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.

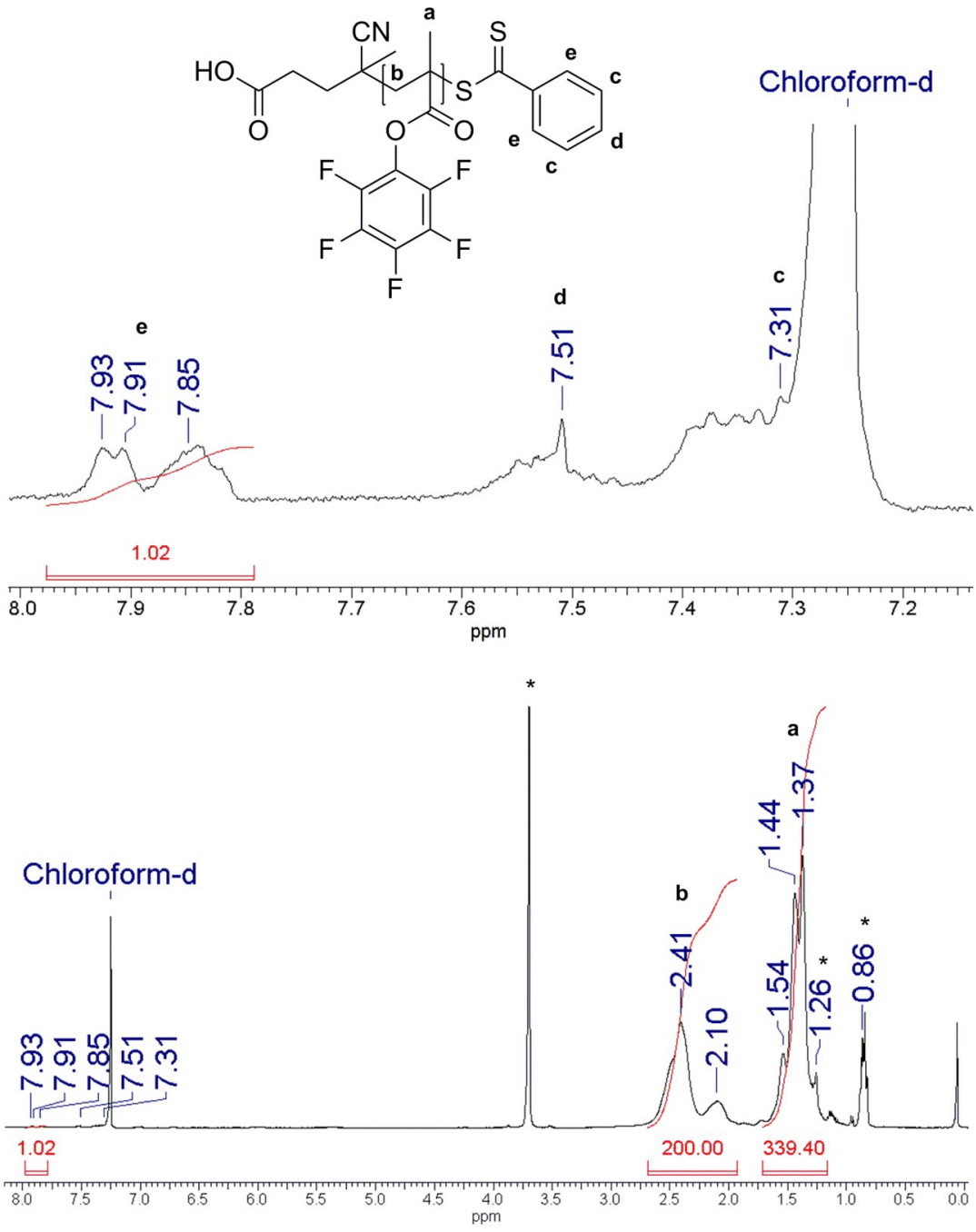

Figure S1: ^{1}H-NMR spectrum of the PPFMA polymer used in this study prior to removal of dithiobenzoate end-groups. **Top:** Enlarged region between 7.15-8.00 ppm highlighting the signals associated to the dithiobenzoate end-groups; **Bottom:** Complete ^{1}H-NMR spectrum of the PPFMA polymer in $CDCl_3$. * = Residual solvent peaks.

