**Supplementary Information**

**Self-assembly of Telechelic Tyrosine End-Capped PEO Star polymers in Aqueous Solution**

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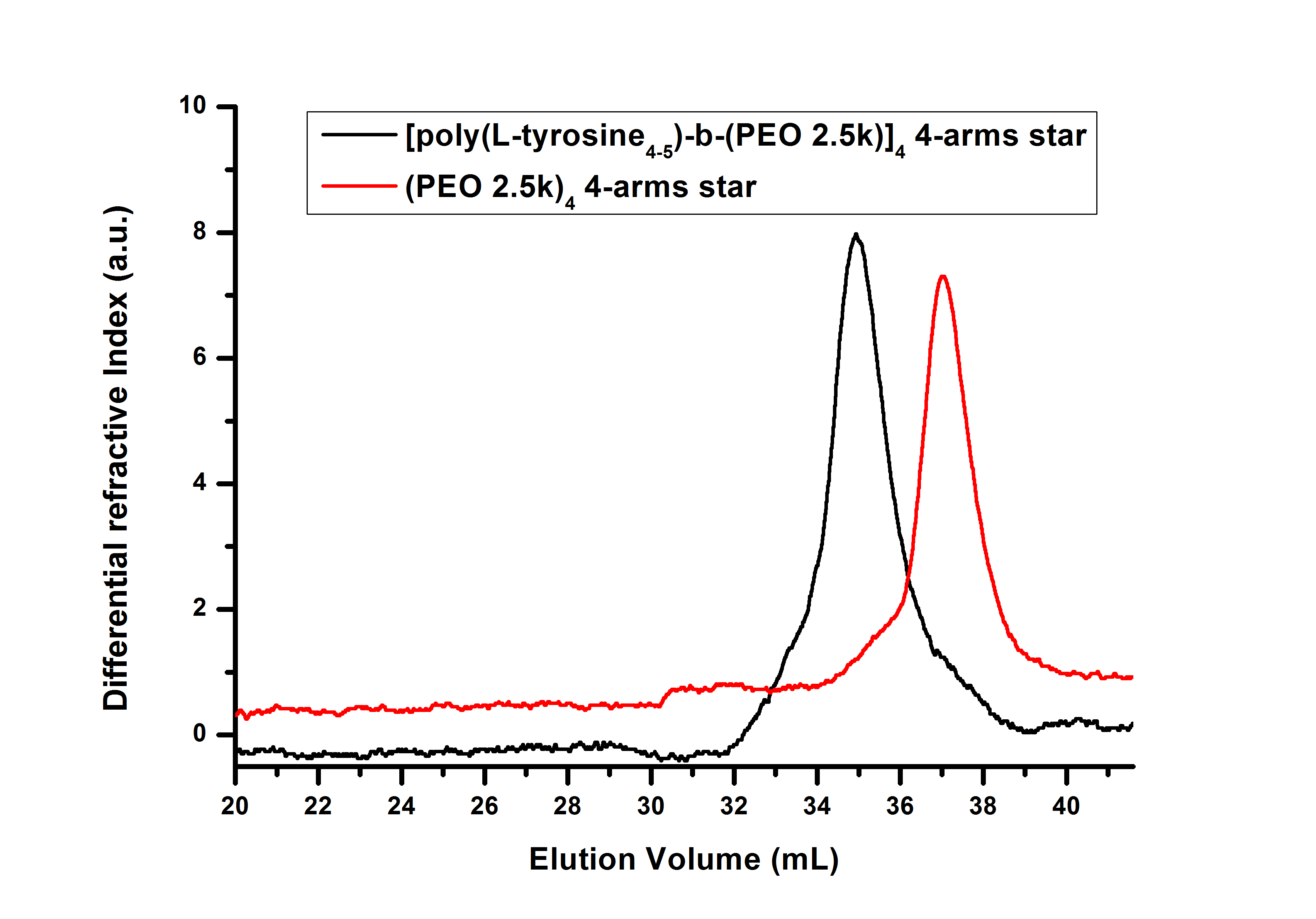
\* Author for correspondence

