Supporting Information for

Controlled Synthesis of pH Responsive Cationic Polymers Containing Side-Chain Peptide Moieties *via* RAFT Polymerization and Their Self Assembly

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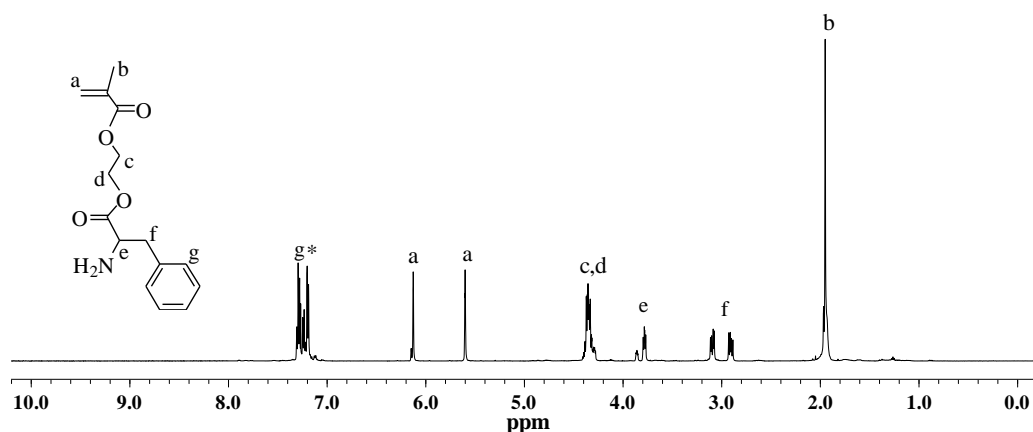
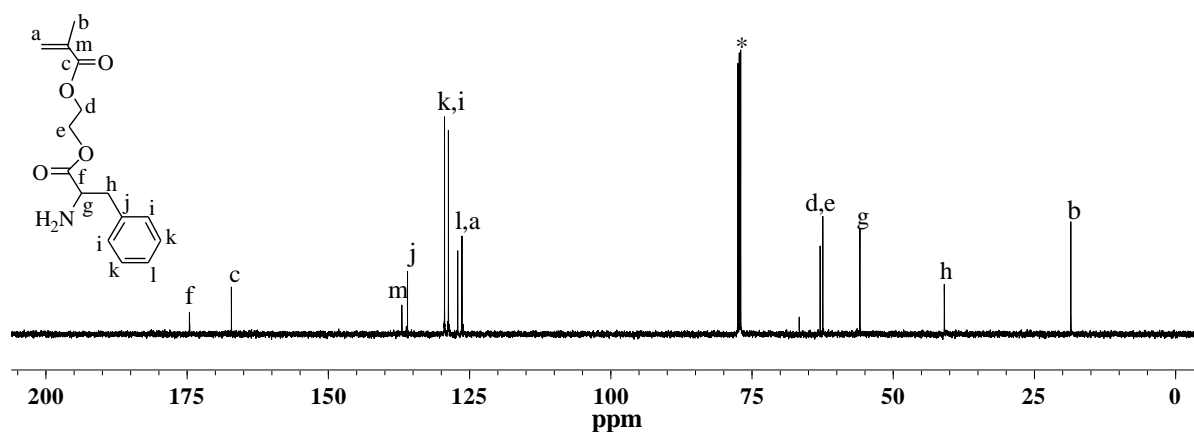**Fig. S1** The ^{1}H NMR spectrum of H_2N-Phe-EMA (* denotes the resonances of $CDCl_3$).

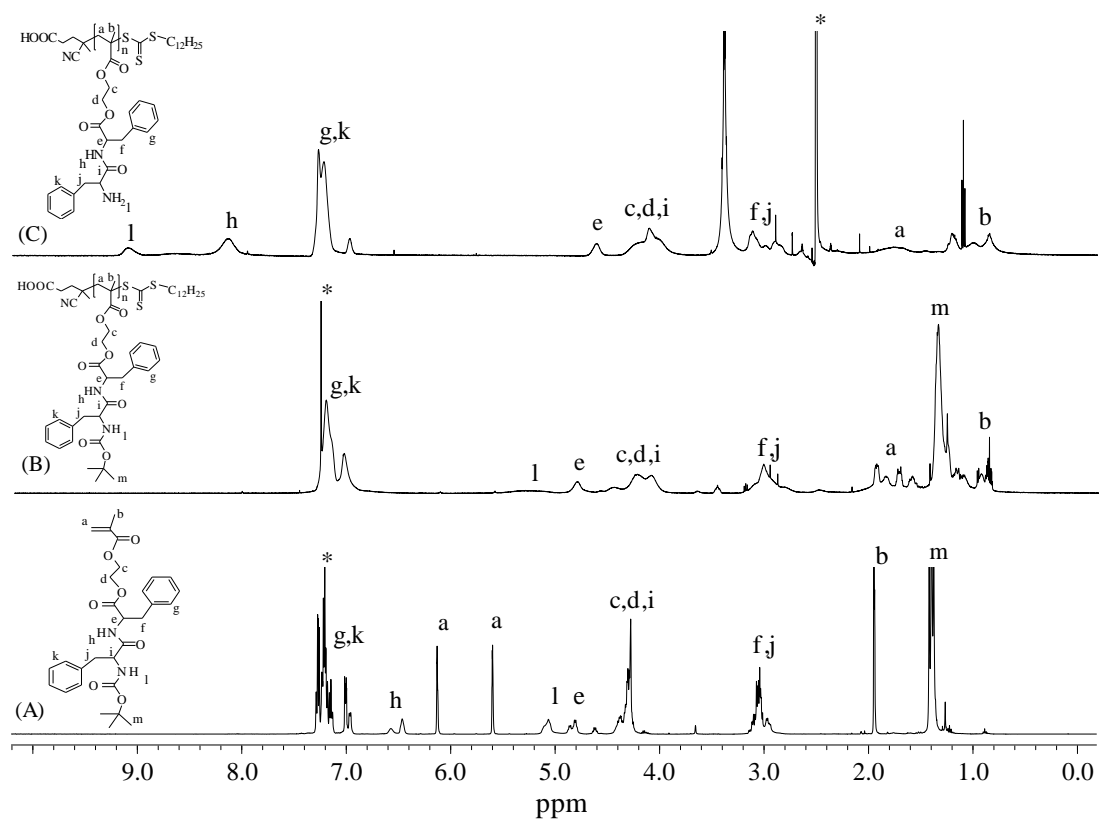**Fig. S2** The ^{13}C NMR spectrum of H_2N-Phe-EMA (* denotes the resonances of $CDCl_3$).

