The Power of Architecture – Cage-shaped PEO and its Application as a Polymer Electrolyte

Supporting Information

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I.   General Information

Reagents and Solvents

3-Azido-5-ethynylbenzoic acid (**AEBA**) was synthetized in accordance with a previously reported procedure[1]. Bis(trifluoromethane)sulfonimide lithium salt (LiTFSI, 99.95%, Merck) was dried at 80 °C under vacuum for 2 days and subsequently stored inside a glove box (MBraun Unilab, < 0.1 ppm H_2O, < 0.1 ppm O_2) under inert argon atmosphere. All other chemicals were purchased from commercial suppliers and were used without further purification. Copper(I) iodide (CuI, Acros Organics, 98%); 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, Merck, ≥99%); *N*-(3-dimethylaminopropyl)-*N'*-ethylcarbodiimide hydrochloride (EDC-HCl, Carl Roth, ≥99%); 4-dimethylaminopyridine (DMAP, Acros Organics, 99%); hydrochloric acid ($HCl_{(aq)}$, Carl Roth, 37%); magnesium sulfate ($MgSO_4$, Carl Roth, ≥99%); 4 arms star-shaped poly(ethylene oxide) 5000 g mol^{-1} (**PEO**$_{star}$, Jenkem Technology, >95%). All solvents were purchased from VWR Chemicals with AnalaR NORMAPUR purity grade and were used without preliminary distillation. Deuterated solvents were obtained from Eurisotop, a subsidiary of Cambridge Isotope Laboratories, Inc. Flash column chromatography was carried out using silica gel (40-63 μm mesh, Geduran® Si 60 from Merck Millipore).

Proton Nuclear Magnetic Resonance (^{1}H-NMR)

All ^{1}H-NMR spectra were recorded on a Bruker Ascend III 400 MHz spectrometer using $CDCl_3$ as deuterated solvents. Chemical shifts were reported in ppm (δ), relative to $CDCl_3$ residual peak as internal standards (δ 7.26 for ^{1}H-NMR). The coupling constants (J) are given in Hz. Splitting patterns are designated as s (singlet), dd (double doublet), t (triplet) and m (multiplet).

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[1] Gauthier-Jaques, M.; Theato, P. Synergy of Macrocycles and Macromolecular Topologies: An Efficient [3$_4$] Triazolophane-Based Synthesis of Cage-Shaped Polymers. *ACS Macro Lett.* **2020**, *9* (5), 700–705

Size Exclusion Chromatography (SEC)

SEC analysis with tetrahydrofuran (THF) as eluent were performed on a PL-SEC 50 Plus Integrated System, comprising an autosampler, a differential Refractive Index (RI) detector, a PLgel 5 µm bead-size guard column (50 × 7.5 mm) followed by three PLgel 5 µm Mixed C column (300 × 7.5 mm) and a PLgel 3 µm Mixed E column (300 × 7.5 mm). THF was used at an operating temperature of 35 °C and a flow rate of 1.0 mL min^{-1}. All samples were prepared with a polymer concentration of 2.0 mg ml^{-1} and 100 µL were typically injected to the columns. All number average molar mass M_n, mass average molar mass M_w and dispersity $Đ$ values were extrapolated from a range of linear polystyrene standard between 370 and 6 × 10^6 g mol^{-1}.

Fourier-Transform Infrared Spectroscopy (FT-IR)

FT-IR measurements were performed on a Bruker ALPHA FT-IR Spectrometer equipped with an ATR unit. All FT-IR spectra were measured though 32 scans from 4000 to 600 cm^{-1} at a resolution of 1 cm^{-1}.

Electrospray Ionization Mass Spectrometry (ESI-MS)

ESI-MS measurements were achieved on a Thermo Fisher Q-Exactive Orbitrap Mass Spectrometer. As sample preparation, a polymer concentration of 0.05 mg ml^{-1} was prepared in a mixture of DCM/MeOH 3:1 enriched with 100 µM sodium trifluoroacetate as cation source.

Differential Scanning Calorimetry (DSC)

DSC measurements were performed by a TA Instruments Q200 incorporating a RCS90 cooling system. Polymer and Polymer Electrolyte samples weighing between 6.00 and 10.00 mg were heated from -75 °C to 70 °C twice with a heating ramp of 5 K min^{-1}. All reported temperature and enthalpy values were taken from the second heating ramp curves.

Thermal Gravimetric Analysis (TGA)

Thermal Gravimetric Analysis (TGA) was carried out by a TGA 5500 (TA Instruments) at a heating rate of 10.0 K min^{-1} under nitrogen atmosphere up to 800 °C. Typically, about 10 mg material were weighted on a palladium pan prior to the measurements.

Polymer electrolyte (PE) preparation

Prior to the PE preparation, the respective polymer was dried at 80 °C under vacuum overnight. The polymer as well as the corresponding amount of LiTFSI with predefined ratios of [Li$^+$]:[EO] 1:20 or 1:25 were both dissolved in acetone. Subsequently, both solutions were combined to yield a homogenous mixture. Acetone was removed slowly under reduced pressure at 50 °C, followed by drying the polymer electrolytes under reduced pressure (10^{-3} mbar) and 80 °C for 24 hours.

## Electrochemical Impedance Spectroscopy (EIS)

For EIS measurements, coin cell-type cells (CR2032) were assembled, where the previously prepared polymer electrolytes were sandwiched between two stainless steel electrodes using a Mylar foil spacer ring (thickness l = 100 µm, inner diameter = 8 mm). Subsequently, these cells were preconditioned in a temperature chamber (Binder MK53, controlled with the Autolab Software Nova 2.1.3) with a gradual increase of temperature from 20 °C – 70 °C in 10 °C steps while maintaining each temperature for 2 h. 1 h after the preconditioning was finished, measurements were carried out by gradually increasing the temperature in 10 °C steps from 0 °C to 70 °C with each temperature being maintained for 2 h to attain a thermal equilibrium. The measurements were performed using a PGSTAT302N potentiostat/galvanostat (Autolab) over a frequency range of 1 MHz – 1 Hz with an amplitude of 10 mV. The ionic conductivity σ was calculated according to the following equation: $\sigma = (1/R_b) \cdot (l\ A^{-1})$; R_b being the bulk resistance that can be accessed from the Nyquist plot, l is the film thickness (l = 100 µm) and A is the film area (A = 5.03 × 10^{-5} m^2). For each SPE three coin cells were prepared and

measured. Subsequently, the mean average ionic conductivity of these three measurements was

derived and discussed.

