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Electronic Supplementary Information

An amino acid-derived ABCBA-type antifouling biohybrid with multi-stimuli responsivity and contaminant removal capability

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Fig. S12 Plot of the hydrodynamic diameter (D_h) as a function of temperature for an aqueous solution of PCysMAM$_{25}$-*b*-PDMAEMA$_{25}$-*b*-PB$_{22}$-*b*-PDMAEMA$_{25}$-*b*-PCysMAM$_{25}$ pentablock copolymer. …….....…S11

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A. Supporting Tables, Schemes and Figures

Table S1. Reaction conditions and molecular characterization data of PDMAEMA-*b*-PB-*b*-PDMAEMA triblock copolymers.[a]

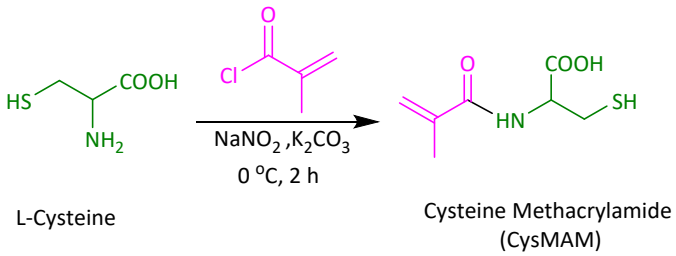
Entry	Polymer	$[DMAEMA]_0/[Br\text{-}PB_{22}\text{-}Br]_0$	Conv.[b] (%)	$M_{n,theo}$[c] (g mol^{-1})	$M_{n,NMR}$[d] (g mol^{-1})	$M_{n,SEC}$[e] (g mol^{-1})	$Đ$[e]
P1	$PDMAEMA_{25}$-*b*-PB_{22}-*b*-$PDMAEMA_{25}$	50: 22	87	10300	9900	10100	1.17
P2	$PDMAEMA_{50}$-*b*-PB_{22}-*b*-$PDMAEMA_{50}$	100: 22	85	22500	21400	22200	1.16
P3	$PDMAEMA_{75}$-*b*-PB_{22}-*b*-$PDMAEMA_{75}$	150: 22	88	32900	32100	32600	1.18
P4	$PDMAEMA_{100}$-*b*-PB_{22}-*b*-$PDMAEMA_{100}$	200: 22	82	40100	37400	38800	1.17

[a]Reaction conditions: solvent = THF; catalyst = Ni-Co alloy; ligand = Me_6TREN; temperature = 25 °C; time = 24 h. [b]Determined gravimetrically based on monomer feed. [c]Calculated using yield as conversion and the following equation: $M_{n,theo} = ([DMAEMA]_0/[Br\text{-}PB_{22}\text{-}Br]_0 \times \text{yield} \times M_{DMAEMA}) + M_{Br\text{-}PB22\text{-}Br}$, where M_{DMAEMA} (= 157 g mol^{-1}) and $M_{Br\text{-}PB22\text{-}Br}$ (= 1350 g mol^{-1}) are the molecular weight of DMAEMA and Br-PB_{22}-Br, respectively. [d]Determined by ^{1}HNMR (see equation 5 in the Experimental Section for details). [e]Obtained from SEC measurements.

Table S2. Catalyst recyclability study for alloy-mediated RDRP of DMAEMA from Br-PB_{22}-Br macroinitiator.[a]

Entry	Cycle	Conv.[b] (%)	$M_{n,theo.}$[c] (g mol^{-1})	$M_{n,SEC}$[d] (g mol^{-1})	$Đ$[d]
P1	1st	86	10250	9900	1.17
P2	2nd	86	10250	9800	1.16
P3	3rd	85	10200	9800	1.17
P4	4th	84	10100	9700	1.16
P5	5th	82	9900	9800	1.15

[a]Reaction conditions: solvent = THF; catalyst = Ni-Co alloy; ligand = Me_6TREN; temperature = 25 °C; time = 24 h. [b]Determined gravimetrically. [c]Calculated using the following equation: $M_{n,theo} = ([DMAEMA]_0/[Br\text{-}PB_{22}\text{-}Br]_0 \times \text{yield} \times M_{DMAEMA}) + M_{Br\text{-}PB22\text{-}Br}$, where M_{DMAEMA} (= 157 g mol^{-1}) and $M_{Br\text{-}PB22\text{-}Br}$ (= 1350 g mol^{-1}) are the molecular weight of DMAEMA and Br-PB_{22}-Br, respectively. [d]Obtained from SEC measurements.



