Supporting information

For

Synthesis of Chitosan-mimicking Cationic Glycopolymers by Cu(0)-LRP for Efficient Capture and Killing of Bacteria

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Experimental section

Materials

Tris(2-(dimethylamino)ethyl)amine (Me_6TREN), dopamine-based initiator 2-bromo-N-(3,4-dihydroxyphenethy)-2-methylpropanamide (DOPA-Br) and mannose-based acrylate (3-(4-((((3S,4S,5S,6R)-3,4,5-trihydroxy-6-(hydroxymethyl)tetrahydro-2H-pyran-2-yl)oxy)methyl)-1H-1,2,3-triazol-1-yl)propyl acrylate, ManA) were synthesized according to literature procedure and stored in the freezer under a nitrogen atmosphere. [1-3] Copper(I) bromide (CuBr, 98%, Aladdin) was washed sequentially with acetic acid and ethanol and dried under vacuum. Copper wire (diameter = 0.25 mm) was pre-treated by washing in hydrochloric acid for 15 min and rinsed thoroughly with MiliQ water, dried under nitrogen and used immediately. Fe_3O_4 nanoparticles were prepared via a modification of procedures reported by Maity et al.[4] 2-Hydroxyethyl acrylate (HEA, 96%), 2-aminoethyl methacrylamide hydrochloride (AEMA，90%) and ethyl α-bromoisobutyrate (EBiB, 99%) were obtained from Aladdin (China) and used directly. Concanavalin A from *Canavalia ensiformis* (ConA, Type VI, lyophilized powder) was obtained from Sigma-Aldrich.

Analytical techniques

^{1}H NMR spectra were recorded at 25 ℃ with a Bruker AV 500M spectrometer using deuterated solvents obtained from Aladdin. The number-average molecular weight (M_n) and the molecular weight distribution (M_w / M_n) were determined by Waters 1515 size

exclusion chromatography (SEC) in deionized water or 100 mM sodium phosphate buffer with 0.2 vol % trifluoroacetic acid (pH = 2) with a flow rate of 1.00 mL/min. The SEC was equipped with refractive index (RI) and UV detectors, a 20 μm guard column (4.6 mm×30 mm, 100-10K) followed by three Waters Styragel columns (HR1, HR3 & HR4) and autosampler. Narrow linear polystyrene standards in range of 540 to 7.4×10^5 g/mol were used to calibrate the system. All samples were passed through 0.45 μm PTFE filter before analysis. Fourier transform infrared (FTIR) spectra were recorded on a Nicolet iS5 FTIR spectrometer using an iD7 diamond attenuated total reflectance optical base. Transition electron microscopy (TEM) images were acquired by FEI TECNAI G2 20 TEM microscope equipped with LaB6 filament. Thermal gravimetric analysis (TGA, Mettler Toledo, Switzerland) was performed at a heating rate of 10 ℃/min from 50 ℃ to 600 ℃ under nitrogen protection. The size and size distribution of Fe_3O_4 particles were measured by dynamic light scattering (DLS) using a ZetaPALS variable temperature analyzer (Brookhaven Instruments, UK).

Synthesis of AEMA-containing polymers by Cu(0)-LRP

The polymerization is performed under nitrogen protection and typical procedures are shown as below.

For the synthesis of poly(AEMA) homo-polymer (designed DP = 40), Me_6TREN (10.7 μL, 0.04 mmol) and CuBr (5.7 mg, 0.04 mmol) were first dispersed in deionized water (1 mL) in a vial. At the same time, AEMA(664 mg, 4 mmol) and EBiB(19.4 mg, 0.1 mmol) were dissolved in water (1 mL) / IPA (2 mL) in another vial. Initiator EBiB

can be replaced by DOPA-Br(30 mg, 0.1 mmol) for the sysnthesis of dopamine-terminal polymers. The mixtures were also purged with nitrogen for 10 min. After that, monomer / initiator aqueous solution was transferred via cannula to the vial with Cu(0) / $CuBr_2$ / Me_6TREN catalyst. The vial was sealed and the mixed solution was allowed to polymerize under ice / water bath cool (0 ℃) for defined time. After reaction, samples were taken for analysis by ^{1}H NMR spectroscopy (500M Hz) in order to determine the monomer conversion and the molecular weight and dispersity of the polymers were characterized by aqueous SEC. The final polymer product was recovered by dialysis against water for two days, following lypholization.

For the synthesis of block copolymer poly(AEMA)-*b*-(HEA) (designed DP = 40:40), after the high-conversion of AEMA, a degassed solution of HEA (464 mg, 4 mmol) in water (1 mL) was added into the vial under nitrogen atmosphere for *in-situ* block copolymerization.

For the synthesis of block copolymer poly(HEA)-*b*-(AEMA) (designed DP = 40:40) using DOPA-Br as the initiator, the polymerization procedure and the amouts of reagents are the same as up-mentioned with only monomer sequence changed, which used HEA as the first monomer and AEMA as the co-monomer for block copolymerization.

