Main-chain degradable star polymers comprised of pH-responsive hyperbranched cores and thermoresponsive polyethylene glycol-based coronas

Ulrike Wais,a,b Lohitha Rao Chennamaneni,a Praveen Thoniyot,a Haifei Zhangb,* and Alexander W. Jacksona,*

a Institute of Chemical and Engineering Sciences, Jurong Island, 627833, Singapore.
b Department of Chemistry, University of Liverpool, Liverpool L69 7ZD, UK.
* Corresponding authors

Electronic Supplementary Information

**Fig. S1** $^1$H NMR (CDCl$_3$) spectra of HB2.
Fig. S2 Expansion of $^1$H NMR (CDCl$_3$) spectra of HB2 used to determine degree of branching (DB).
**Fig. S3** $^1$H NMR (CDCl$_3$) spectra of SHB2.

**Fig. S4** (a) Size exclusion chromatography (in THF) refractive index traces of LP1 (dashed line) and DB1 (solid line) after chain-extension. (b) Dynamic light scattering analysis (in H$_2$O) of DB1 (3 mg/mL) at pH 5.0 (dotted line) and pH 9.0 (solid line).
Fig. S5 (a) UV-Vis calibration curve of IMC in EtOH (+ 1 % H₂O by volume) and (b) IMC control experiment displaying no IMC in H₂O without the presence of SHB2 or DB1.

Fig. S6 Photographic visual evidence of IMC uptake facilitated by SHB2 and subsequent pH-triggered release.

Fig. S7 Hydrogel formation of SHB2-SH at 5 and 10 wt %, and unsuccessful gel formation at wt 1 %.
Fig. S8 $^1$H NMR (CDCl$_3$) spectra of LP4.

Fig. S9 Lower critical solution temperatures (LCST) of LP3 and LP4, determined by dynamic light scattering (DLS). Phase transition from hydrophilic to hydrophobic, and subsequent precipitation, occurs when the count rate drastically increases.
Fig. S10 $^1$H NMR (CDCl$_3$) spectra of LP6.

Fig. S11 Size exclusion chromatography (in THF) refractive index traces of (a) LP2, (b) LP3, (c) LP4 and (d) LP5. Each image displays the polymer trace (solid line) and corresponding oligomer sample after hydrolysis (dashed line).
Fig. S12 $^1$H NMR (CDCl$_3$) spectra of DB2.

Fig. S13 Size exclusion chromatography (in THF) refractive index traces of (a) HB5, SHB5 and SHB5 Hydrolysis and (b) HB6, SHB6 and SHB6 Hydrolysis.
Fig. S14 Size exclusion chromatography (in THF) refractive index traces of (a) hyperbranched polymer HB8 (dashed line) followed by chain-extension to SHB8 (solid line) and subsequent hydrolysis of SHB8 (dotted line). DLS analysis in H$_2$O (3 mg/mL) of SHB8 at pH 5.0 (dotted lines) and pH 9.0 (solid lines) and pH 5.0 at 45 °C (dashed lines).