Scheme S1 Synthesis of L-cysteine methacrylamide (CysMAM).

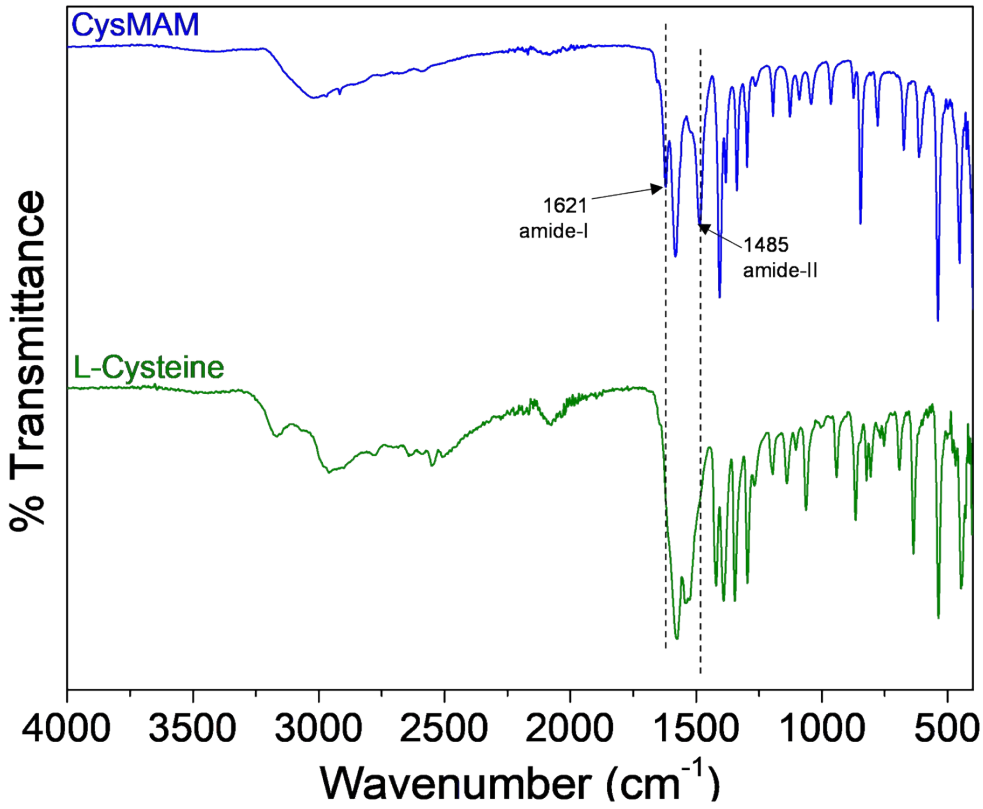


Fig. S1 ATR-IR spectra of L-cysteine and CysMAM.

L-Cysteine methacrylamide was prepared by coupling with L-cysteine monomer with methacryloyl chloride. This was confirmed by two characteristic amide I and amide II absorption bands at 1621 and 1485 cm^{-1}, respectively (Fig. S1).[1]