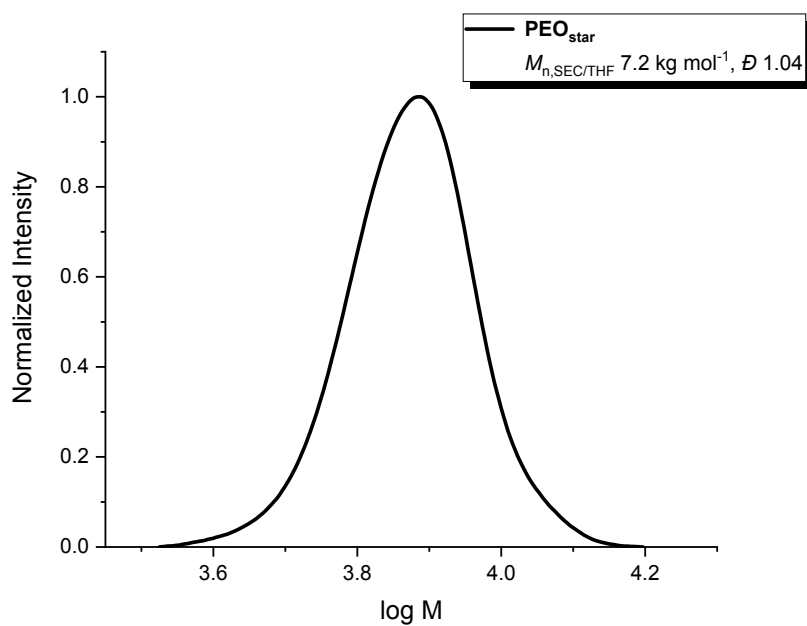## II. Polymer synthesis and characterization

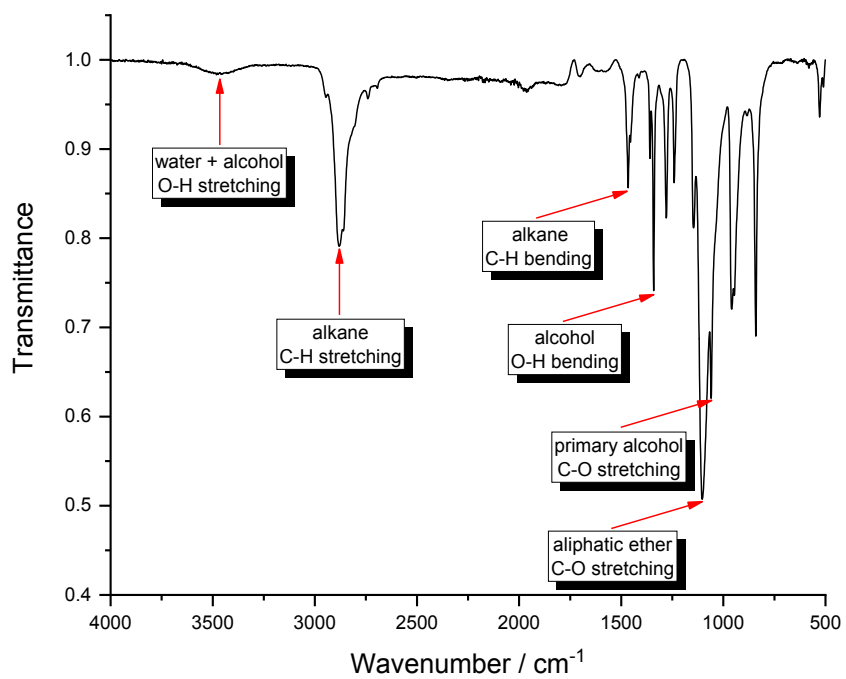### 1. (PEO$_{star}$) Analysis of commercial *star*-shaped PEO 5000 g mol^{-1}

^{1}H-NMR analysis
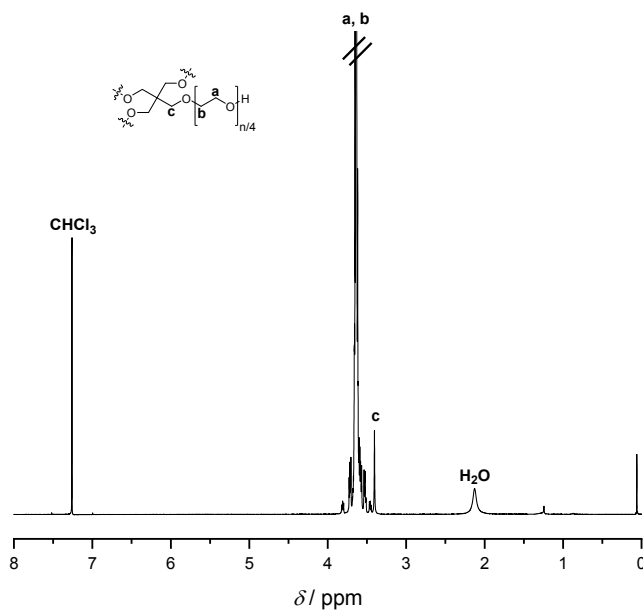
^{1}H NMR (400 MHz, CDCl$_3$) δ 3.84 – 3.43 (m), 3.40 (s).
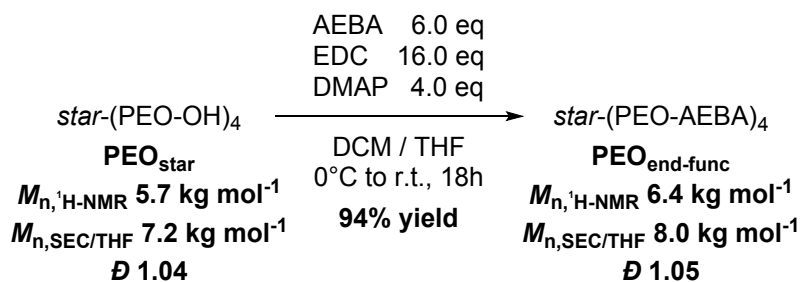
SEC analysis
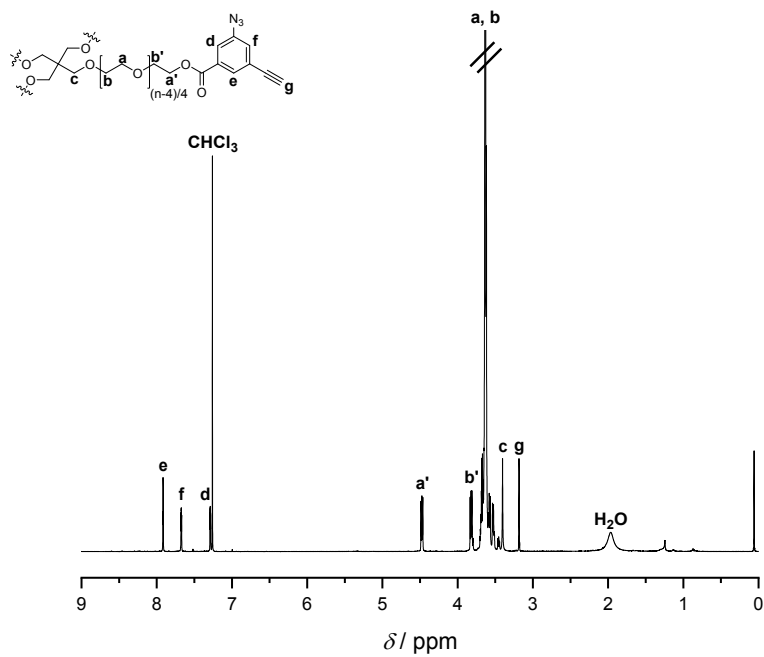
FT-IR analysis

