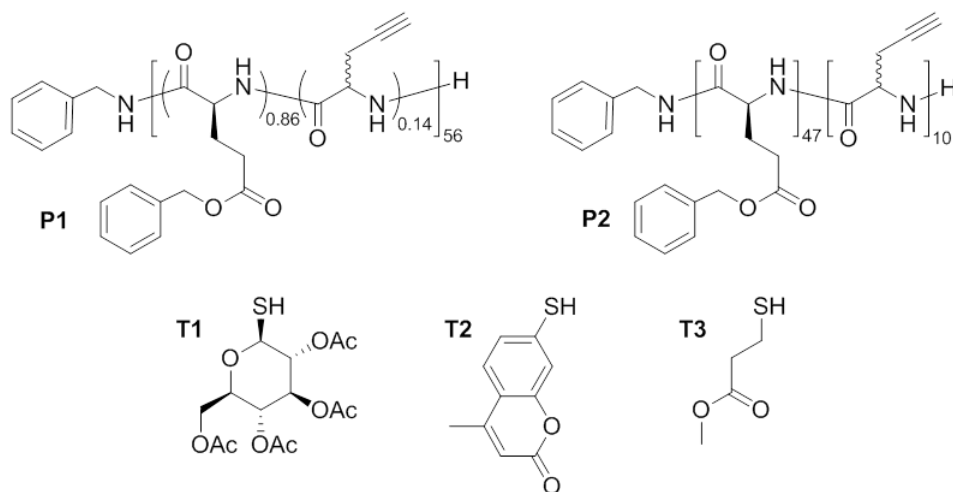


Electronic Supporting Information to

Photochemical thiol-yne functionalization of polypeptide scaffolds

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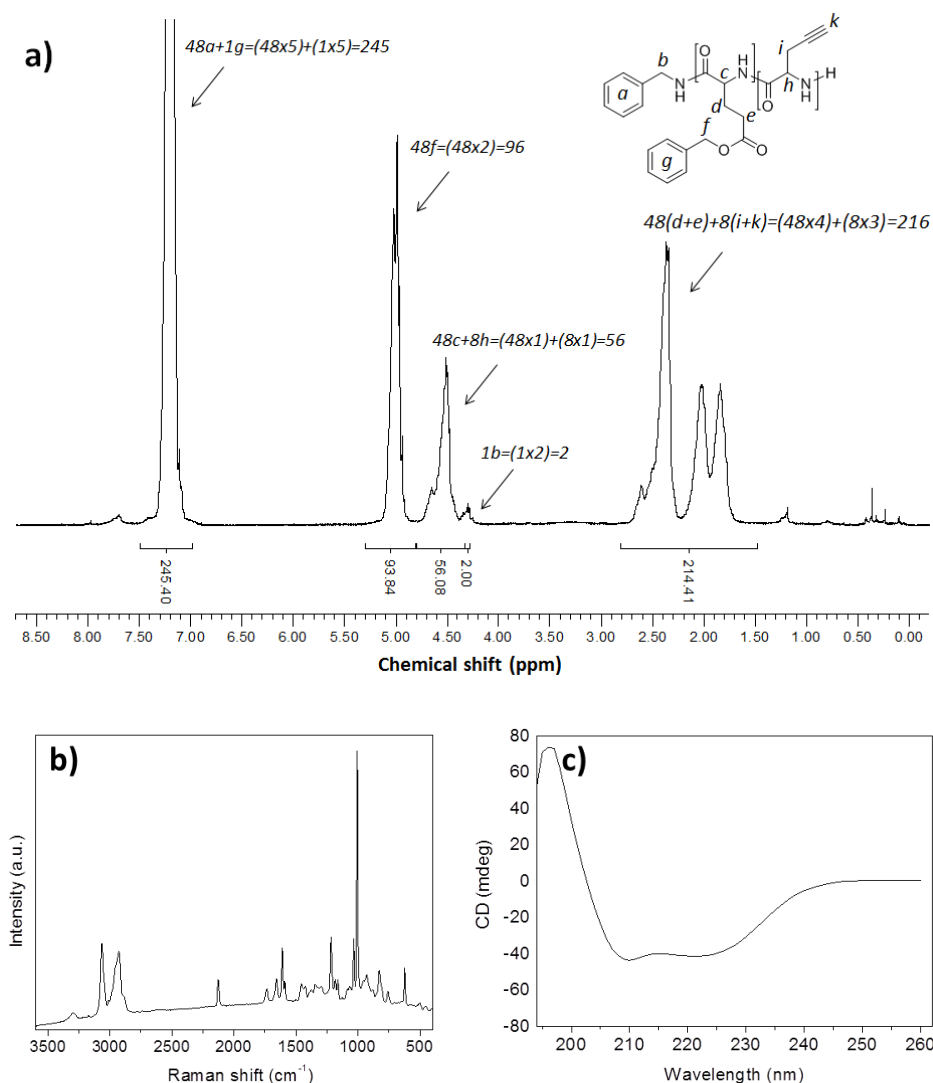


Figure S1: ¹H NMR (400.1 MHz, TFA-d) (a), Raman (b), and CD spectra (acetonitrile, 25 °C) (c) of copolypeptide **P1**.

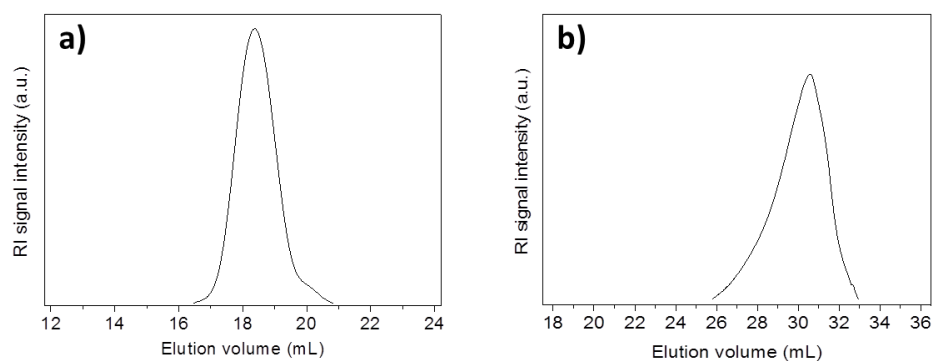


Figure S2: SEC traces of **P1**, eluent: NMP + LiBr, 70 °C (a) and THF, 25 °C (b).

