

Supporting Information for

Cationic Methacrylate Polymers Containing Chiral Amino Acid Moieties:

Controlled Synthesis via RAFT Polymerization

Sonu Kumar, Saswati Ghosh Roy, Priyadarsi De*

Polymer Research Centre, Department of Chemical Sciences

Indian Institute of Science Education and Research – Kolkata

PO: BCKV Campus Main Office, Mohanpur - 741252, Nadia, West Bengal, India

* Corresponding author: Fax: +91-33-25873020, E-mail: p_de@iiserkol.ac.in (P. De).

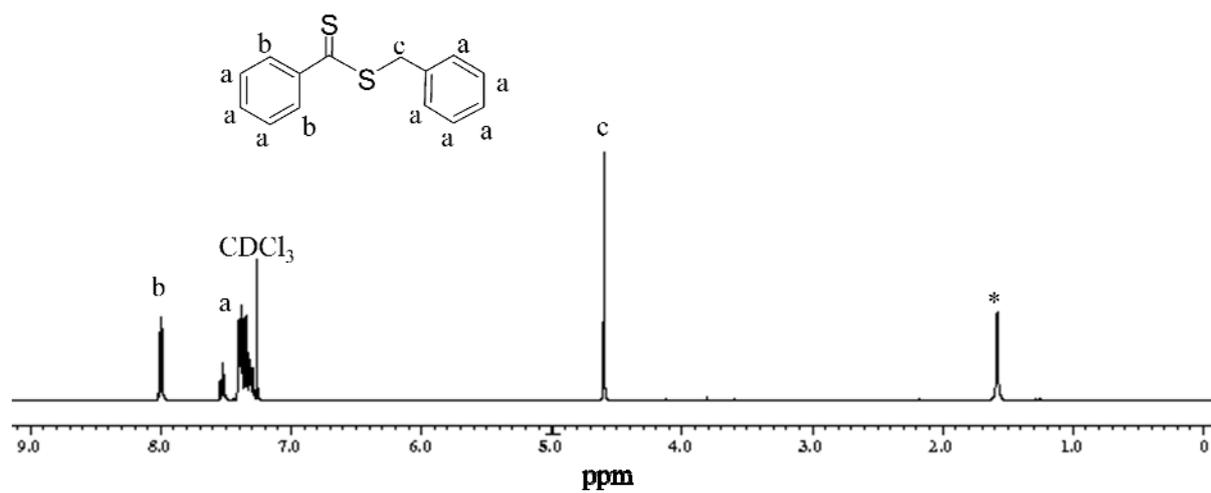


Figure S1. ¹H NMR spectrum of BDB in CDCl₃ (* denotes H₂O resonance).