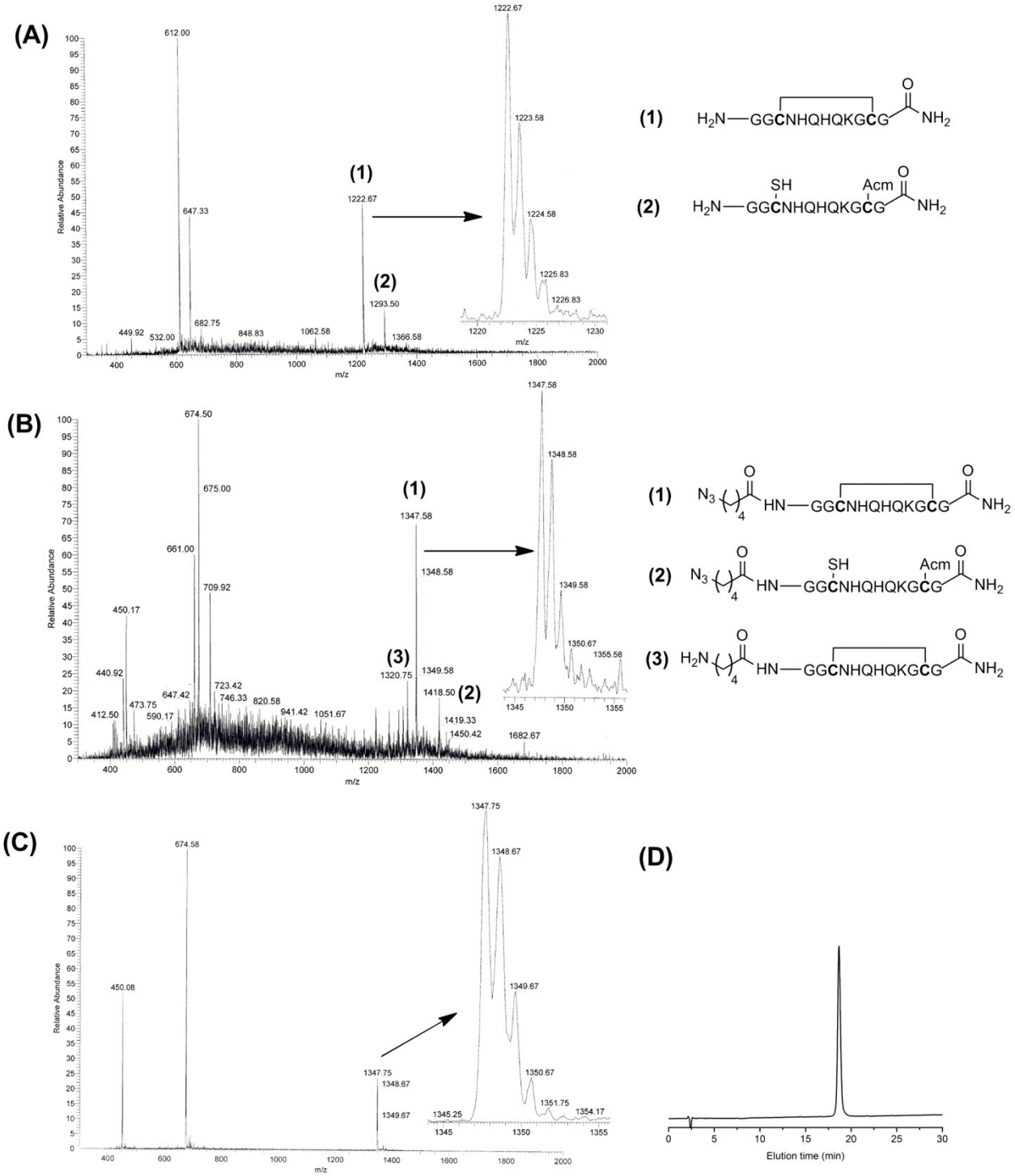

Figure S2: (A) ESI-MS spectrum of crude **Pep1** after $Tl(CF_3COO)_3$ mediated oxidation. (B) ESI-MS spectrum of crude **Pep1** after N-terminal azide functionalization. (C) ESI-MS spectrum and (D) HPLC elution chromatogram of pure **Pep1**.

