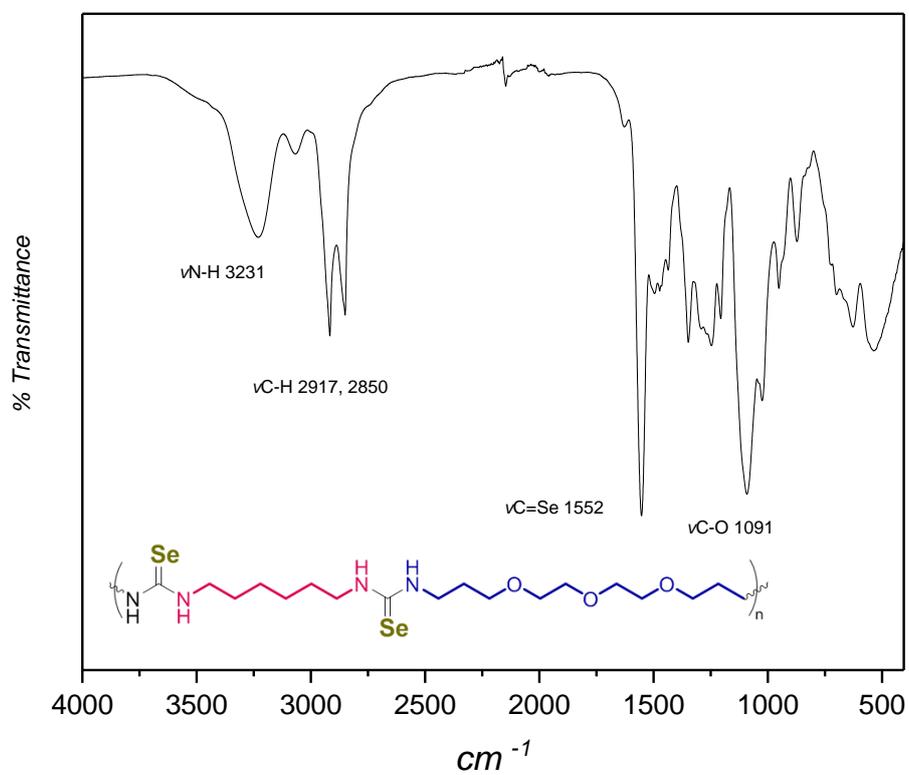


Figure S29 IR spectrum of P2

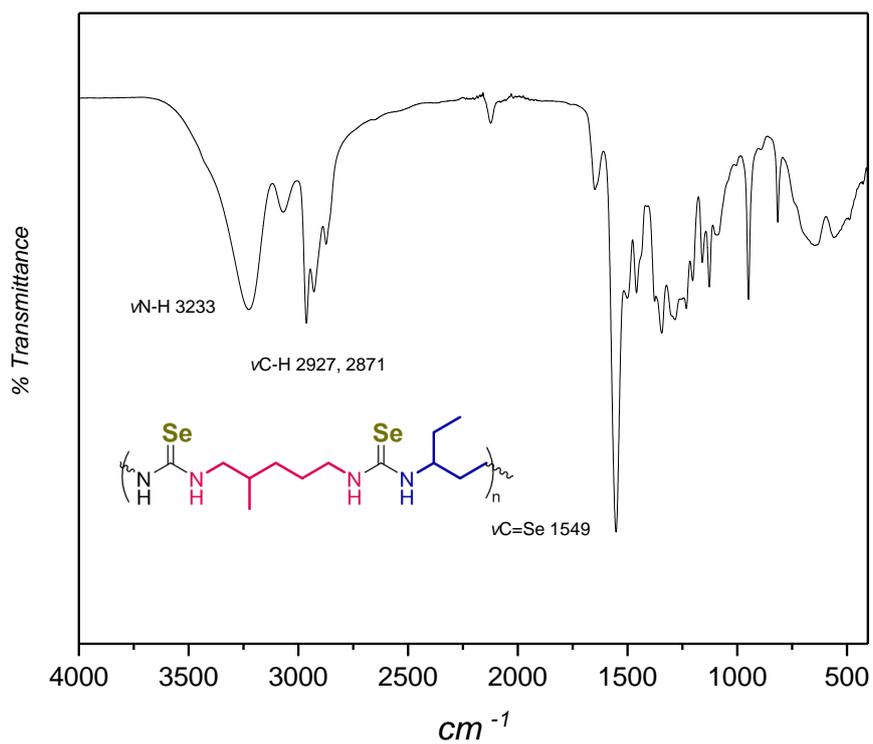


Figure S30 IR spectrum of P3

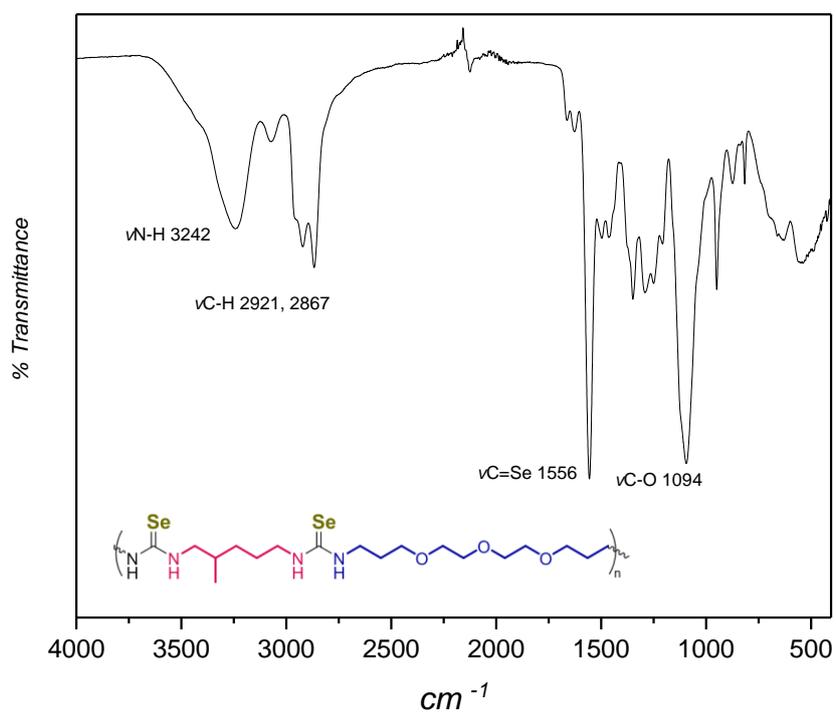