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Fig. S3 The ^{1}H NMR spectra of (A) Boc-FF-EMA monomer, (B) P(Boc-FF-EMA) homopolymer in CDCl$_3$, and (C) P(FF-EMA) in DMSO-d_6 (* denotes the solvent resonances).
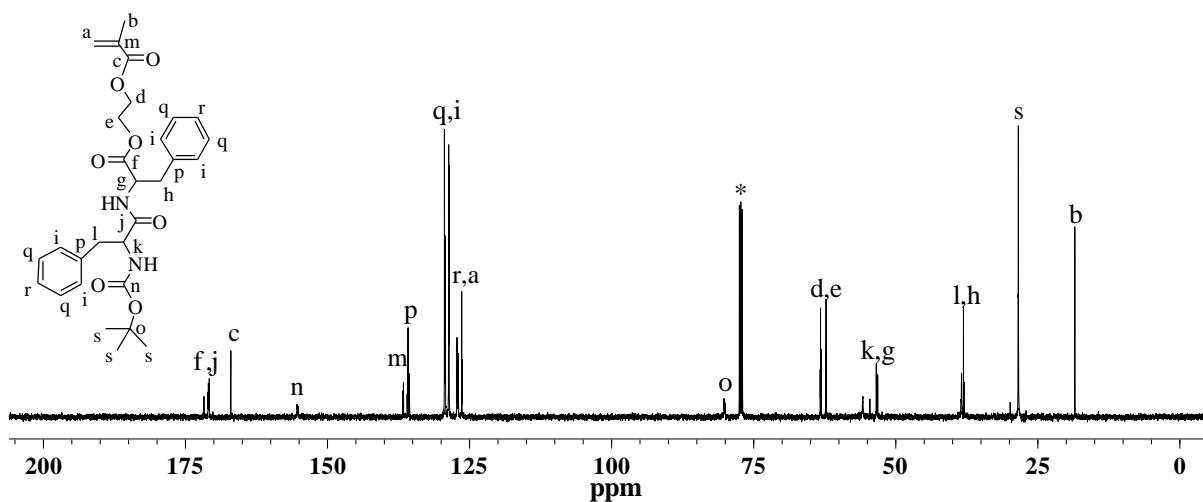

Fig. S4 The ^{13}C NMR spectrum of Boc-FF-EMA (* denotes the resonances of CDCl$_3$).
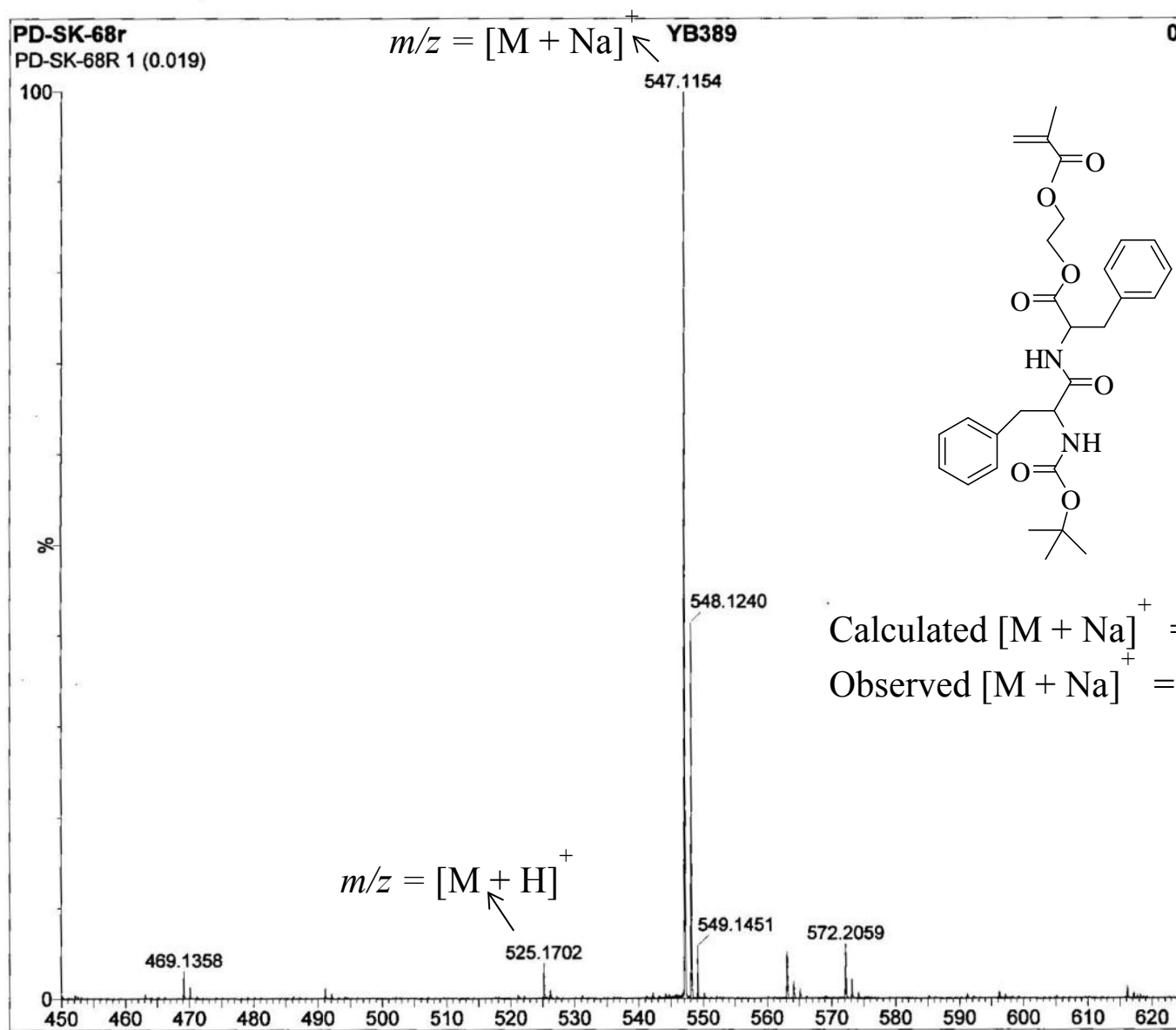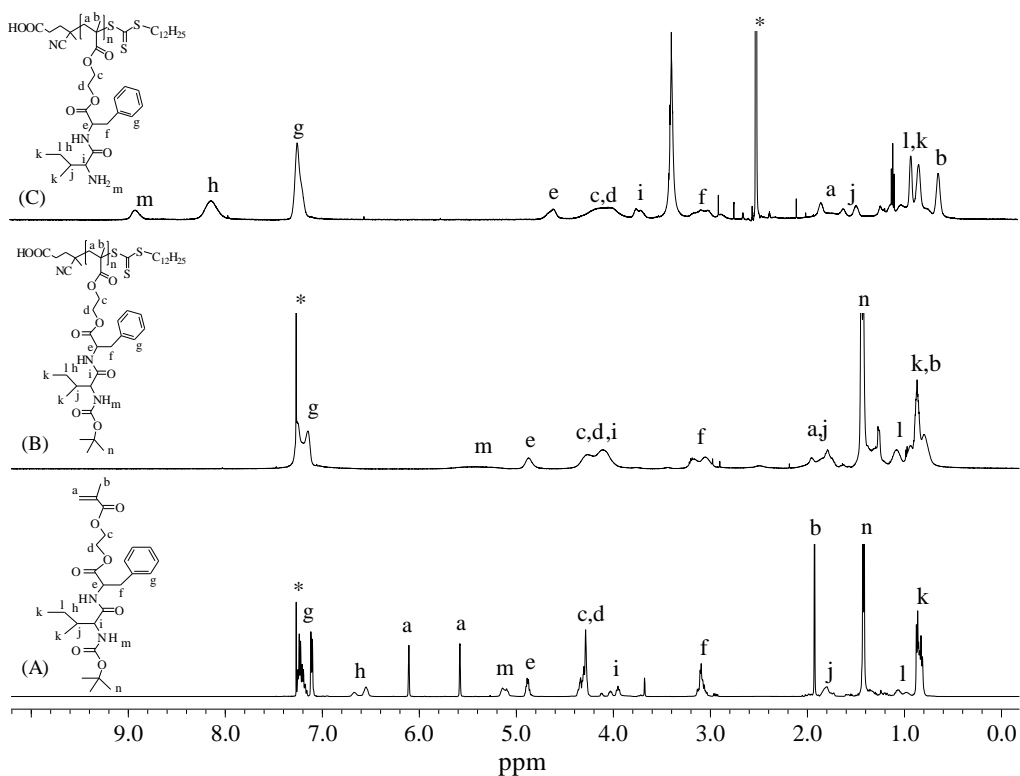
Fig. S5 The ESI-MS spectrum of Boc-FF-EMA.