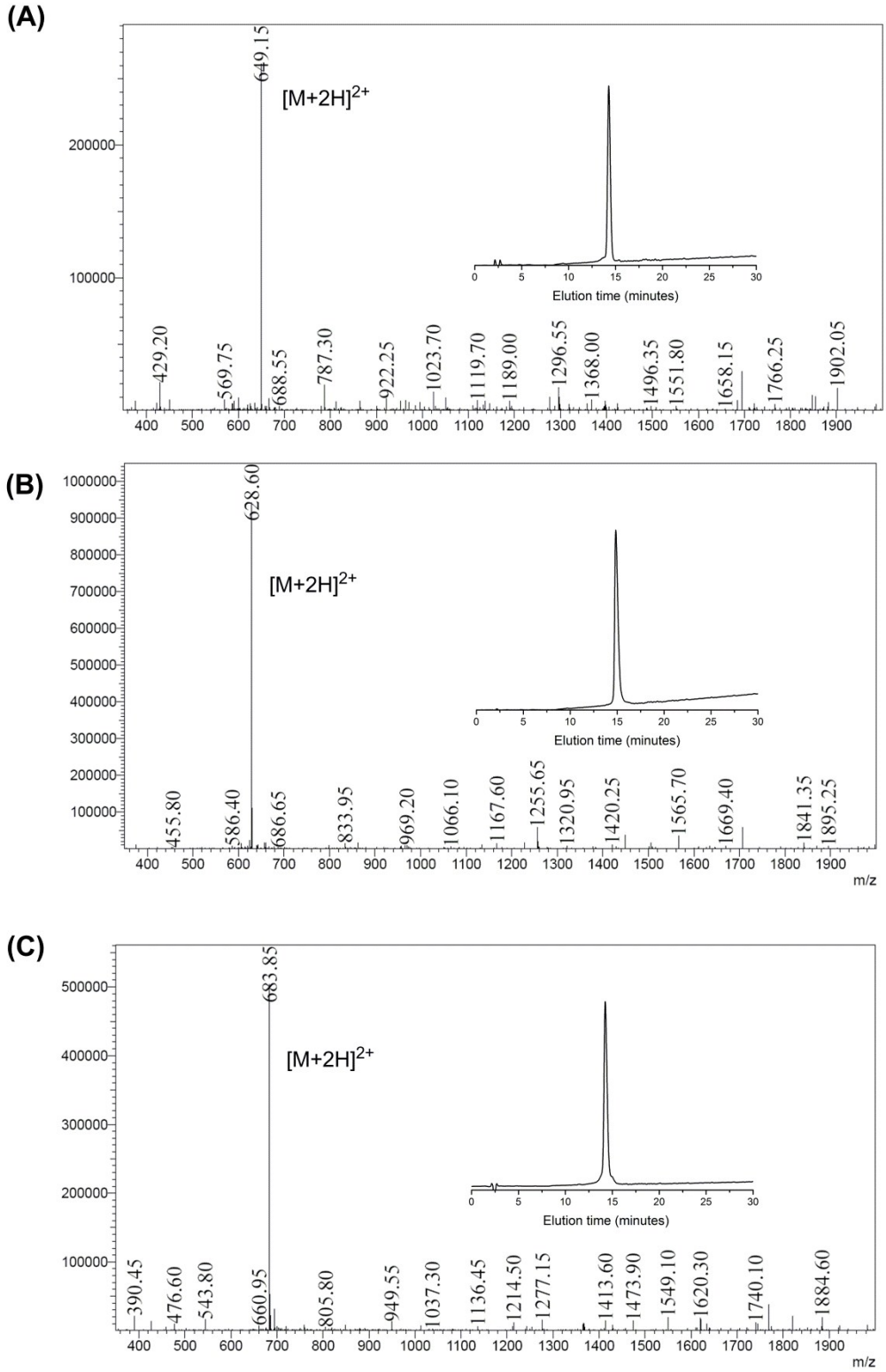

Figure S3: HPLC elution profiles and corresponding ESI-MS spectra of purified cyclic peptide disulfides (A) **Pep2,** (B) **Pep3** and (C) **Pep4**.

