Supplementary Information

Synthesis and Characterization of Reactive PEO-PMCL Polymersomes

Matthew A. Petersen, Ligeng Yin, Efrosini Kokkoli, Marc A. Hillmyer

Department of Chemical Engineering and Materials Science and Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455-0431

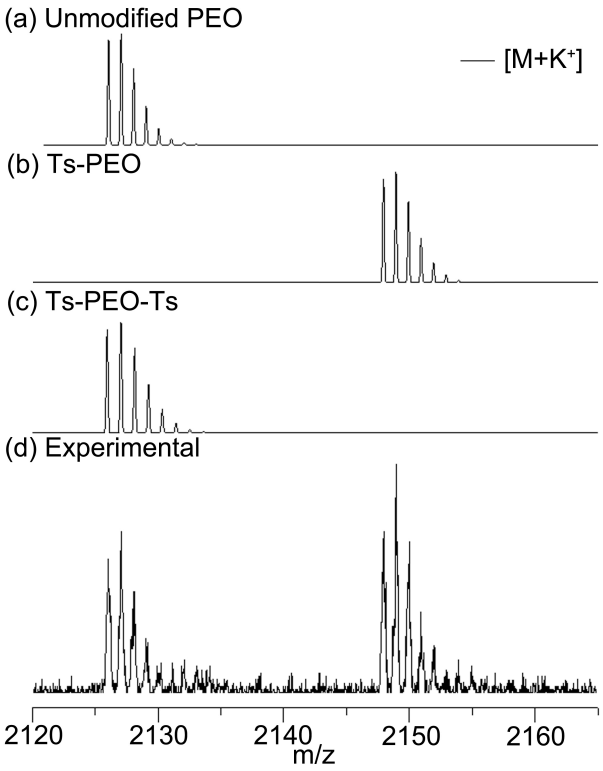

Figure S1. Predicted (a)-(c) and experimental ESI-MS data (d) for tosylated PEO. While Ts-PEO is clearly distinguishable, Ts-PEO-TS and unmodified PEO overlap.

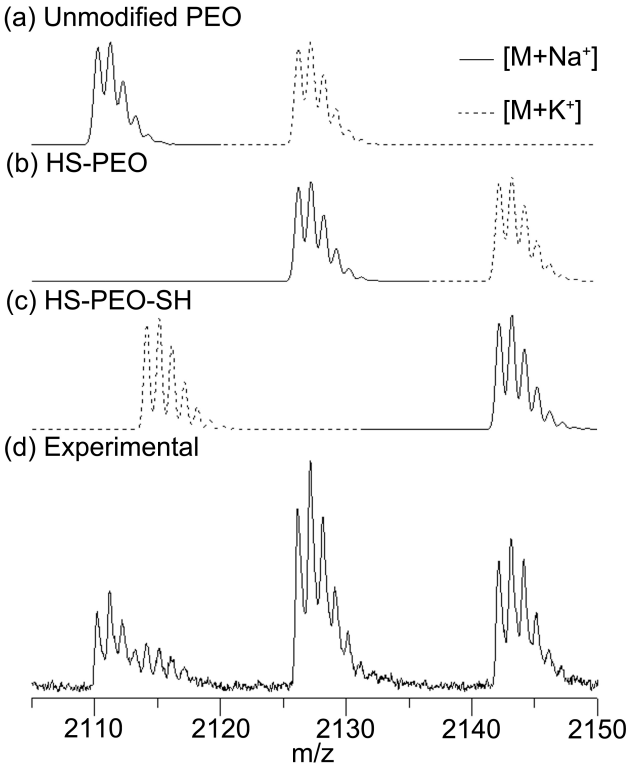

Figure S2. Predicted (a)-(c) and experimental MALDI-MS data (d) for a combination of unmodified PEO, S-PEO and S-PEO-S.