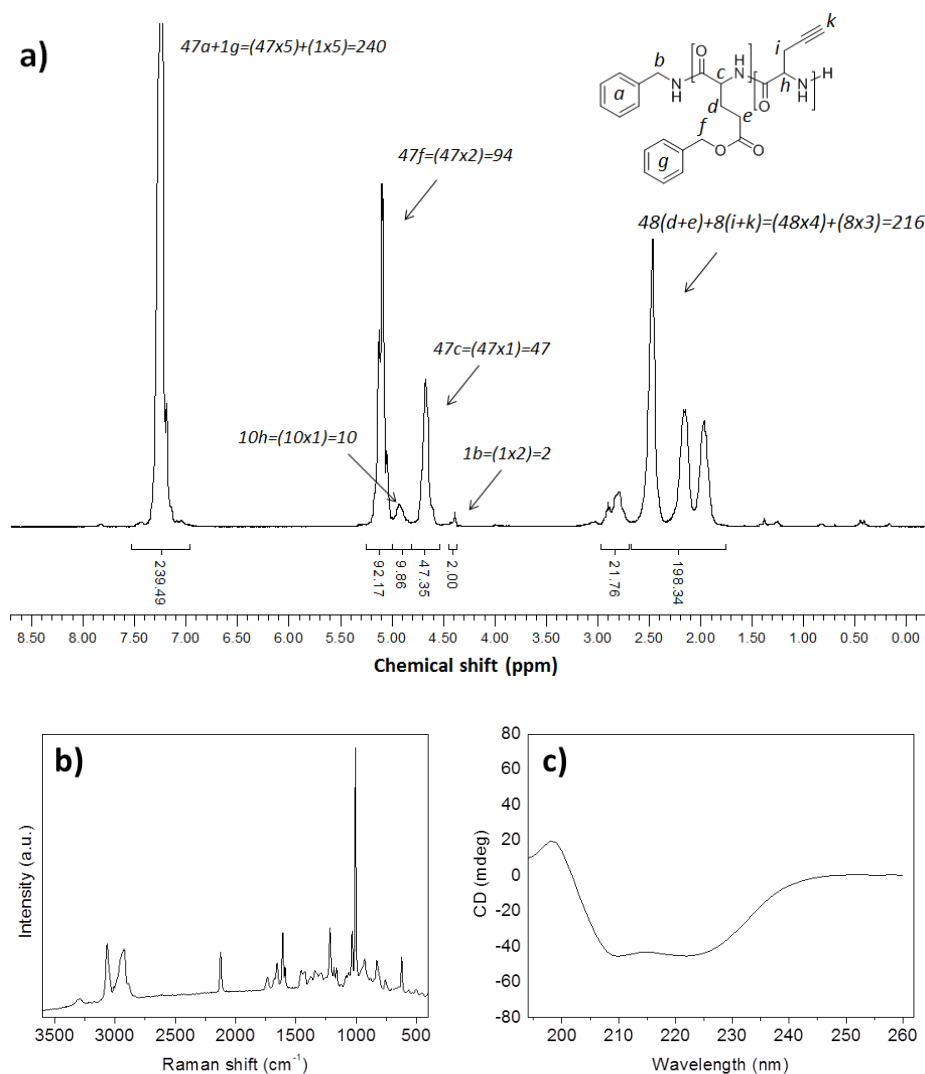


Figure S3: ¹H NMR (400.1 MHz, TFA-d) (a), Raman (b), and CD spectra (acetonitrile, 25 °C) (c) of block copolypeptide **P2**.

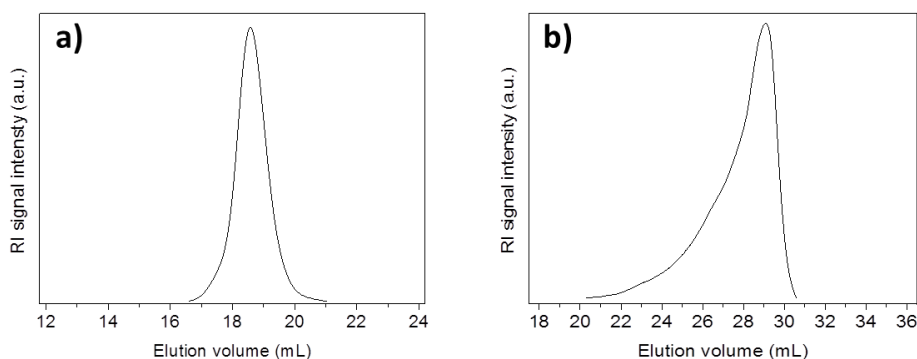


Figure S4: SEC traces of **P2**, eluent: NMP + LiBr, 70 °C (a) and THF, 25 °C (b).

