Supporting Information for

Facile RAFT synthesis of side-chain amino acid containing pH responsive hyperbranched and star architectures

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Fig. S1 $^1$H NMR spectrum of Boc-Val-HEA in CDCl$_3$. 

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**Fig. S2** $^{13}$C NMR spectrum of Boc-Val-HEA in CDCl$_3$.

**Fig. S3** ESI-MS spectrum of Boc-Val-HEA.
Fig. S4 $^1$H NMR spectrum of VBBT CTA in CDCl$_3$.

Fig. S5 $^{13}$C NMR spectrum of VBBT CTA in CDCl$_3$. 
**Fig. S6** ESI-MS spectrum of VBBT.

**Fig. S7** GPC-RI traces of the polymers prepared by SCVP-RAFT of Boc-Val-HEA with VBBT as function of time at [Boc-Val-HEA]/[VBBT] = 10/1 (A) and 25/1 (B).

**Fig. S8** DSC thermograms of P(Boc-Val-HEA) homopolymer and hyperbranched copolymers P(Boc-Val-HEA-co-VBBT) with the different feed ratios.
**Fig. S9** FT-IR spectra of (A) Boc-Val-HEA (B) VBBT CTA (C) HB5, and (D) DHB5.

**Fig. S10** Size distribution detected by DLS with the solution of 0.1 mg mL\(^{-1}\) at different pH for P(DHB5-star-PEGMA).

**Thermo-responsive property of P(DHB10-star-MEO\(_2\)MA) and P(DHB25-star-MEO\(_2\)MA) stars:** Thermoresponsive property of P(DHB10-star-MEO\(_2\)MA) and P(DHB25-star-MEO\(_2\)MA) star polymers has been investigated by UV-Vis spectroscopy by analyzing their aqueous solution (2 mg/mL) as a function of temperature. Initially, the pH of the solution was adjusted to pH = 7.5 and temperature of the solution was set to 16 °C. Then, temperature of the solution was increased at 2 °C intervals, allowed to equilibrate at that temperature for 6 min followed by the measurement of % transmittance (%T) at 500 nm. Reduction of 50% T of polymer solution was considered as lower critical solution temperature (LCST) of the polymer (Figure S11).
**Fig. S11** Plot of % transmittance at 500 nm *versus* temperature for the aqueous solutions (2 mg/mL) of P(DHB10-*star*-MEO₂MA) and P(DHB25-*star*-MEO₂MA) star polymers.

**Fig. S12** (A) SEM and (B) AFM images of P(DHB5-*star*-PEGMA). Samples were prepared from 0.1 mg mL⁻¹ polymer solutions in DI water at pH = 7.5 and 16 °C.

**Fig. S13** AFM images of (A) P(DHB10-*star*-MEO₂MA) at pH = 7.5 and 16 °C (B) P(DHB10-*star*-MEO₂MA) at pH = 7.5 and 26 °C (C) P(DHB25-*star*-MEO₂MA) at pH = 7.5 and 16 °C, and (D) P(DHB25-*star*-MEO₂MA) at pH = 7.5 and 26 °C. AFM samples were prepared from 0.1 mg mL⁻¹ polymer solutions.