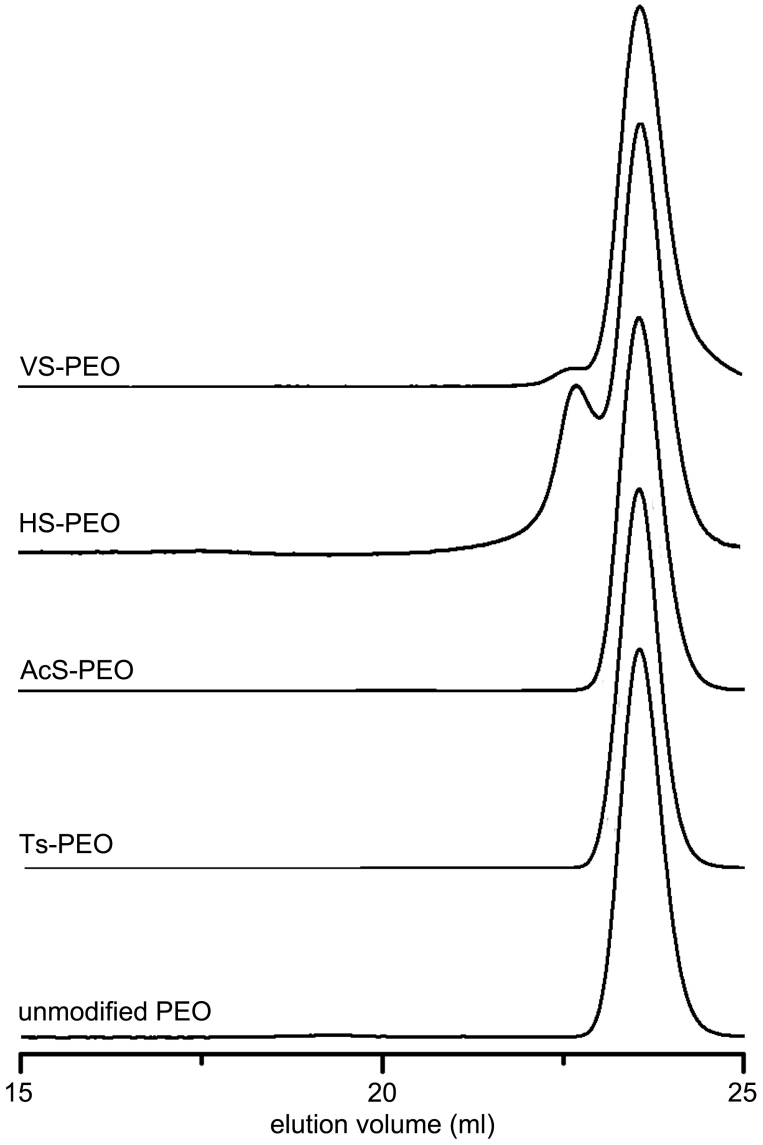

Figure S3. SEC traces for each form of modified PEO.

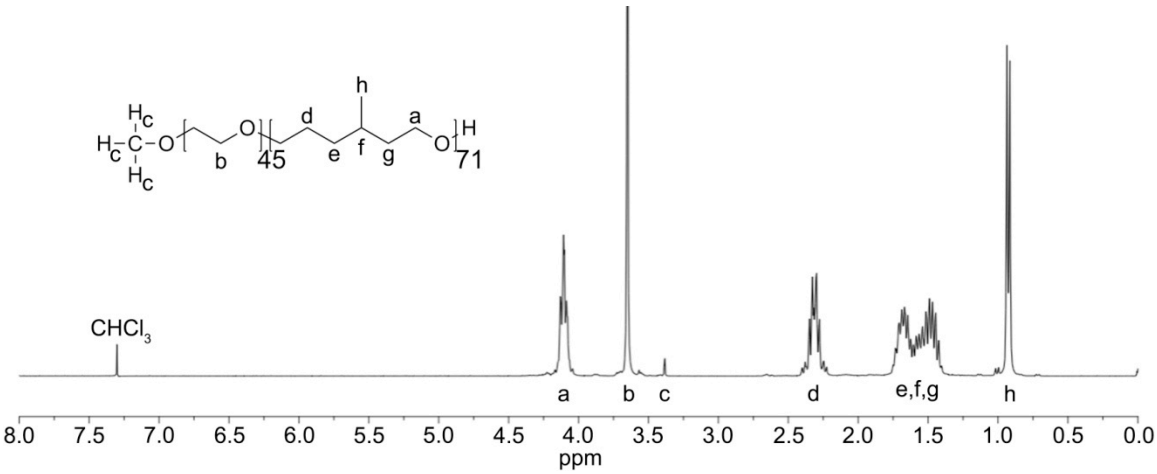

Figure S4. 300 MHz ^{1}H NMR spectrum and assignments for nonreactive PEO-PMCL.

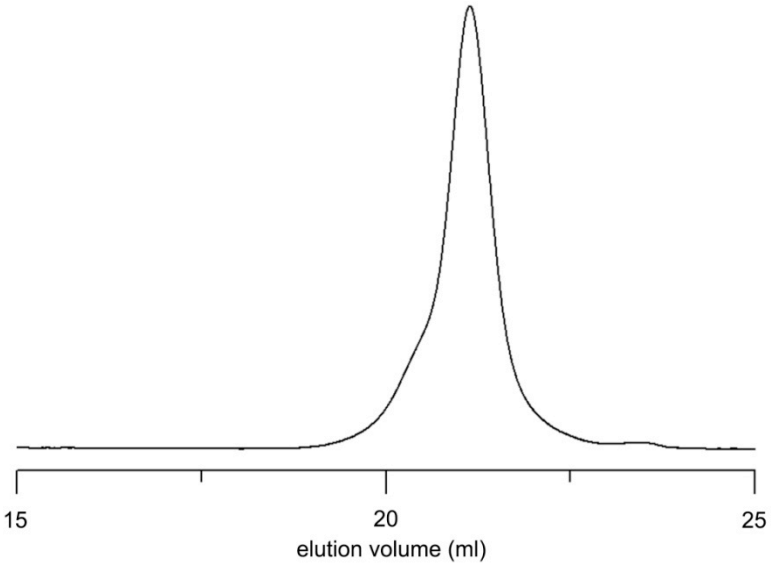

Figure S5. SEC trace for nonreactive PEO-PMCL.