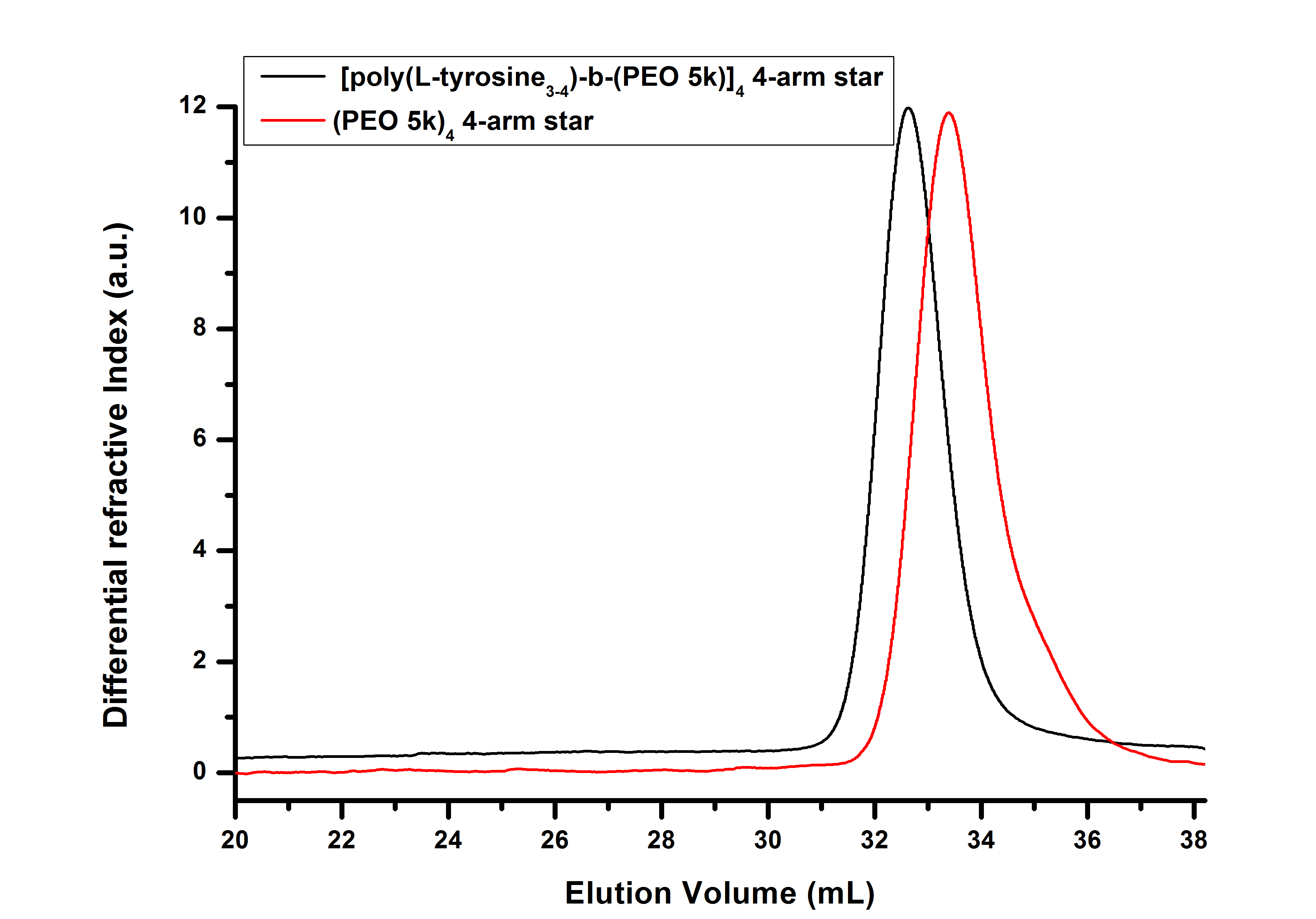


**Figure S1**.1H NMR spectrum of the4-arm star [poly(L-tyrosine4-5)-*b*-(PEO 2.5k)]4in DMSO-d6.

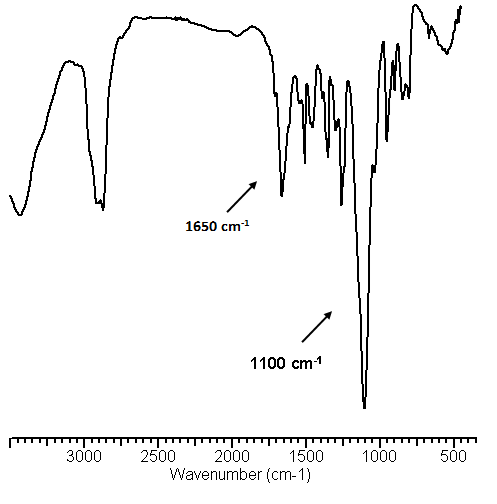


**Figure S2.** 1H NMR spectrumof the 4-arm star [poly(L-tyrosine3-4)-*b*-(PEO 5k)]4 in DMSO-d6.

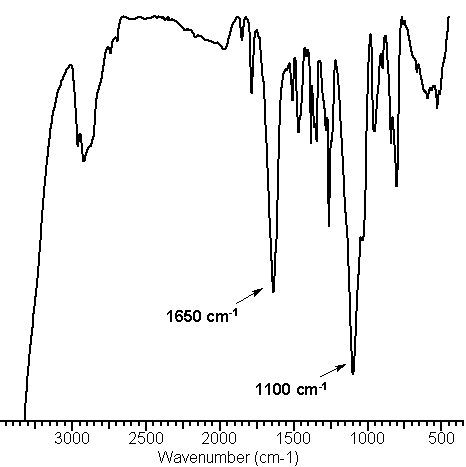
  
**Figure S3.** Size exclusion chromatographs of the 4-arm star [poly(L-tyrosine4-5)-*b*-(PEO 2.5k)]4 and precursor. A 0.1 N LiBr DMF solution was used as an eluent at a rate of 1 mL/min (SEC-TALLS).



**Figure S4.** Size exclusion chromatographs of the 4-arm star [poly(L-tyrosine3-4)-*b*-(PEO 5k)]4 and precursor. A 0.1 N LiBr DMF solution was used as an eluent at a rate of 1 mL/min (SEC-TALLS).

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**Figure S5.** FTIR spectrum of [poly(L-tyrosine4-5)-*b*-(PEO 2.5k). FTIR shows the development of the characteristic peaks of the peptide bonds at 1650 cm-1 and the ether bonds at 1100 cm-1 of PEO.



**Figure S6.** FTIR spectrum of the 4-arm star [poly(L-tyrosine4)-*b*-(PEO 5K)]4. FTIR shows the development of the characteristic peaks of the peptide bonds at 1650 cm-1 and the ether bonds at 1100 cm-1 of PEO.



**Figure S7**. CD spectra showing the reversibility of pH-induced conformational transitions. The reversibility of the CD spectra shows that the peptide does not decompose at high pH but rather unfolds and refolds.



**Figure S8.