IR (ATR, cm^{-1}) 2881, 1466, 1359, 1341, 1279, 1241, 1146, 1104, 1060, 959, 841, 529.

2. (PEO_{end-func}) End-functionalization of PEO_{star} with AEBA

$$\textit{star-}(PEO\text{-}OH)_4 \xrightarrow[\substack{DCM / THF \\ 0°C \text{ to r.t., 18h} \\ \textbf{94\% yield}}]{\substack{AEBA \quad 6.0 \text{ eq} \\ EDC \quad 16.0 \text{ eq} \\ DMAP \quad 4.0 \text{ eq}}} \textit{star-}(PEO\text{-}AEBA)_4$$

PEO_{star}

$M_{n,{}^1H\text{-NMR}}$ **5.7 kg mol⁻¹**

$M_{n,SEC/THF}$ **7.2 kg mol⁻¹**

Đ **1.04**

PEO_{end-func}

$M_{n,{}^1H\text{-NMR}}$ **6.4 kg mol⁻¹**

$M_{n,SEC/THF}$ **8.0 kg mol⁻¹**

Đ **1.05**

Commercial grade *star*-shaped (PEO-OH)$_4$ (**PEO_{star}**, 3.446 g, 0.606 mmol, 5687 g mol⁻¹, 1.0 eq), 3-azido-5-ethynylbenzoic acid (**AEBA**, 680 mg, 3.63 mmol, 6.0 eq) and 4-dimethylaminopyridine (**DMAP**, 296 mg, 2.42 mmol, 4.0 eq) were dissolved in dry DCM (15 mL) and dry THF (10 mL). The solution was cooled down to 0 °C and *N*-(3-dimethylaminopropyl)-*N'*-ethylcarbodiimide hydrochloride (**EDC**, 1.86 g, 9.69 mmol, 16.0 eq) was added portionwise. The mixture was then stirred for 18 hours from 0 °C to room temperature. Afterwards, the resulting mixture was quenched with HCl 1 M and the aqueous phase was extracted with DCM (3 × 30 mL). The organic fractions were collected, dried over MgSO$_4$ and the solvent was removed under reduced pressure. The crude material was then washed on silica gel. To do so, a chromatography column (40 × 3 cm) was packed with silica gel (30 cm) and the crude material was deposited on the upper silica gel layer and covered with sand (1 cm). Then, CHCl$_3$ was eluted though the chromatography column until no more reagents could be noticed (500 mL). Afterwards, the PEO material was recovered from the silica gel. In this regard, a solvent mixture of 10 vol% MeOH and 90 vol% CHCl$_3$ was eluted until no more polymer could be recovered (400 mL). The resulting material was filtrated through a 0.2 µm PFTE filter, yielding **PEO_{end-func}** as a yellow solid. **(3.62 g, 0.569 mmol, 94% yield)**
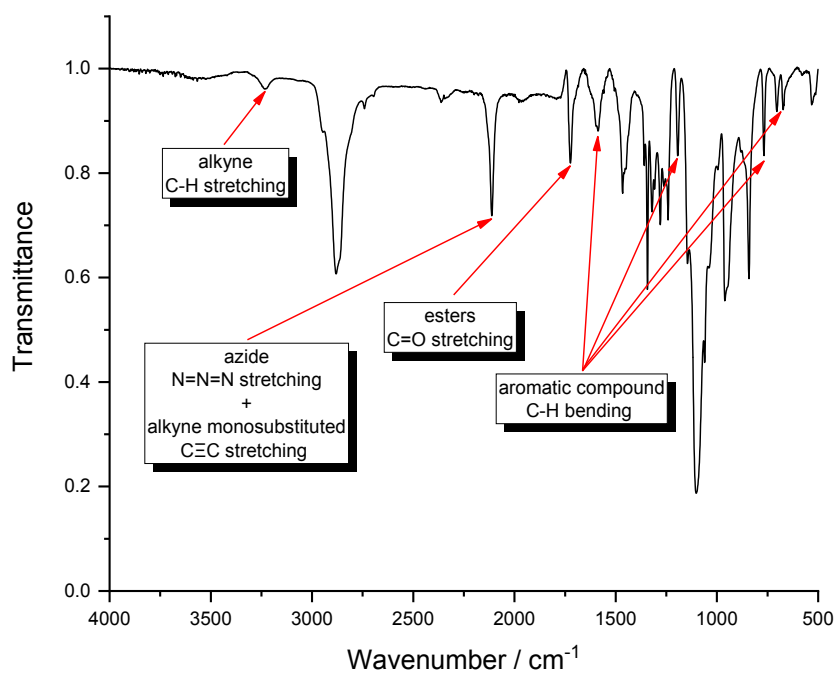
¹H-NMR analysis