Fig. S6 The ^{1}H NMR spectra of (A) Boc-IF-EMA monomer, (B) P(Boc-IF-EMA) homopolymer in CDCl$_3$, and (C) P(IF-EMA) in DMSO-d_6 (* denotes the solvent resonances).
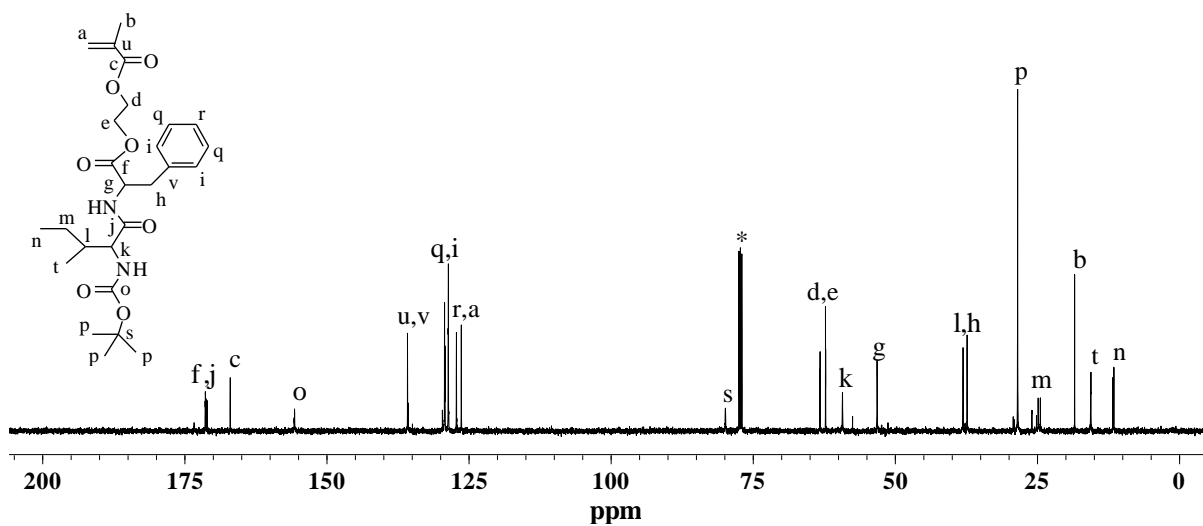

Fig. S7 The ^{13}C NMR spectrum of monomer Boc-IF-EMA (* denotes the resonances of CDCl$_3$).
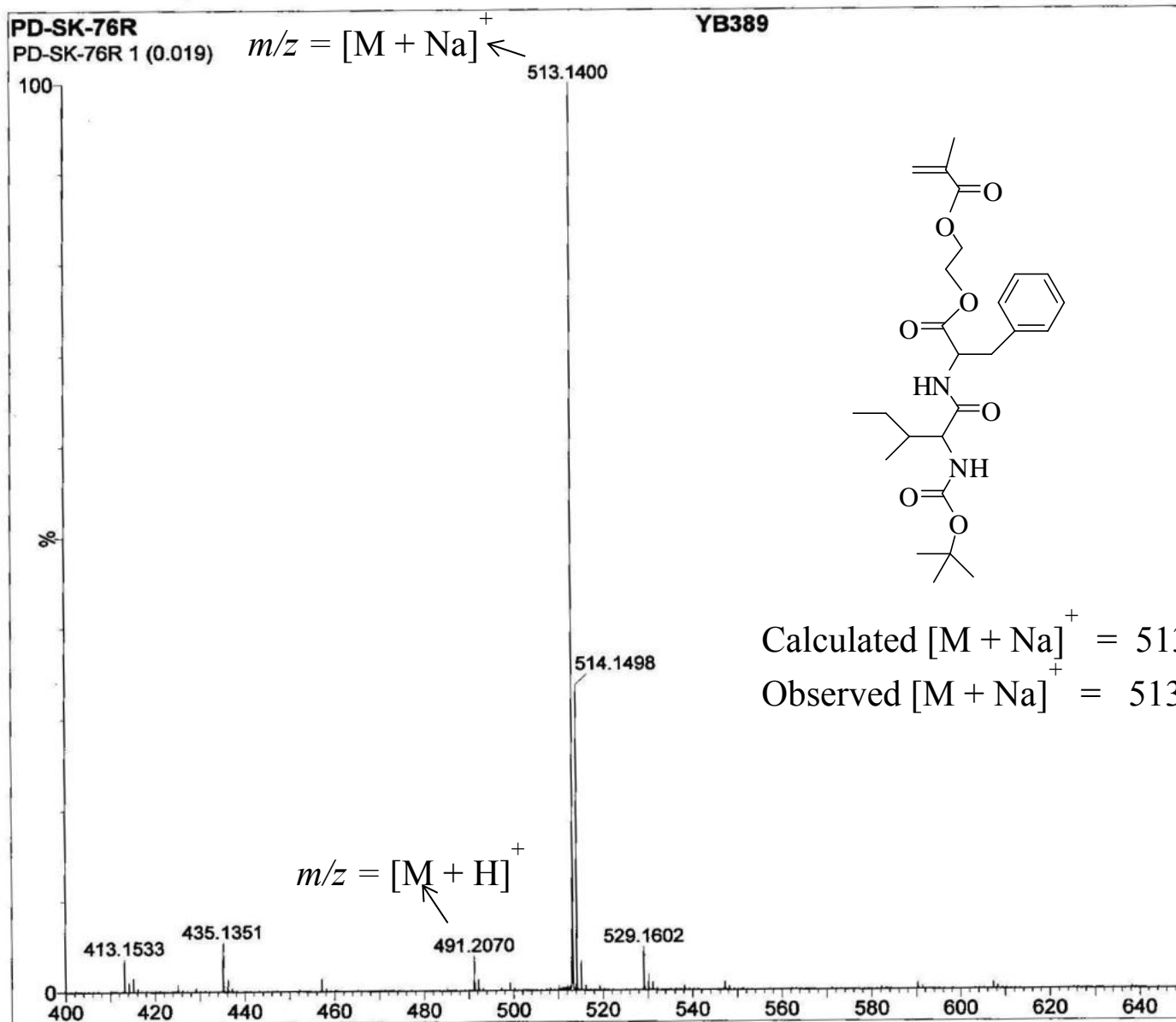
PD-SK-76R
PD-SK-76R 1 (0.019) YB389

$m/z = [M + Na]^+$

513.1400

Calculated $[M + Na]^+ = 51$

Observed $[M + Na]^+ = 513$

514.1498

$m/z = [M + H]^+$

413.1533 435.1351 491.2070 529.1602

Fig. S8 The ESI-MS spectrum of Boc-IF-EMA.