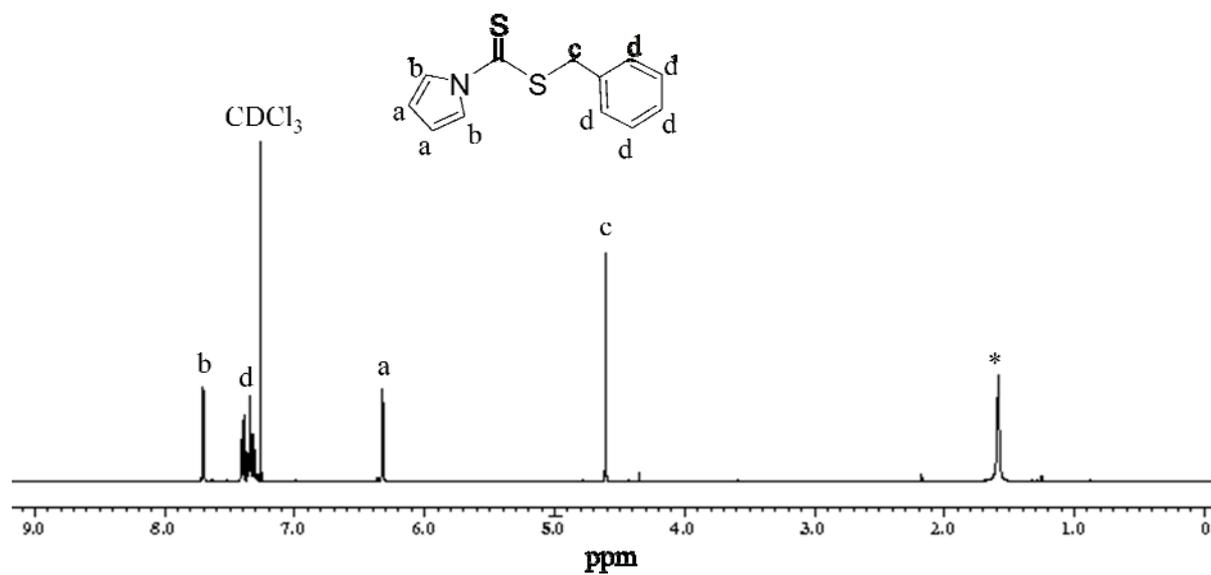


Figure S2. ¹H NMR spectrum of BPC in CDCl₃ (* denotes H₂O resonance).

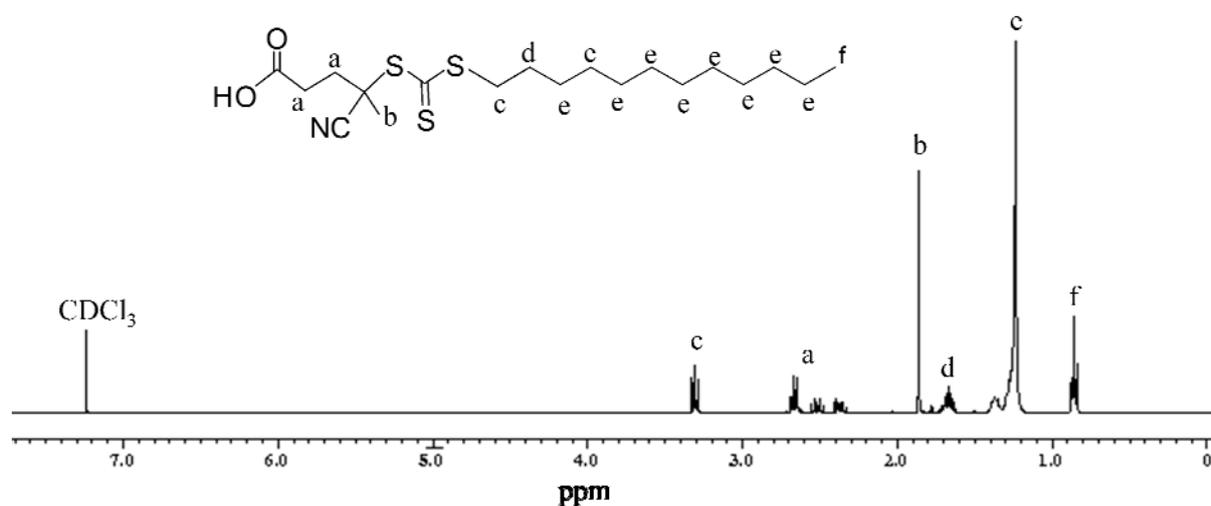


Figure S3. ¹H NMR spectrum of CDP in CDCl₃.

