Electronic Supplementary Information

Synthesis of Cyclic Peptide Disulfide-PHPMA Conjugates via Sequential Active Ester Aminolysis and CuAAC Coupling

Kemal Arda Günay, Harm-Anton Klok*

École Polytechnique Fédérale de Lausanne (EPFL), Institut des Matériaux and Institut des Sciences et Ingénierie Chimiques, Laboratoire des Polymères, Bâtiment MXD, Station 12, CH-1015 Lausanne, Switzerland

*To whom correspondence should be addressed: E-mail: harm-anton.klok@epfl.ch; Fax: + 41 21 693 5650; Tel: + 41 21 693 4866.
Figure S1: $^1$H-NMR spectrum of the PPFMA polymer used in this study prior to removal of dithiobenzoate end-groups. **Top:** Enlarged region between 7.15-8.00 ppm highlighting the signals associated to the dithiobenzoate end-groups; **Bottom:** Complete $^1$H-NMR spectrum of the PPFMA polymer in CDCl$_3$. * = Residual solvent peaks.
Figure S2: (A) ESI-MS spectrum of crude Pep1 after Tl(CF₃COO)₃ mediated oxidation. (B) ESI-MS spectrum of crude Pep1 after N-terminal azide functionalization. (C) ESI-MS spectrum and (D) HPLC elution chromatogram of pure Pep1.
Figure S3: HPLC elution profiles and corresponding ESI-MS spectra of purified cyclic peptide disulfides (A) Pep2, (B) Pep3 and (C) Pep4.
**Figure S4:** $^1$H-NMR spectrum of P1 in methanol-d$_4$. * = 1 H peaks associated with the hydrogen of the amide groups.

**Figure S5:** $^1$H-NMR spectrum of the copolymer obtained using CuAAC condition C5 (PC5) in methanol-d$_4$. * = 1H peaks associated with the hydrogen of the amide groups.
Figure S6: $^1$H-NMR spectrum of PPepl\textsubscript{a} in methanol-d\textsubscript{4}. * = 1H peaks associated with the hydrogen of the amide groups.

Figure S7: $^1$H-NMR spectrum of PPepl\textsubscript{b} in methanol-d\textsubscript{4}. * = 1H peaks associated with the hydrogen of the amide groups.
Figure S8: $^1$H-NMR spectrum of PPep2 in methanol-d$_4$. * = 1H peaks associated with the hydrogen of the amide groups.

Figure S9: $^1$H-NMR spectrum of PPep3 in methanol-d$_4$. 
Figure S10: $^1$H-NMR spectrum of PPe4 in methanol-d$_4$. 