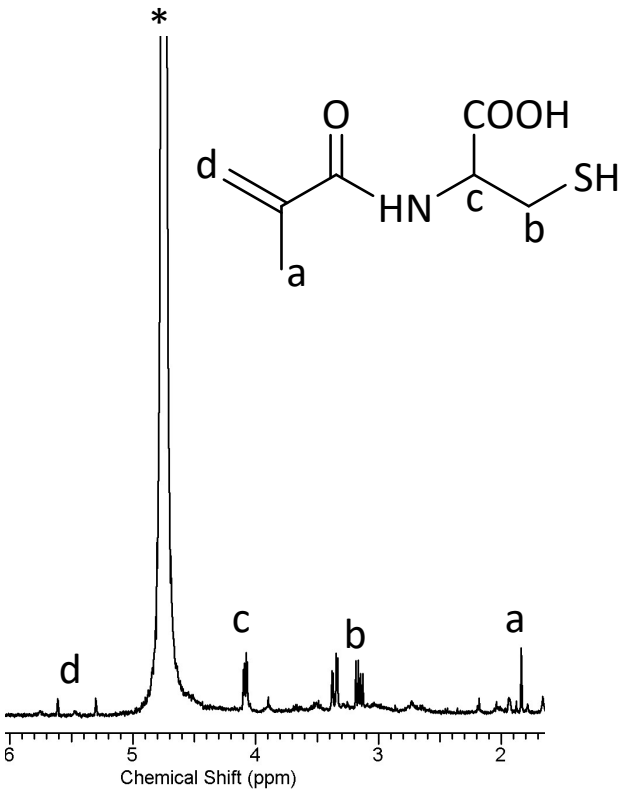


Fig. S2 ^{1}H NMR spectrum of CysMAM. (∗) Solvent (D_2O) peak.

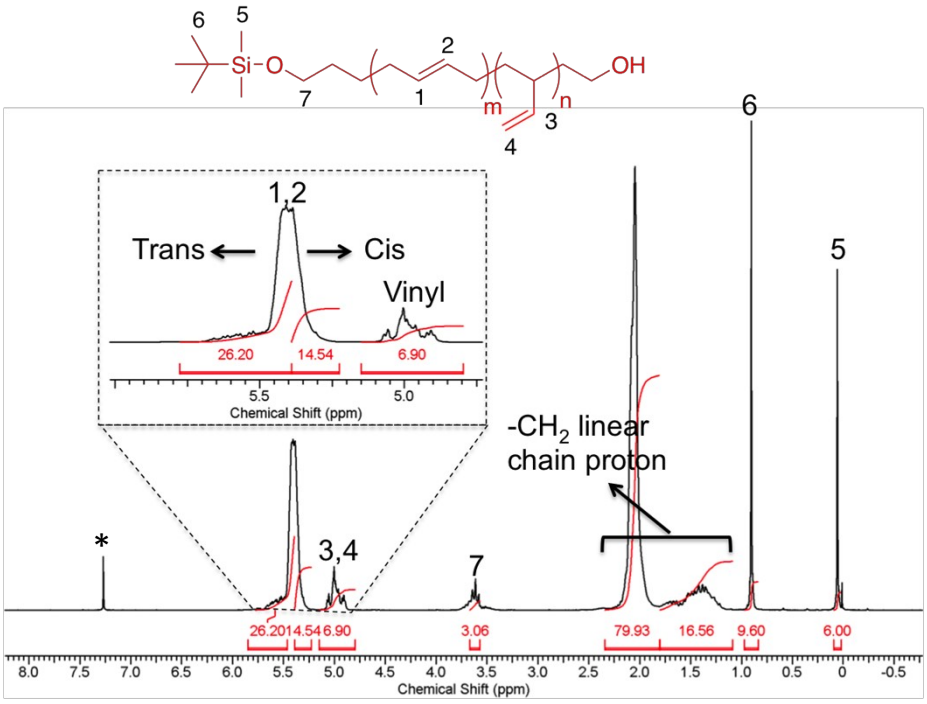


Fig. S3 ^{1}H NMR spectrum of monohydroxyl-terminated polybutadiene polymer. (∗) Solvent ($CDCl_3$) peak.

