Supporting Information

The label matters: μPET imaging of the biodistribution of low molar mass ^{89}Zr and ^{18}F-labeled poly(2-ethyl-2-oxazoline)

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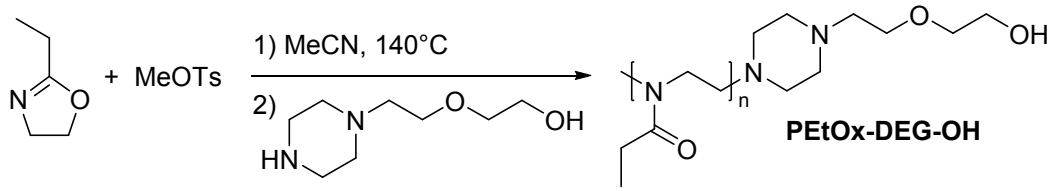
Polymer Synthesis

PEtOx-OH was synthesized by termination of the living polymerization with tetramethylammonium hydroxide as described previously.[1] PEG-OTs was synthesized by tosylation of commercial poly(ethylene glycol) monomethyl ether (2 kDa) according to the literature.[2]

Synthesis of PEtOx-DEG-OH



A solution of EtOx (1.05 g, 10.6 mmol) and MeOTs (80 µL, 0.53 mmol) in acetonitrile with an initial monomer concentration of 4 M was prepared in a microwave vial and closed with a crimp cap under argon. The polymerization mixture was heated to 140 °C for 2 min under microwave irradiation and subsequently cooled to ambient temperature. A solution of 1-[2-(2-Hydroxyethoxy)ethyl]piperazine (185 mg, 1.06 mmol) in 1 mL acetonitrile was stirred over barium oxide for 30 min under argon, filtered, added to the polymerization mixture and stirred at ambient temperature for 1 h. The solution was concentrated under reduced pressure and the residue dissolved in dichloromethane. The solution was filtered through a short pad of alumina and the polymer was precipitated in diethyl ether. DMAc-SEC: M_n = 3.2 kDa, Đ = 1.06; MALDI-TOF MS: M_n = 2.0 kDa, Đ = 1.03.

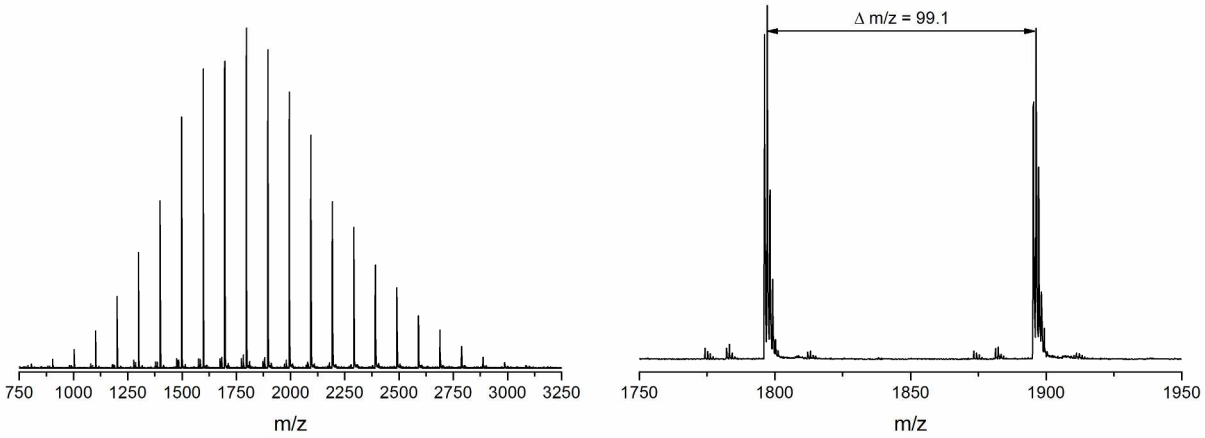
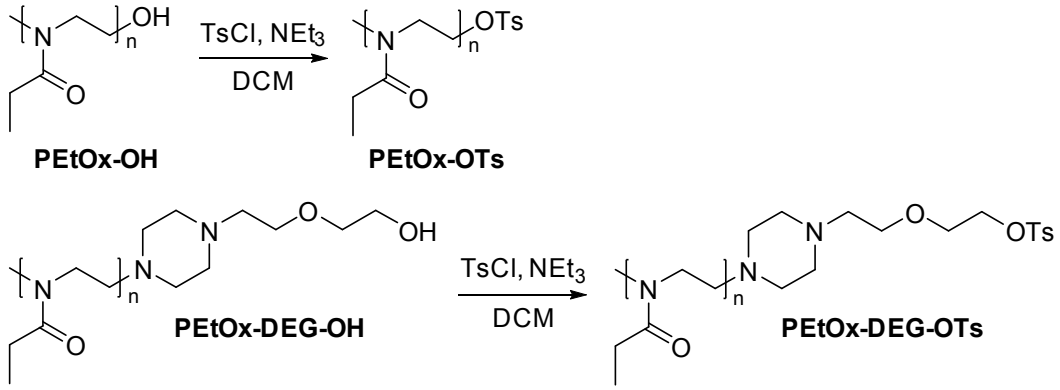