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Fig. S9 The ^{13}C NMR spectrum of monomer Boc-VF-EMA (* denotes the resonances of CDCl$_3$).
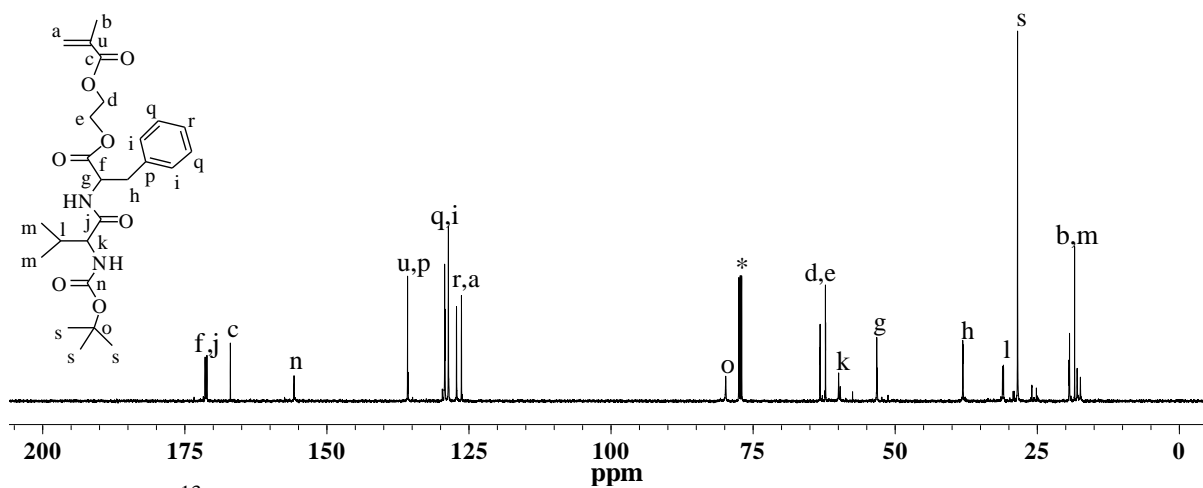
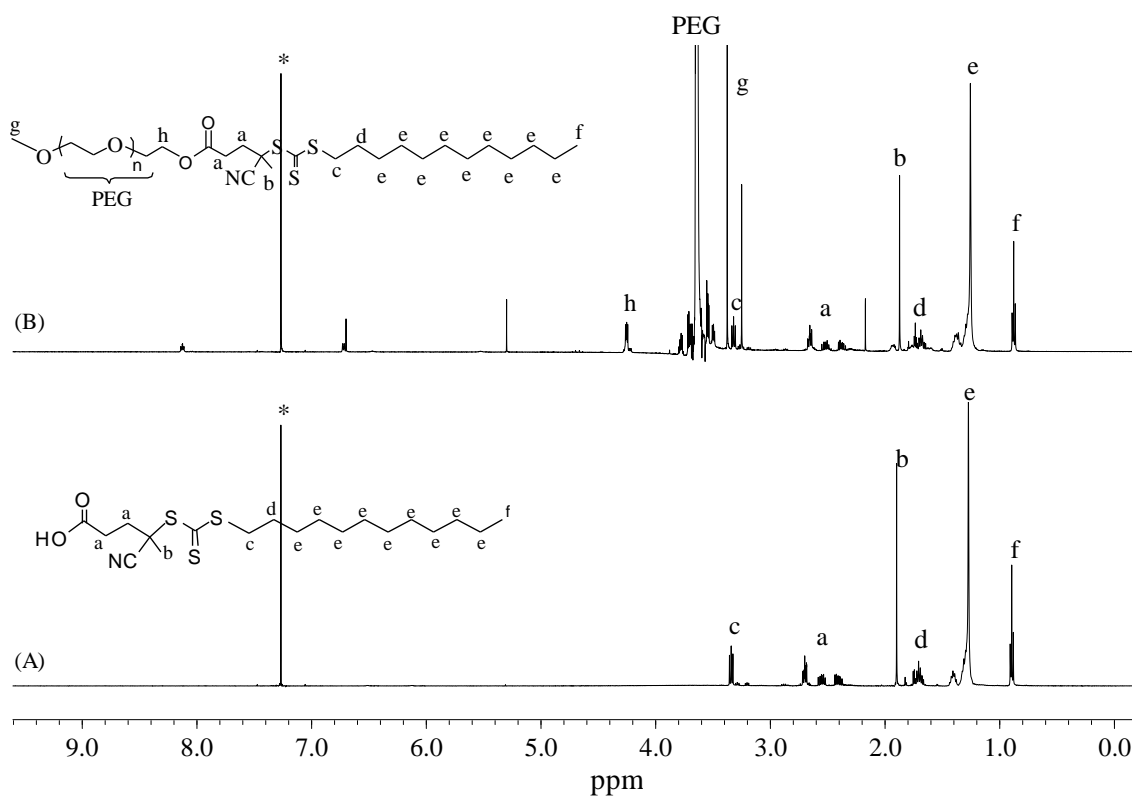**Fig. S10** The ESI-MS spectrum of Boc-VF-EMA.

Fig. S11 The ^{1}H NMR spectra of chain transfer agent (A) CDP, and (B) mPEG-CDP macro-CTA (* denotes the resonances of CDCl$_3$).
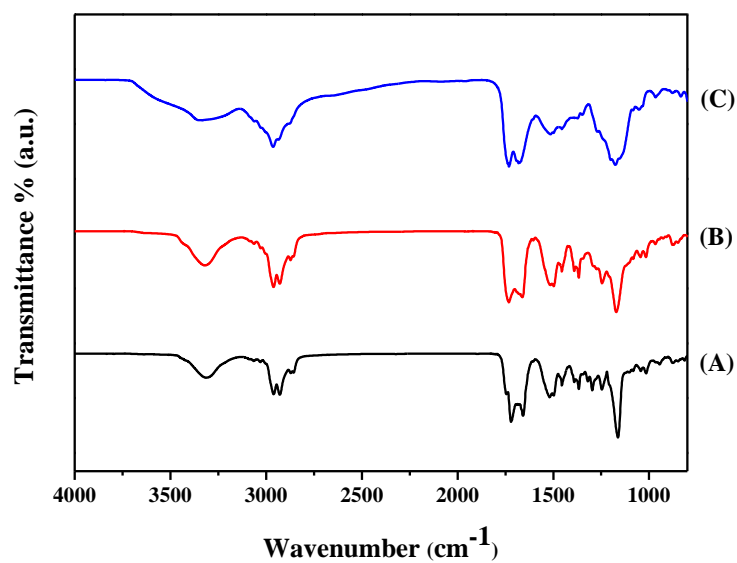