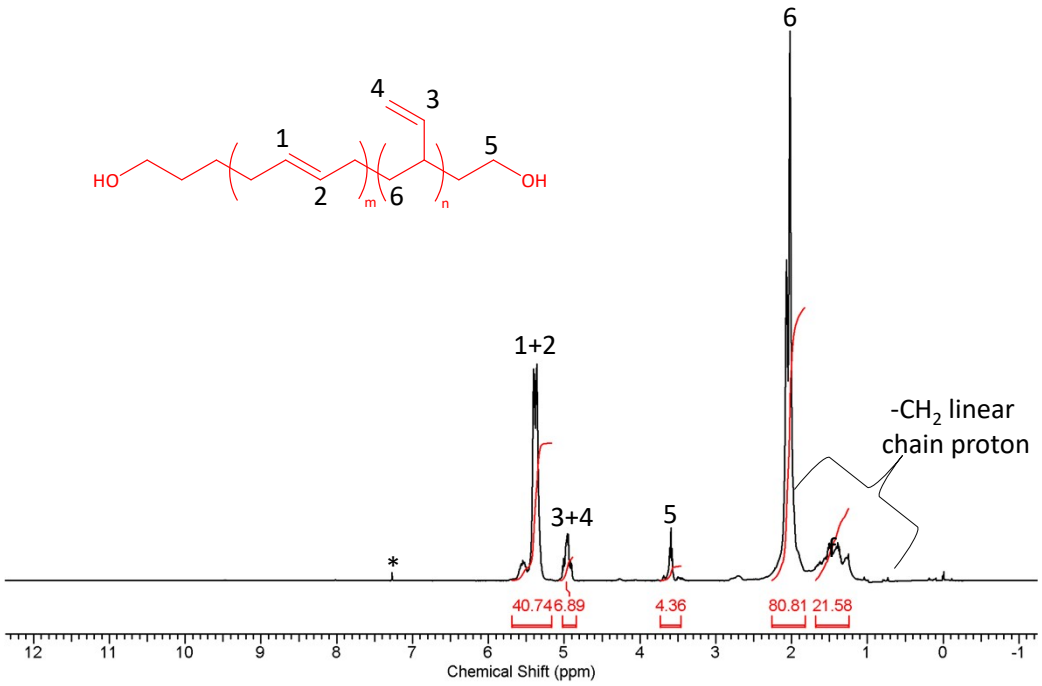


Fig. S4 ^{1}H NMR spectrum of dihydroxyl-terminated polybutadiene polymer (PB). (∗) Solvent ($CDCl_3$) peak.