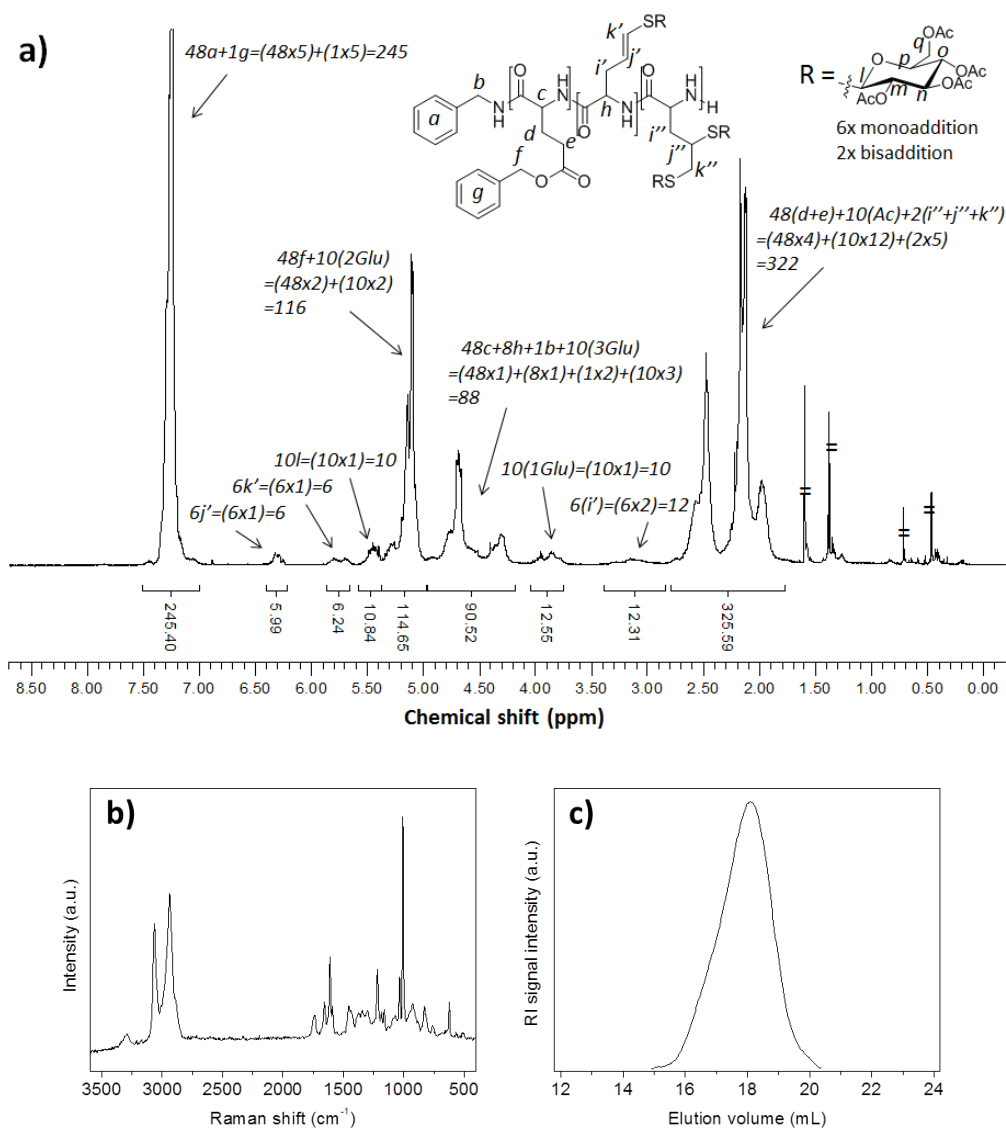


Figure S5: ^1H NMR (400.1 MHz, TFA- d) (a), Raman spectra (b), and SEC trace (NMP + LiBr, 70 °C) (c) of copolypeptide **P1T1/a** (1.23 eq **T1**).

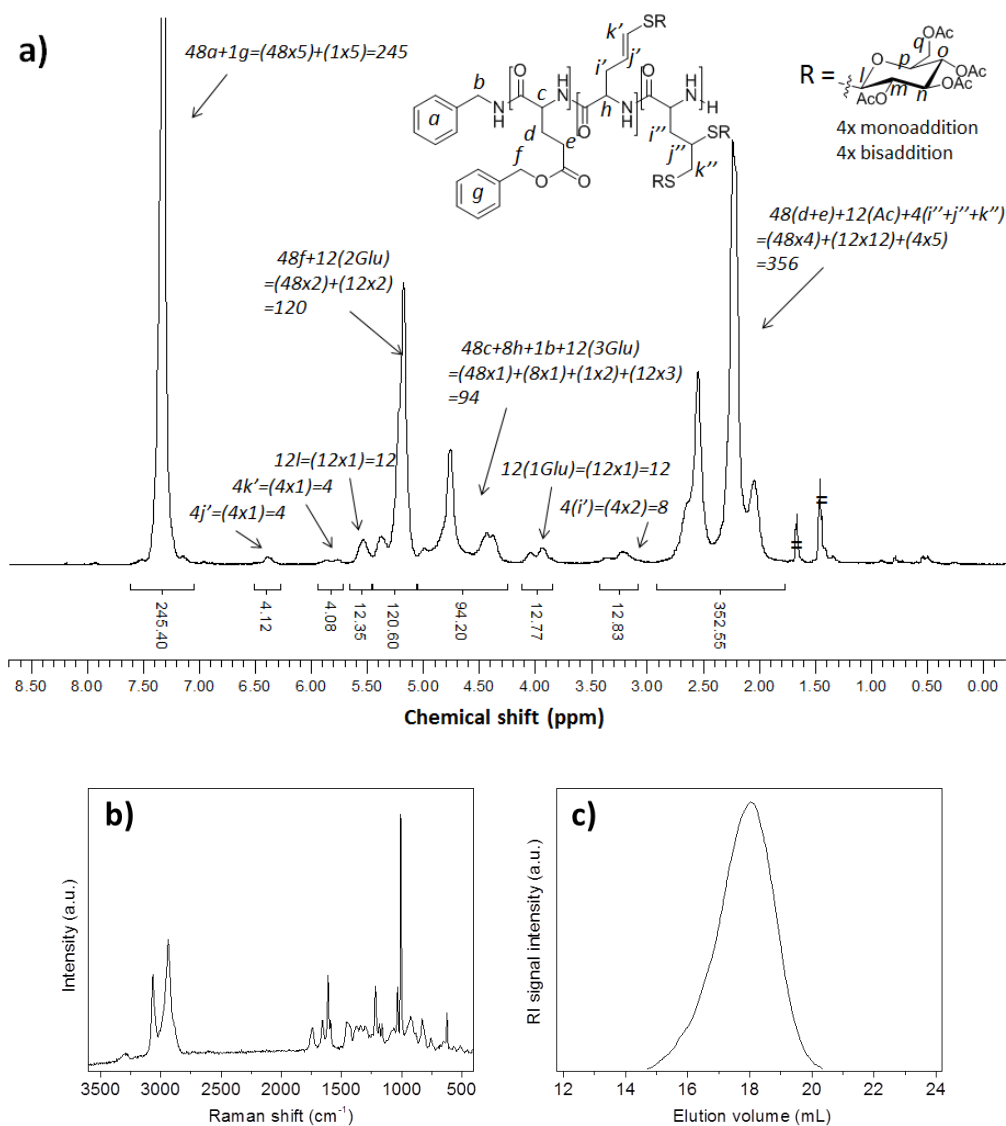


Figure S6: ^1H NMR (400.1 MHz, TFA- d) (a), Raman spectra (b), and SEC trace (NMP + LiBr, 70 °C) (c) of copolypeptide **P1T1/b** (1.5 eq **T1**).

