

Supporting Information for

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

Saswati Ghosh Roy and Priyadarsi De*

Polymer Research Centre, Department of Chemical Sciences, Indian Institute of Science
Education and Research Kolkata, Mohanpur - 741246, Nadia, West Bengal, India

* Corresponding Author: e-mail: p_de@iiserkol.ac.in (P.D.).

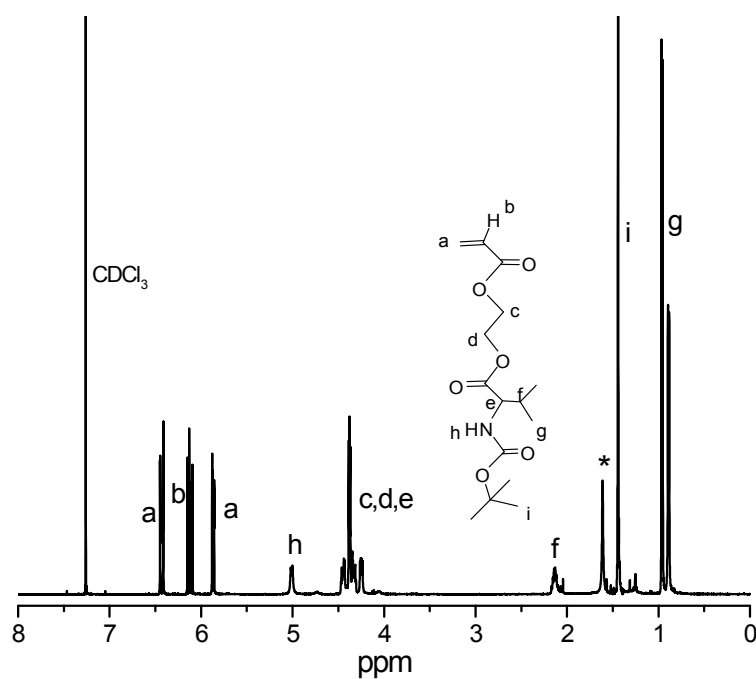


Fig. S1 ^1H NMR spectrum of Boc-Val-HEA in CDCl_3 .

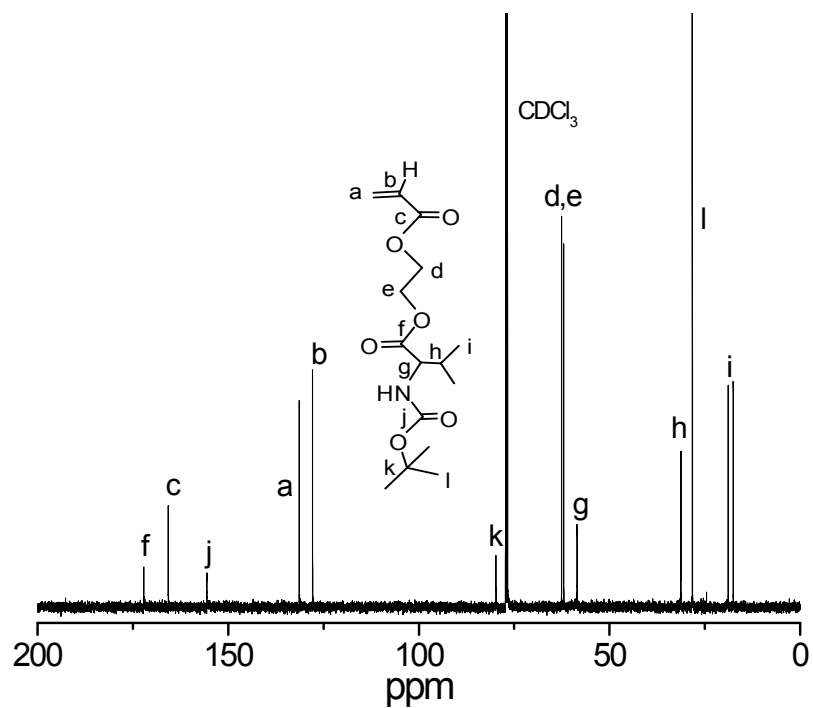


Fig. S2 ^{13}C NMR spectrum of Boc-Val-HEA in CDCl_3 .

