

Supporting information for

Advantages of poly(vinyl phosphonic acid)-based double hydrophilic block copolymers for the stabilization of iron oxide nanoparticles

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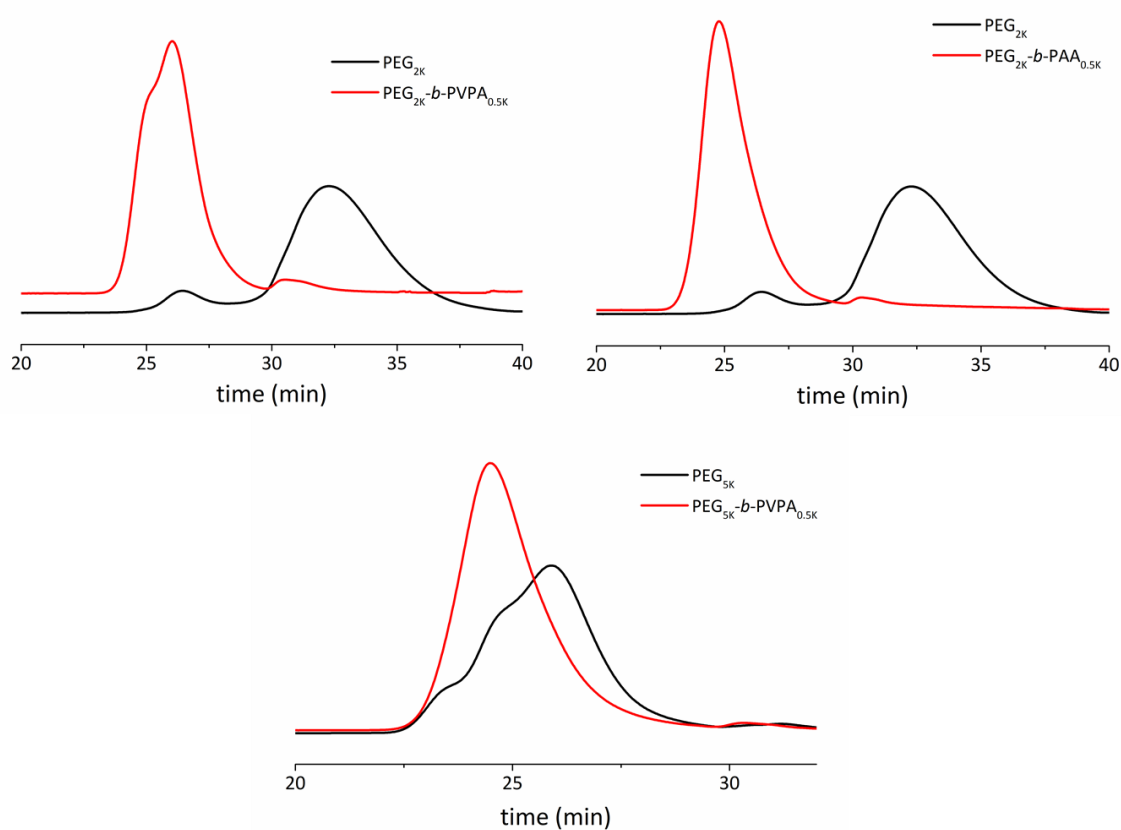


Figure S1A. SEC-RI chromatograms of polymers and copolymers used in reported study.

markiewicz_k_300b.50.fid
PEG2k-X

^1H NMR PEG_{2K}-X

CCOC(=S)SC(C)C(=O)OCCO

Integration values: 2.49, 0.91, 2.02, 185.14, 3.16, 3.00, 3.79

The figure displays a ^1H NMR spectrum of PEG_{2K}-X. The x-axis represents the chemical shift in ppm, ranging from 5.5 to 0.5. The y-axis represents the intensity, ranging from 0 to 3400. The spectrum shows several peaks: a large peak at approximately 3.6 ppm (integration 185.14), a smaller peak at approximately 3.4 ppm (integration 3.16), and a cluster of peaks between 1.2 and 1.6 ppm (integrations 3.00 and 3.79). There are also smaller peaks at approximately 4.6 ppm (integration 2.49), 4.3 ppm (integration 0.91), and 4.1 ppm (integration 2.02). The chemical structure of PEG_{2K}-X is shown as an inset, featuring a poly(ethylene glycol) chain with a terminal ester group and a thioether linkage.