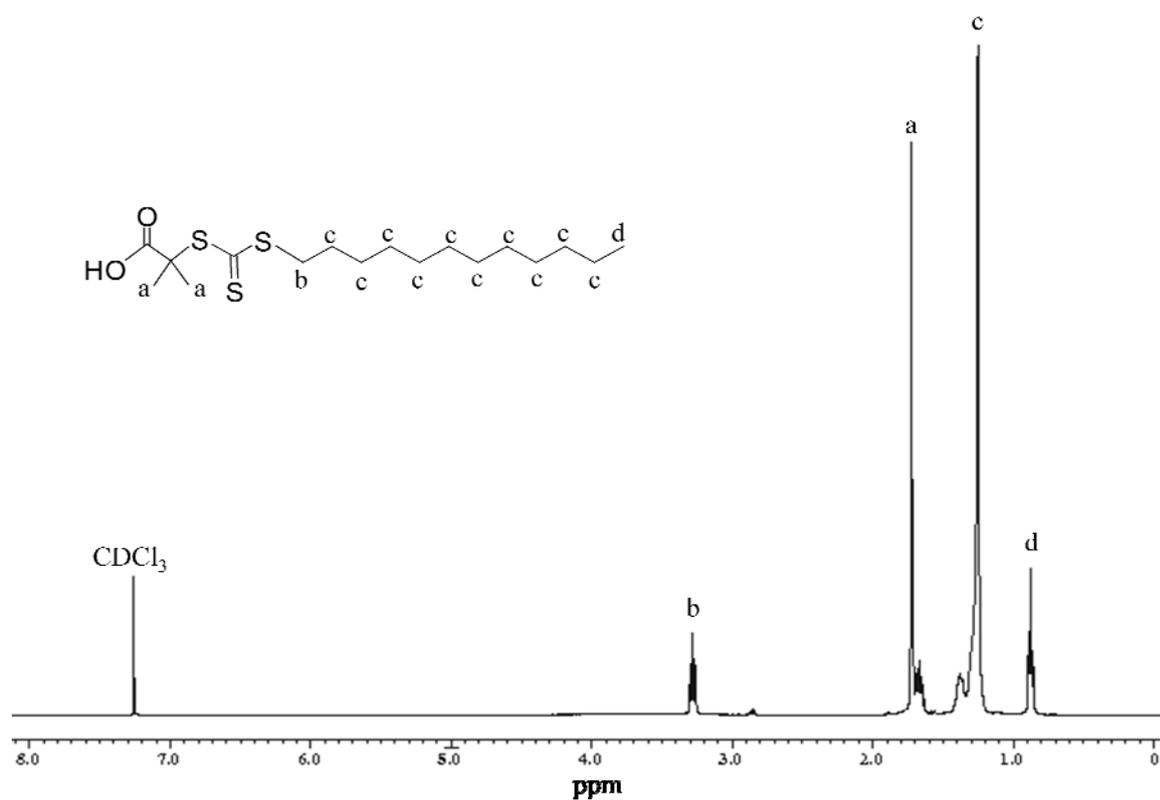


Figure S4. ¹H NMR spectrum of DMP in CDCl₃.