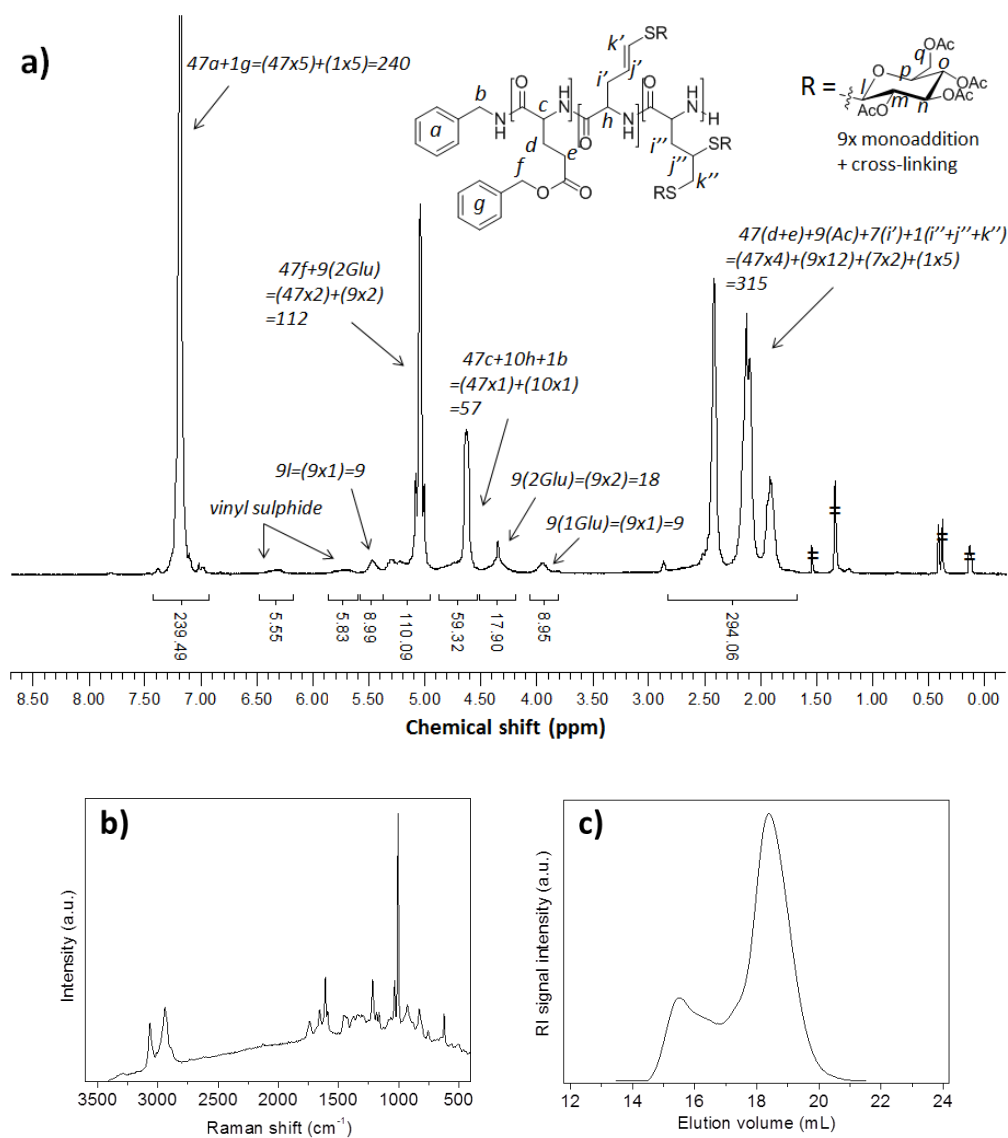


Figure S7: ^1H NMR (400.1 MHz, TFA- d) (a), Raman spectra (b), and SEC trace (NMP + LiBr, 70 °C) (c) of block copolypeptide **P2T1/a** (0.9 eq **T1**) (Photoaddition reaction performed in THF solution).

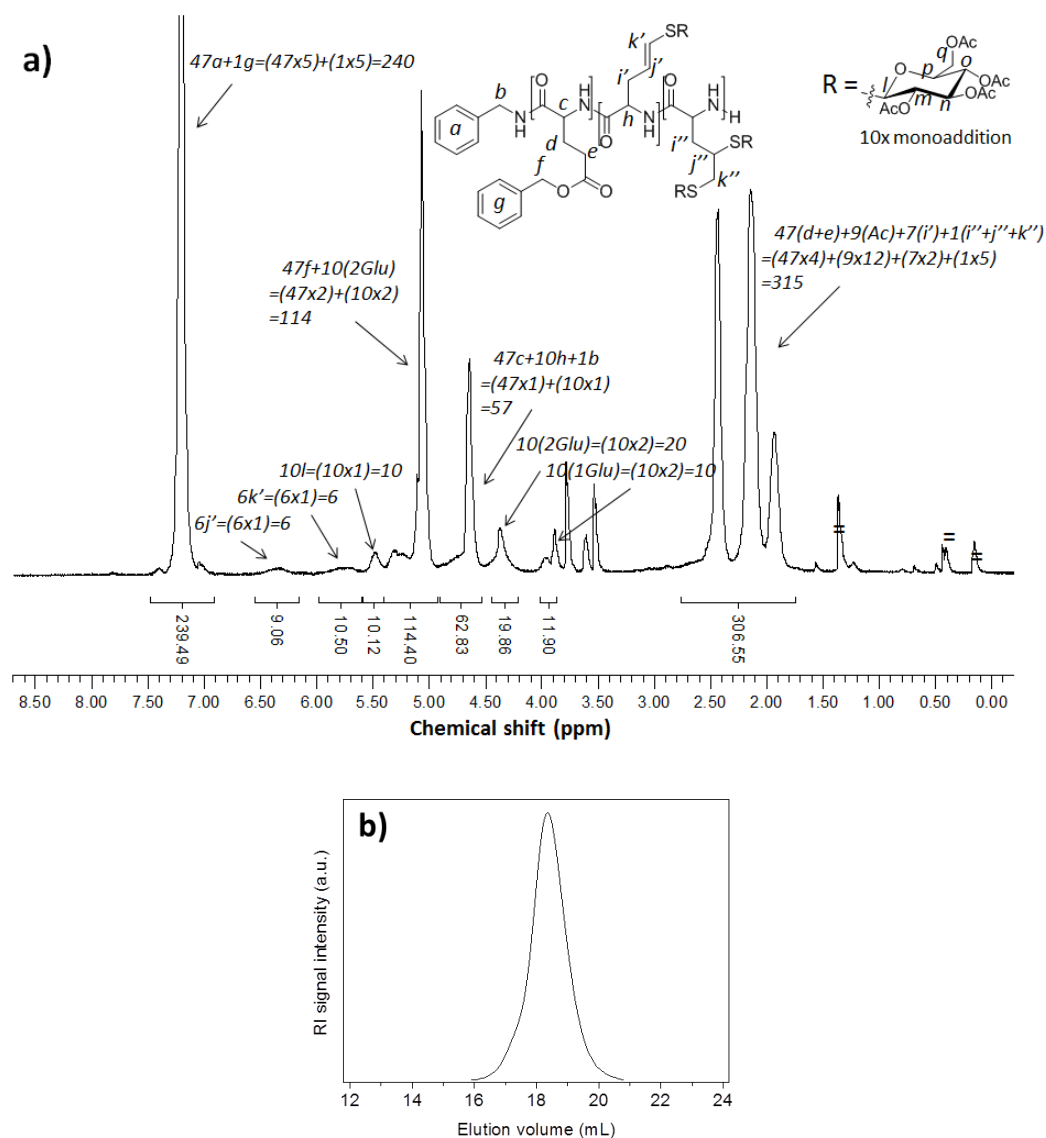


Figure S8: ^1H NMR (400.1 MHz, TFA-d) (a) and SEC trace (NMP + LiBr, 70 °C) (b) of block copolypeptide **P2T1/b** (1.0 eq **T1**). (Photoaddition reaction performed in DMF solution).