For the synthesis of dopamine-terminal poly(ManA)-*r*-(AEMA) (designed DP = 10:10), Me_6TREN (10.7 μL, 0.04 mmol) and CuBr (5.7 mg, 0.04 mmol) were first dispersed in deionized water (1 mL) in a vial. At the same time, ManA(373 mg, 1 mmol), AEMA(116 mg, 1 mmol) and DOPA-Br(30 mg, 0.1 mmol) were dissolved in

water (1 mL) / IPA (2 mL) in another vial. The mixtures were also purged with nitrogen for 10 min. After that, monomer / initiator aqueous solution was transferred via cannula to the vial with Cu(0) / $CuBr_2$ / Me_6TREN catalyst. The vial was sealed and the mixed solution was allowed to polymerize under ice / water bath cool (0 ℃) for 24 hours. The final polymer product was recovered by dialysis against water for two days, following lypholization.

For the synthesis of dopamine-terminal poly(ManA) and poly(HEA) (designed DP = 10), Me_6TREN (10.7 μL, 0.04 mmol) and CuBr (5.7 mg, 0.04 mmol) were first dispersed in deionized water (1 mL) in a vial. At the same time, ManA(373 mg, 1 mmol) or HEA(116mg, 1 mmol) and DOPA-Br(30 mg, 0.1 mmol) were dissolved in water (1 mL) / IPA (2 mL) in another vial. The mixtures were also purged with nitrogen for 10 min. After that, monomer / initiator aqueous solution was transferred via cannula to the vial with Cu(0) / $CuBr_2$ / Me_6TREN catalyst. The vial was sealed and the mixed solution was allowed to polymerize under ice / water bath cool (0 ℃) for 3 hours. After reaction, the final polymer product was recovered by dialysis against water for two days, following lypholization.

For the synthesis of poly(HEA) in the presence of HCl (designed DP = 20), Me_6TREN (10.7 μL, 0.04 mmol), HCl(0.04 mmol) and CuBr (5.7 mg, 0.04 mmol) were first dispersed in deionized water (1 mL) in a vial. At the same time, HEA(232mg, 2 mmol) and EBiB(19.4 mg, 0.1 mmol) were dissolved in water (1 mL) / IPA (2 mL) in another vial. The mixtures were also purged with nitrogen for 10 min. After that, monomer / initiator aqueous solution was transferred via cannula to the vial with Cu(0) / $CuBr_2$ /

Me_6TREN catalyst. The vial was sealed and the mixed solution was allowed to polymerize under ice / water bath cool (0 ℃) for 24 hours. After reaction, samples were taken for analysis by ^{1}H NMR and SEC analysis.

Preparation of Fe_3O_4/polymer hybrid nanoparticles *via* "Grafting to" strategy

Fe_3O_4 nanoparticles (70mg) and Dopamine-initiated polymers (70mg) [poly(ManA), poly(AEMA), poly(ManA)-*r*-(AEMA) and poly(AEMA) / poly(ManA)] were dispersed into 5ml deionized water to produce a stable suspension and stirred under nitrogen atmosphere at 70 ℃ for 48 hours. The particles are separated by magnet adsorption. After discarding the supernatant, the sediments were dispersed in deionized water and centrifuged once more. The above purification was repeated for five times in order to remove the excess polymers. Finally, the products were recovered by lyophilization for further characterization.

Antibacterial activity determination

The antibacterial activity of hybrid nanocomposites was evaluated against *E.coli* by suspending the bacteria in PBS and inoculating given concentrations of the samples. During the test, *E.coli* was first cultivated in sterilized Luria-Bertani (LB) broth and incubated for 12 hours at 37 ℃ with a shaking incubator.

To investigate the antibacteria performance of Fe_3O_4@polymer nanocomposites [poly(HEA), poly(ManA), poly(AEMA)], the samples (1, 3, 5mg) were dispersed in 1 mL physiological saline and then 1 mL diluted microbial solution (1 x 10^6 CFUs per mL) was added. Blank and pristine Fe_3O_4 nanoparticles were made as control. The resultant suspensions were incubated at 37 ℃ in a shaking incubator for 30 minutes and

then the suspensions were separated by a magnet. The supernatant and the substrate were diluted with 2 mL of physiological saline respectively. After that, 5 μL suspensions were taken to spread on the LB agar plate and incubated for 12 hours at 37 ℃.

To investigate the antibacteria performance of Fe_3O_4@polymer nanocomposites [poly(AEMA), poly(AEMA) / poly(ManA), poly(ManA)-*r*-(AEMA)] at relatively lower density of *E.Coli*, the diluted microbial solution ($1x10^4$ CFUs per mL) was also used. The incubation procedures were the same as previously mentioned.