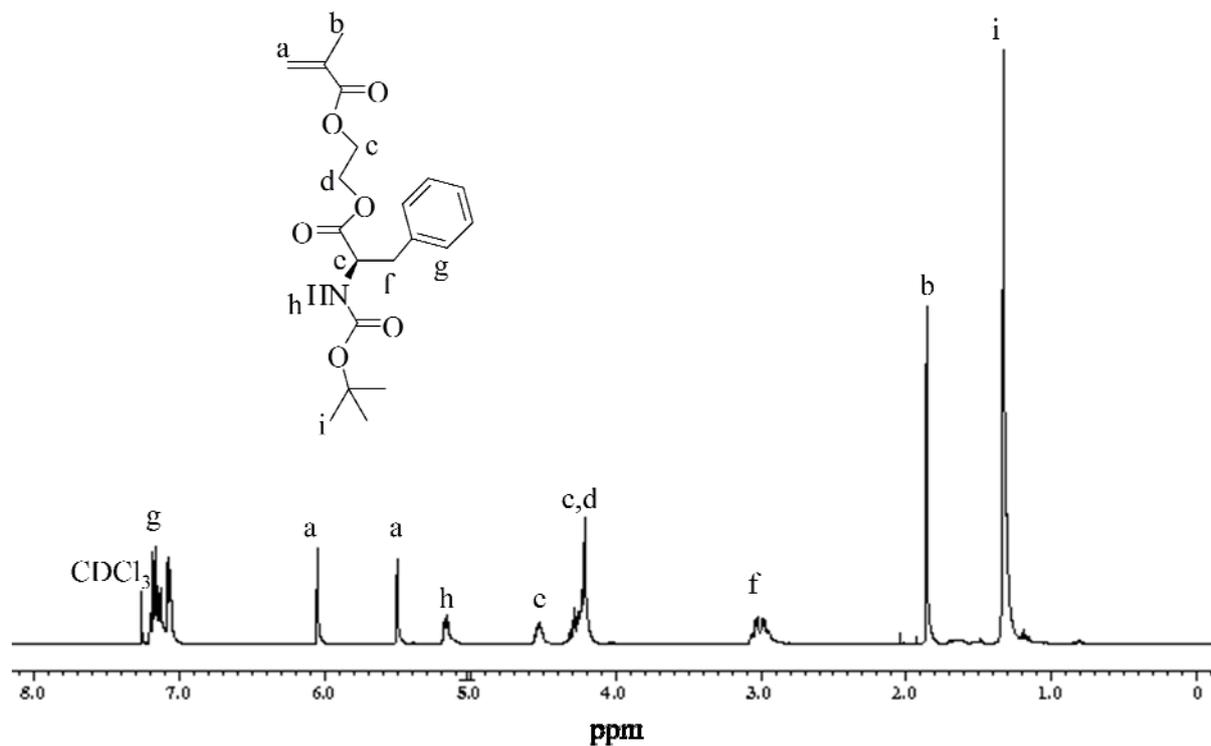


Figure S5. ¹H NMR spectrum of Boc-Phe-HEMA in CDCl₃.

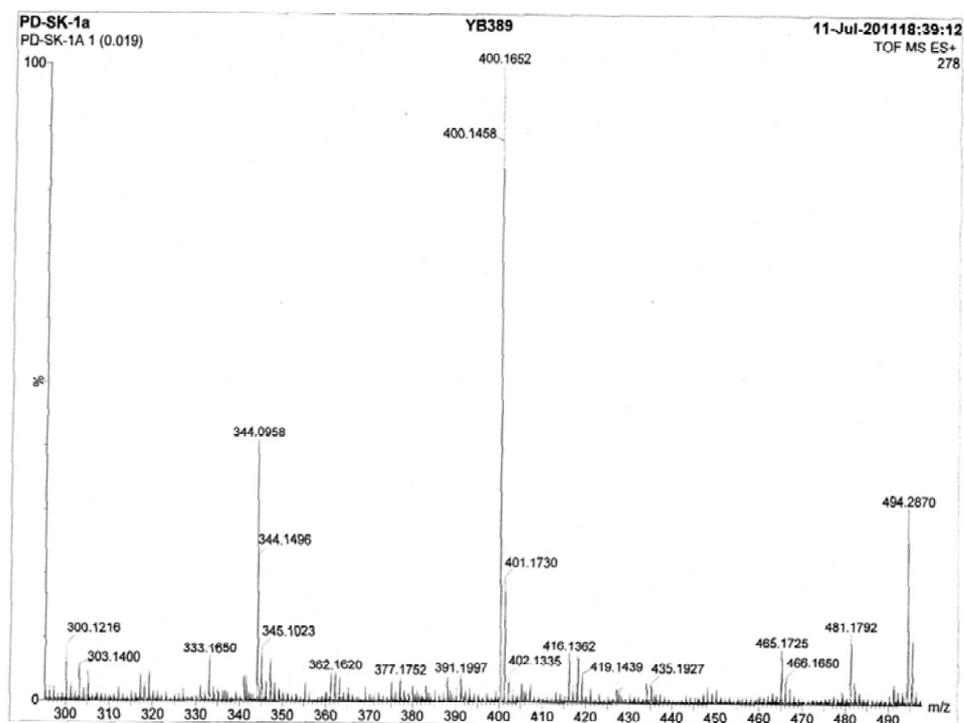


Figure S6. ESI-MS spectrum of Boc-Phe-HEMA (calculated for $[M + Na^+]$: 400.18 m/z , observed 400.16 m/z).