¹H NMR (400 MHz, CDCl₃) δ 7.92 (t, J = 1.4 Hz), 7.67 (dd, J = 2.2, 1.5 Hz), 7.29 (dd, J = 2.2, 1.4 Hz), 4.52 − 4.43 (m), 3.86 − 3.77 (m), 3.75 − 3.43 (m), 3.40 (s), 3.18 (s).
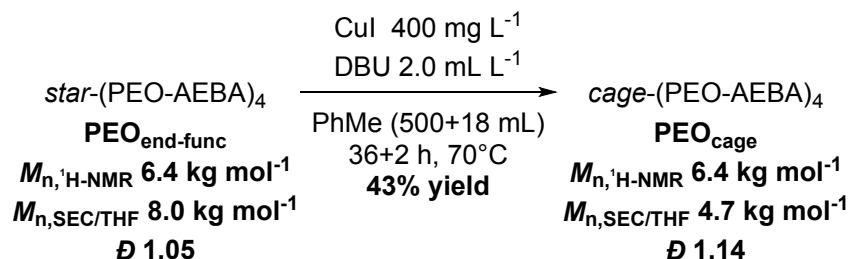
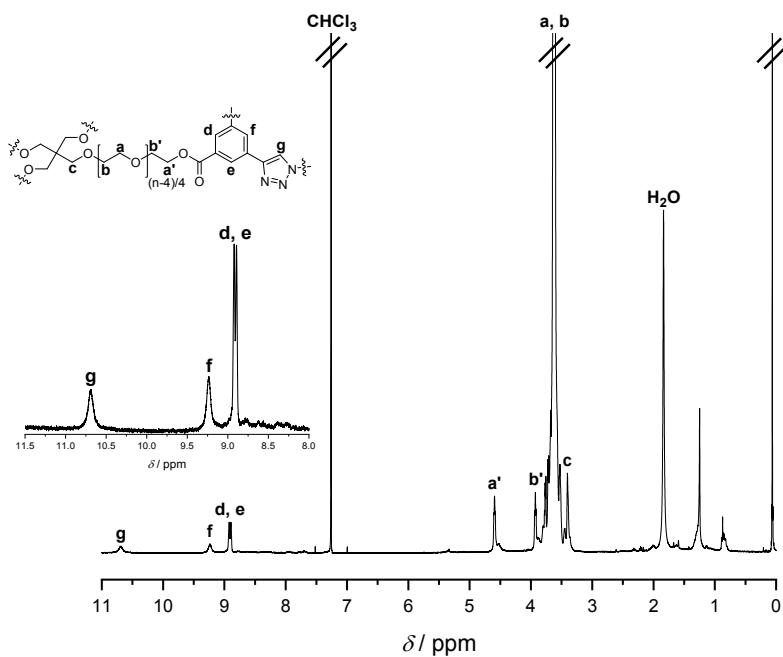## SEC analysis
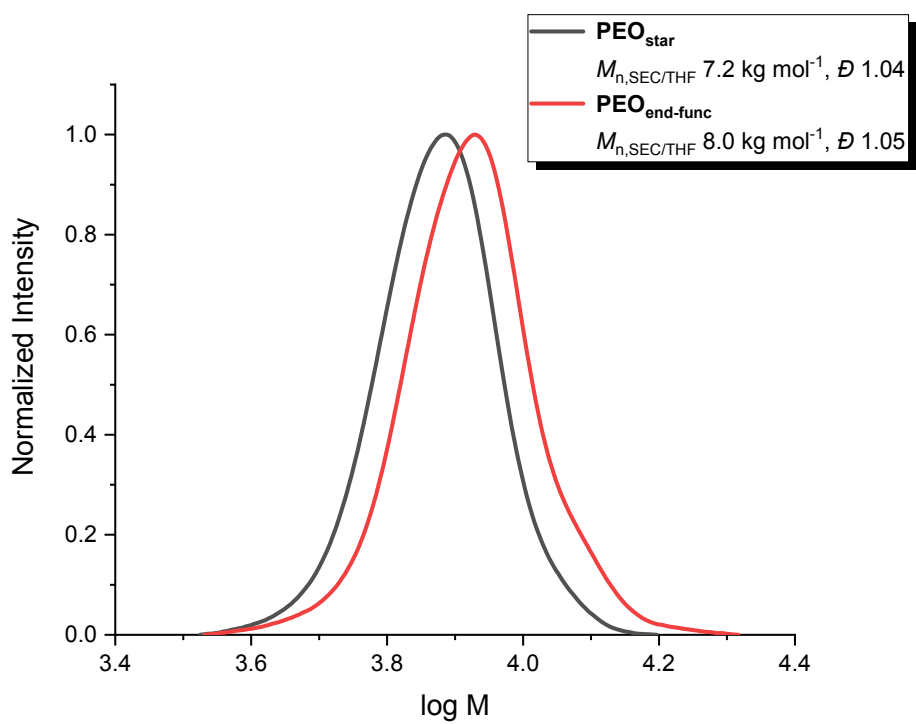
FT-IR analysis

IR (ATR, cm^{-1}) 2881, 2112, 1724, 1587, 1466, 1359, 1343, 1321, 1280, 1241, 1193, 1102, 1060, 961, 842, 768, 704, 673, 532.

## 3. (PEO$_{cage}$) *Cage*-shaped polymer synthesis from PEO$_{end-func}$ via CuAAC

$$\text{star-(PEO-AEBA)}_4 \xrightarrow[\substack{\text{PhMe (500+18 mL)} \\ \text{36+2 h, 70°C} \\ \textbf{43\% yield}}]{\substack{\text{CuI 400 mg L}^{-1} \\ \text{DBU 2.0 mL L}^{-1}}} \text{cage-(PEO-AEBA)}_4$$