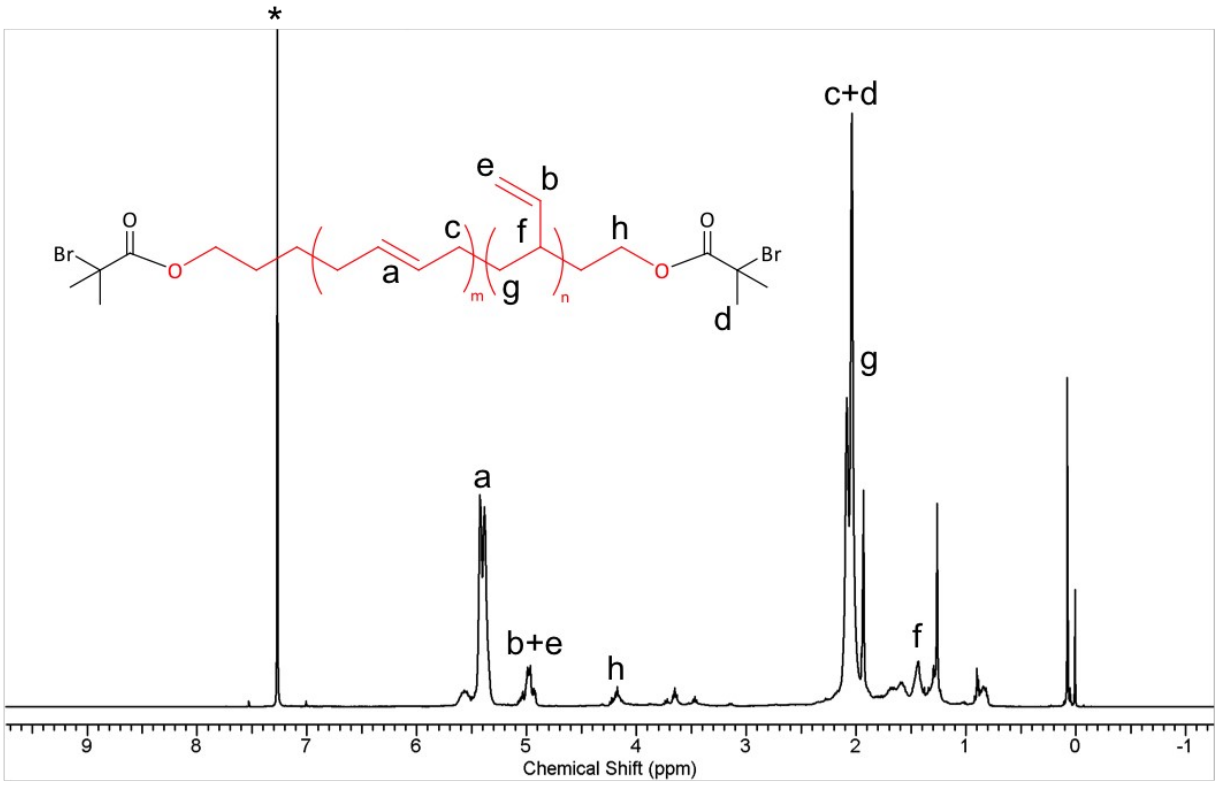


Fig. S5 ^{1}H NMR spectrum of dibromo-terminated polybutadiene polymer (Br-PB_{22}-Br). (∗) Solvent ($CDCl_3$) peak.

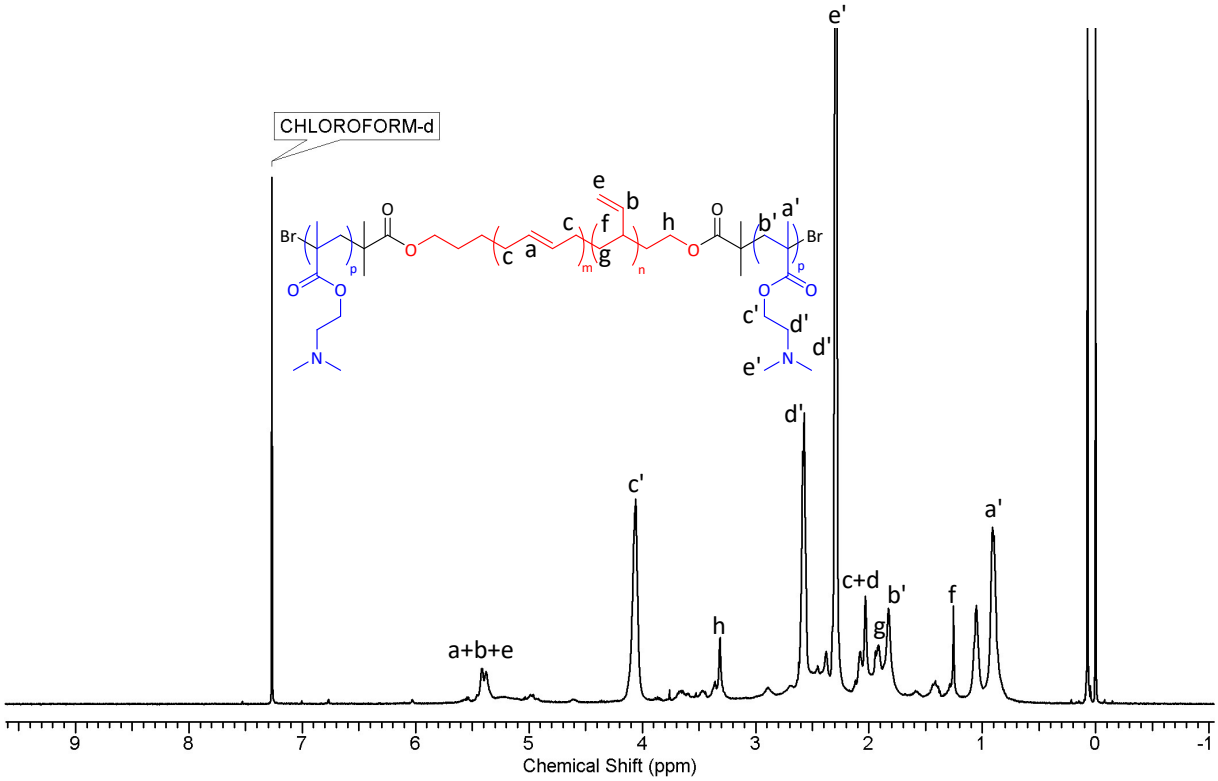


Fig. S6 ^{1}H NMR spectrum of PDMAEMA$_{25}$-*b*-PB$_{22}$-*b*-PDMAEMA$_{25}$ triblock copolymer (P1, Table S1).