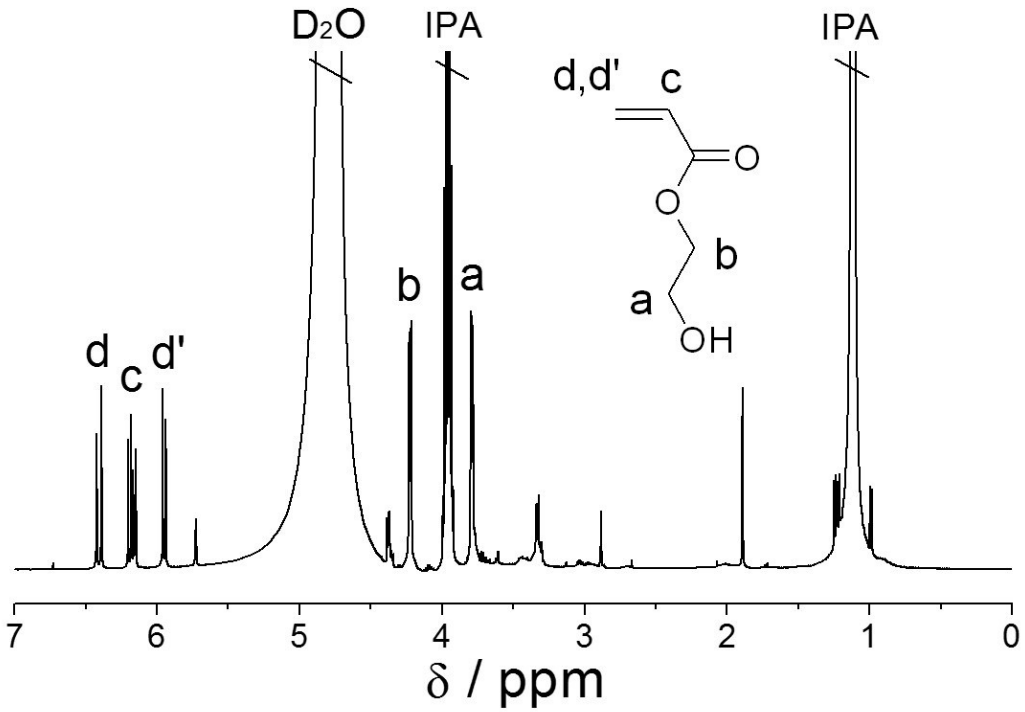

Figure S1. ^{1}H NMR spectrum of the sample taken after polymerization of EBiB-poly(HEA) in the presence of HCl (0.02mmol/L concentration) in D_2O.

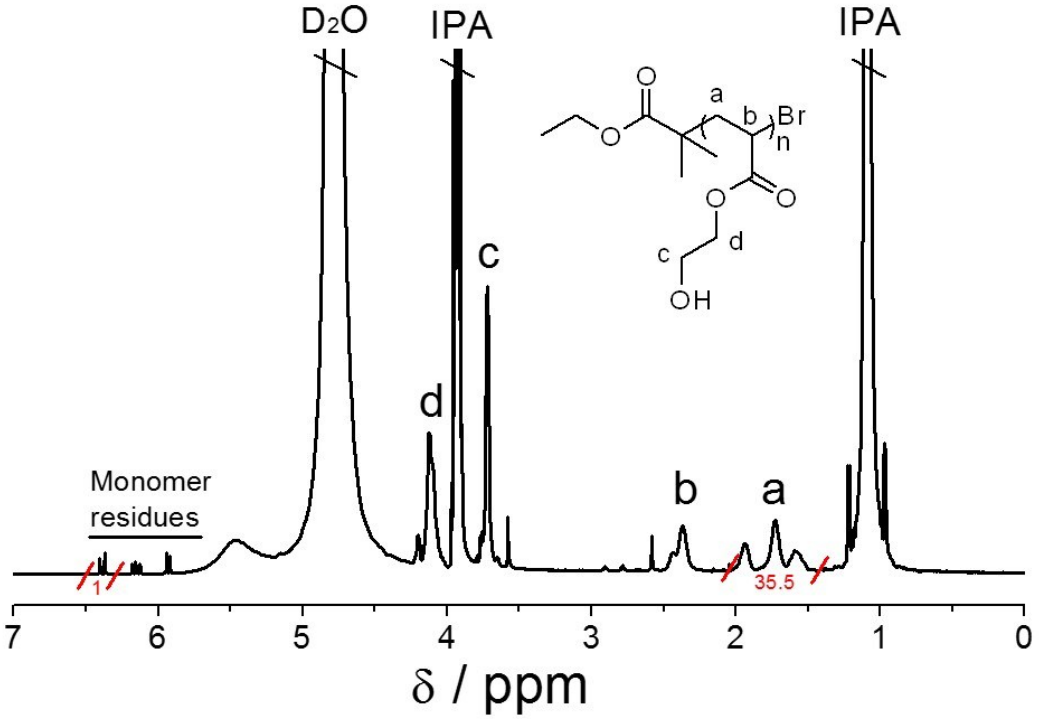

Figure S2. ^{1}H NMR spectrum (D_2O) for the synthesis of EBiB-poly(HEA) after 3 hours.