Equation S1. Due to the uncertainty of quantifying the fraction of each form of modified PEO (VS-PEO-VS, VS-PEO and unmodified PEO) by mass spectrometry we wished to use ^{1}H NMR spectroscopy to determine these fractions. We collected the following data by ^{1}H NMR spectroscopy before and after polymerization of MCL using modified PEO: a PEO chain end had a 42.5% chance of bearing a vinyl sulfone moiety, the remaining chain ends initiated

polymerization of MCL, the initial ratio of MCL monomer to PEO was 91 and polymerization was carried out to 75% conversion. These data allowed us to formulate and solve three simultaneous equations to approximate relative mole fraction of each molecule without the assumptions necessary for quantification using MS techniques. In (a) we state that only these three molecules are active in the system and that following polymerization from PEO precursors we generate MCL from each hydroxyl group while vinyl sulfone groups remain intact. In (b) we relate the ratio of vinyl sulfone groups to the number of PEO chains (*via* their respective 1H NMR proton integrations) to the fractions of each form of modified PEO. In (c) we relate the relative number of PMCL protons following polymerization from the crude VS-PEO to those of PEO, including the contribution to the PEO resonance of VS-PEO-VS. The amount of MCL consumed during polymerization is known, as is the final molecular weight of a PMCL block. Solving these three equations results in (d), the mole fraction of each component. In the following, '*f*' refers to the mole fraction of a given component. $^1H_{VS}$ refers to the integrated area of the proton resonance at 6.46 ppm. $^1H_{PEO}$ refers to the integrated area of the proton resonance at 3.65 ppm. N_{MCL} refers to the average number of repeat units in a block of MCL.

$$\text{(a)}\ f_{VS-PEO-VS} + f_{VS-PEO-PMCL} + f_{PMCL-PEO-PMCL} = 1$$

$$\text{(b)}\ {}^1H_{VS} = 2 \cdot f_{VS-PEO-VS} \cdot \frac{{}^1H_{PEO}}{180} + f_{VS-PEO-PMCL} \cdot \frac{{}^1H_{PEO}}{180} + 0 \cdot N_{PEO} \cdot f_{PMCL-PEO-PMCL}$$

$$\text{(c)}\ \frac{{}^1H_{MCL}}{{}^1H_{PEO}} = \frac{2 \cdot N_{MCL} \cdot f_{VS-PEO-PMCL}}{180 + 180 \cdot f_{VS-PEO-VS}} + \frac{4 \cdot N_{MCL} \cdot f_{PMCL-PEO-PMCL}}{180 + 180 \cdot f_{VS-PEO-VS}}$$

$$\text{(d)}\ f_{VS-PEO-VS} \approx 0.1 \quad f_{VS-PEO-PMCL} \approx 0.7 \quad f_{PMCL-PEO-PMCL} \approx 0.2$$

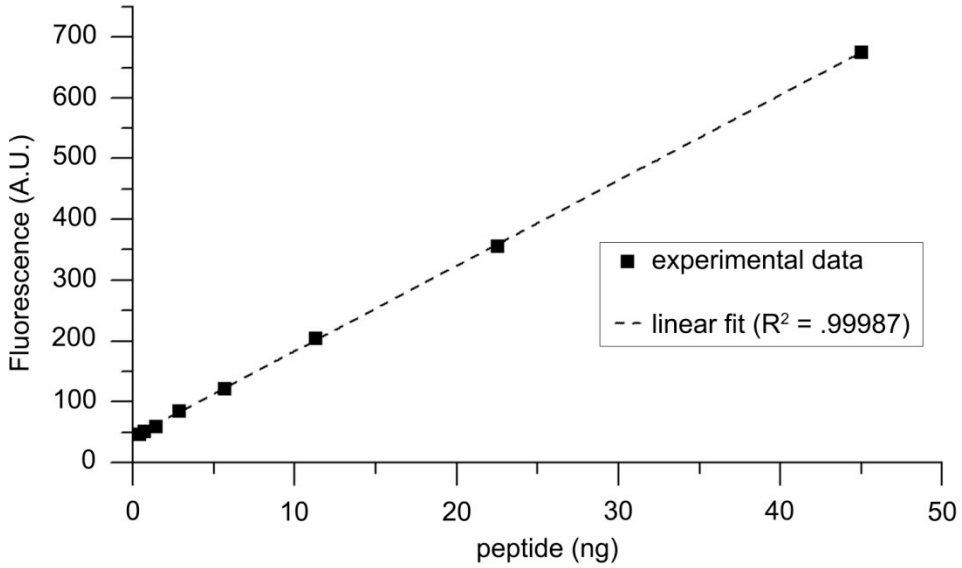

Figure S6. Calibration curve used to quantify attached peptide using fluorescamine.