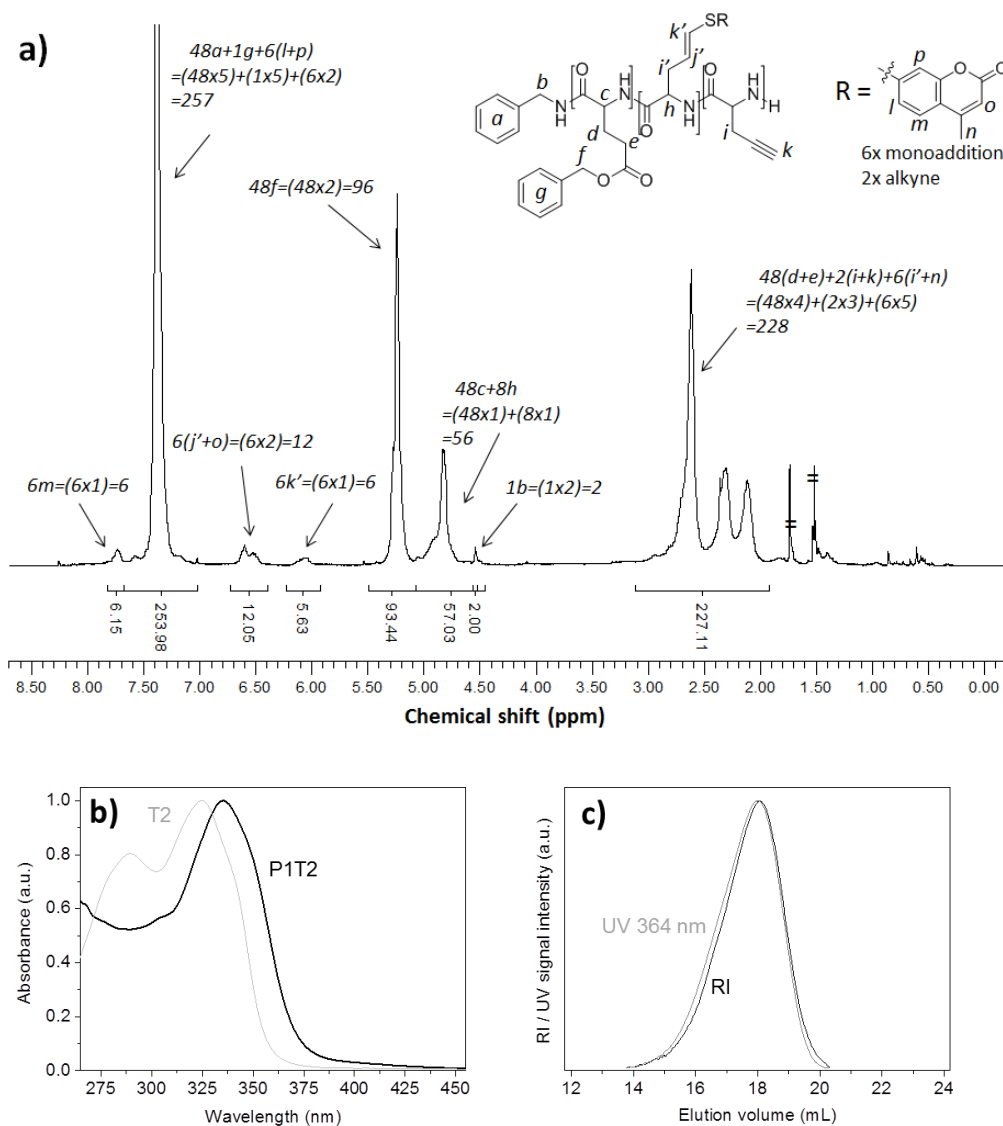


Figure S9: ^1H NMR (400.1 MHz, TFA- d) (a), UV-visible spectra (THF, 25 °C) (b), and SEC trace (NMP + LiBr, 70 °C) (c) of copolypeptide **P1T2** (0.75 eq **T2**).

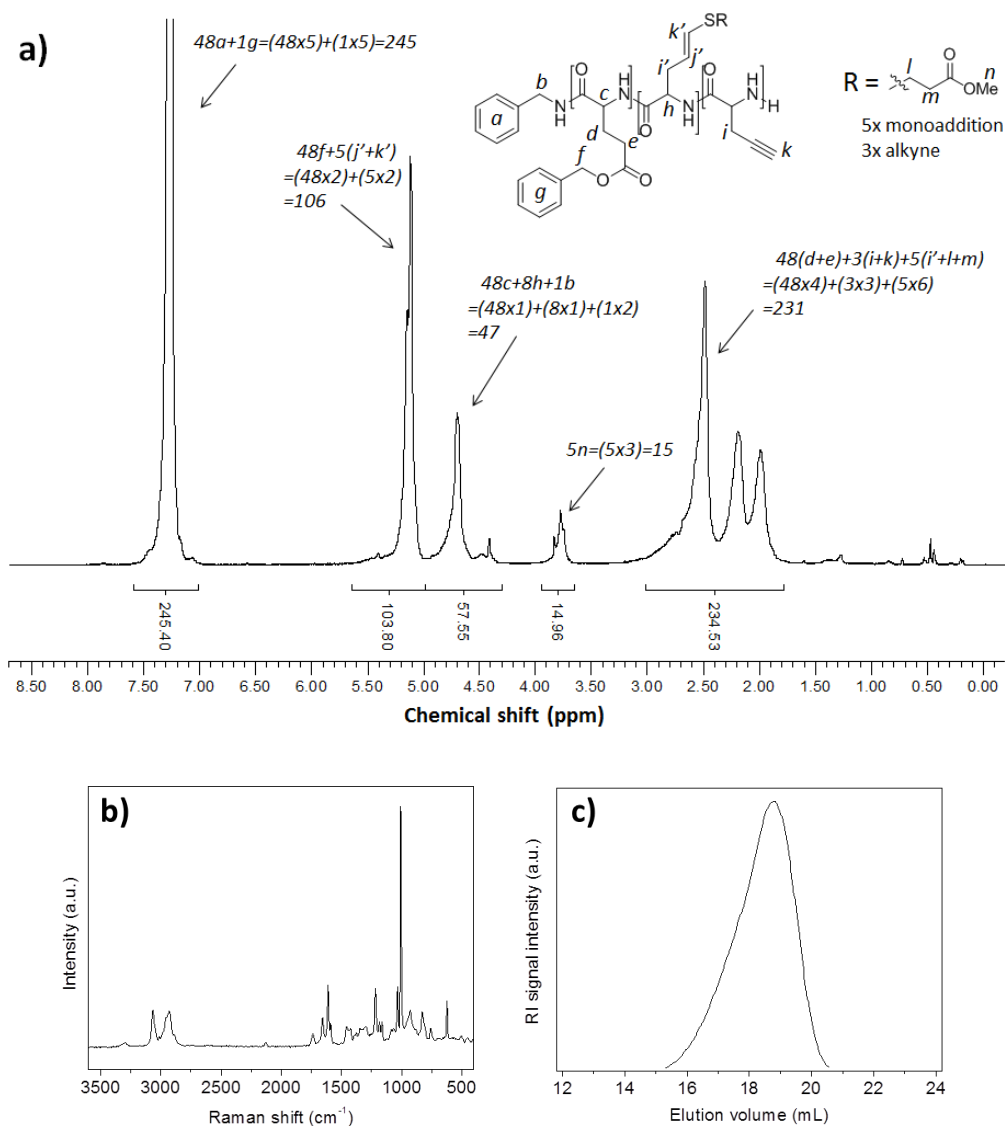


Figure S10: ^1H NMR (400.1 MHz, TFA-d) (a), Raman spectra (b), and SEC trace (NMP + LiBr, 70 °C) (c) of copolypeptide **P1T3/a** (0.63 eq **T3**).