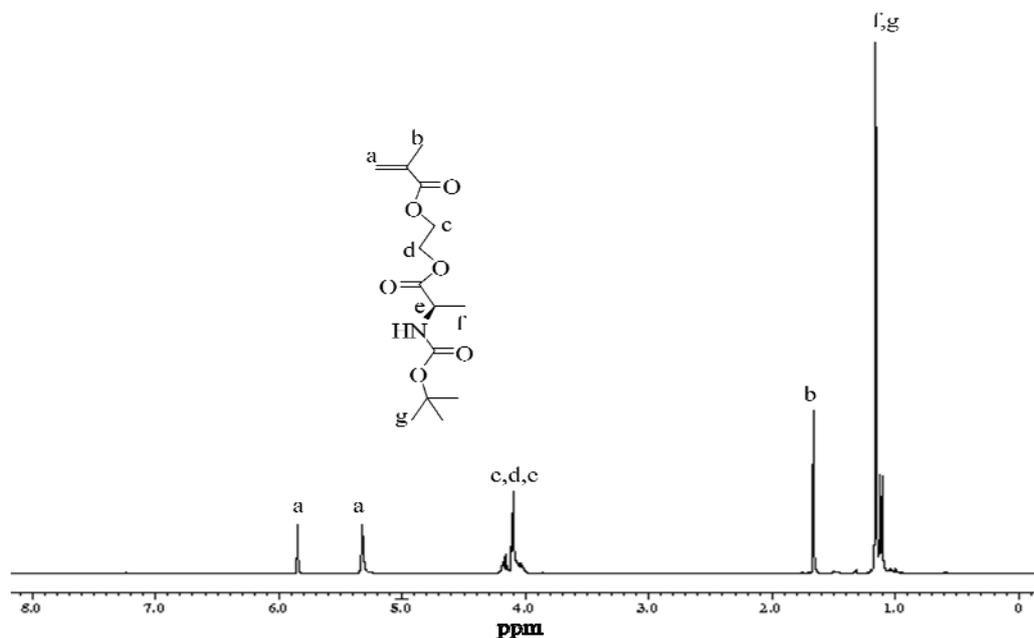


Figure S7. ¹H NMR spectrum of Boc-Ala-HEMA in CDCl₃.

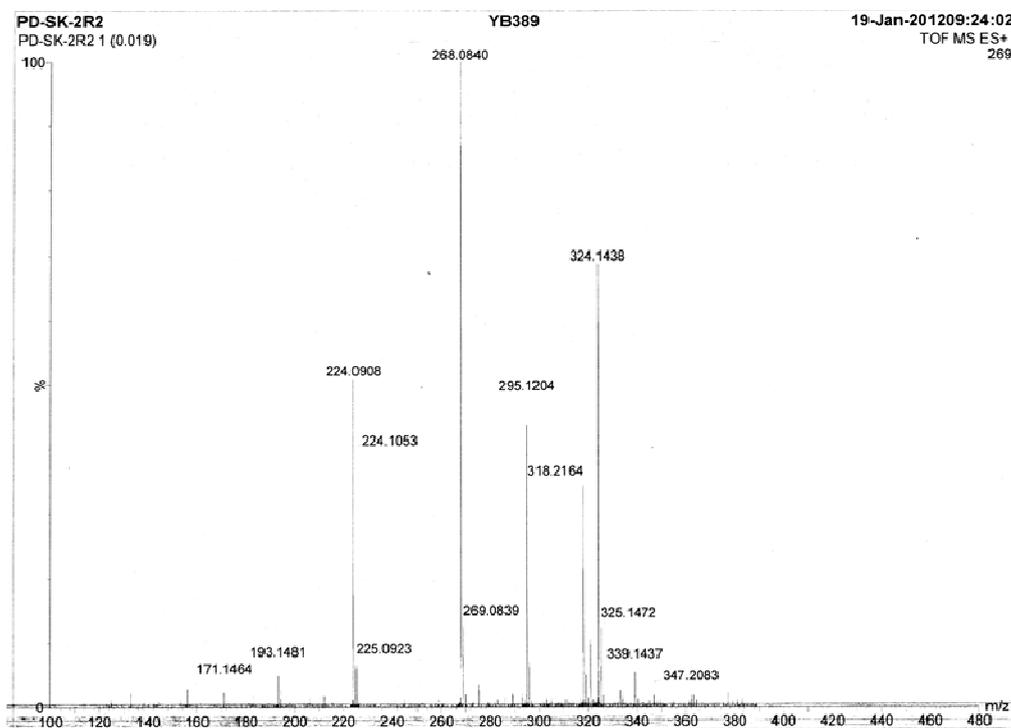


Figure S8. ESI-MS spectrum of Boc-Ala-HEMA (calculated for [M + Na⁺]: 324.15 *m/z*, observed 324.14 *m/z*).