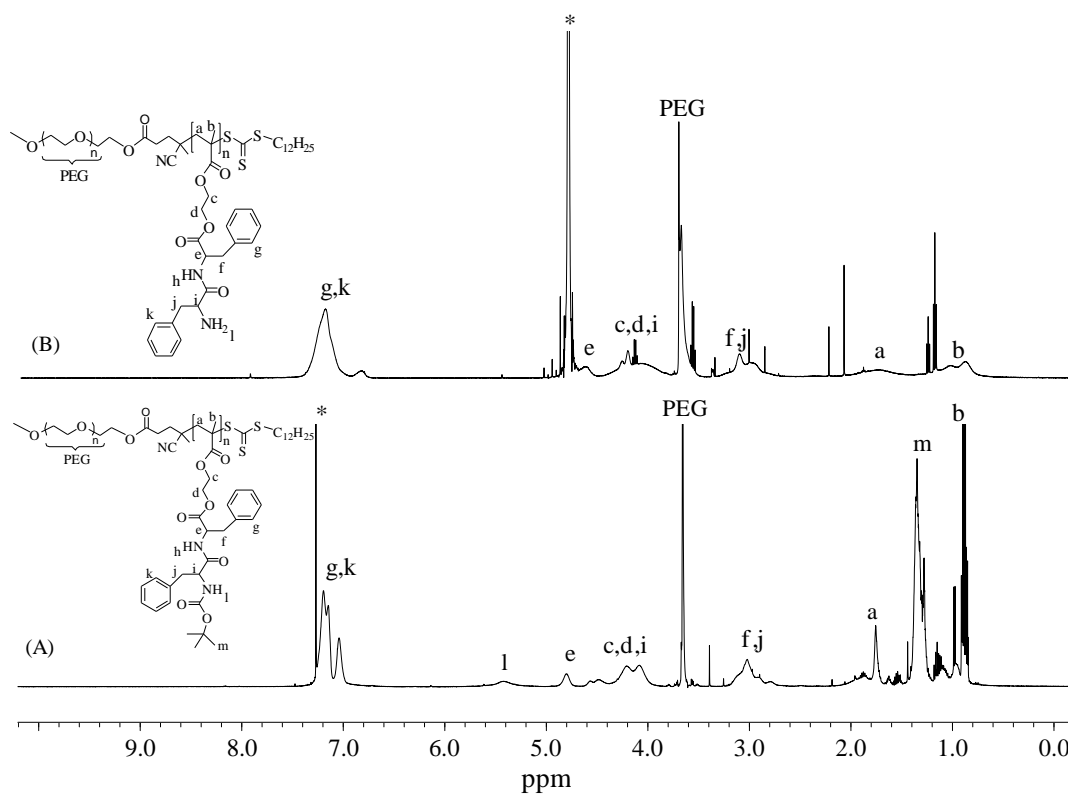**Fig. S12** FT-IR spectra of (A) Boc-VF-EMA, (B) P(Boc-VF-EMA), and (C) P(VF-EMA).

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Fig. S13 The ^{1}H NMR spectra of (A) mPEG-*b*-P(Boc-FF-EMA) block copolymer in CDCl$_3$ and (B) mPEG-*b*-P(FF-EMA) in D$_2$O (* denotes the solvent resonances).

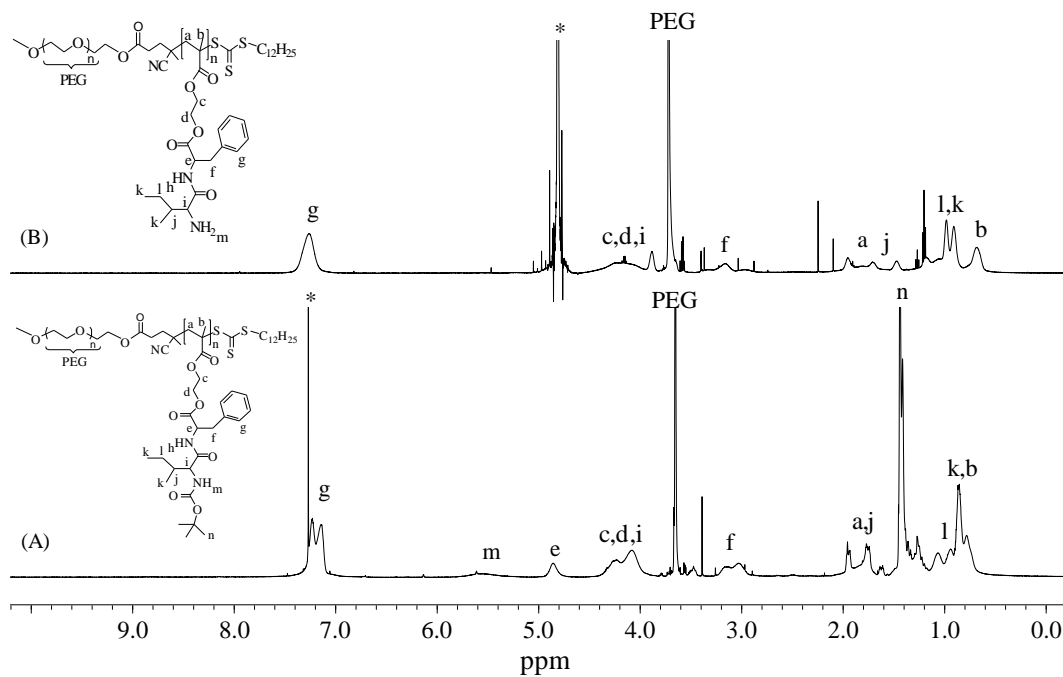**Fig. S14** ^{1}H NMR spectra of block copolymers (A) mPEG-*b*-P(Boc-IF-EMA) in CDCl$_3$ (B) mPEG-*b*-P(IF-EMA) in D$_2$O (* denotes the solvent resonances).
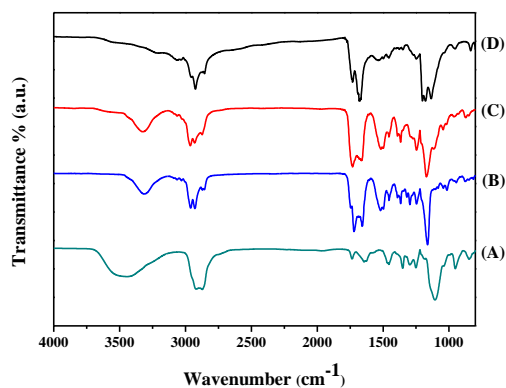
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Fig. S15 FT-IR spectra of (A) mPEG-CDP, (B) Boc-VF-EMA, (C) mPEG-*b*-P(Boc-VF-EMA) and (D) mPEG-*b*-P(VF-EMA).
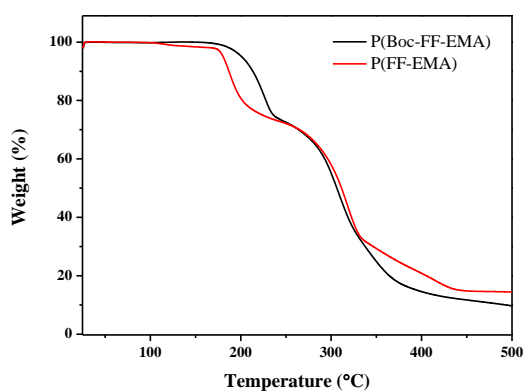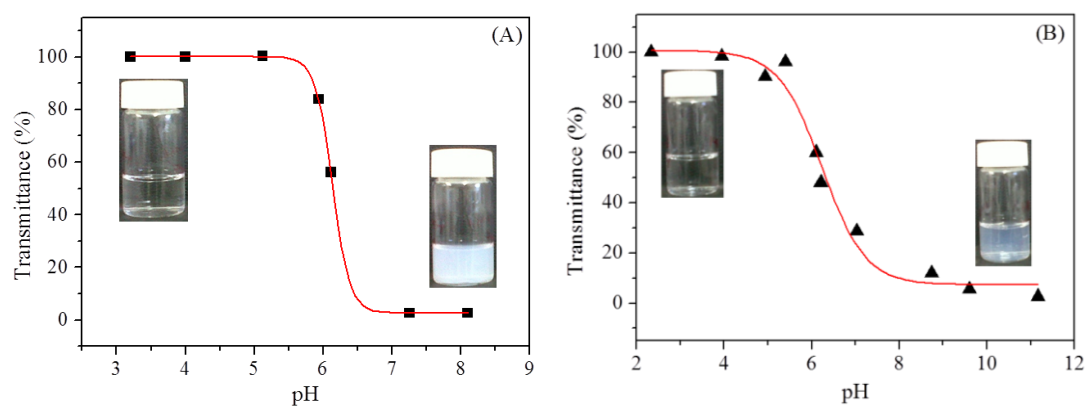

Fig. S16 TGA curves of dipeptide based homopolymers.