Figure S31 IR spectrum of P4

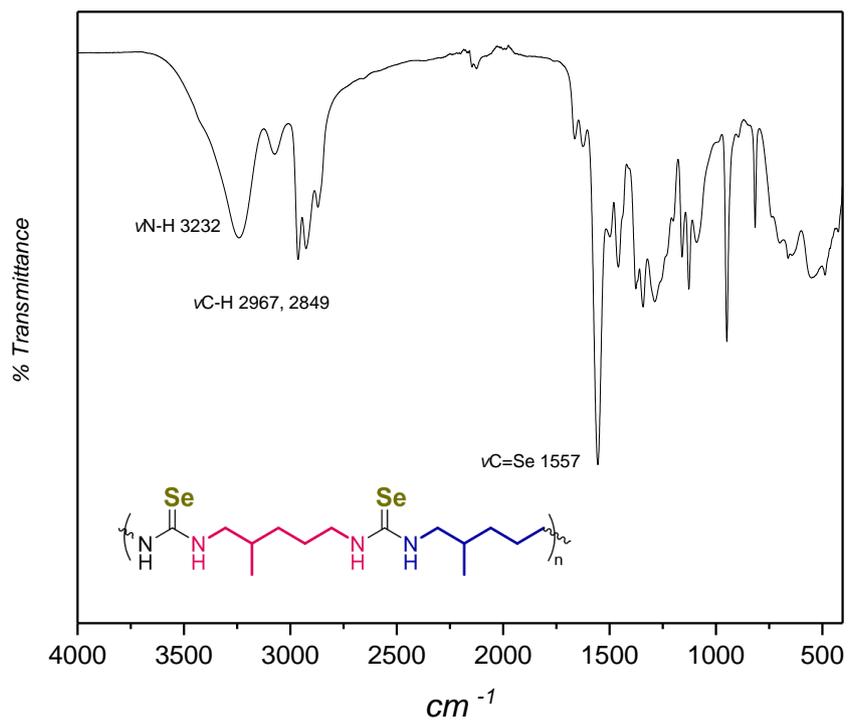


Figure S32 IR spectrum of P5

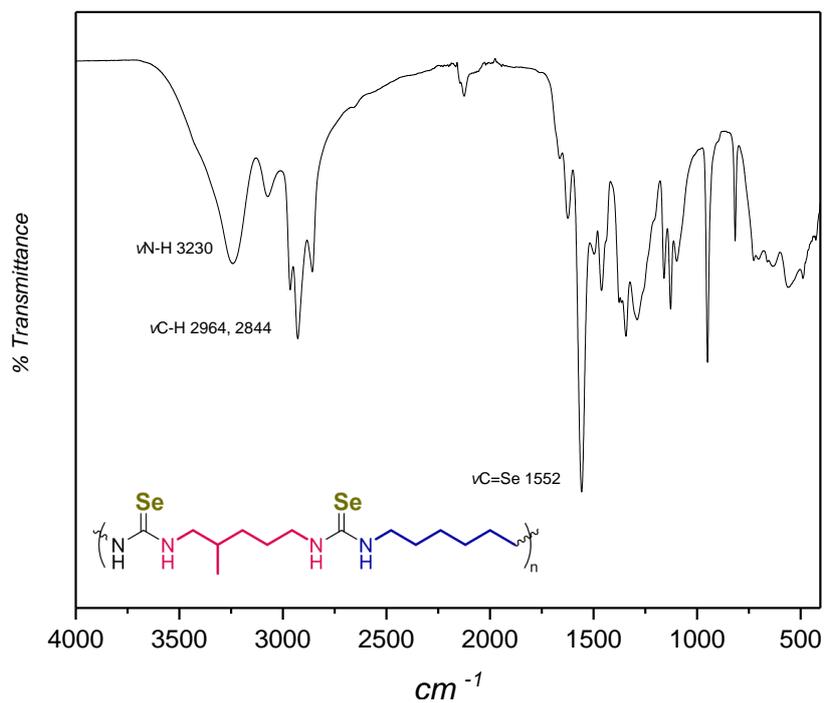