Figure S1 MALDI-TOF MS spectrum of PEtOx-DEG-OH. A zoom of the spectrum on the left is shown on the right.

Synthesis of PEtOx-OTs and PEtOx-DEG-OTs



Tosyl chloride (95 mg, 0.5 mmol) was added to a solution of PEtOx-OH or PEtOx-DEG-OH (M_n = 2 kDa, 200 mg, 0.1 mmol) and triethylamine (69 µL, 0.5 mmol) in 2 mL dichloromethane and the mixture was stirred 48 h at ambient temperature. The solution was filtered through a short pad of alumina and the polymer was precipitated in diethyl ether.

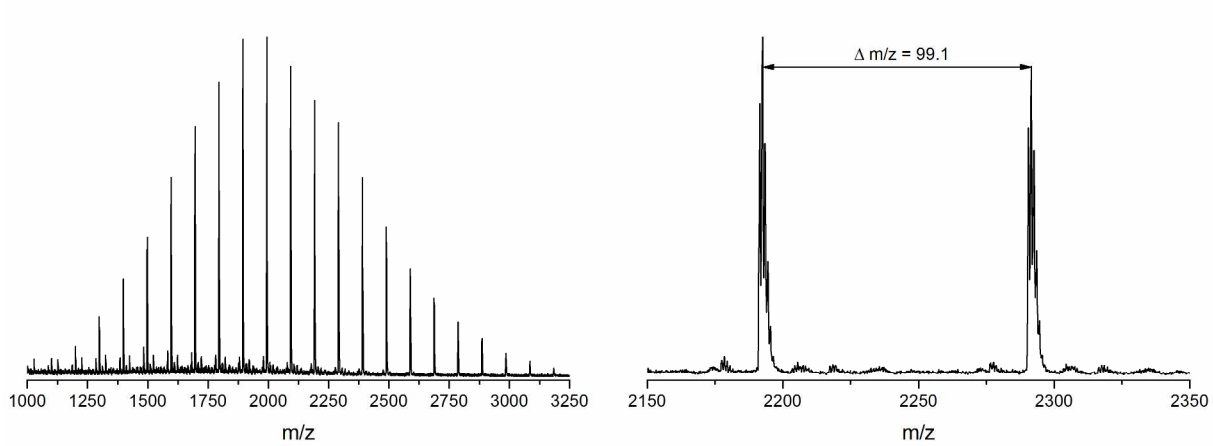


Figure S2 MALDI-TOF MS spectrum of PEtOx -OTs. A zoom of the spectrum on the left is shown on the right.

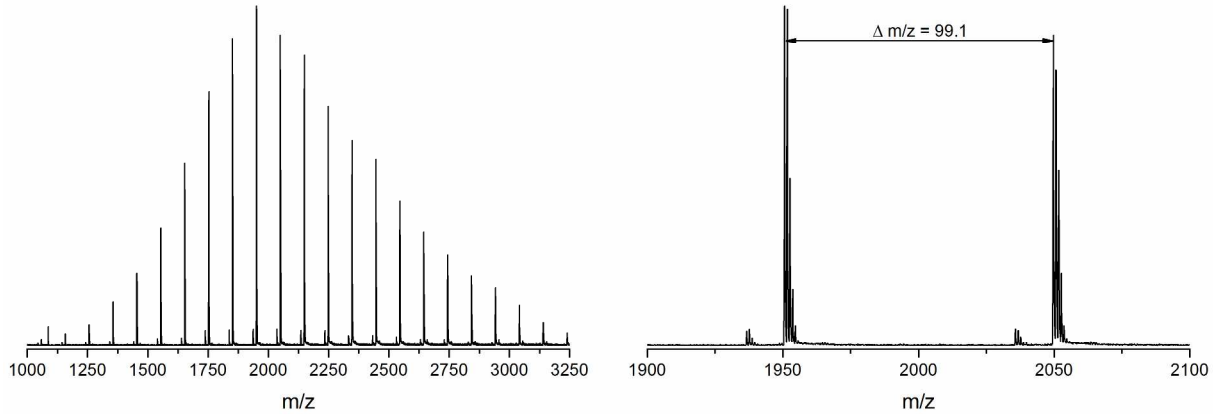
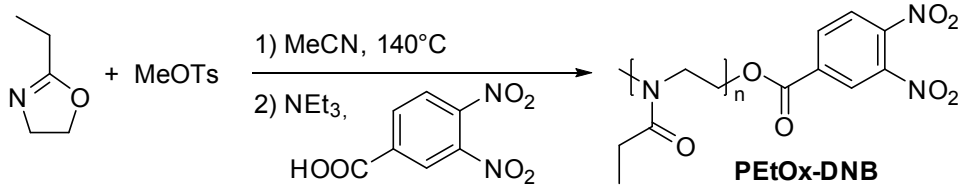