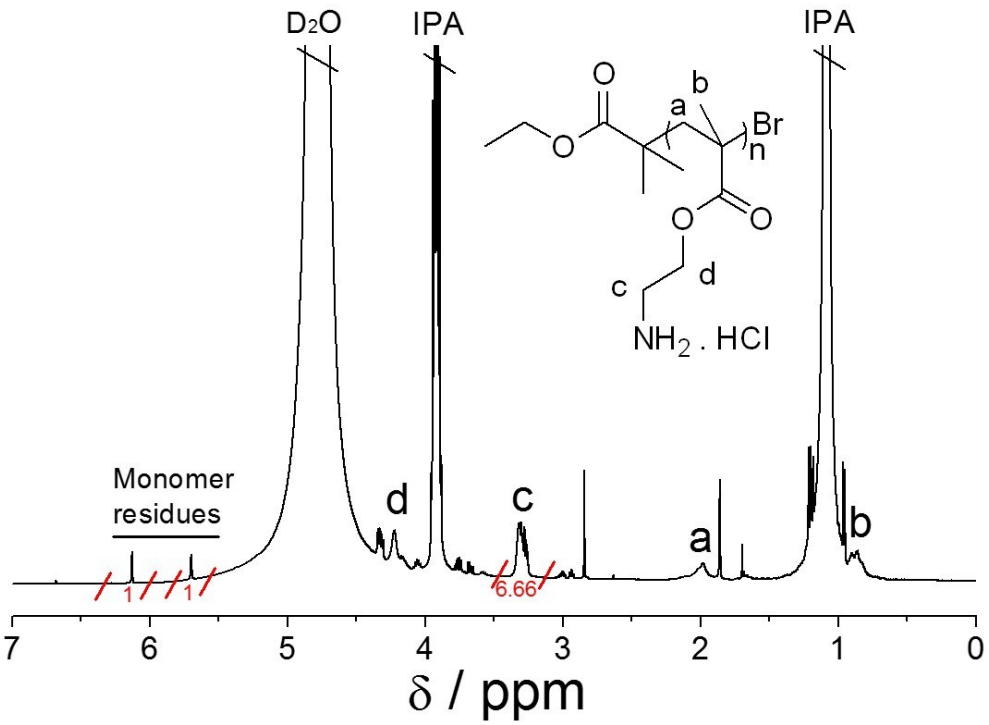

Figure S3. ^{1}H NMR spectrum (D_2O) for the sample taken during the synthesis of EBiB-poly(AEMA).

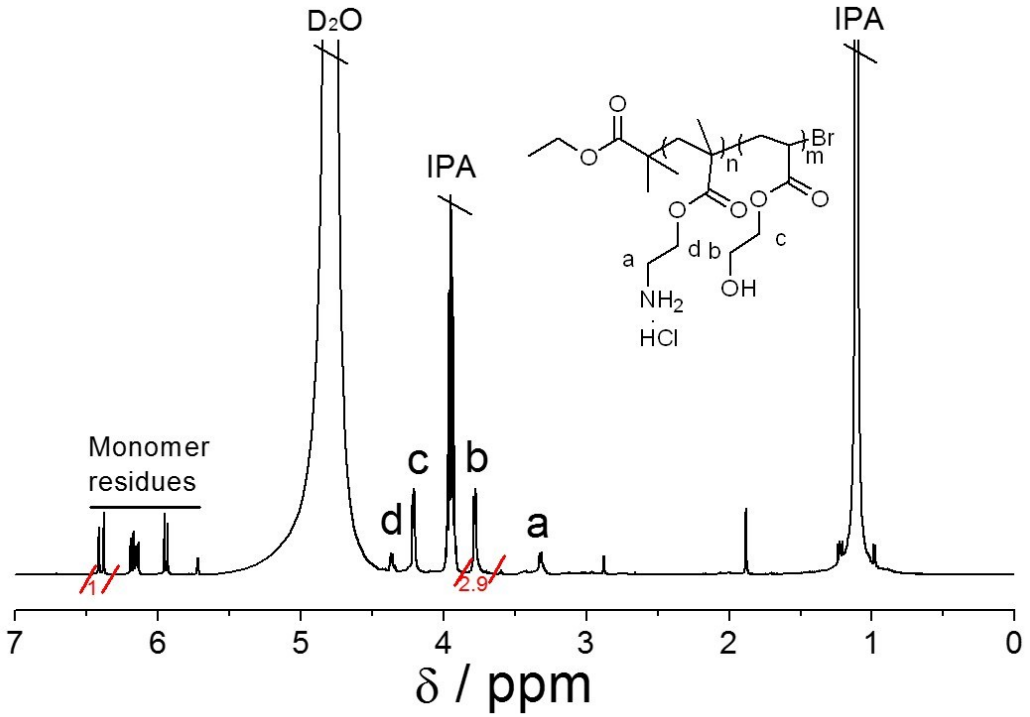

Figure S4. ^{1}H NMR spectrum (D_2O) for the sample taken during the synthesis of EBiB-poly(AEMA)-*b*-(HEA).