Figure S33 IR spectrum of P6

XPS

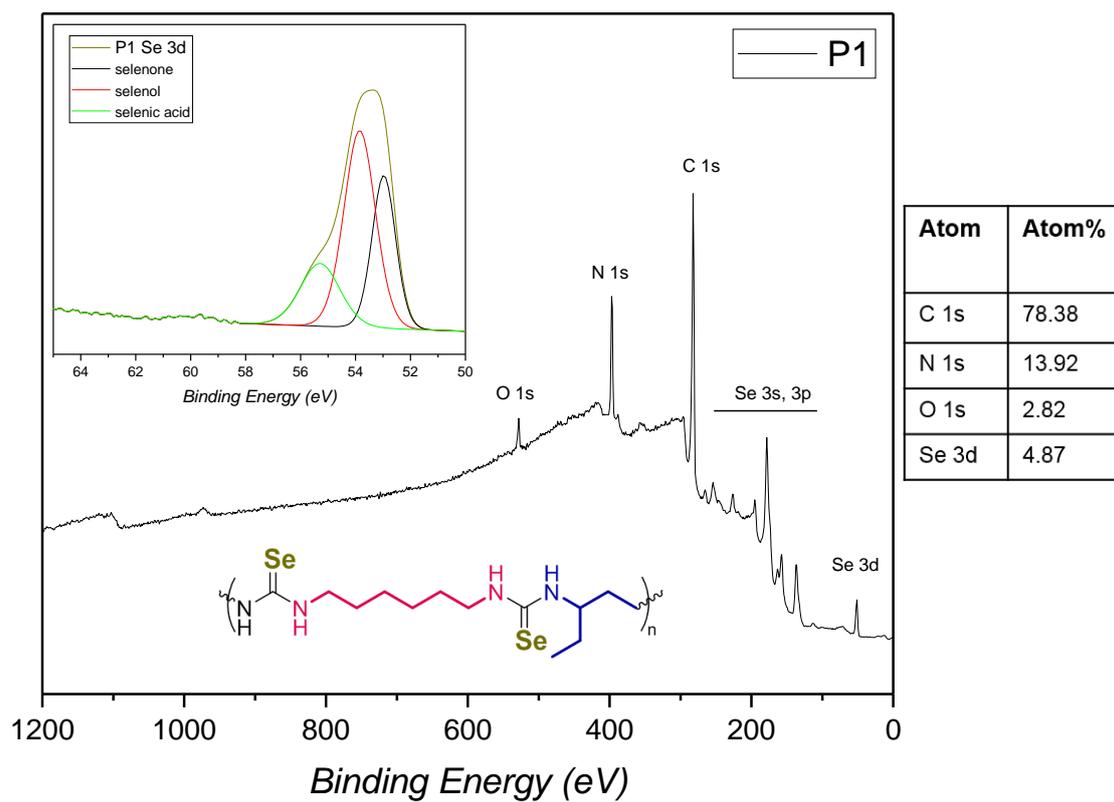


Figure S34 Survey (wide) scan with Se 3d high-resolution scan insert of P1 with peak deconvolution.