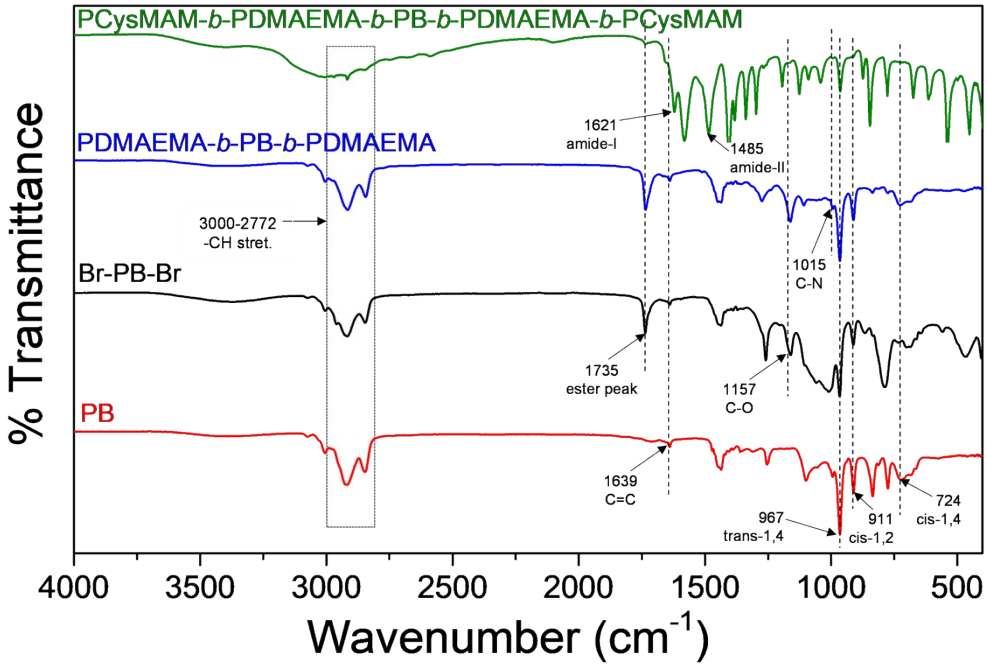


Fig. S7 ATR-IR spectra of PB$_{22}$ (a), Br-PB$_{22}$-Br macroinitiator (b), PDMAEMA$_{25}$-*b*-PB$_{22}$-*b*-PDMAEMA$_{25}$ (c) and PCysMAM$_{25}$-*b*-PDMAEMA$_{25}$-*b*-PB$_{22}$-*b*-PDMAEMA$_{25}$-*b*-PCysMAM$_{25}$ (d).

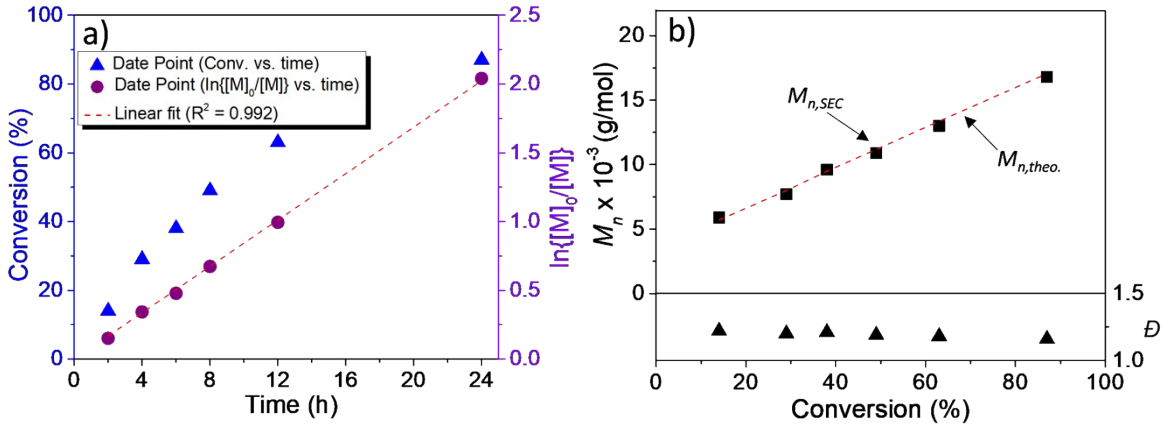


Fig. S8 Plot of a) conversion vs. time, ln{[M]0/[M]} vs. time and b) evolution of M_n and $Đ$ with increasing monomer conversion for alloy-mediated RDRP of DMAEMA in THF at 25 °C using Br-PB-Br as the macroinitiator. The non-zero value of M_n at zero conversion is because the Br-PB-Br macroinitiator was used in the polymerization.

