

# Electronic Supplemental Information

Poly(ethylene glycol)-*block*-poly(4-vinyl pyridine) as a versatile  
block copolymer to prepare nanoaggregates of  
superparamagnetic iron oxide nanoparticles

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### **Synthesis of poly(ethylene glycol) monomethyl ether chloride (mPEG<sub>113</sub>-Cl)**

The mPEG<sub>113</sub>-Cl was prepared through an adaptation of a reported method [35]. DMAP (0.916 g, 7.5 mmol), DCM (20 mL) and TEA (0.7 mL, 5 mmol) were placed into a round-bottom flask. A solution of CPC (1.21 mL, 12.5 mmol) in DCM (20 mL) was then added dropwise and a yellow dispersion was formed. After, mPEG<sub>113</sub> (10.0 g, 5.0 mmol) and DCM (30 mL) were added, under a N<sub>2</sub> atmosphere in an ice bath (0°C). After the CPC solution addition, the temperature was raised to 25°C and the reaction continued under magnetic stirring for 18 h. The obtained dispersion was then filtered, concentrated by solvent evaporation and the product recovered by precipitation in cold diethyl ether. The crude product was purified by recrystallization overnight in absolute ethanol. After being filtered and washed with cold diethyl ether, the macroinitiator was collected and dried for 48 h, under vacuum, at 40°C. The same procedure was used for the preparation of mPEG<sub>45</sub>-Cl.

### **Synthesis of mPEG<sub>113</sub>-*b*-P4VP<sub>124</sub> block copolymer**

mPEG<sub>113</sub>-*b*-P4VP block copolymers were prepared by Atom Transfer Radical Polymerization (ATRP) using the previously reported Cu(0) and [CuCl<sub>2</sub>]/[Me<sub>6</sub>TREN]=1/1 catalytic system [36]. In a typical procedure, a mixture of mPEG<sub>113</sub>-Cl (0.472 g, 0.09 mmol), CuCl<sub>2</sub> (12.47 mg, 0.09 mmol), Me<sub>6</sub>TREN (21.36 mg, 0.09 mmol) and IPA (3.11 mL) was placed in a Schlenk reactor and immediately frozen in liquid nitrogen. Activated Cu(0) wire was placed in the reactor and the system was deoxygenated with four freeze-vacuum-thaw cycles and purged with nitrogen. 4VP (3.0 mL, 28 mmol) was then added to a Schlenk reaction vessel under a nitrogen atmosphere and the reaction mixture was immediately frozen in liquid nitrogen and deoxygenated by conducting two freeze-vacuum-thaw cycles and purged with nitrogen. The Schlenk reactor was placed in a pre-heated oil bath at 50°C and left reacting under magnetic stirring. After 90 minutes, a sample was taken to determine the monomer conversion by <sup>1</sup>H NMR spectroscopy. Then the block copolymer was precipitated in cold diethyl ether and the solid dissolved in chloroform and passed through an alumina column to remove the copper catalyst. The solution was concentrated by rotary evaporation and the product recovered by precipitation in cold diethyl ether, followed by filtration. Further catalysts removal was achieved by re-dissolving the product in methanol and dialysis for 12 h (molecular weight cut-off (MWCO) = 3500 Da). Finally, the crude product was obtained by precipitation in cold diethyl ether, filtered and then dried, under vacuum, at 40°C for 48 h.

### **Synthesis of hydrophilic Fe<sub>3</sub>O<sub>4</sub> SPIONs (hSPIONs)**

Hydrophilic Fe<sub>3</sub>O<sub>4</sub> SPIONs were synthesized using a micro-emulsion technique in which two water in oil microemulsions, with the same water/toluene/CTAB-butanol composition, were prepared, according to our previous work [37]. One of the microemulsions contained 1.9 mL of an aqueous internal phase of ferric chloride hexahydrate (0.75 mmol, 111 mg/mL) and ferrous chloride tetrahydrate (0.37 mmol, 52.2 mg/mL). The other micro-emulsion contained the ammonium hydroxide (NH<sub>4</sub>OH) reducing agent (30% v/v, 1.9 ml). SPIONs were formed and precipitated by blending the two microemulsions under a high purity (99.9%) argon atmosphere, at 50 °C for 1 h. The product was washed 3 times with 20 mL of ethanol and then washed under reflux with ethanol to remove any surfactant residues and any unreacted byproduct, before being finally collected using an external magnet.