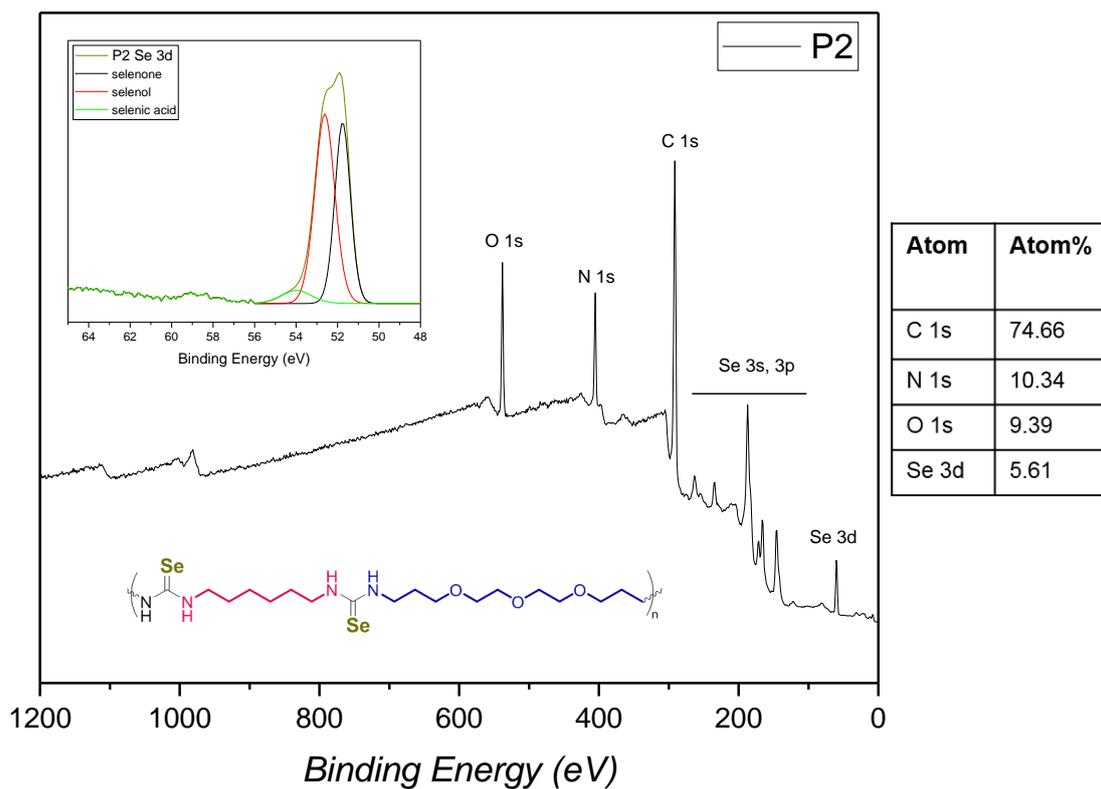


Figure S35 Survey (wide) scan with Se 3d high-resolution scan insert of **P2** with peak deconvolution.