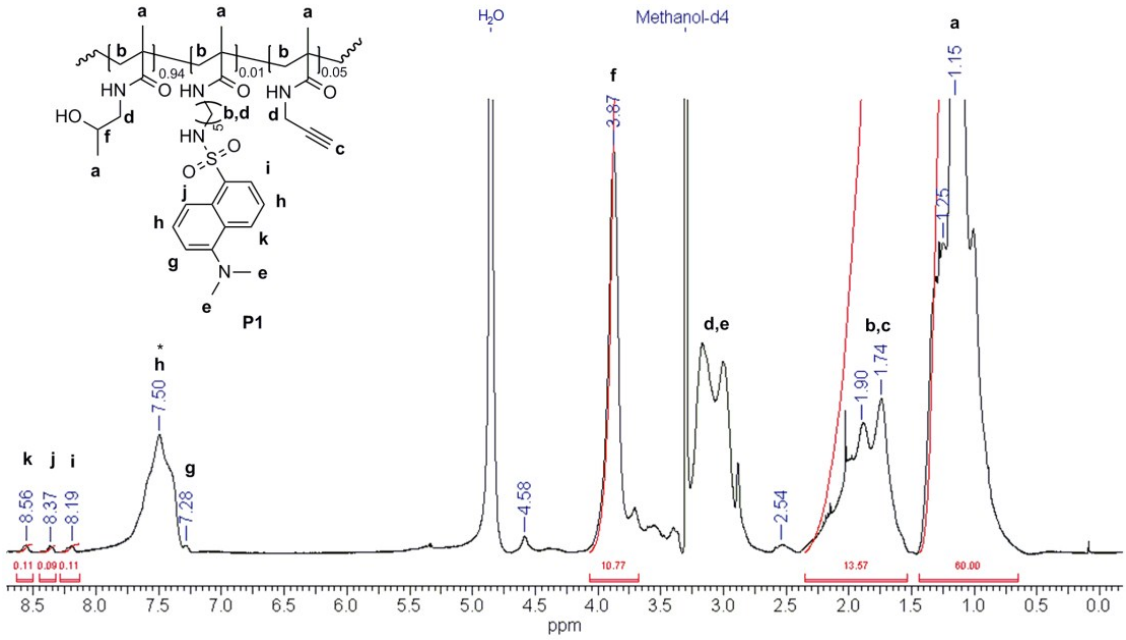

Figure S4: ^{1}H-NMR spectrum of **P1** in methanol-d_4. * = 1 H peaks associated with the hydrogen of the amide groups.

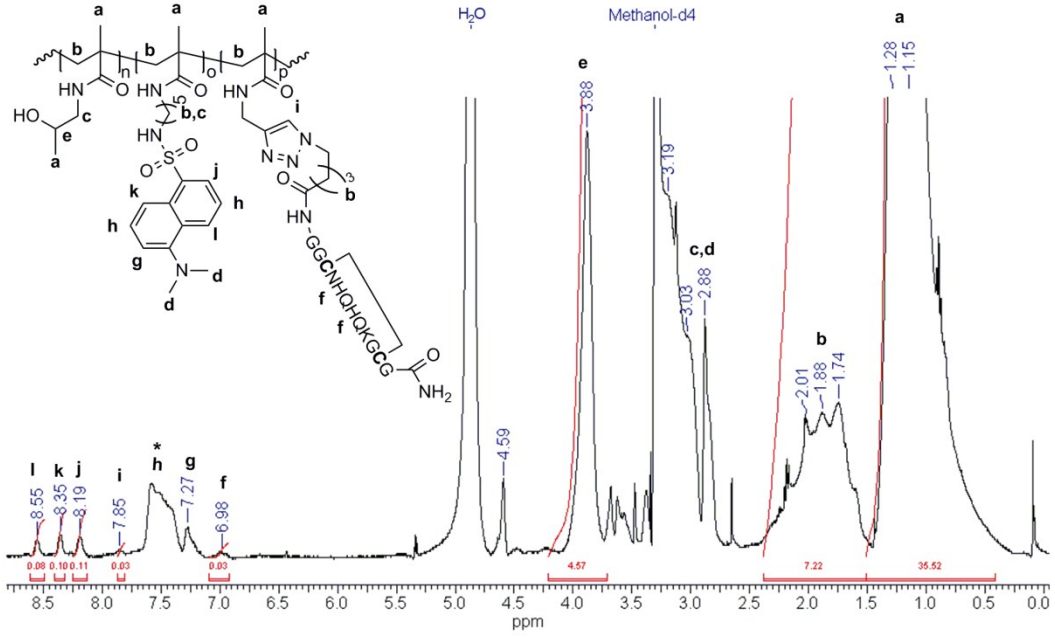

Figure S5: ^{1}H-NMR spectrum of the copolymer obtained using CuAAC condition **C5 (PC5)** in methanol-d_4. * = 1H peaks associated with the hydrogen of the amide groups.