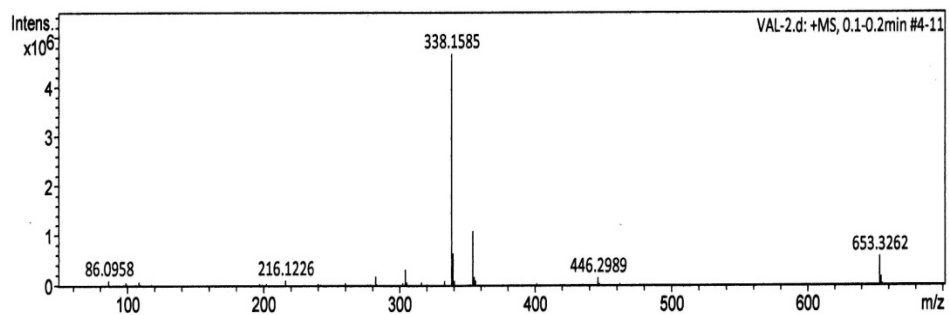


Fig. S3 ESI-MS spectrum of Boc-Val-HEA.

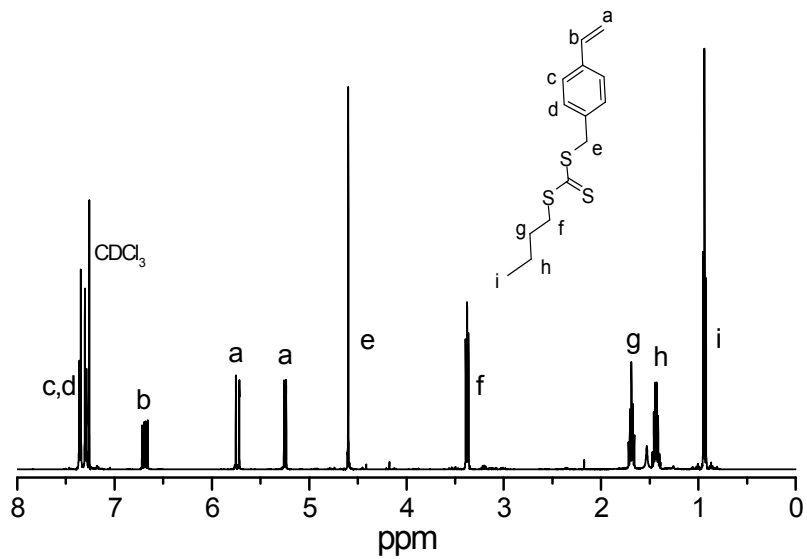


Fig. S4 ^1H NMR spectrum of VBBT CTA in CDCl_3 .

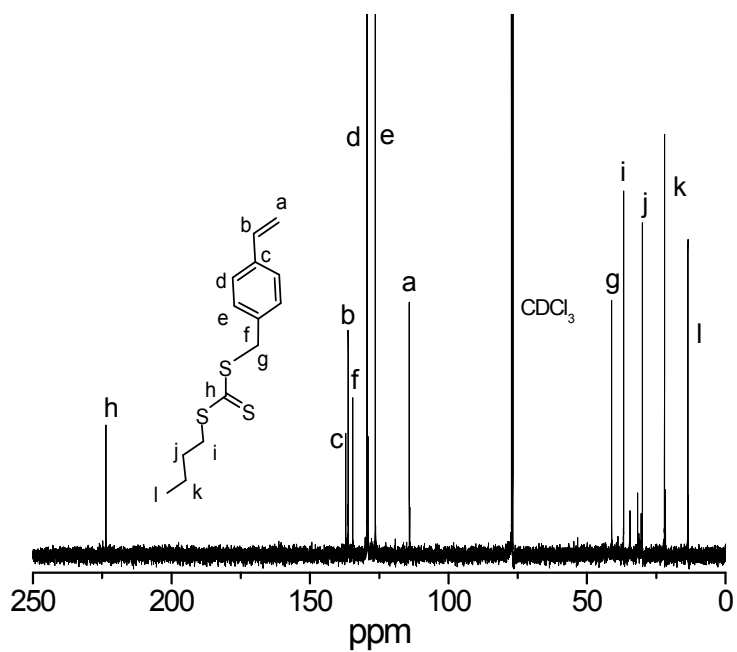


Fig. S5 ^{13}C NMR spectrum of VBBT CTA in CDCl_3 .