Figure S3 MALDI-TOF MS spectrum of PEtOx –DEG-OTs. A zoom of the spectrum on the left is shown on the right.

Synthesis of PEtOx-DNB



A solution of EtOx (1.05 g, 10.6 mmol) and MeOTs (80 µL, 0.53 mmol) in acetonitrile with an initial monomer concentration of 4 M was prepared in a microwave vial and crimped under argon. The polymerization mixture was heated to 140 °C for 2 min under microwave irradiation and subsequently cooled to ambient temperature. A solution of 3,4-dinitrobenzoic acid (225 mg, 1.06 mmol) and triethylamine (147 µL, 1.06 mmol) in 0.5 mL acetonitrile was added to the polymerization mixture and stirred at 60 °C overnight. The solution was concentrated under reduced pressure and the residue dissolved in dichloromethane. The solution was filtered through a short pad of alumina and the polymer was precipitated in diethyl ether. DMAc-SEC: M_n = 3.2 kDa, Đ = 1.08; ^{1}H NMR MS: M_n = 2.0 kDa.

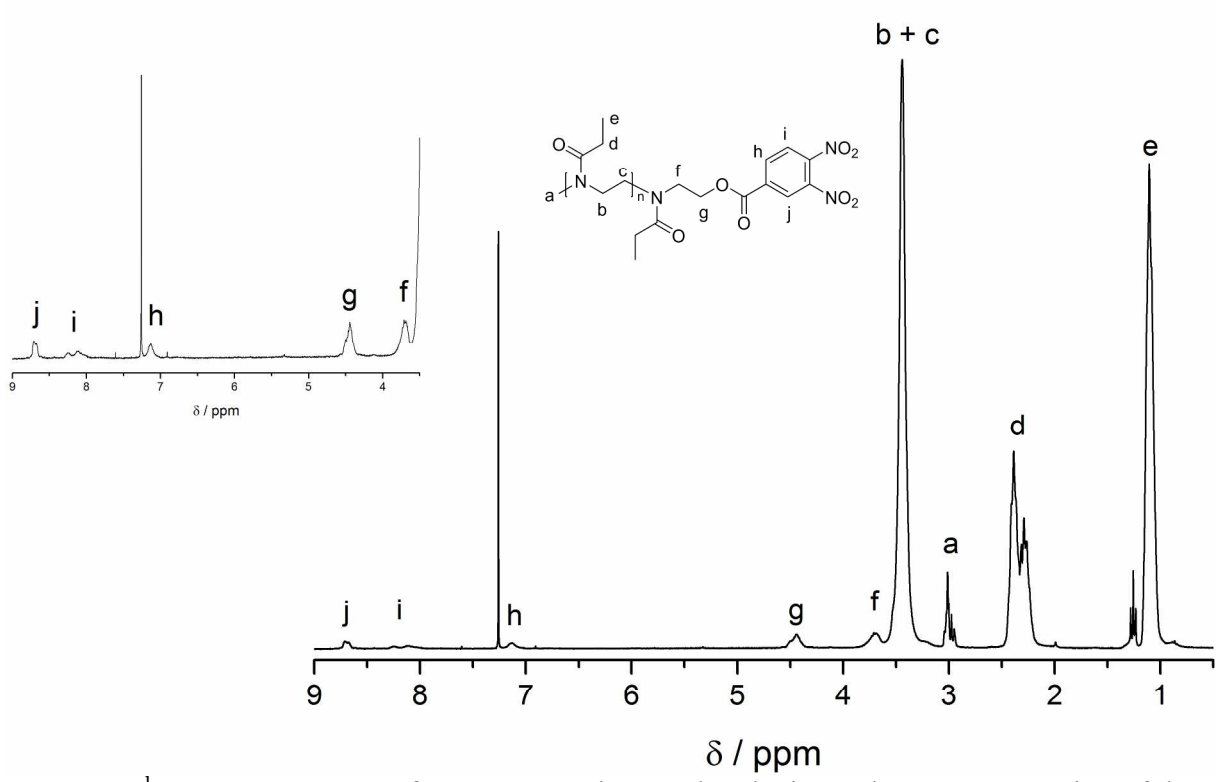


Figure S4 ^{1}H NMR spectrum of PEtOx-DNB in $CDCl_3$. The inset shows an expansion of the region of the peaks originating from the dinitrobenzoate end-group.

Fluorination test reactions of tosylated polymers

TBAF method: PEtOx-OTs or PEtOx-DEG-OTs or PEG-OTs (50 mg, 0.025 mmol) was dissolved in 0.5 mL dry acetonitrile under argon. TBAF (1.0 M in THF, 0.125 mL, 0.125 mmol) was added and the solution was stirred at 80 °C for 1 h. The solvents were removed under

reduced pressure. The residue was dissolved in milli-Q water, passed through Sephadex G-25 (PD-10 column) and the macromolecular fraction lyophilized.

KF/K[2.2.2] method: PEtOx-OTs or PEtOx-DEG-OTs or PEG-OTs (50 mg, 0.025 mmol), KF (predried in a vacuum oven at 150 °C, 7.3 mg, 0.125 mmol) and K[2.2.2] (47 mg, 0.125 mmol) were dissolved in 0.5 mL dry acetonitrile under argon and the solution was stirred at 80 °C for 1 h. The solvents were removed under reduced pressure. The residue was dissolved in milli-Q water, passed through Sephadex G-25 (PD-10 column) and the macromolecular fraction lyophilized.