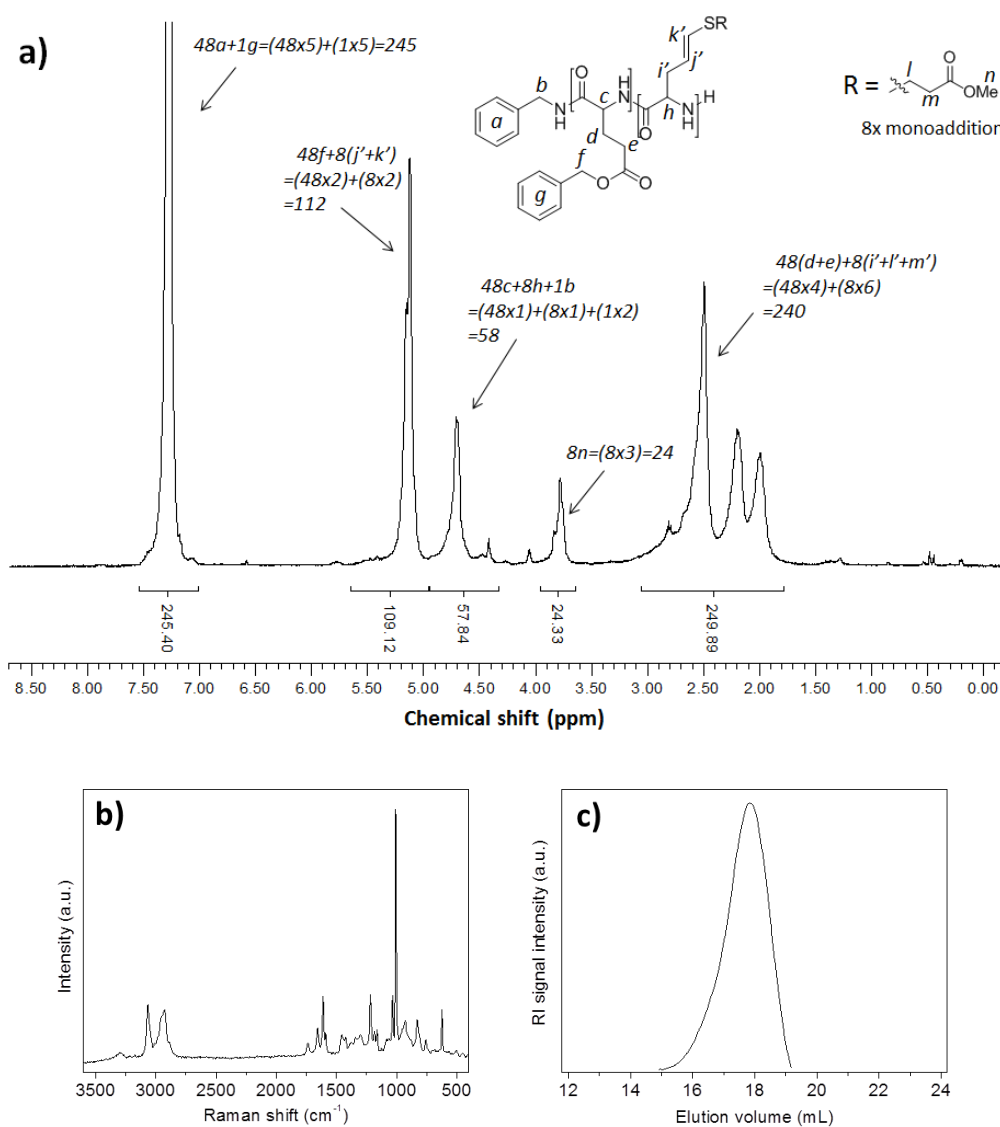


Figure S11: ¹H NMR (400.1 MHz, TFA-d) (a), Raman spectra (b), and SEC trace (NMP + LiBr, 70 °C) (c) of copolypeptide **P1T3/b** (1.0 eq **T3**).