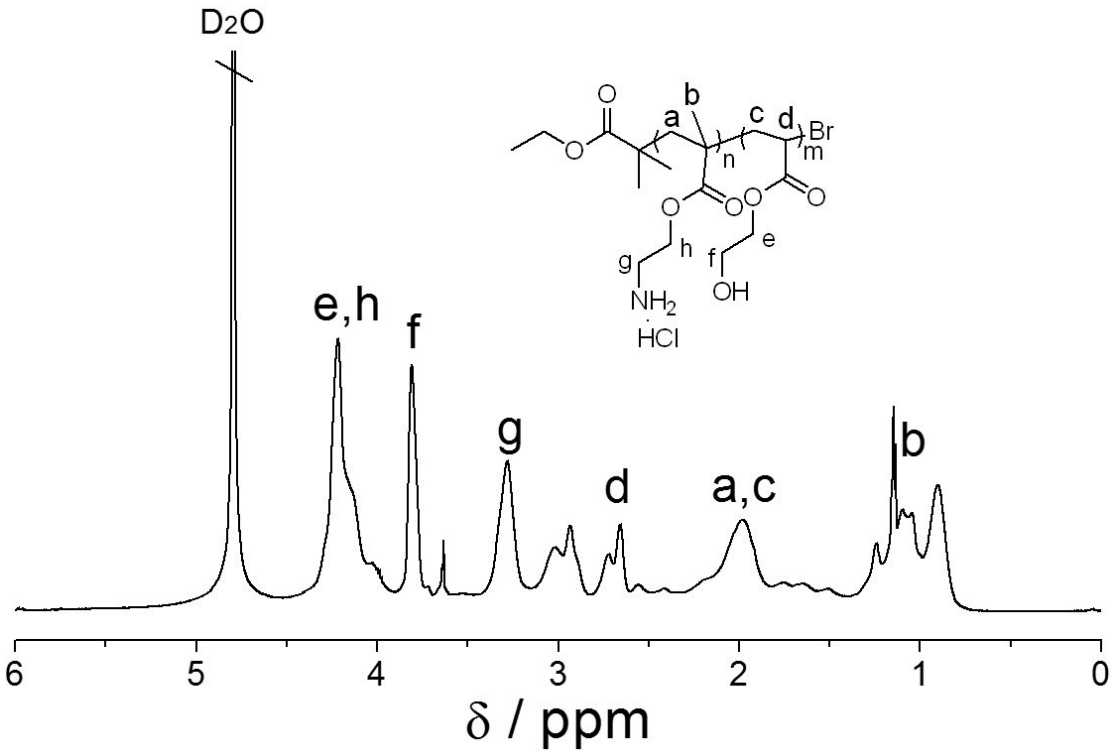

Figure S5. ^{1}H NMR spectrum of EBiB-poly(AEMA)-*b*-(HEA) in D_2O.