** X-ray fibre diffraction data obtained from dried stalks made from 3 wt% solutions of [poly(L-tyrosine4-5)-*b*-(PEO 2.5K)]4 and precursor molecule (PEO 2.5K)4. Selected *d*-spacings in Å are indicated



**Figure S9.** X-ray fibre diffractiondata obtained from dried stalks made from 3 wt% solutions of [poly(L-tyrosine3-4)-*b*-(PEO 5k)]4 and precursor molecule (PEO 5k)4. Selected *d*-spacings in Å are indicated.

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**Figure S10.** Less common self-assembled structures observed by cryo-TEM for the conjugates. a) [poly(L-tyrosine4-5)-*b*-(PEO 2.5k)]4 pH 12 shows occasional spherical structures. b) (PEO 2.5k)4 shows occasional spherical clusters. c) [poly(L-tyrosine3-4)-*b*-(PEO 5k)]4 pH 7 shows occasional short straight fibres and longer fibres. d) [poly(L-tyrosine4)-*b*-(PEO 5k)]4 shows occasional very long fibers, e) (PE0 5k)4 shows occasional large clusters.



**Figure S11.** Kratky plots of the SAXS data for precursor molecules, consistent with branched conformation.



**Figure S12.** Cytotoxicity profile of tyrosine showing that it does not have a significant effect on cell viability. Concentrations were chosen based on the tyrosine content in each of the precursor molecules. The highest concentration of tyrosine, present in 5 mg/ml of the [poly(L-tyrosine4-5)-*b*-(PEO 2.5k)]4 could not be tested with the MTT assay due to tyrosine solubility, the limit of which is 0.45 mg/ml in water.