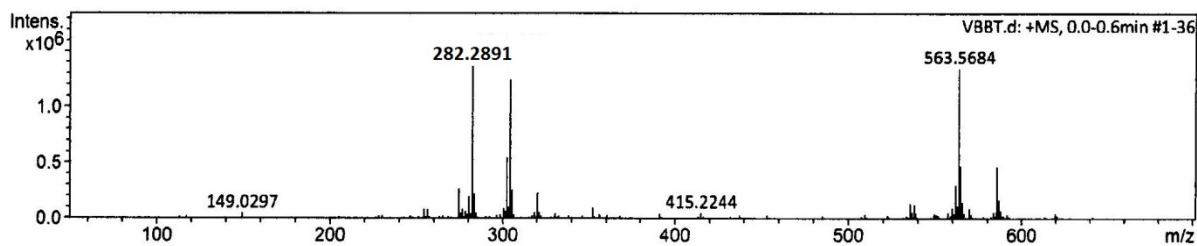


Fig. S6 ESI-MS spectrum of VBBT.

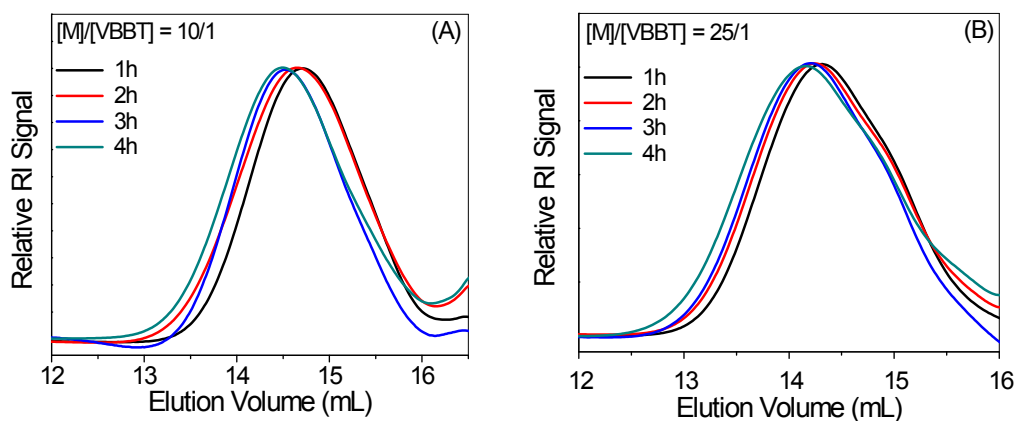


Fig. S7 GPC-RI traces of the polymers prepared by SCVP-RAFT of Boc-Val-HEA with VBBT as function of time at $[\text{Boc-Val-HEA}]/[\text{VBBT}] = 10/1$ (A) and $25/1$ (B).

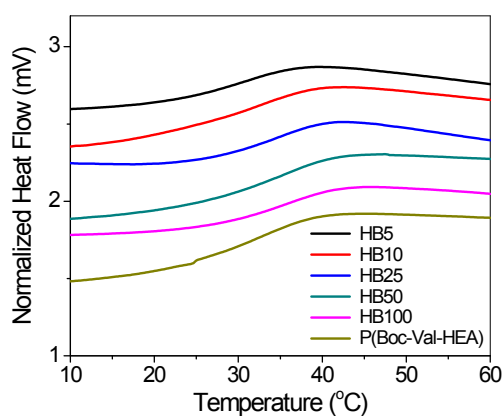


Fig. S8 DSC thermograms of P(Boc-Val-HEA) homopolymer and hyperbranched copolymers P(Boc-Val-HEA-*co*-VBBT) with the different feed ratios.

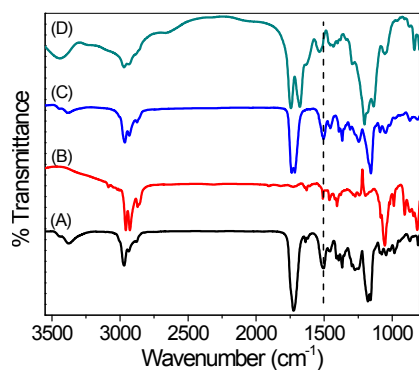


Fig. S9 FT-IR spectra of (A) Boc-Val-HEA (B) VBBT CTA (C) HB5, and (D) DHB5.