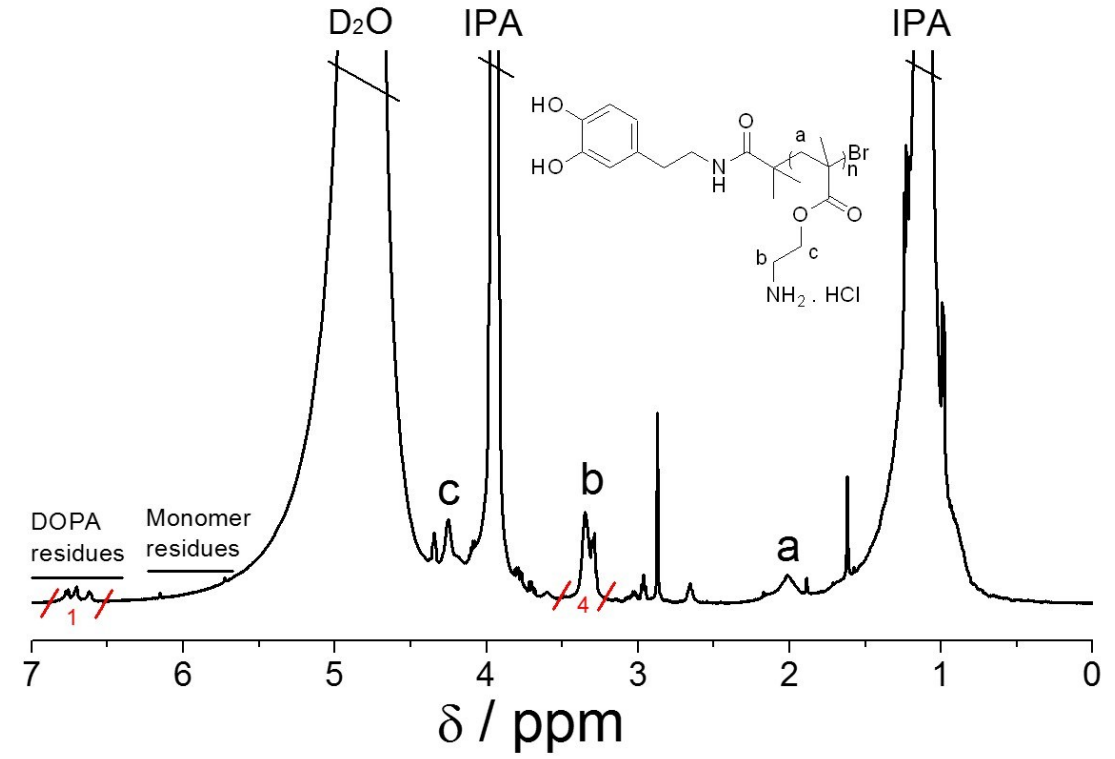

Figure S6. ^{1}H NMR spectrum (D_2O) for the sample taken during the synthesis of DOPA-poly(AEMA).

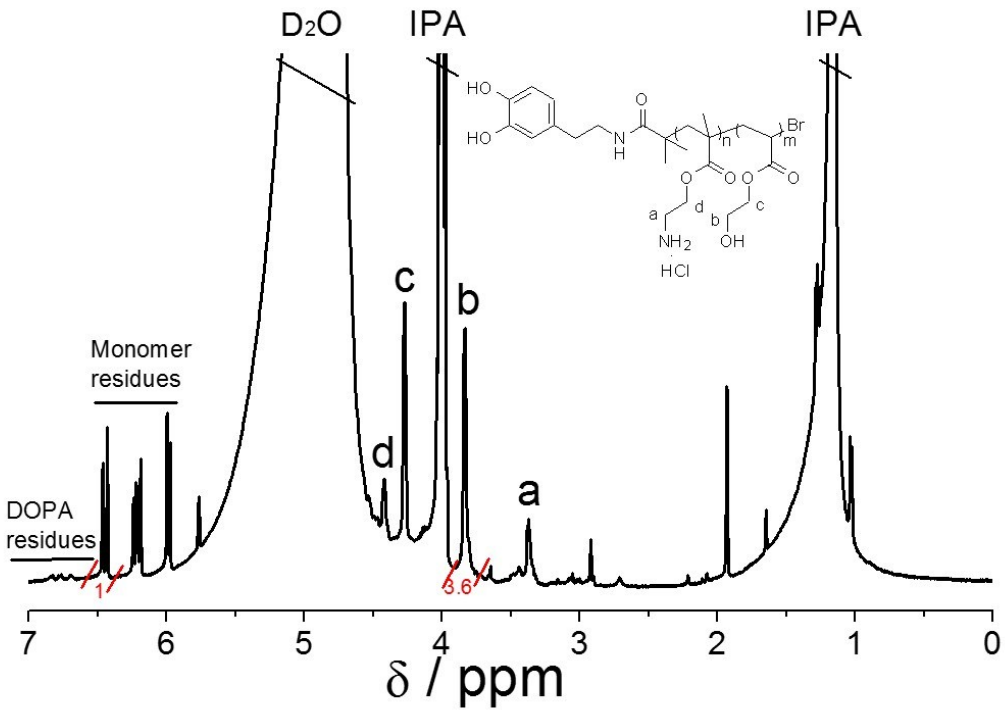

Figure S7. ^{1}H NMR spectrum (D_2O) for the sample taken during the synthesis of DOPA-poly(AEMA)-*b*-(HEA).