Fig. S17 Effect of pH on the absorbance at 550 nm of (A) P(IF-EMA) homopolymer, and (B) block copolymer mPEG-*b*-P(IF-EMA).
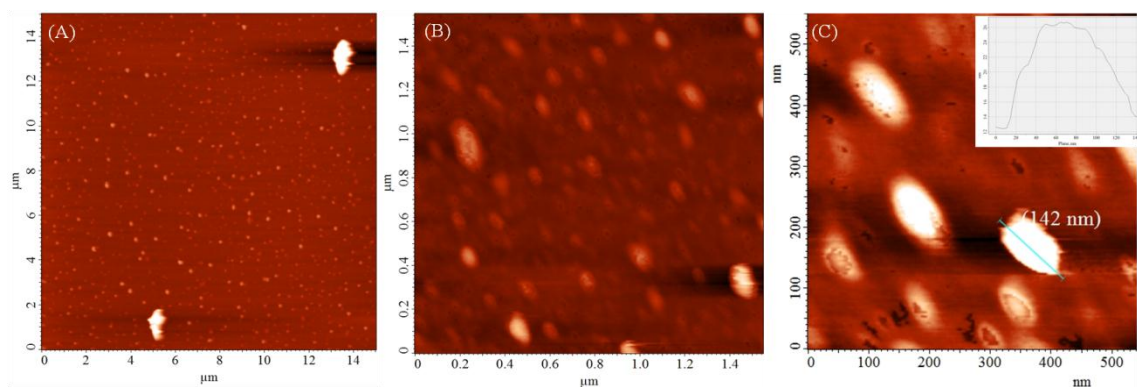
Fig. S18 AFM height images of mPEG-*b*-P(Boc-FF-EMA) block copolymer in different magnification (prepared from 0.1 mg mL^{-1} aqueous solution). Inset in C: height profile plot (line marked in C).
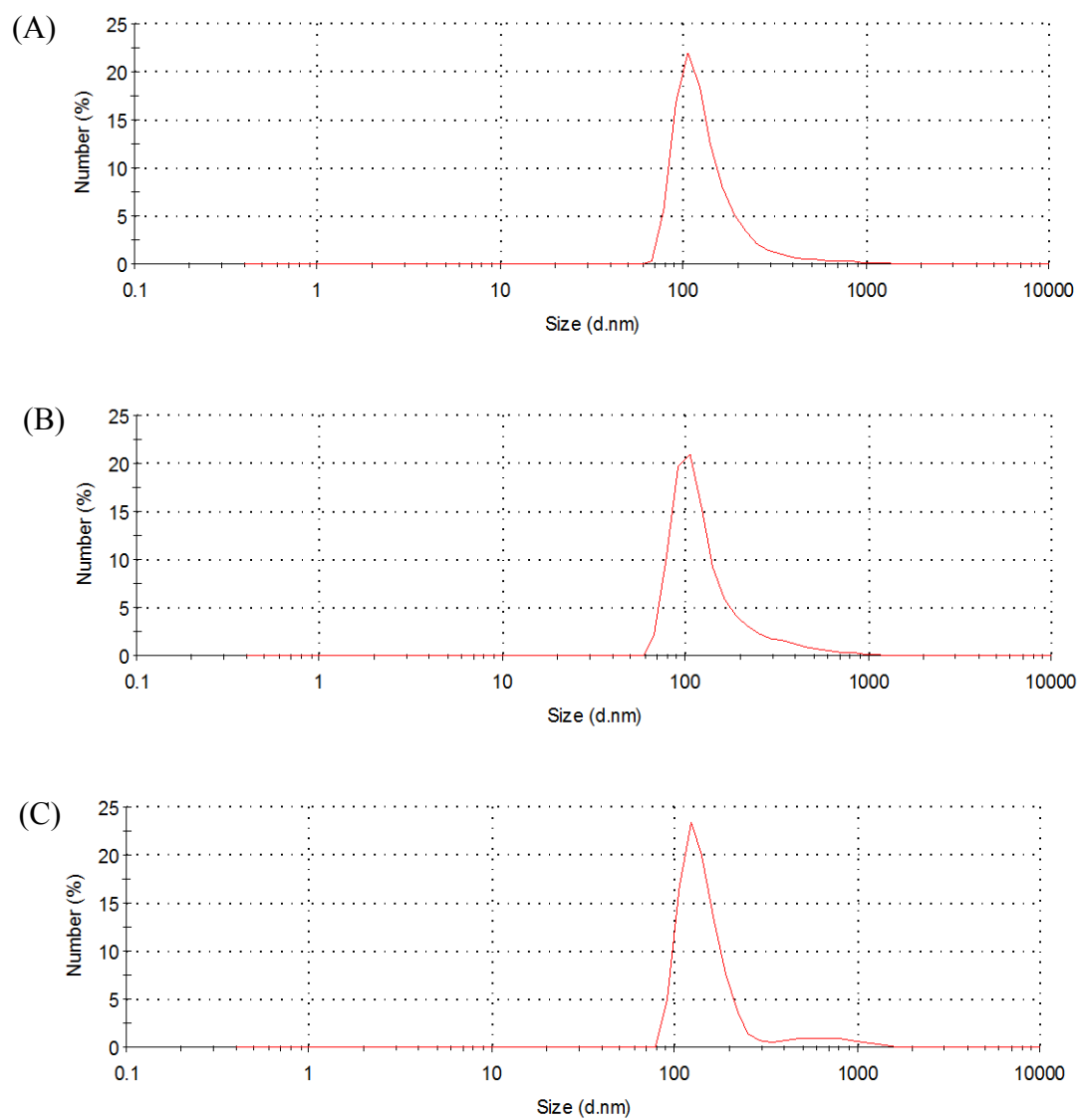
(A)

(B)

(C)