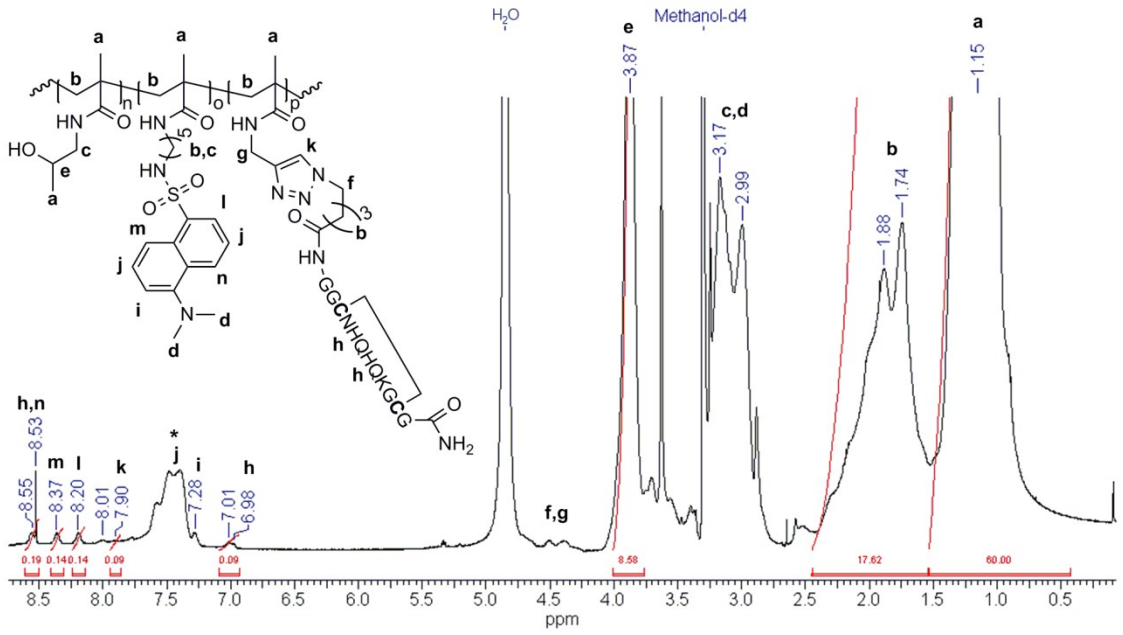

Figure S6: ^{1}H-NMR spectrum of **PPep1a** in methanol-d_4. * = 1H peaks associated with the hydrogen of the amide groups.