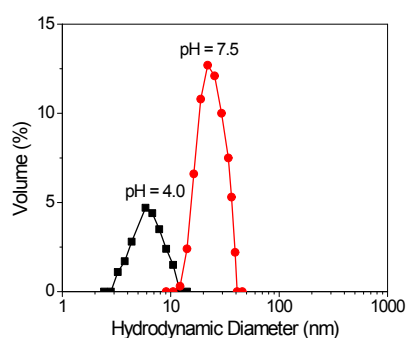


Fig. S10 Size distribution detected by DLS with the solution of 0.1 mg mL^{-1} at different pH for P(DHB5-*star*-PEGMA).

Thermo-responsive property of P(DHB10-*star*-MEO₂MA) and P(DHB25-*star*-MEO₂MA) stars: Thermoresponsive property of P(DHB10-*star*-MEO₂MA) and P(DHB25-*star*-MEO₂MA) 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 $\text{pH} = 7.5$ and temperature of the solution was set to $16 \text{ }^\circ\text{C}$. Then, temperature of the solution was increased at $2 \text{ }^\circ\text{C}$ 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).

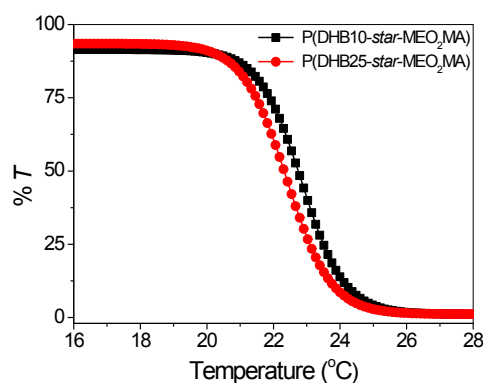


Fig. S11 Plot of % transmittance at 500 nm *versus* temperature for the aqueous solutions (2 mg/mL) of P(DHB10-*star*-MEO₂MA) and P(DHB25-*star*-MEO₂MA) star polymers.

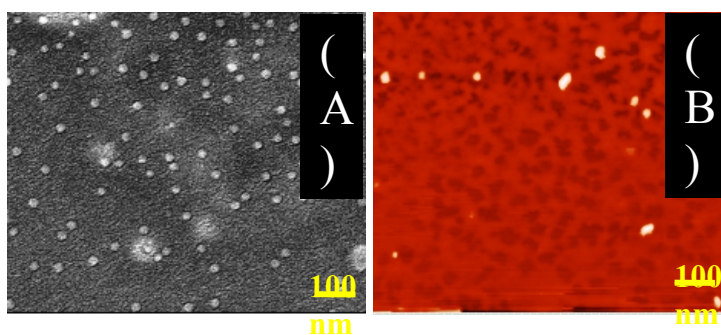


Fig. S12 (A) SEM and (B) AFM images of P(DHB5-*star*-PEGMA). Samples were prepared from 0.1 mg mL⁻¹ polymer solutions in DI water at pH = 7.5 and 16 °C.

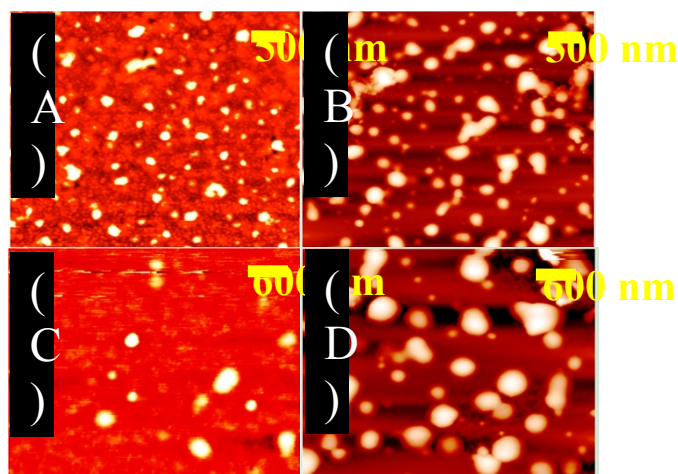


Fig. S13 AFM images of (A) P(DHB10-*star*-MEO₂MA) at pH = 7.5 and 16 °C (B) P(DHB10-*star*-MEO₂MA) at pH = 7.5 and 26 °C (C) P(DHB25-*star*-MEO₂MA) at pH = 7.5 and 16 °C, and (D) P(DHB25-*star*-MEO₂MA) at pH = 7.5 and 26 °C. AFM samples were prepared from 0.1 mg mL⁻¹ polymer solutions.