Fig. S19 DLS study of (A) mPEG-*b*-P(Boc-FF-EMA), (B) mPEG-*b*-P(Boc-IF-EMA), and
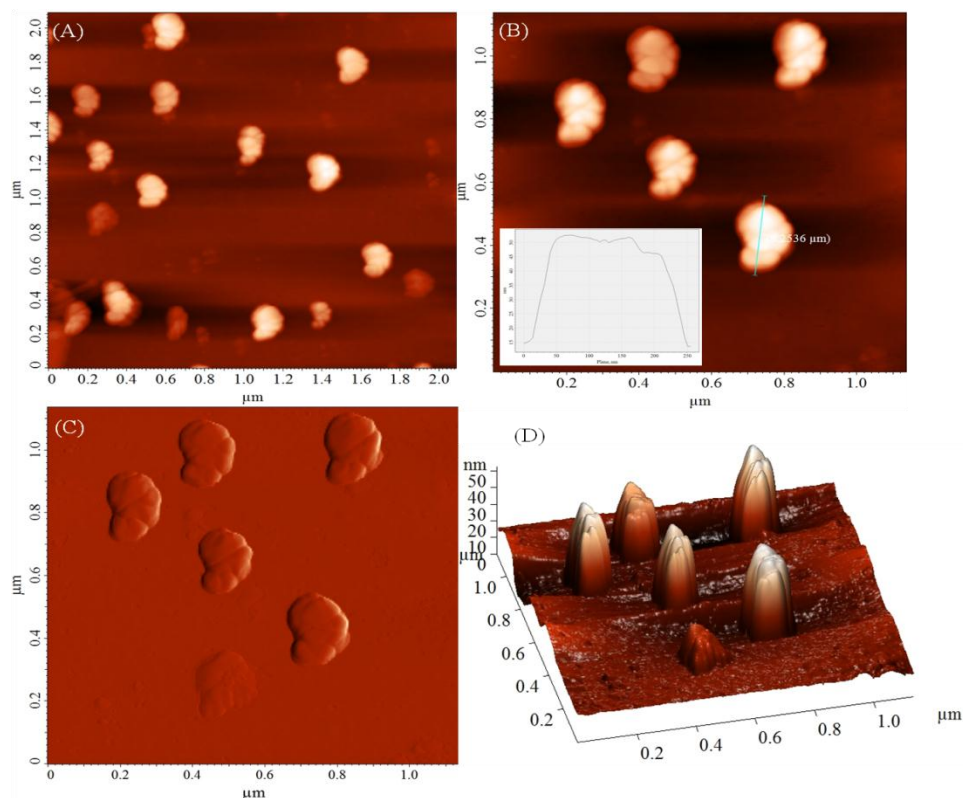
(C) mPEG-*b*-P(Boc-VF-EMA), at a concentration 1 mg mL^{-1}.

Fig. S20 AFM height (A and B), magnitude (C) and 3D (D) images of mPEG-*b*-P(Boc-IF-EMA) block copolymer (prepared from 0.1 mg mL^{-1} aqueous solution). Inset in B: height profile plot (line marked in B).

Fig. S21 AFM height (A and B), and 3D (C) images of mPEG-*b*-P(Boc-VF-EMA) block copolymer (prepared from 0.1 mg mL^{-1} aqueous solution). Inset in B: height profile plot (line marked in B).
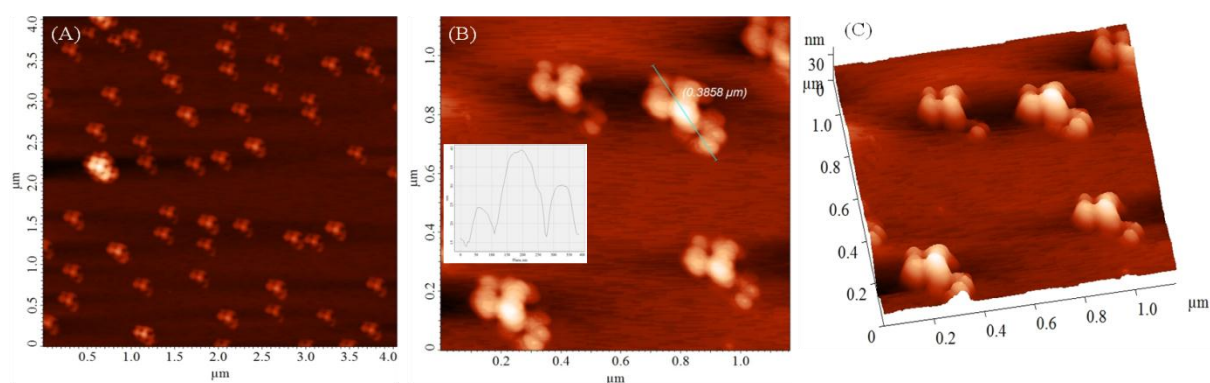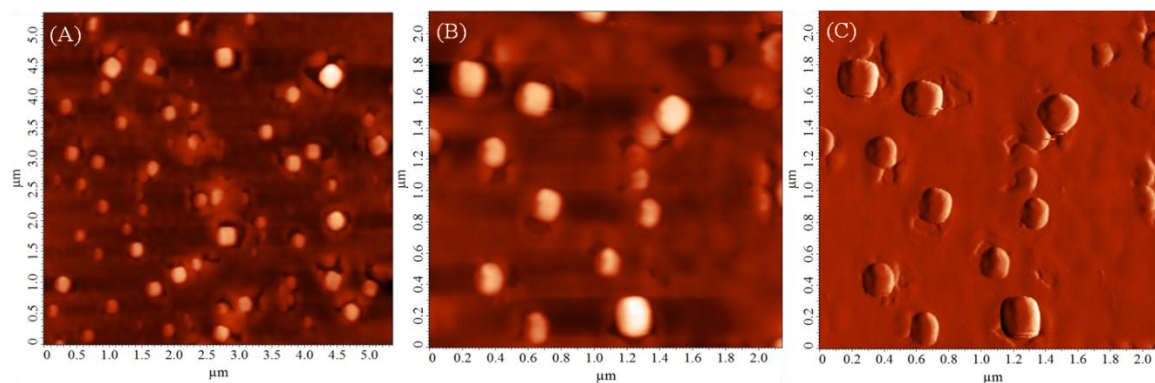
Fig. S22 AFM height (A and B), and magnitude (C) images of block copolymer mPEG-*b*-P(FF-EMA) (prepared from 0.1 mg mL^{-1} aqueous solution).
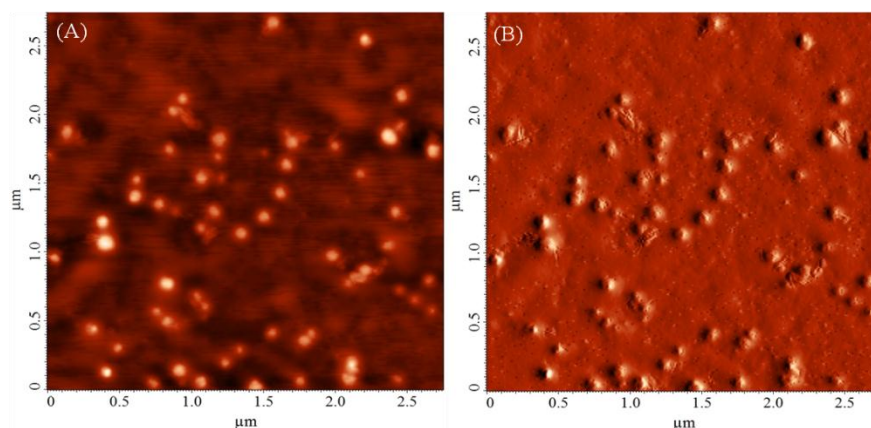