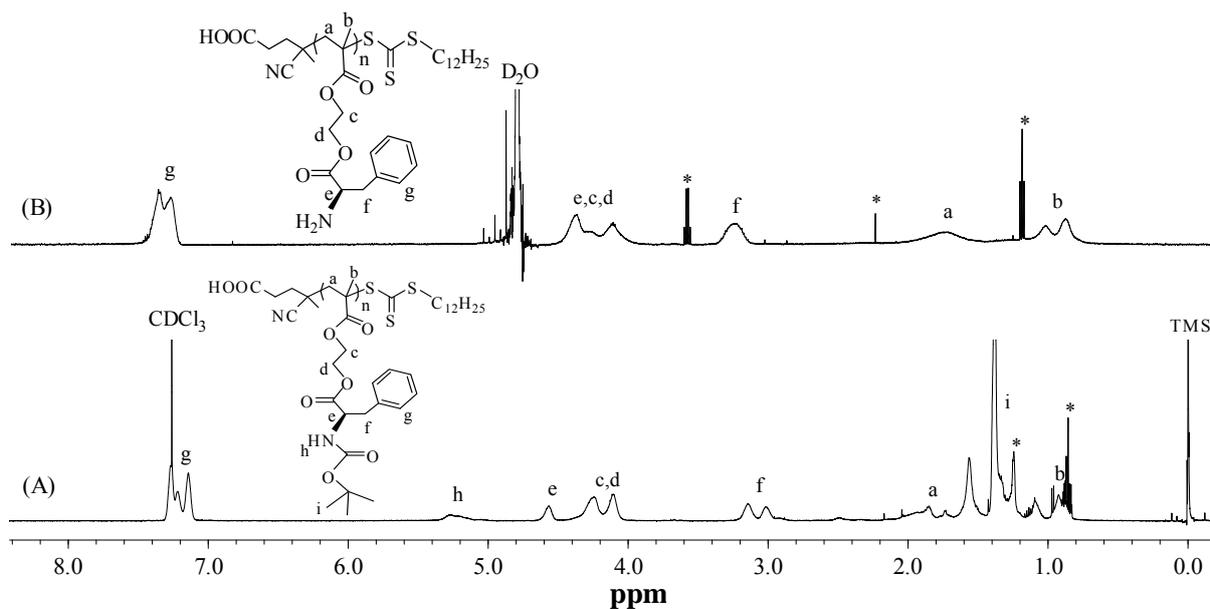


Figure S9. ^1H NMR spectra of homopolymers (A) P(Boc-Phe-HEMA) in CDCl_3 and (B) P(Phe-HEMA) in D_2O (* denotes the solvent resonances).