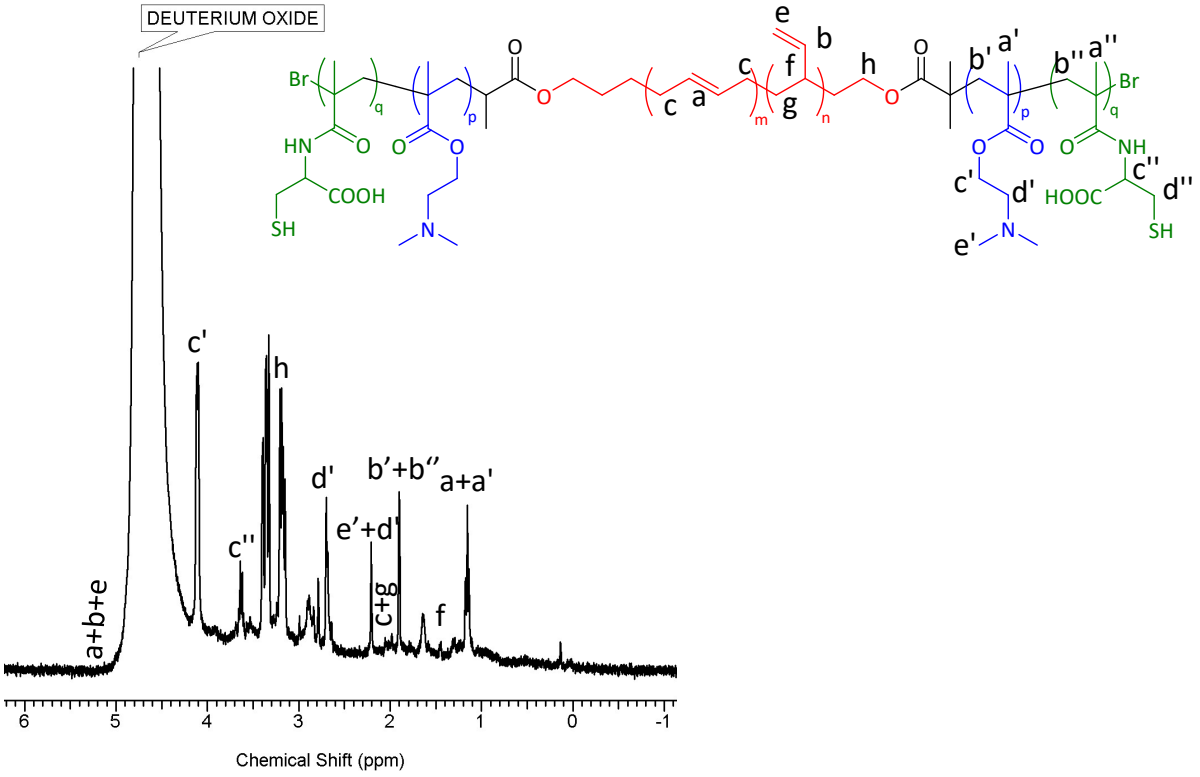


Fig. S9 ^{1}H NMR spectrum of PCysMAM$_{25}$-*b*-PDMAEMA$_{25}$-*b*-PB$_{22}$-*b*-PDMAEMA$_{25}$-*b*-PCysMAM$_{25}$ pentablock copolymer (P2, Table 1). (∗) Solvent (D_2O) peak.