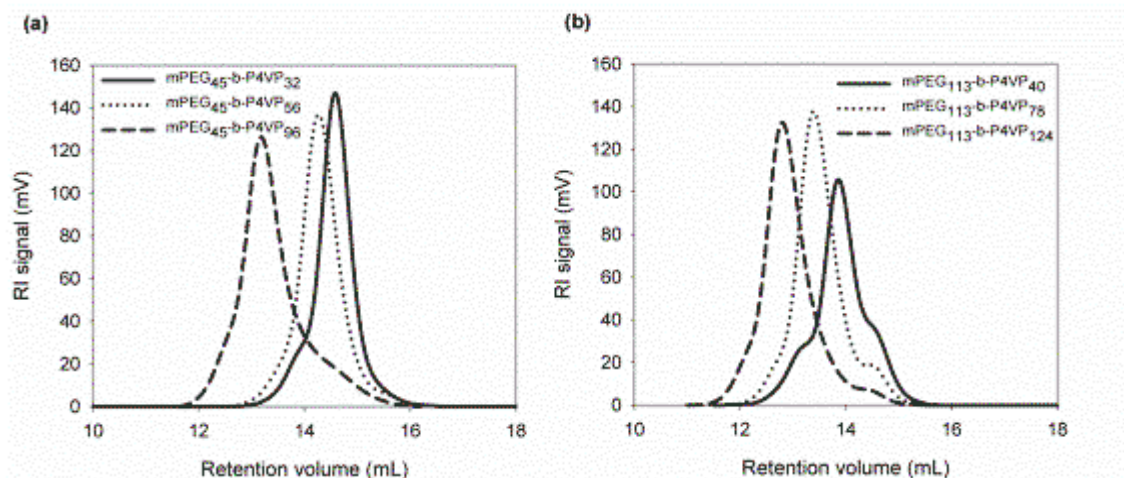


Figure S1 - GPC traces that were obtained for the mPEG-*b*-P4VP block copolymers obtained from (a) mPEG<sub>45</sub>-Cl and (b) mPEG<sub>113</sub>-Cl macroinitiators

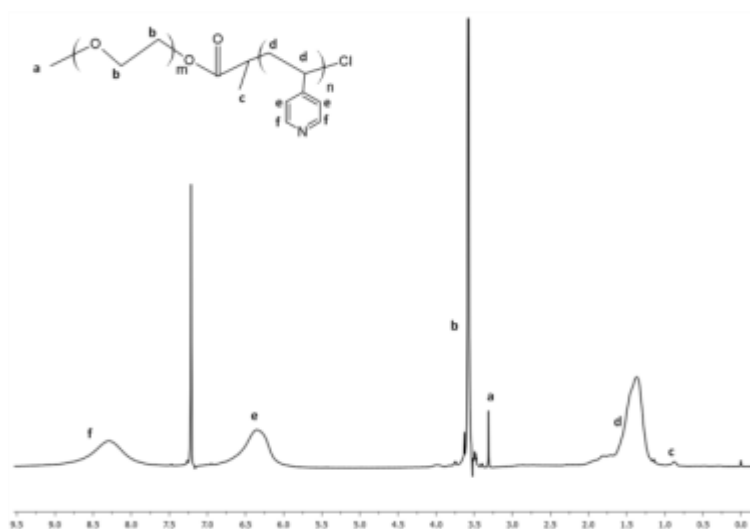
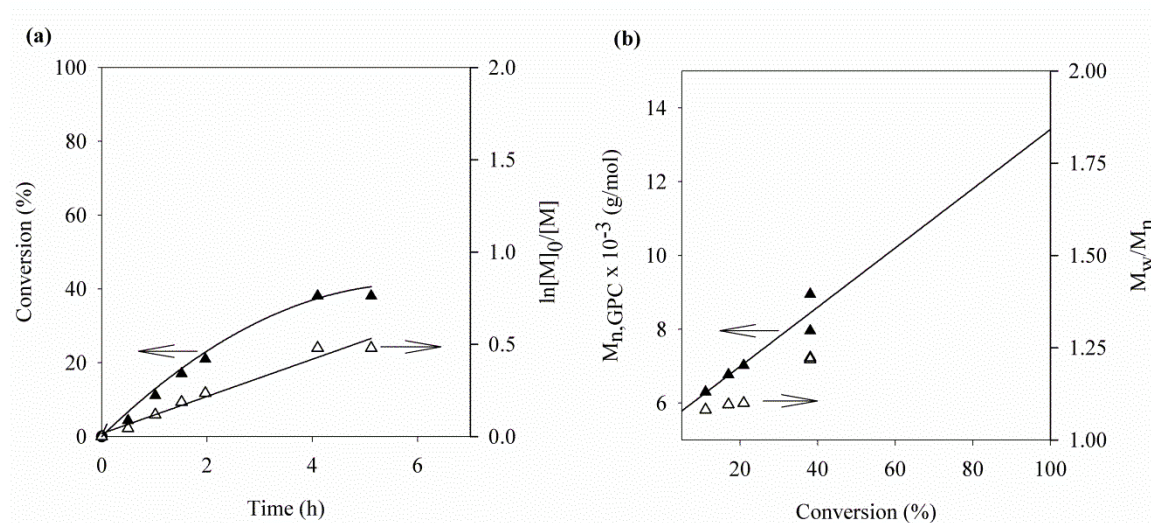
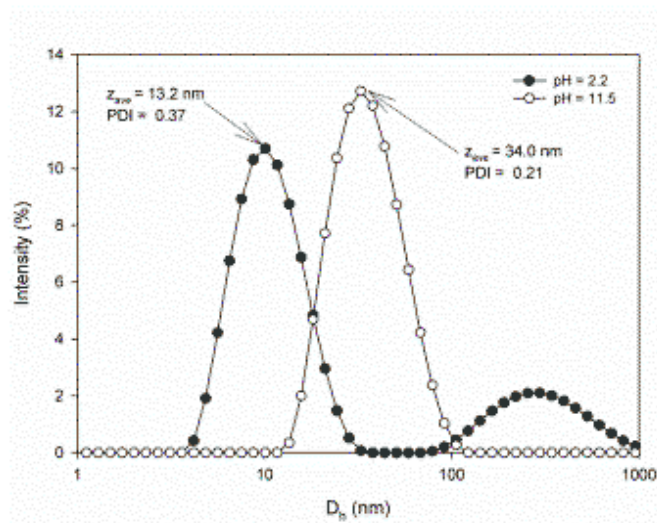