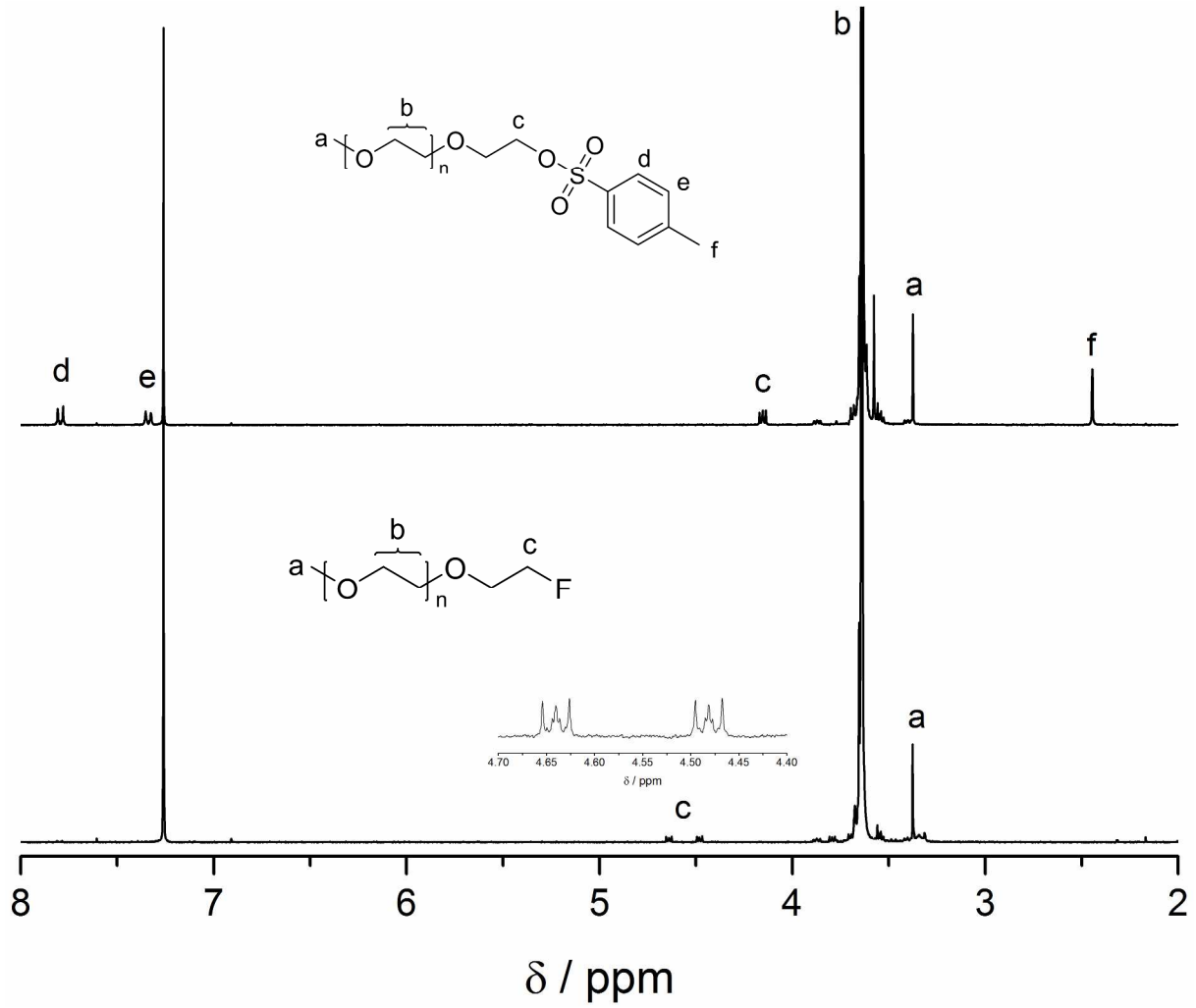


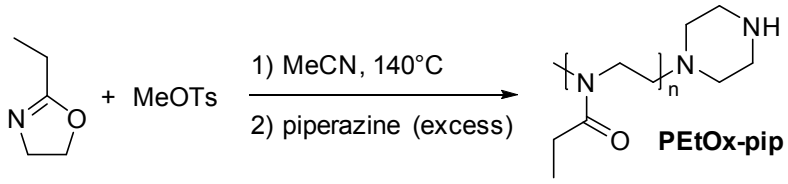
Figure S5 ^{1}H NMR spectra of PEG-OTs (top) and PEG-F (bottom) in $CDCl_3$. The zoom shows the peaks of CH_2F (c).

Fluorination test reactions by S_NAr

TBAF method: PEtOx-DNB (50 mg, 0.025 mmol) was dissolved in 0.5 mL dry DMSO under argon. TBAF (1.0 M in THF, 0.125 mL, 0.125 mmol) was added and the solution was stirred at 150 °C for 1 h. Water was added and the reaction mixture was extracted with dichloromethane. The organic phases were dried over magnesium sulfate and the solvents were removed under reduced pressure. The residue was dissolved in milli-Q water, passed through Sephadex G-25 (PD-10 column) and the macromolecular fraction lyophilized.

KF/K[2.2.2] method: PEtOx-DNB, KF (predried in a vacuum oven at 150 °C, 7.3 mg, 0.125 mmol) and K[2.2.2] (47 mg, 0.125 mmol) were dissolved in 0.5 mL dry acetonitrile under argon and the solution was stirred at 80 °C for 1 h. Water was added and the reaction mixture was extracted with dichloromethane. The organic phases were dried over magnesium sulfate and the solvents were removed under reduced pressure. The residue was dissolved in milli-Q water, passed through Sephadex G-25 (PD-10 column) and the macromolecular fraction lyophilized.

Synthesis of PEtOx-pip



See main manuscript for experimental.