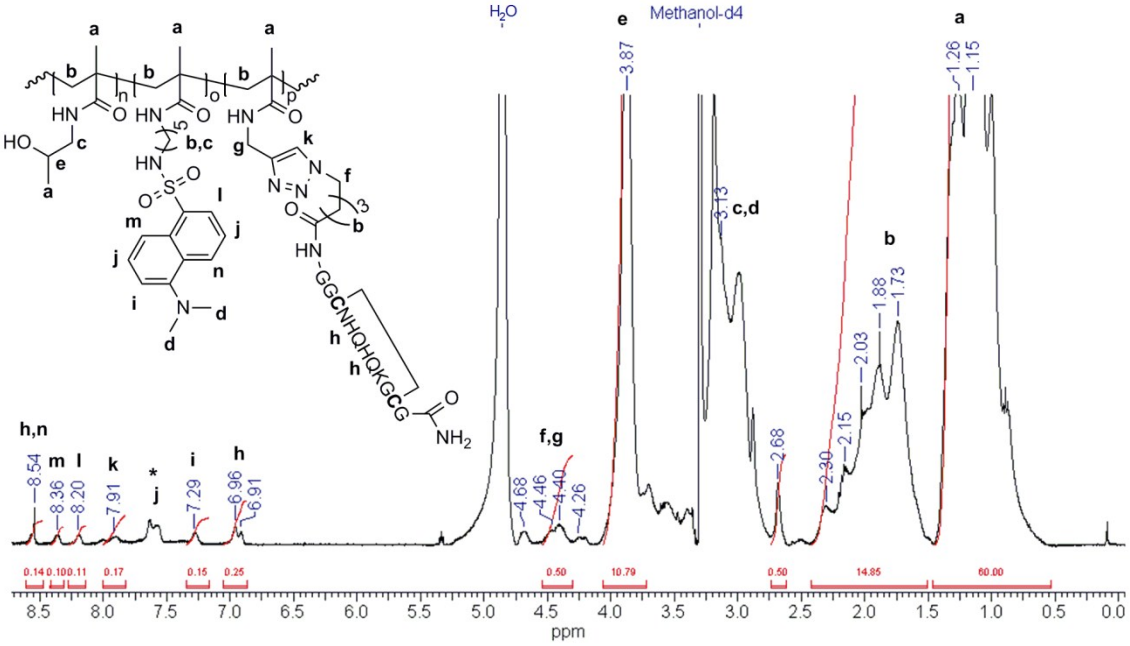

Figure S7: ^{1}H-NMR spectrum of **PPep1b** in methanol-d_4. * = 1H peaks associated with the hydrogen of the amide groups.

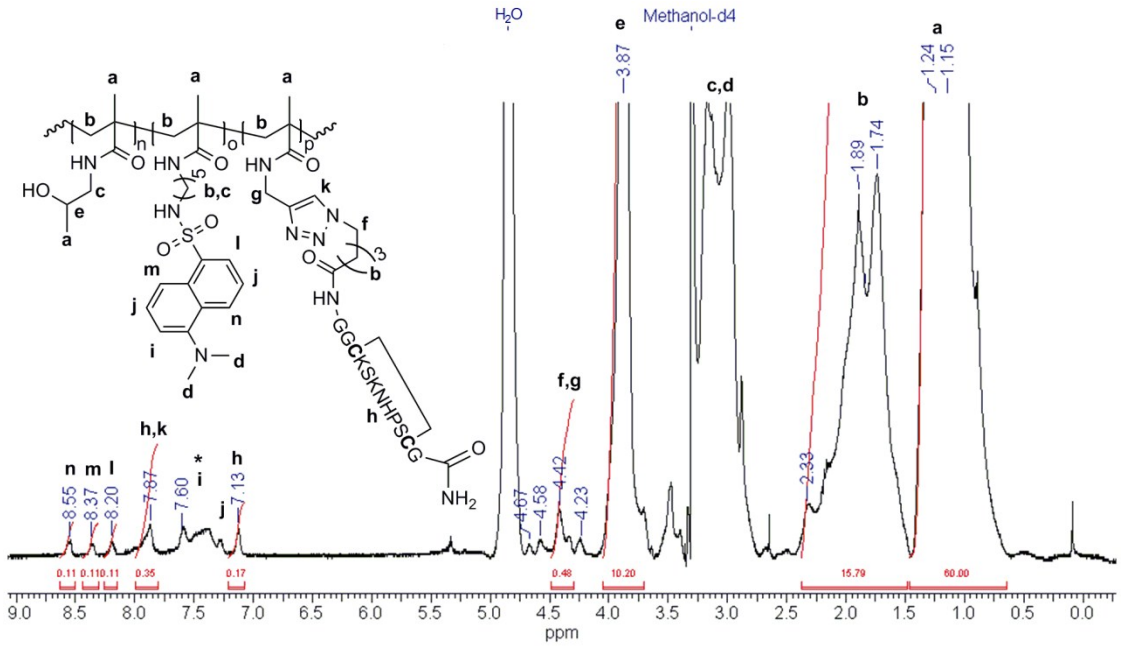

Figure S8: ^{1}H-NMR spectrum of **PPep2** in methanol-d_4. * = 1H peaks associated with the hydrogen of the amide groups.