<div align="center">

star-(PEO-AEBA)$_4$ → **cage-(PEO-AEBA)$_4$**

PEO$_{end-func}$ **PEO$_{cage}$**

$M_{n,^1H-NMR}$ **6.4 kg mol^{-1}** $M_{n,^1H-NMR}$ **6.4 kg mol^{-1}**

$M_{n,SEC/THF}$ **8.0 kg mol^{-1}** $M_{n,SEC/THF}$ **4.7 kg mol^{-1}**

Đ **1.05**   Đ **1.14**

</div>

DBU (1.0 mL, 2.0 mL L^{-1}) was dissolved in toluene (500 mL). The mixture was flushed with argon for 15 min and CuI (200 mg, 400 mg L^{-1}) was added. The mixture was then flushed with argon for another 15 min before being heated at 70 °C. **PEO$_{end-func}$** (3.600 g) was dissolved in toluene (18 mL) and flushed with argon for 15 min before being placed in a 20 mL syringe. The syringe mixture was injected at a regular rate (100 mg h^{-1} polymer, 0.50 mL h^{-1}) to the first mixture over 36 hours. Then, the resulting mixture was heated for two more hours at 70 °C before being cooled down to room temperature. Afterwards, the solvent was removed under reduced pressure, HCl 1 M (50 mL) was added and the crude was extracted with DCM (3 × 50 mL). The organic fractions were collected, dried over MgSO$_4$ and the solvent was removed under reduced pressure. The crude material was then washed on silica gel. To do so, a chromatography column (40 × 3 cm) was packed with silica gel (30 cm) and the crude material was deposed on the upper silica gel layer and covered with sand (1 cm). Then, CHCl$_3$ was eluted though the chromatography column until no more DBU, nor DBU degradation products could be noticed (500 mL). Afterwards, the PEO material was recovered from the silica gel. In this regard, a solvent mixture of 10 vol% MeOH and 90 vol% CHCl$_3$ was eluted until no more polymer could be recovered (400 mL). The process was repeated a second time in order to ensure a maximal purity of the material. At last, the resulting material was reprecipitated once in cold Et$_2$O (-20 °C) with EtOH as solubilizing agent and filtrated through a 0.2 μm PFTE filter, yielding **PEO$_{cage}$** as a brown solid. **(1.548 g, 43% yield)**
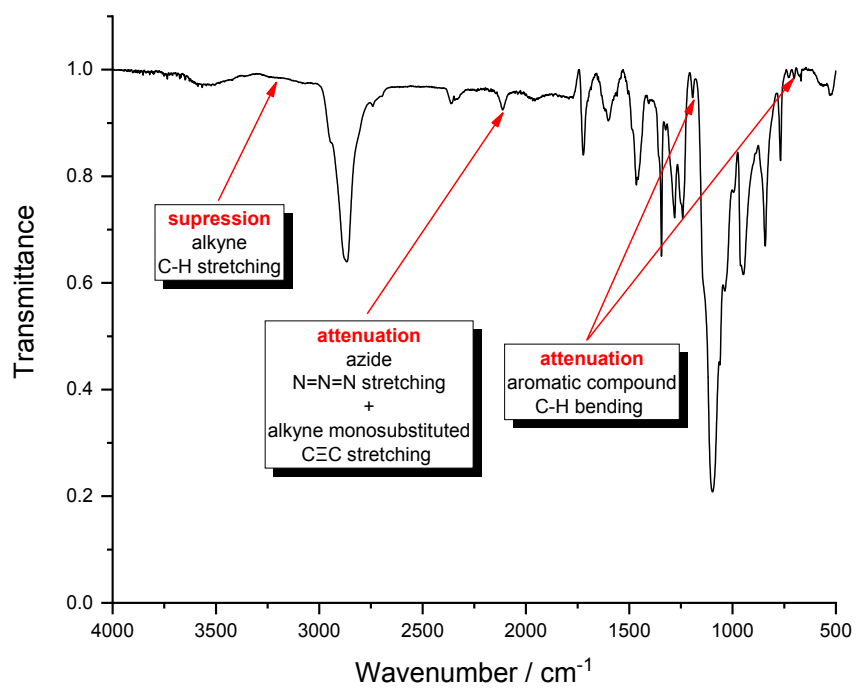
¹H-NMR analysis