Fig. S23 AFM height (A), and magnitude (B) images of block copolymer mPEG-*b*-P(IF-EMA) (prepared from 0.1 mg mL^{-1} aqueous solution).
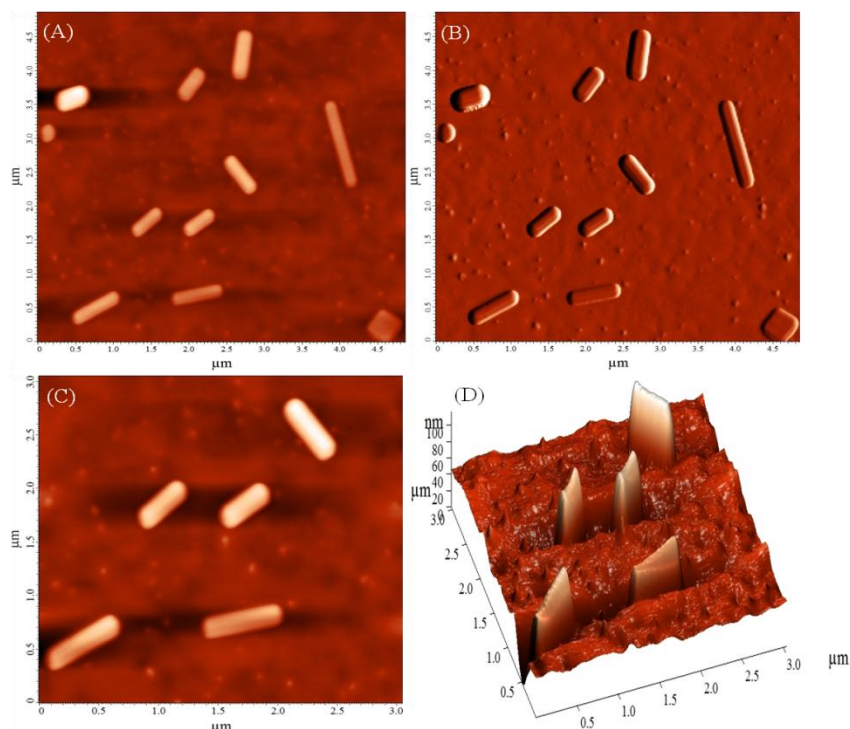
Fig. S24 AFM image of double hydrophilic block copolymer mPEG-*b*-P(VF-EMA) in aqueous solution, (A and C) height image, (B) magnitude image, and (D) 3D image (0.1 mg mL^{-1}).
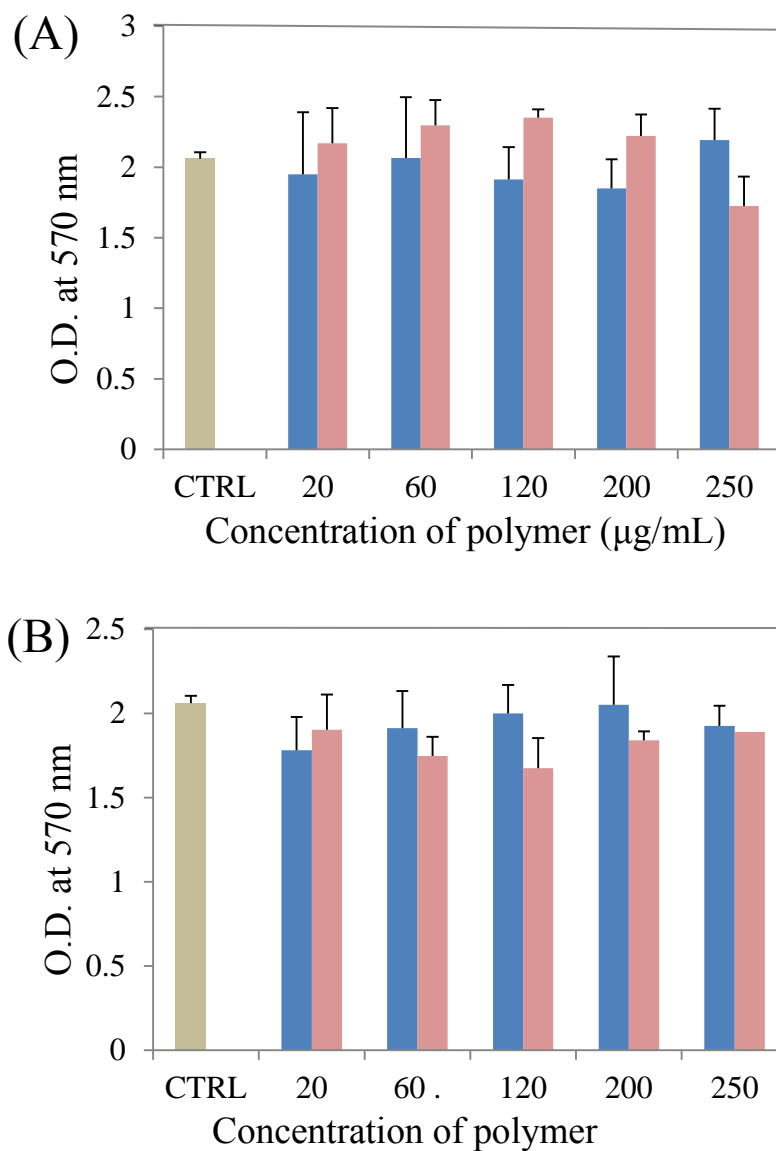
Fig. S25 Cytotoxicity of various polymers on HeLa cells: (A) P(IF-EMA) (blue color) and P(VF-EMA) (pink color), and (B) mPEG-*b*-P(IF-EMA) (blue color) and mPEG-*b*-P(VF-EMA) (pink color).
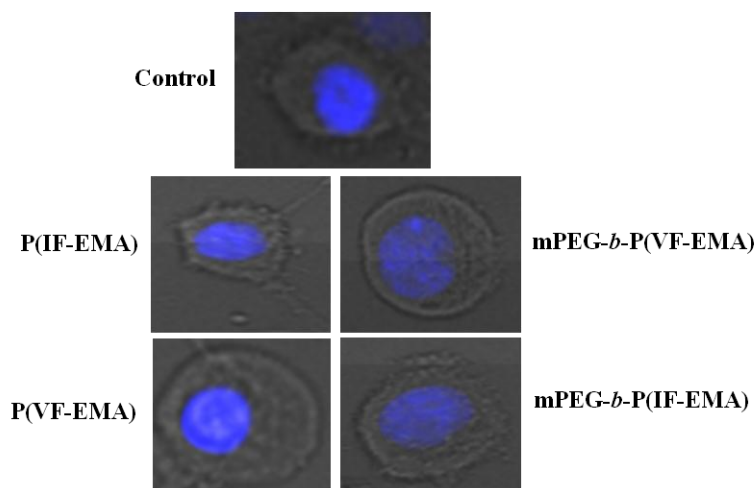
Fig. S26 Fluorescence microscopic merged images of a single ME-180 cells taken at 72 h post-incubation of control and polymer treatment with 60 μg/mL concentrations.

Spectroscopic Analysis of ω-Trithiocarbonate Moiety. For the homopolymers, the percentage of living chain ends was calculated using UV-Vis spectroscopy. The molar absorptivity value (ε) was calculated as 12326 M^{-1} cm^{-1} for CDP in DMF at 27 ^{o}C (S. Kumar, S. G. Roy and P. De, *Polym. Chem.,* 2012, **3**, 1239-1248.), and used in this study. We have prepared two different stock solutions of P(Boc-dipep-EMA) homopolymers and absorptions values at 309 nm were determined by UV-Vis spectroscopic analysis. Then, number-average molecular weight ($M_{n,UV\text{-}vis}$) was determined for both the concentrations and the average value was determined.