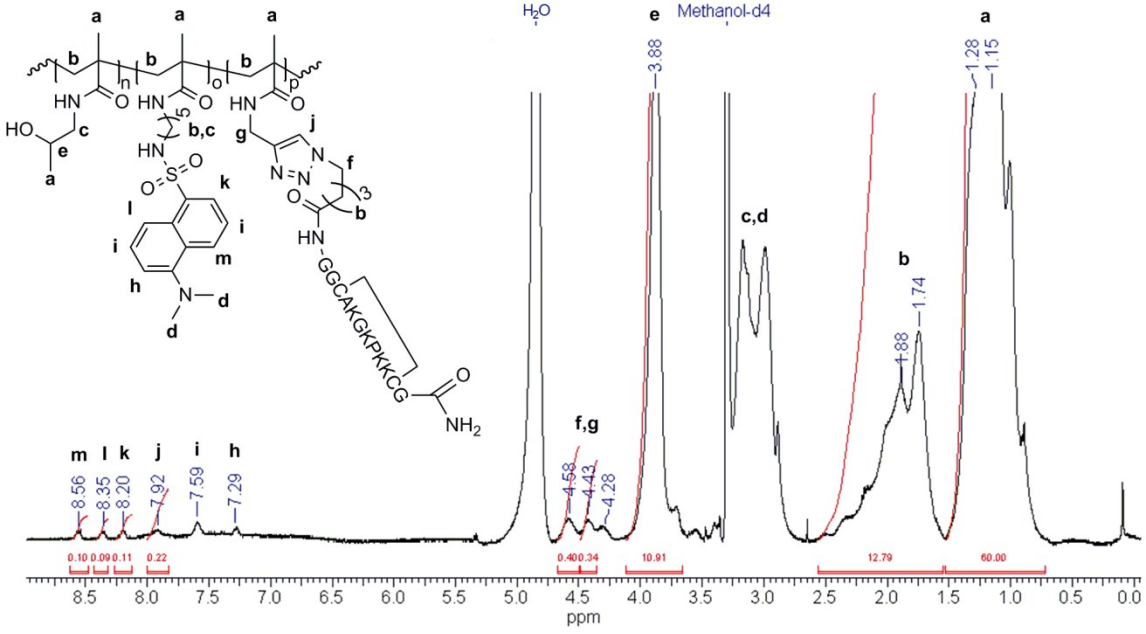

Figure S9: ^{1}H-NMR spectrum of **PPep3** in methanol-d_4.

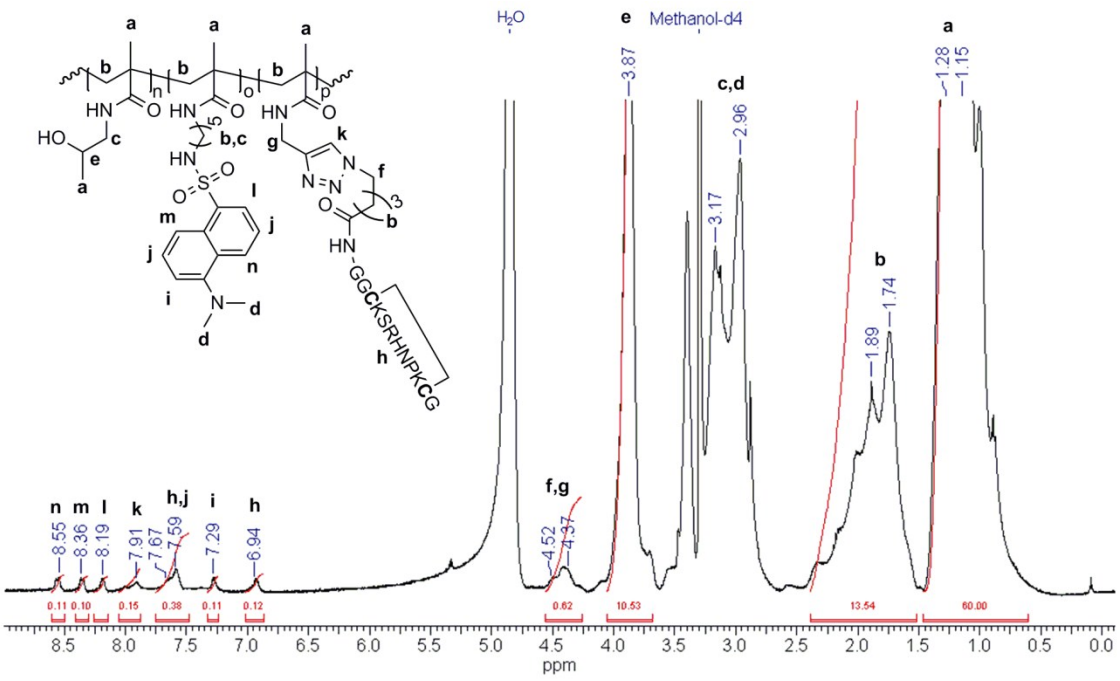

Figure S10: ^{1}H-NMR spectrum of **PPep4** in methanol-d_4.