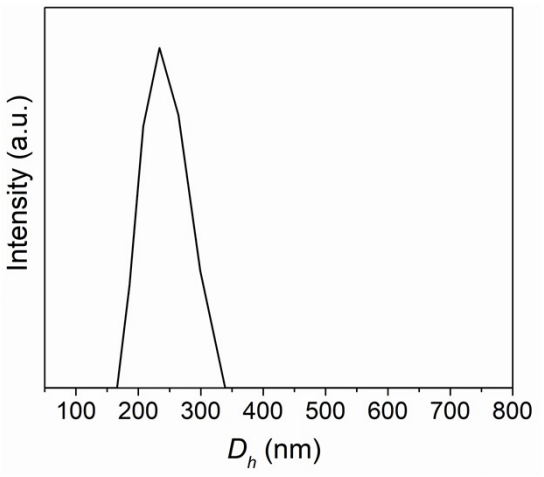


Fig. S10 Size distributions of the PCysMAM$_{25}$-*b*-PDMAEMA$_{25}$-*b*-PB$_{22}$-*b*-PDMAEMA$_{25}$-*b*-PCysMAM$_{25}$ pentablock copolymer aggregates by DLS.

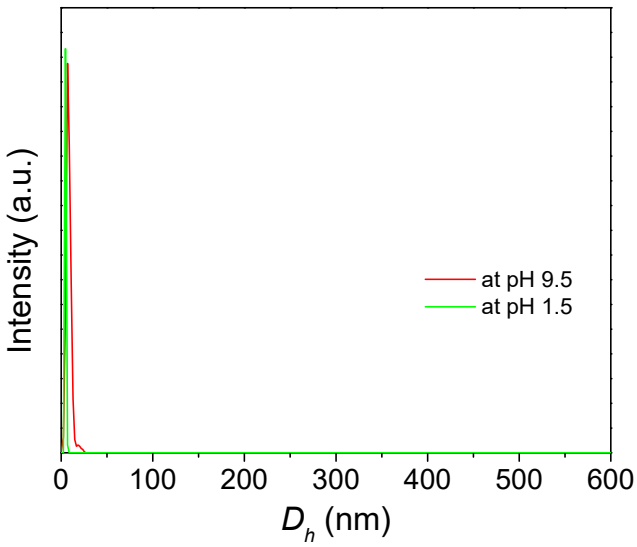


Fig. S11 Size distributions of the PCysMAM$_{25}$-*b*-PDMAEMA$_{25}$-*b*-PB$_{22}$-*b*-PDMAEMA$_{25}$-*b*-PCysMAM$_{25}$ pentablock copolymer aggregates at pH 9.5 and 1.5 by DLS.

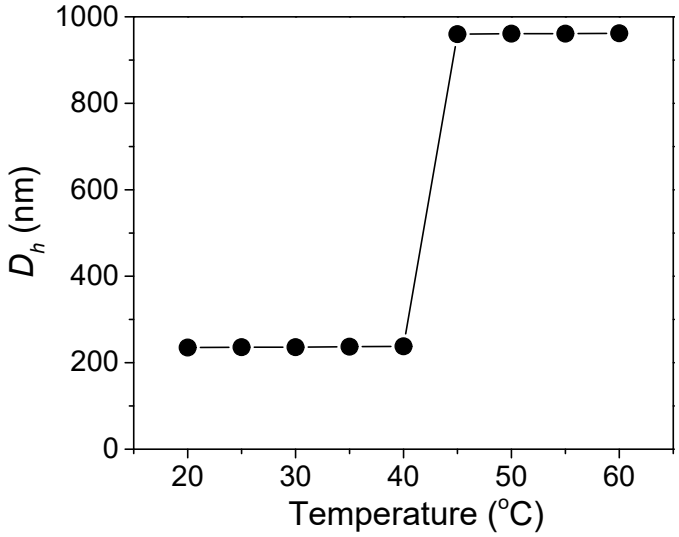


Fig. S12 Plot of the hydrodynamic diameter (D_h) as a function of temperature for an aqueous solution of PCysMAM$_{25}$-*b*-PDMAEMA$_{25}$-*b*-PB$_{22}$-*b*-PDMAEMA$_{25}$-*b*-PCysMAM$_{25}$ pentablock copolymer at pH 7.

B. References.

1. B. B. Prasad, D. Jauhari and M. P. Tiwari, *Biosens. Bioelectron.*, 2014, **59**, 81-88.