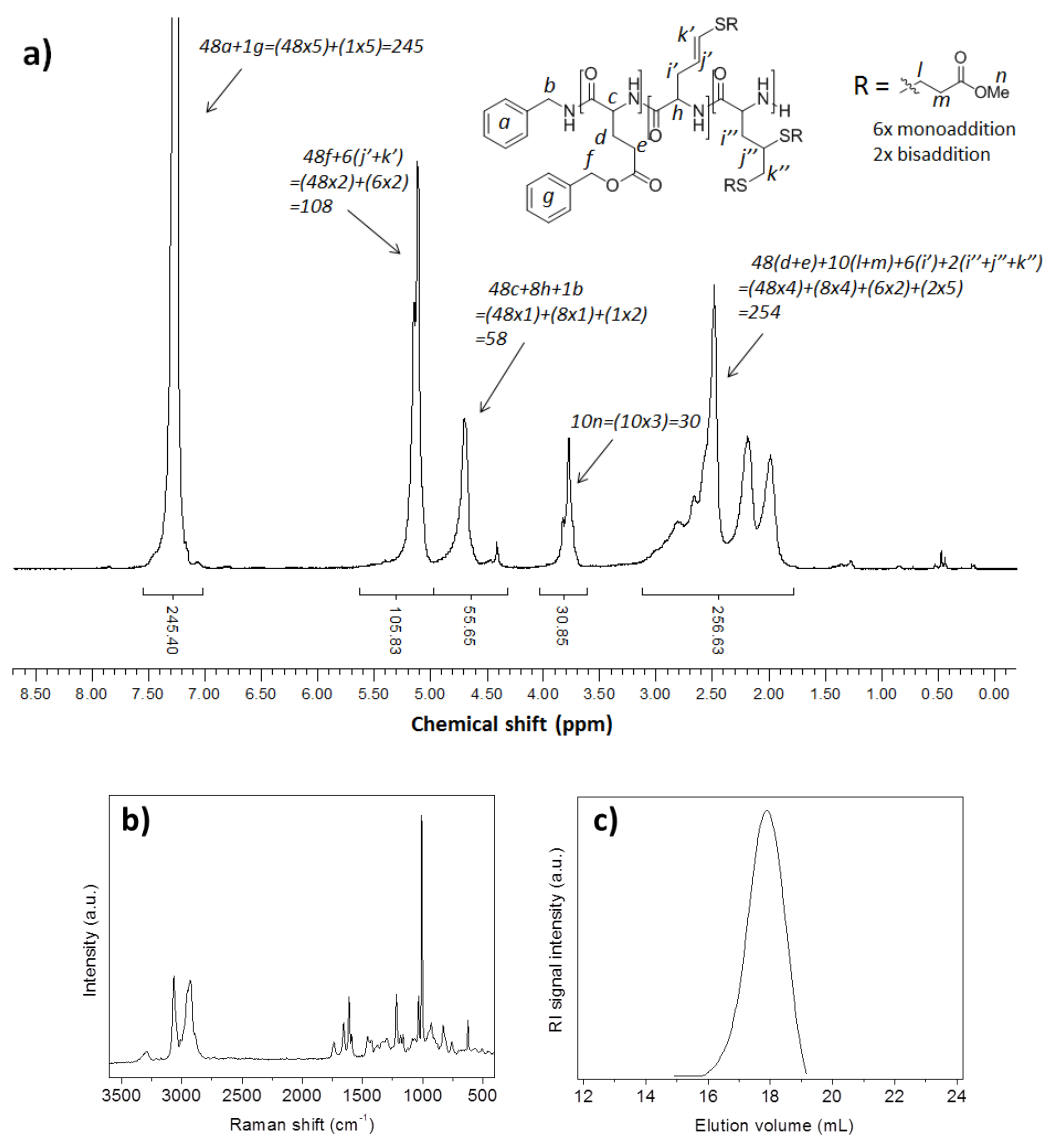


Figure S12: ^1H NMR (400.1 MHz, TFA- d) (a), Raman spectra (b), and SEC trace (NMP + LiBr, 70 $^\circ\text{C}$) (c) of copolypeptide **P1T3/c** (1.25 eq **T3**).

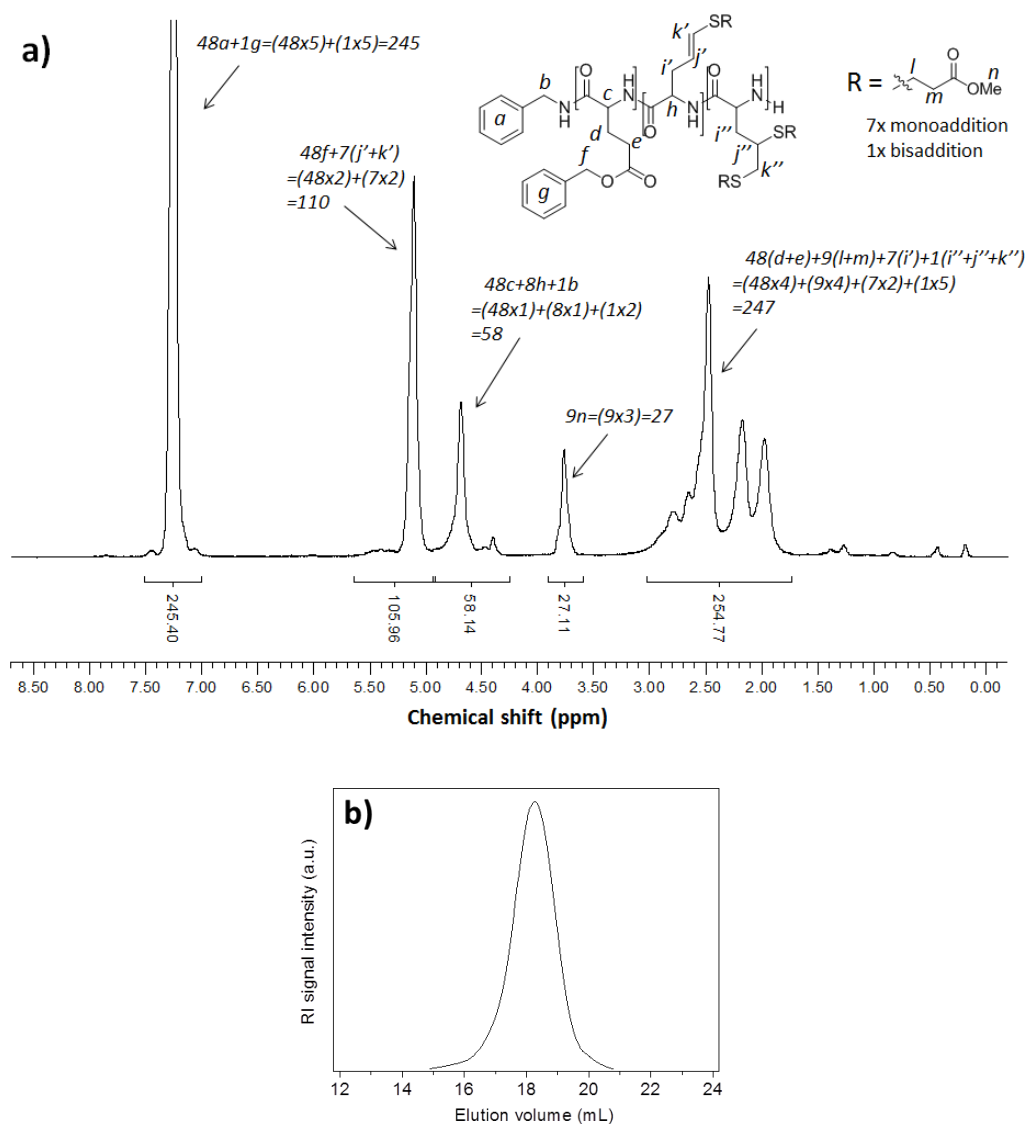


Figure S13: ^1H NMR (400.1 MHz, TFA-d) (a) and SEC trace (NMP + LiBr, 70 °C) (b) of copolypeptide **P1T3/d** (1.13 eq **T3**). (Photoaddition reaction performed in DCM solution).