¹H NMR (400 MHz, CDCl₃) δ 10.69 (s), 9.24 (s), 8.92 (s), 8.89 (s), 4.65 − 4.46 (m), 3.97 − 3.85 (m), 3.83 − 3.33 (m), 3.40 (s).
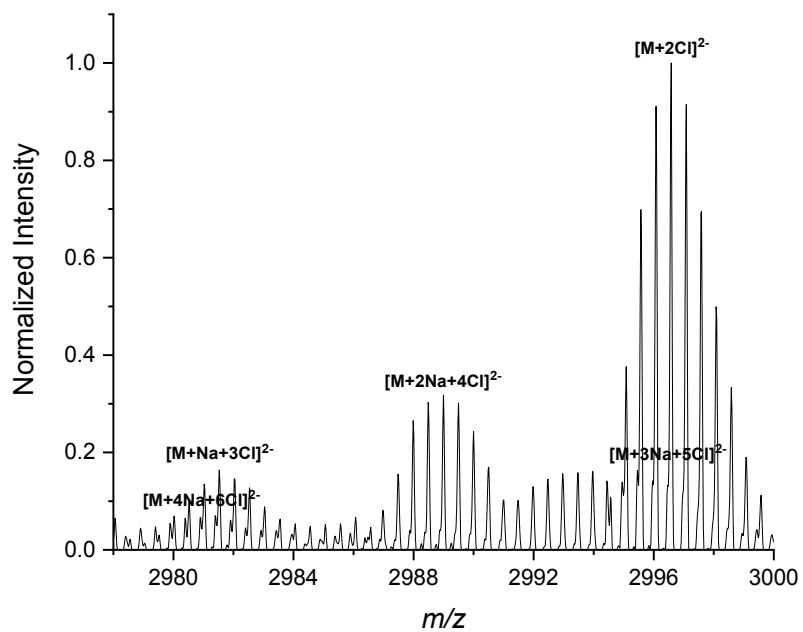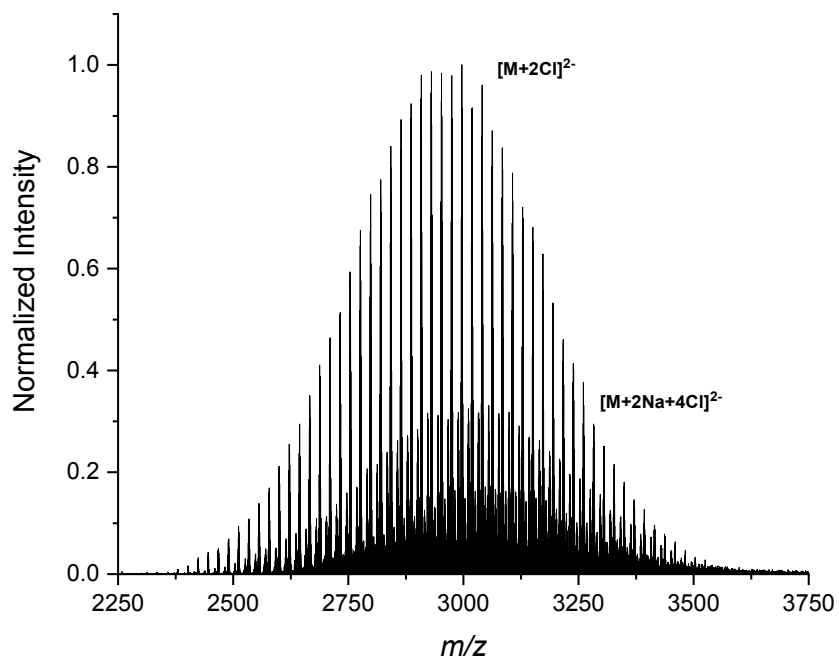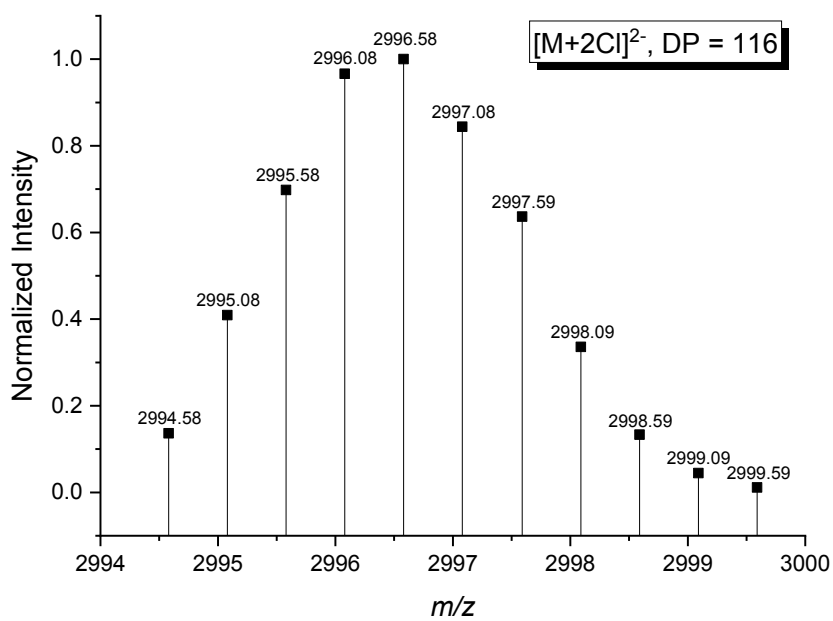
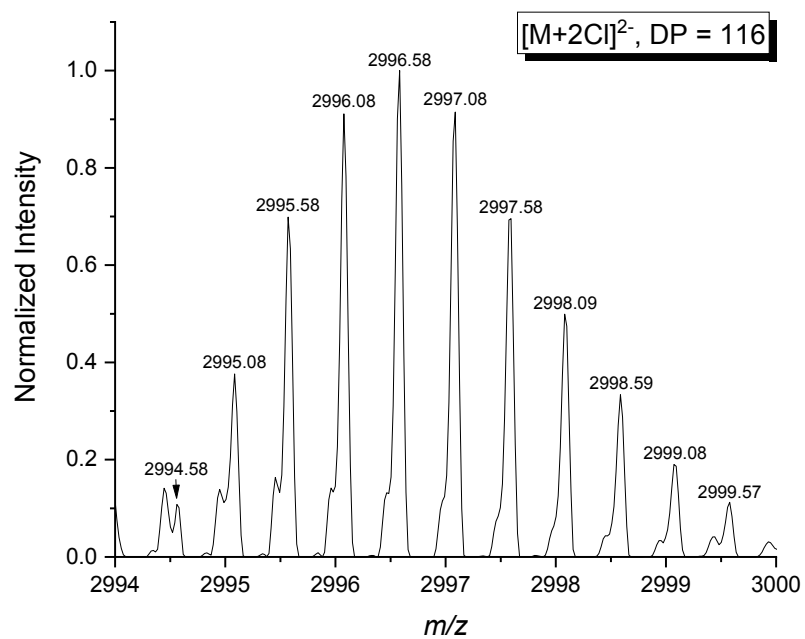## SEC analysis
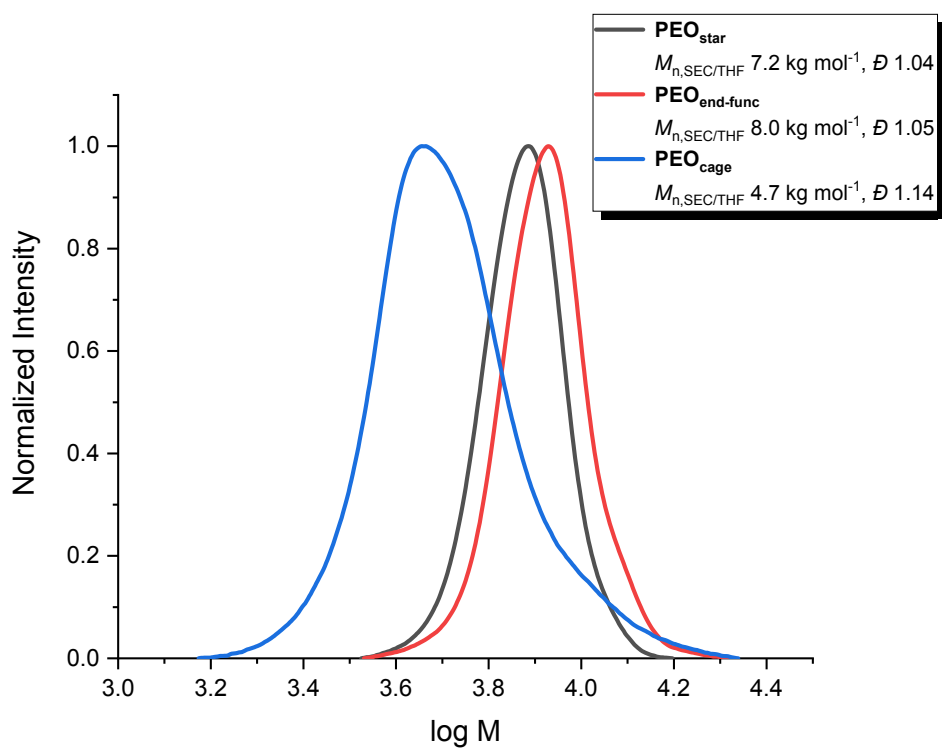
FT-IR analysis

**IR (ATR, cm^{-1})** 2867, 1723, 1602, 1466, 1344, 1281, 1242, 1097, 948, 842, 768.

4. (PEO_{cage}) ESI-MS analysis – distribution overview

The spectra show the normalized intensity versus m/z distributions for the PEO cage species.