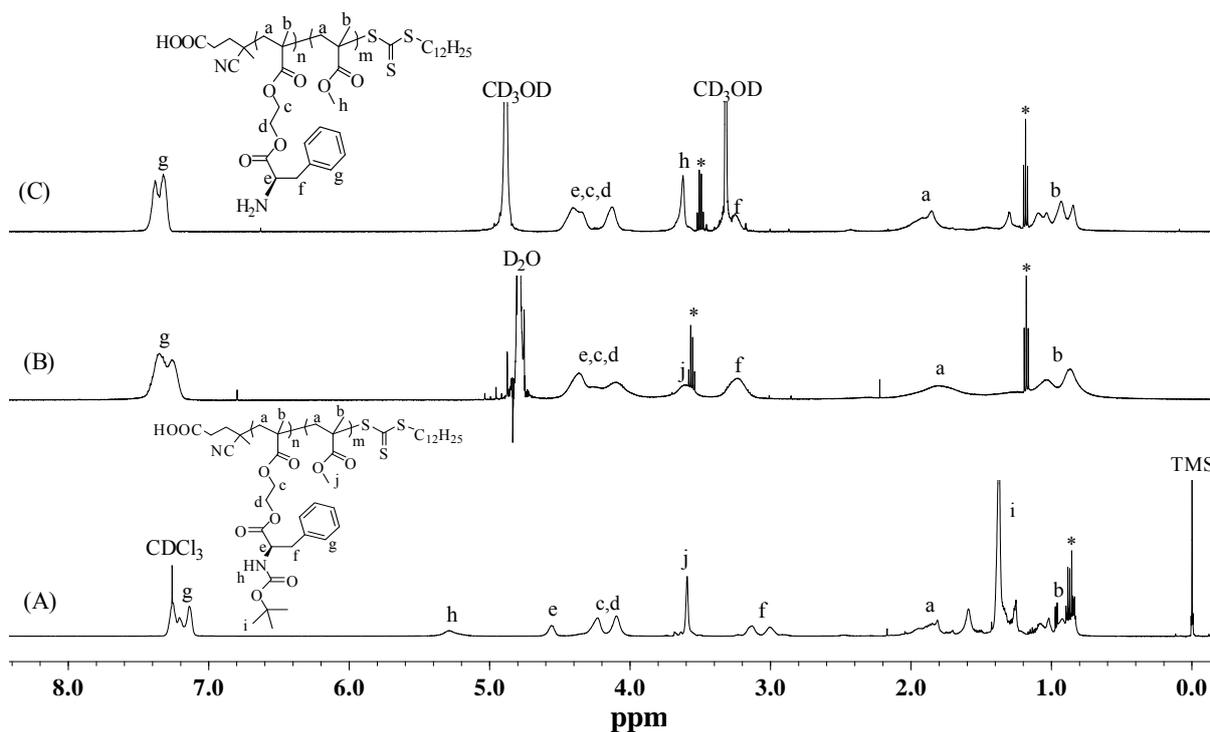


Figure S10. ^1H NMR spectra of block copolymer; (A) P(Boc-Phe-HEMA)-*b*-PMMA in CDCl_3 , (B) P(Phe-HEMA)-*b*-PMMA in D_2O , and (C) P(Phe-HEMA)-*b*-PMMA in CD_3OD . (* denotes the solvent resonances)

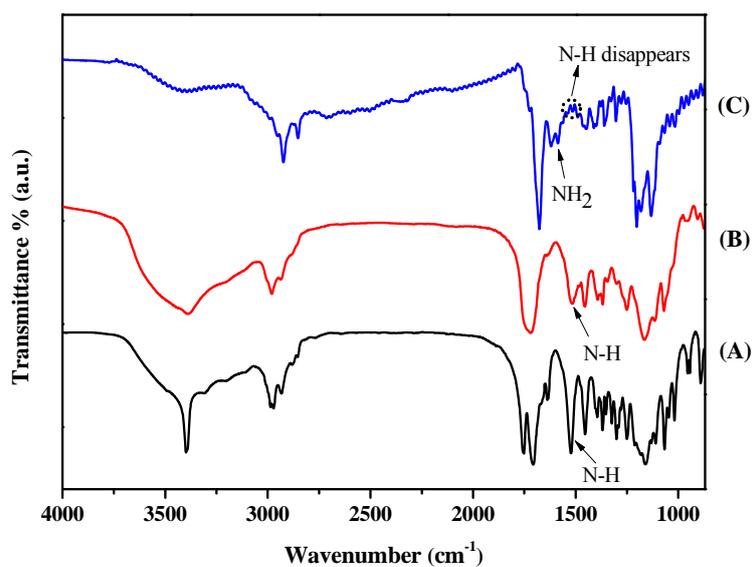


Figure S11. FT-IR spectra of (A) Boc-Ala-HEMA (B) P(Boc-Ala-HEMA) and (C) P(Ala-HEMA).