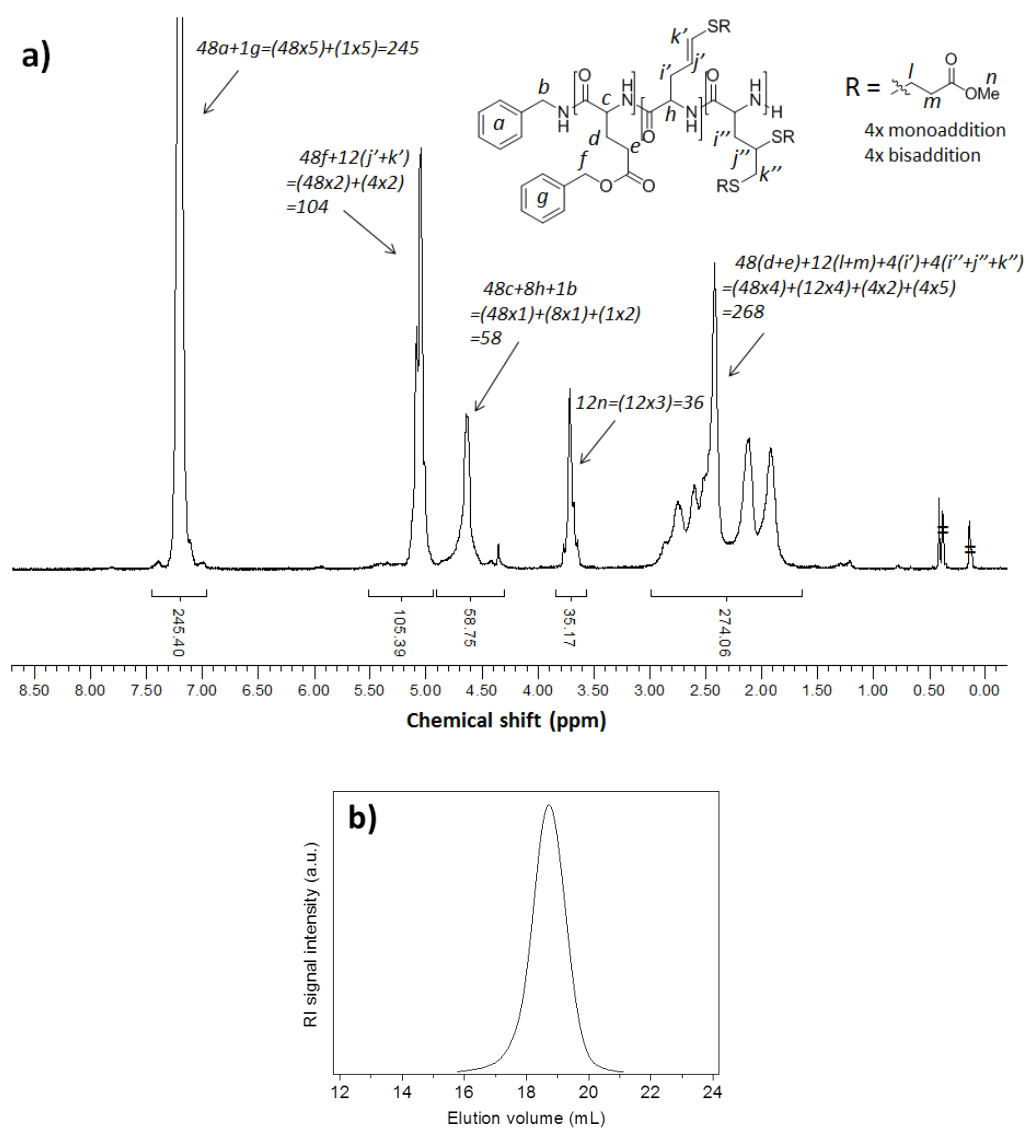


Figure S14: ^1H NMR (400.1 MHz, TFA-d) (a) and SEC trace (NMP + LiBr, 70 °C) (b) of copolypeptide **P1T3/e** (added 1.5 eq **T3**). (Addition reaction performed in DMF solution at 70 °C, radical source: AIBN).

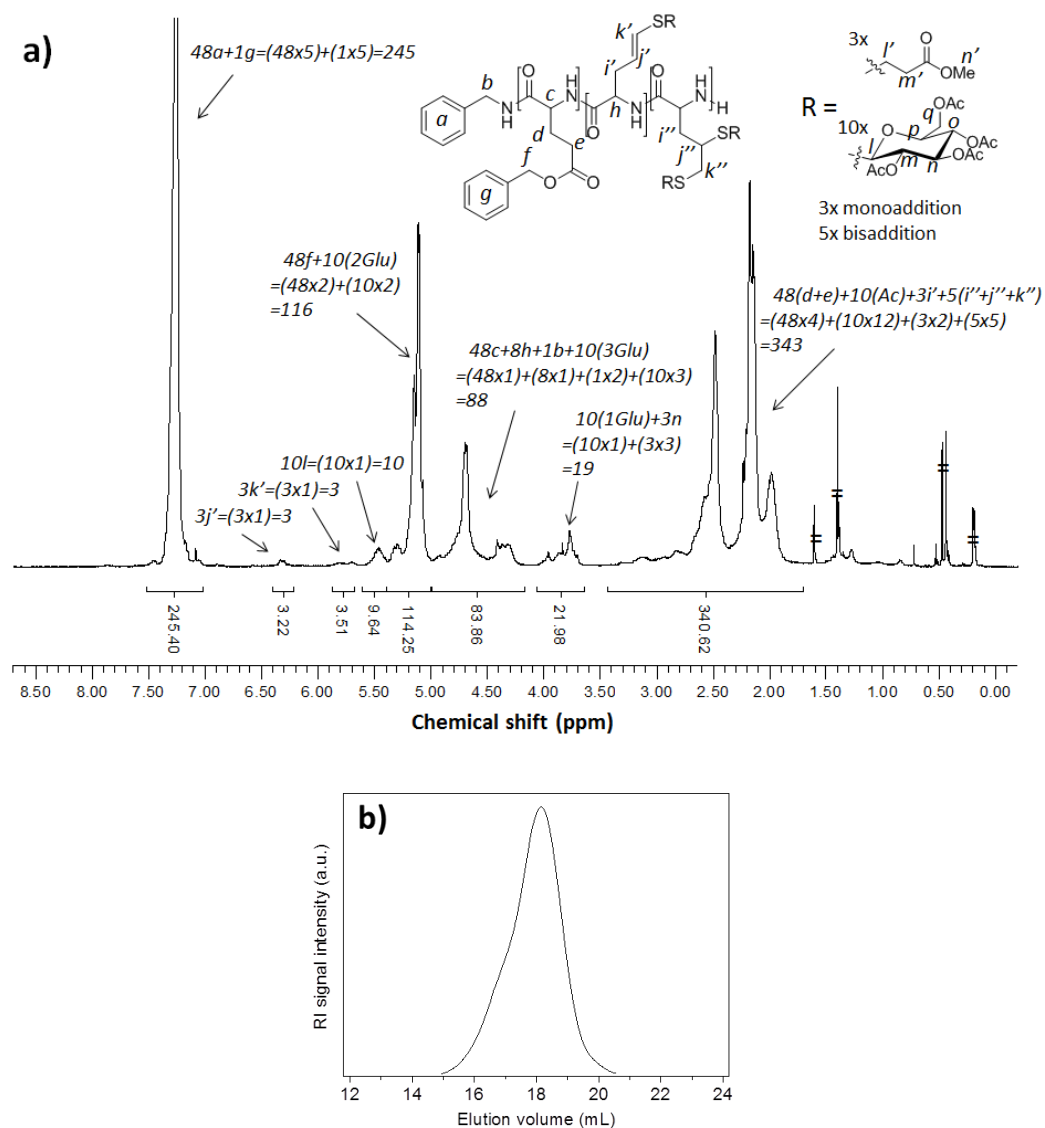


Figure S15: ^1H NMR (400.1 MHz, TFA-*d*) (a) and SEC trace (NMP + LiBr, 70 °C) (b) of copolypeptide **P1T1T3** (1.25 eq **T1** and 0.38 eq **T3**).