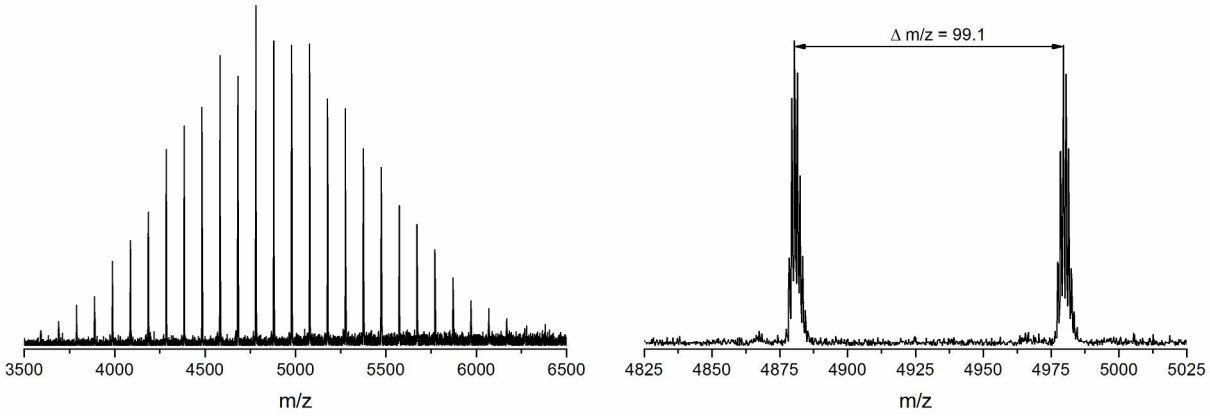
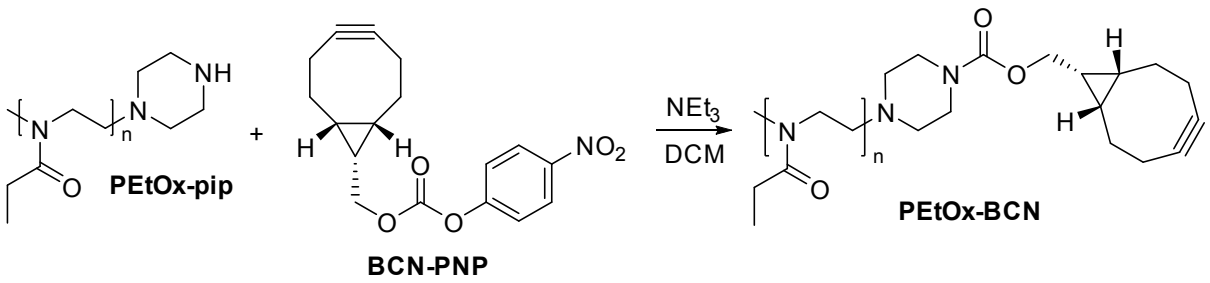


Figure S6 MALDI-TOF MS spectrum of PEtOx -pip. A zoom of the spectrum on the left is shown on the right.

Synthesis of PEtOx-BCN



See main manuscript for experimental.

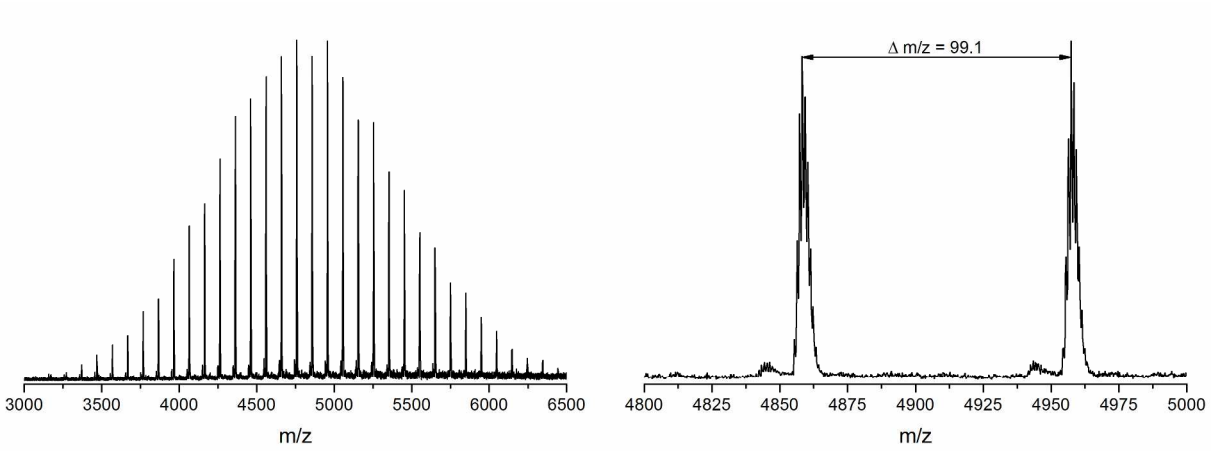


Figure S7 MALDI-TOF MS spectrum of PEtOx -BCN. A zoom of the spectrum on the left is shown on the right.

(1) de la Rosa, V. R.; Tempelaar, S.; Dubois, P.; Hoogenboom, R.; Mespouille, L.; *Polym. Chem.* **2016,** *7*, 1559-1568.
(2) Glassner, M.; Delaittre, G.; Kaupp, M.; Blinco, J. P.; Barner-Kowollik, C.; *J. Am. Chem. Soc.* **2012,** *134*, 7274-7277.