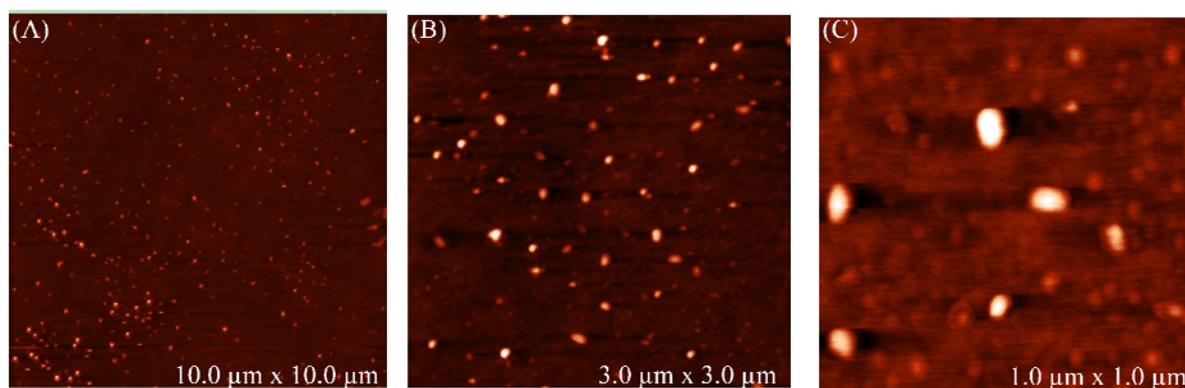


Figure S12. AFM images (height) of block copolymer P(Ala-HEMA)-*b*-PMMA in aqueous solution (0.08 mg/mL).

Table S1. Solubility studies for P(Boc-AA-HEMA)^a

Solvent	Solubility of	
	P(Boc-Phe-HEMA)	P(Boc-Ala-HEMA)
water	-	-
Acetone	+	+
CHCl ₃	+	+
CH ₂ Cl ₂	+	+
CCl ₄	+	+
Methanol	+	+
Ethanol	+	+
DMF	+	+
DMSO	+	+
THF	+	+
Pet Ether	-	-
Diethyl Ether	+	+
Ethyl Acetate	+	+
Hexane	-	-
Benzene	+	+
Toluene	+	+
1,4-Dioxane	+	+
Acetonitrile	+	+

^aThe symbols (+) and (-) indicate soluble and insoluble, respectively.

Spectroscopic Analysis of ω -Trithiocarbonate Moiety.

The % living chain ends were calculated using UV-Vis spectroscopy.

1 mg of CDP (MW = 403.67) was dissolved in 1 ml of DMF and from this solution 50 μ L was taken out and was added in 2 ml of DMF (0.0604 mM solution). UV-Vis spectrophotometer (path length = 1 cm) was used to determine absorbance at 307 nm, which was 0.752. From this result, the molar absorptivity was calculated as $12450 \text{ M}^{-1} \text{ cm}^{-1}$.

1.3 mg of CDP (MW = 403.67) was dissolved in 1.3 ml of DMF and from this solution 50 μ L was taken out and was added in 2 ml of DMF (0.0604 mM solution). UV-Vis spectrophotometer (path length = 1 cm) was used to determine absorbance at 307 nm, which was 0.737. From this result, the molar absorptivity was calculated as $12202 \text{ M}^{-1} \text{ cm}^{-1}$.

Average molar absorptivity = $12326 \text{ M}^{-1} \text{ cm}^{-1}$ was used for further calculations.

P(Boc-Ala-HEMA) (from two different measurements in DMF): Using molar absorptivity = $12326 \text{ M}^{-1} \text{ cm}^{-1}$, the $M_{n,UV-VIS} = 4,340 \text{ g/mol}$ was determine from the UV-Vis spectrophotometer. From GPC, $M_n = 4,300 \text{ g/mol}$ was determine (Table 2 in the manuscript). This indicates $\approx 100\%$ of P(Boc-Ala-HEMA)-macro CTA has living chain ends.

P(Boc-Phe-HEMA) (from two different measurements in DMF): Using molar absorptivity = $12326 \text{ M}^{-1} \text{ cm}^{-1}$, the $M_{n,UV-VIS} = 4,460 \text{ g/mol}$ was determine from the UV-Vis spectrophotometer. From GPC, $M_n = 4,650 \text{ g/mol}$ was determine (Table 2 in the manuscript). This indicates $\approx 96\%$ of P(Boc-Phe-HEMA)-macro CTA has living chain ends.