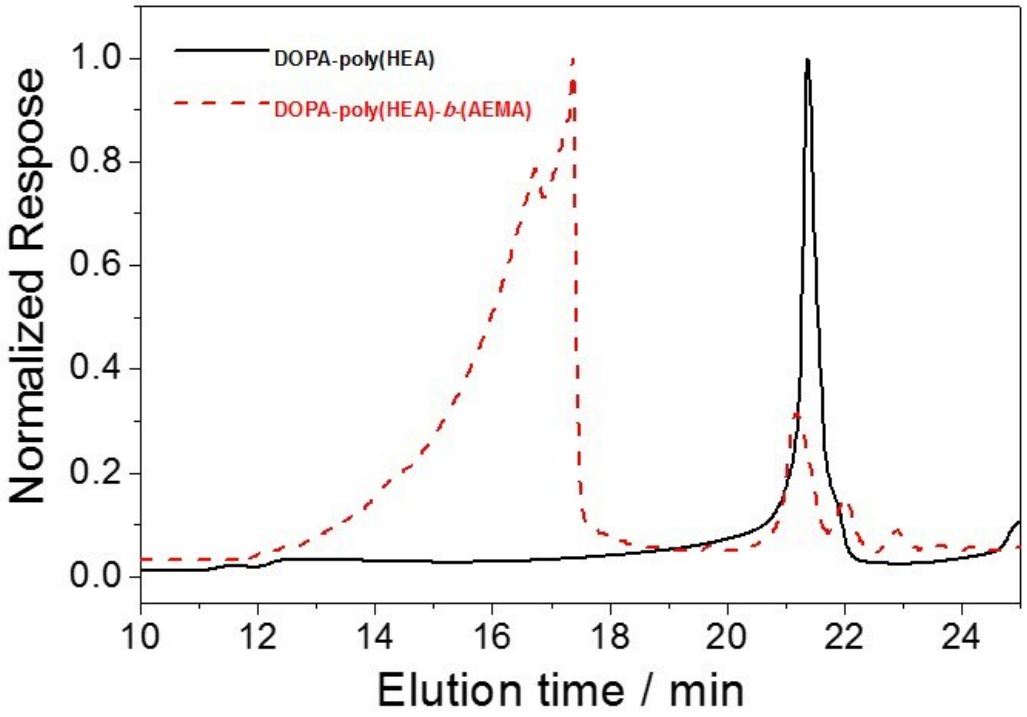

Figure S8. SEC elution traces of DOPA-poly(HEA) and DOPA-poly(HEA)-*b*-(AEMA).

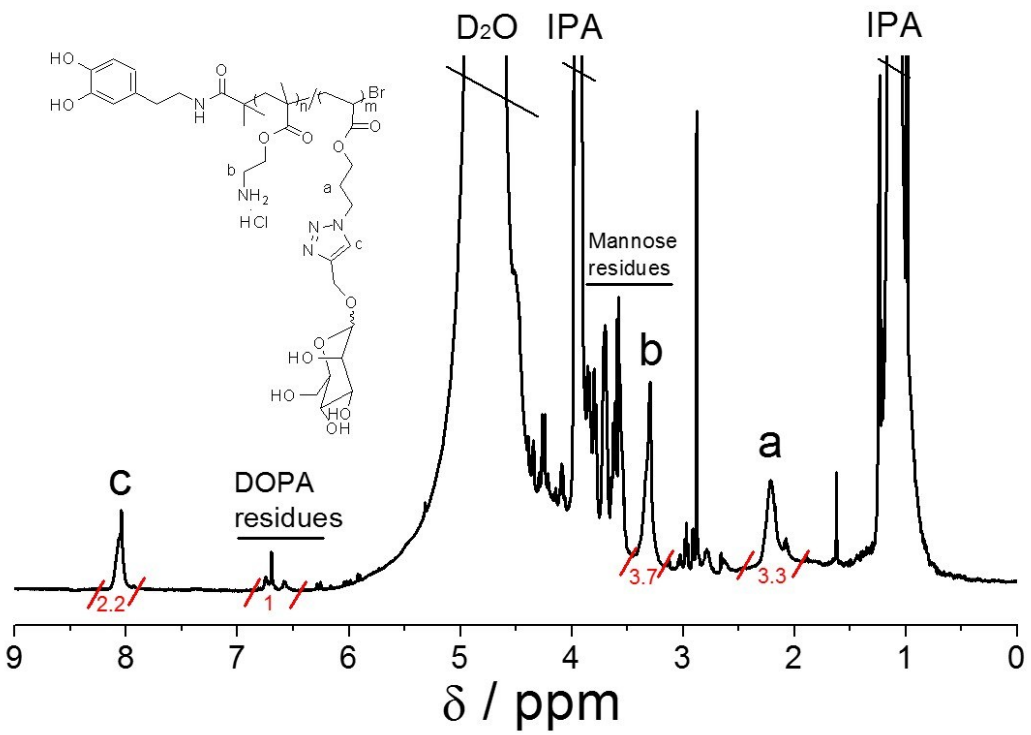

Figure S9. ^{1}H NMR spectrum (D_2O) for the sample taken during the synthesis of DOPA-poly(ManA)-*r*-(AEMA).