Top spectrum (range 2250–3750 m/z):
- $[M+2Cl]^{2-}$
- $[M+2Na+4Cl]^{2-}$

Bottom spectrum (range 2978–3000 m/z):
- $[M+2Cl]^{2-}$
- $[M+2Na+4Cl]^{2-}$
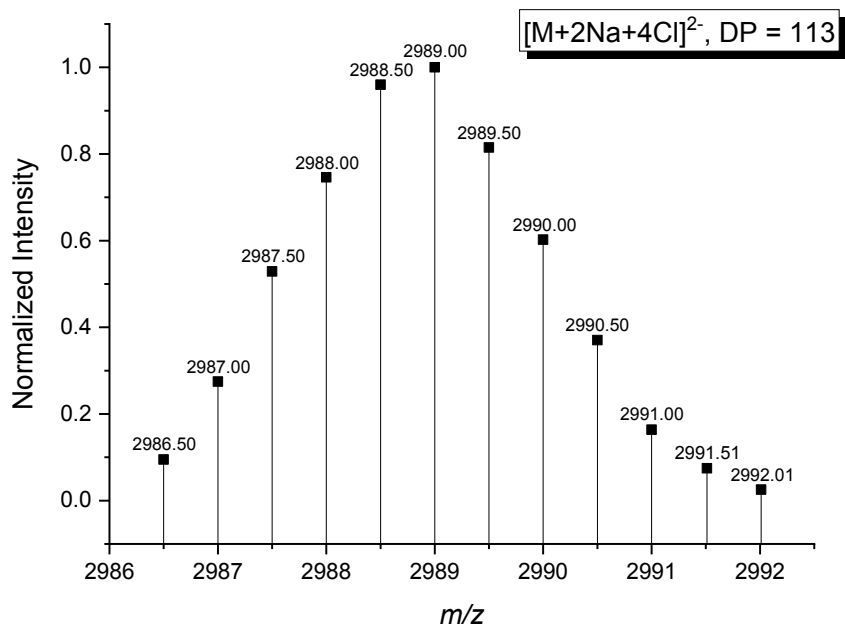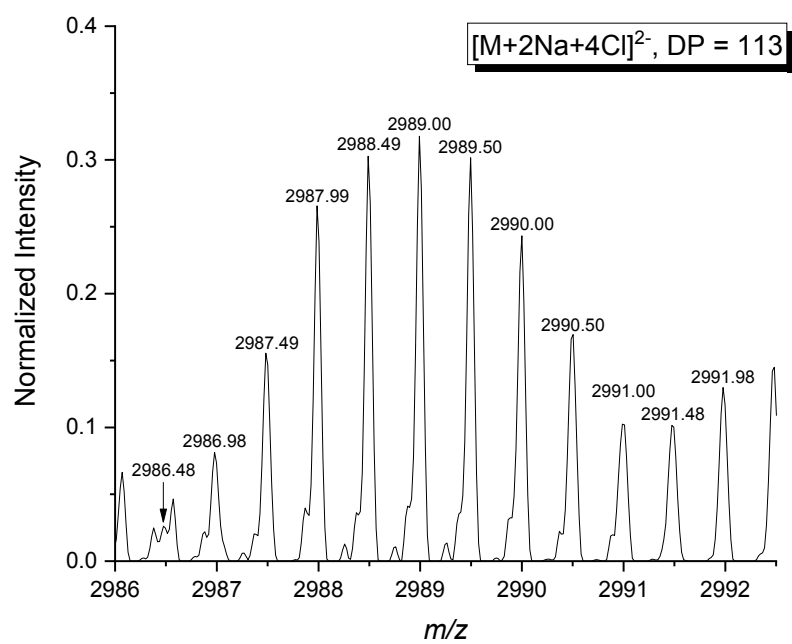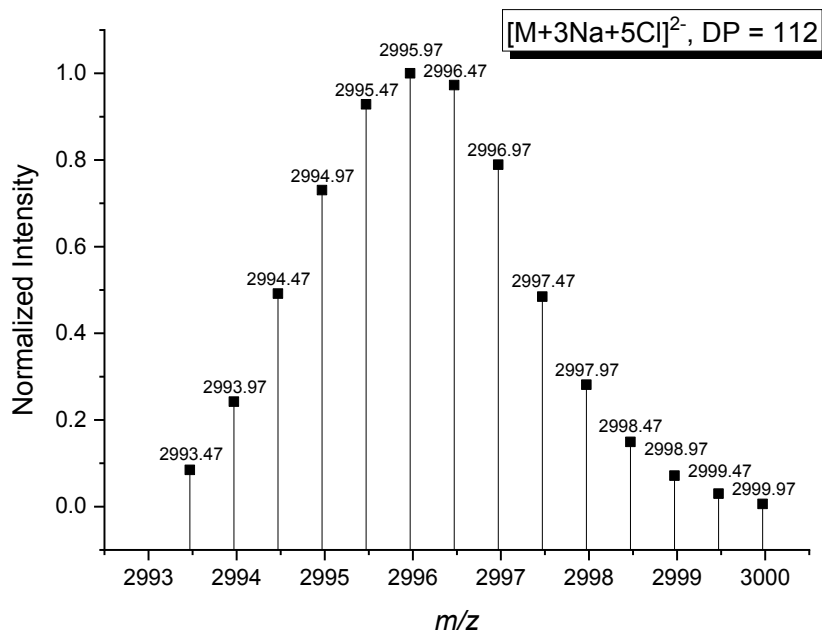- $[M+Na+3Cl]^{2-}$
- $[M+4Na+6Cl]^{2-}$
- $[M+3Na+5Cl]^{2-}$