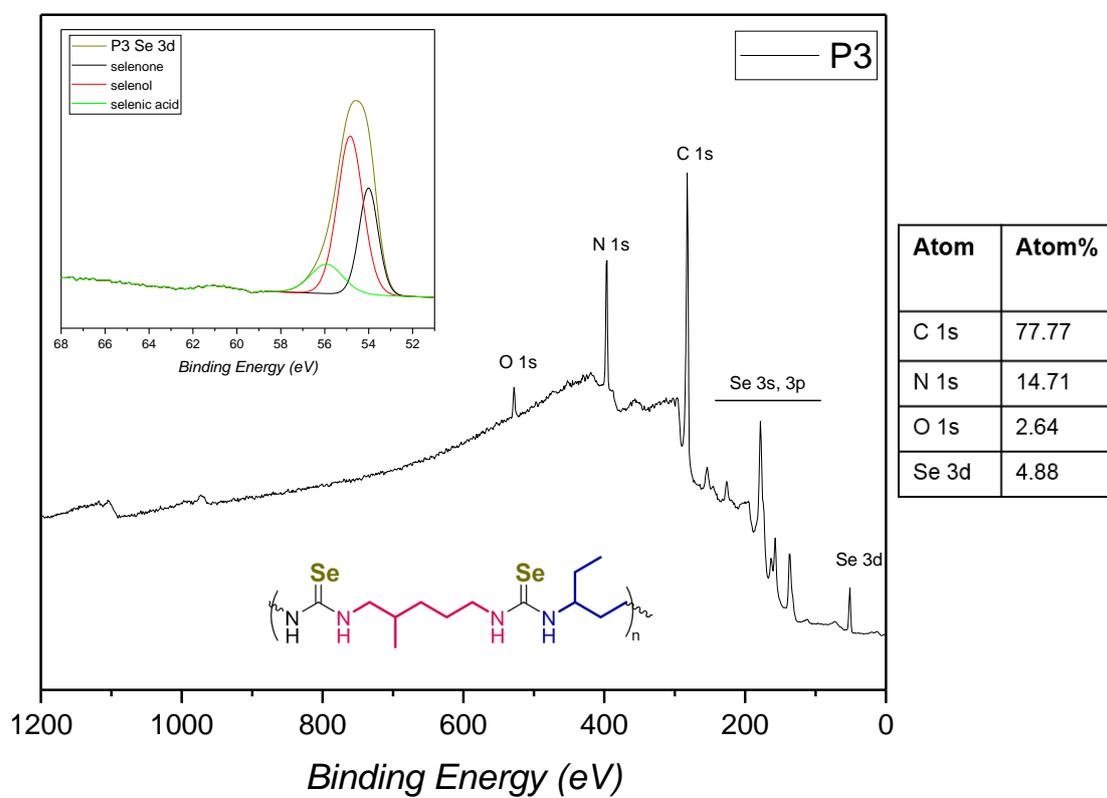


Figure S36 Survey (wide) scan with Se 3d high-resolution scan insert of **P3** with peak deconvolution.

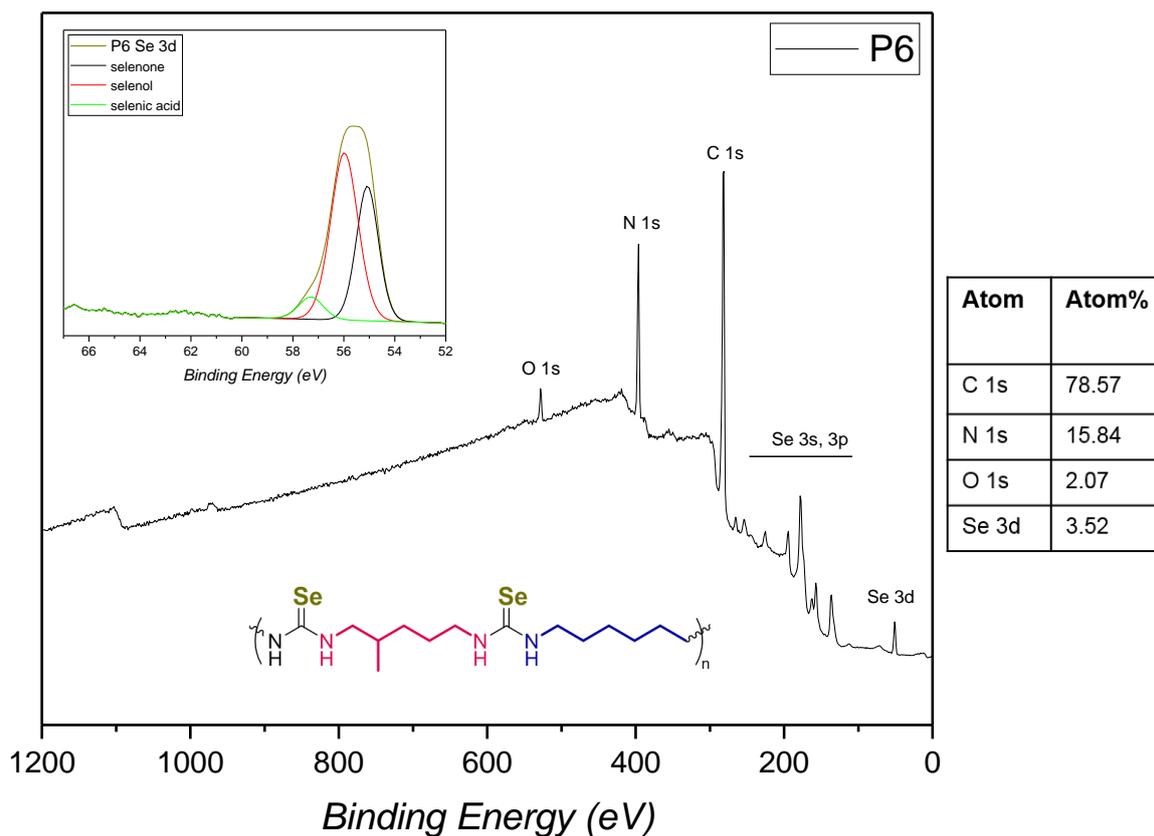


Figure S39 Survey (wide) scan with Se 3d high-resolution scan insert of P6 with peak deconvolution.

References

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