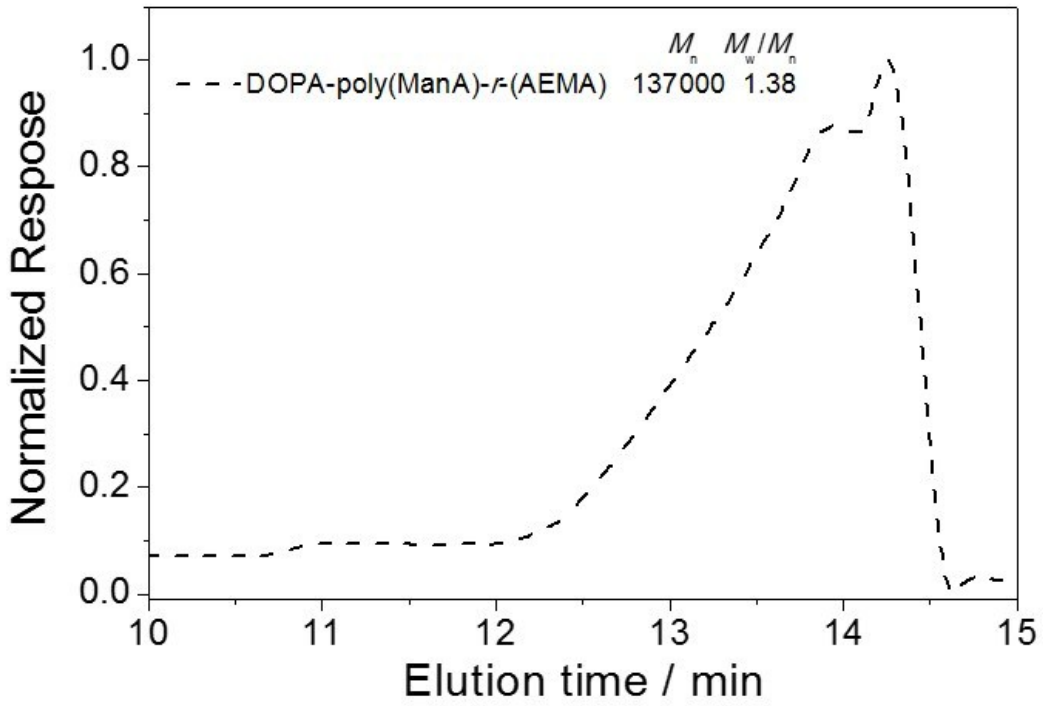

Figure S10. SEC elution traces of DOPA-poly(ManA)-*r*-(AEMA).

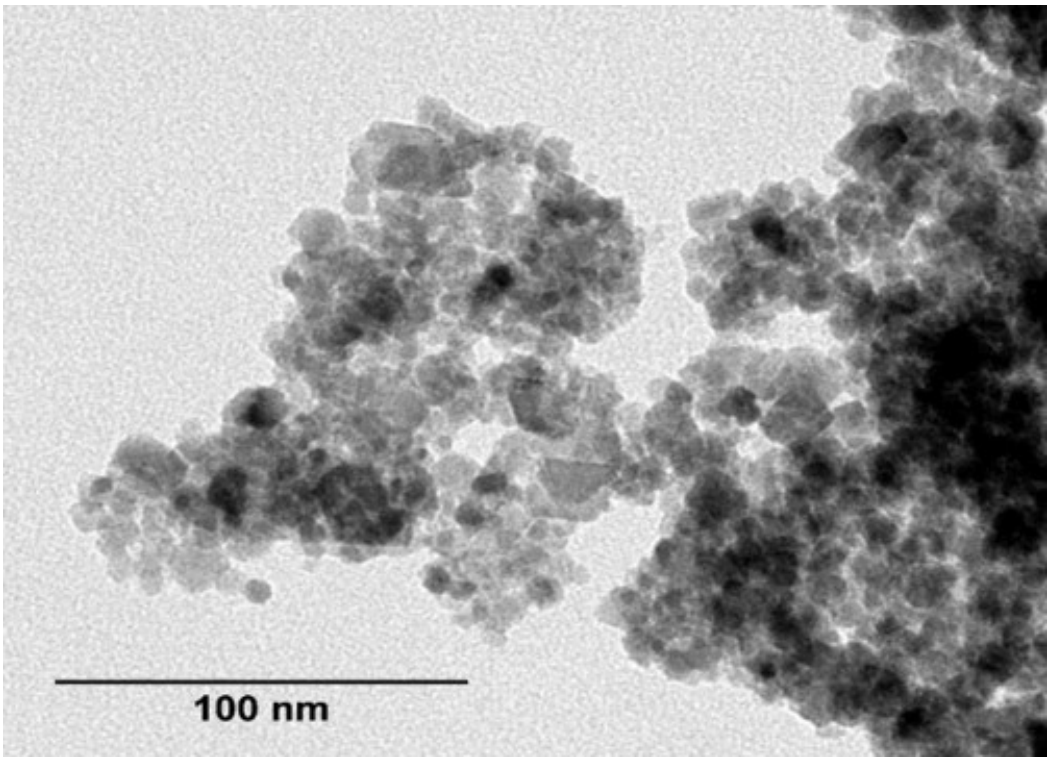

Figure S11. TEM image of Fe_3O_4 nanoparticles.

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