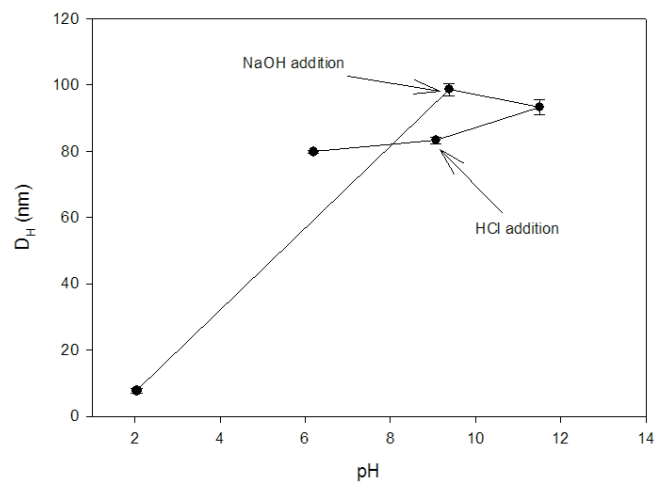
Figure S2 – <sup>1</sup>H NMR spectrum of mPEG<sub>45</sub>-*b*-P4VP<sub>56</sub>-Cl block copolymer. Their chemical structure and the proton identification scheme adopted for the NMR spectral assignments are also indicated.



**Figure S3 – mPEG<sub>113</sub>-b-P4VP<sub>40</sub> ATRP kinetic plots of (a) conversion and  $\ln[M]_0/[M]$  vs. time and plot of (b) number average molecular weights ( $M_{n, GPC}$ ) and  $M_w/M_n$  vs. conversion (%) in IPA. Conditions:  $[4VP]_0/[IPA] = 1/1$  (v/v);  $[4VP]_0/[PEG_{113}\text{-Cl}]_0/[CuCl_2]_0/[Me_6TREN] = 100/1/1/1$  (molar).**



**Figure S4 - Particle size distribution in intensity determined by DLS for mPEG<sub>113</sub>-b-P4VP<sub>40</sub> at different pH conditions**



**Figure S5 - Hydrodynamic diameter ( $D_h$ ) of mPEG<sub>113</sub>-b-P4VP<sub>78</sub> self-assembled in the presence of hSPIONs measured at different pH values using the titration method.**