ESI-MS analysis - [M+2Cl]$^{2-}$ experimental and theoretical distributions

ESI-MS analysis - [M+Na+3Cl]²⁻ experimental and theoretical distributions

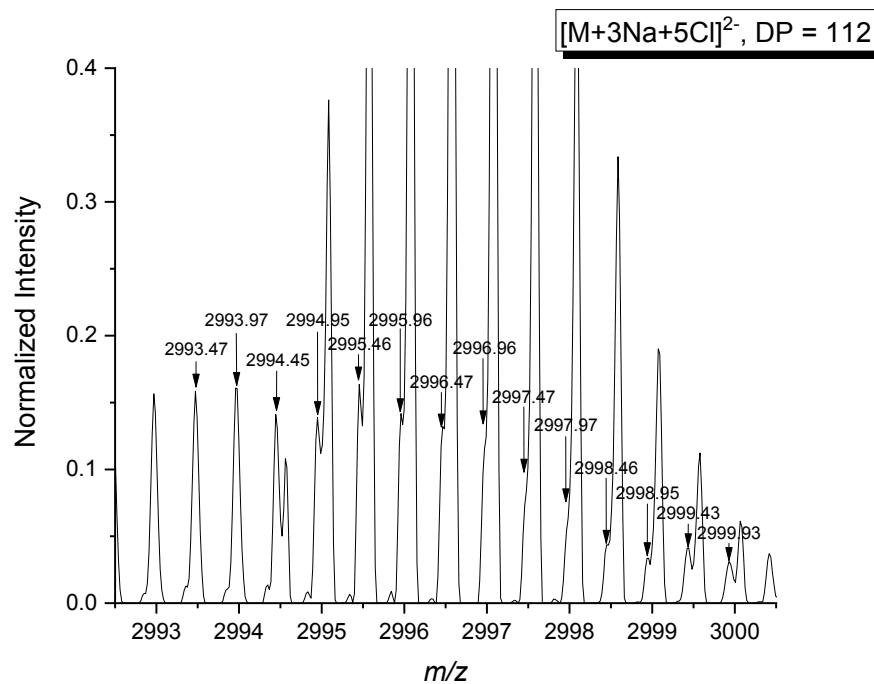$[M+Na+3Cl]^{2-}$, DP = 114

$[M+Na+3Cl]^{2-}$, DP = 114
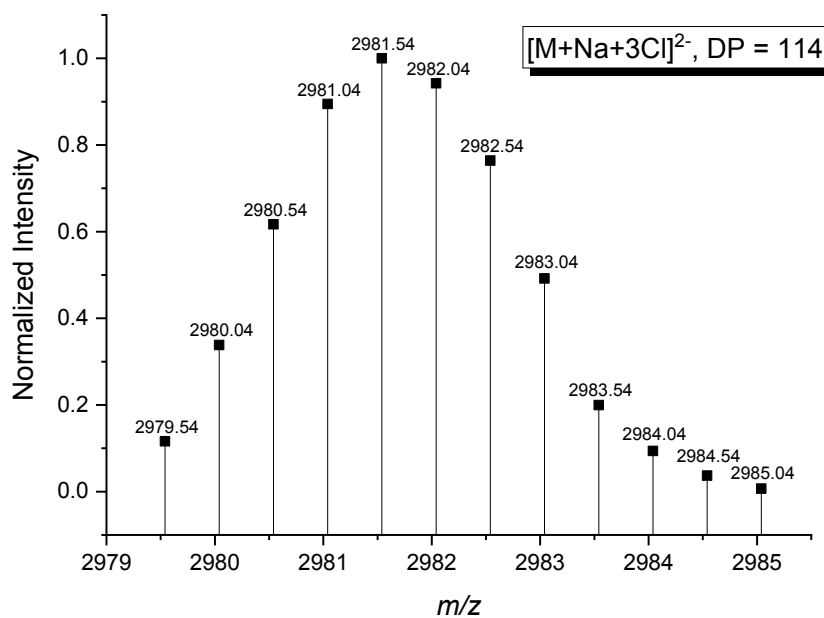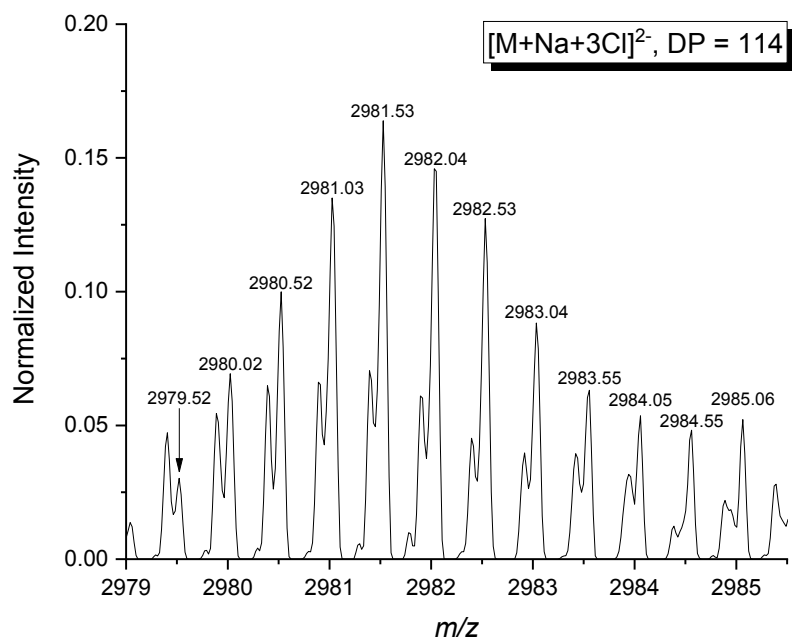
ESI-MS analysis - [M+2Na+4Cl]$^{2-}$ experimental and theoretical distributions

ESI-MS analysis - [M+3Na+5Cl]$^{2-}$ experimental and theoretical distributions

ESI-MS analysis - [M+4Na+6Cl]$^{2-}$ experimental and theoretical distributions