markiewicz_k_300b.20.fid
KM_FR_17 ap 100

^1H NMR PVPA_{2k}-X

Chemical structure of PVPA_{2k}-X is shown, featuring a poly(vinylphosphonic acid) backbone with a carboxylic acid group and a phosphonic acid group. The structure is labeled with 'n' for the repeating unit and 'X' for the end group.

markiewicz_k_300a.56.fid
KM_FR_17 ap 100 HCl (2)

^{31}P NMR PVPA_{2k}-X

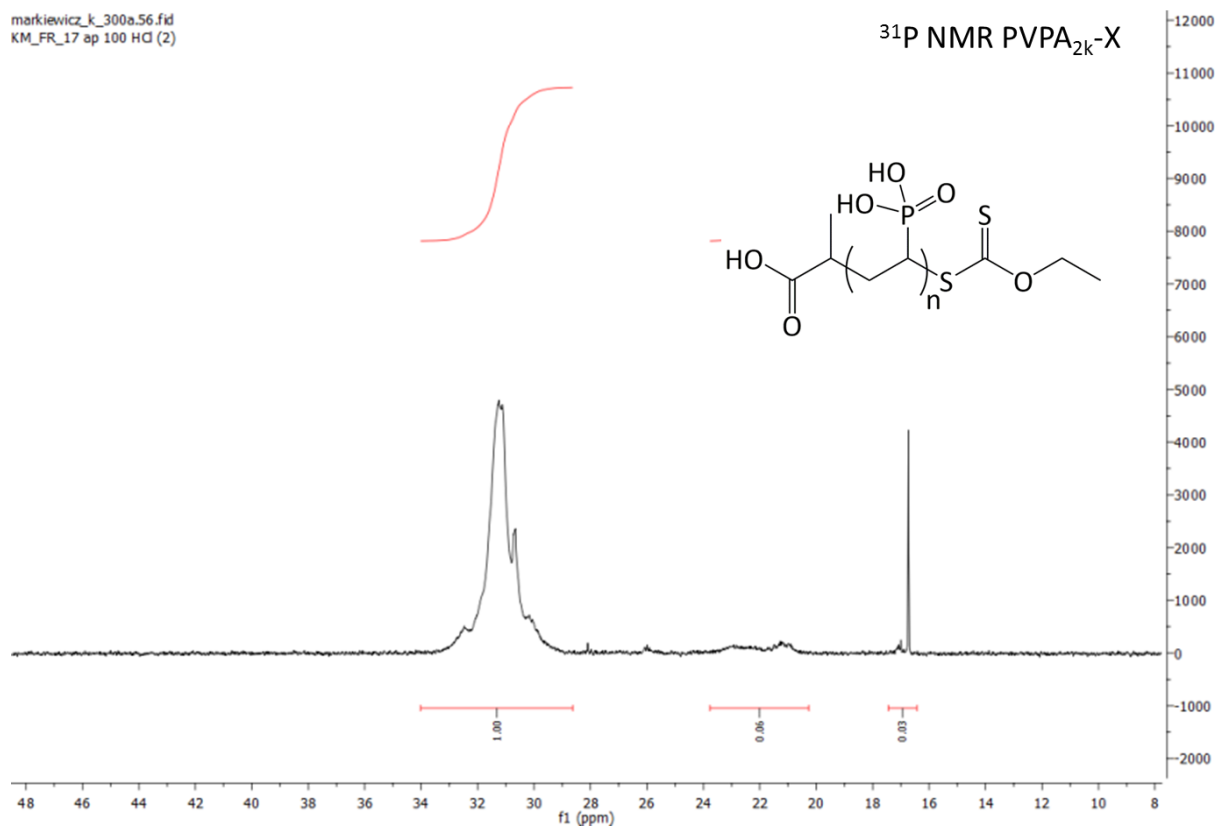
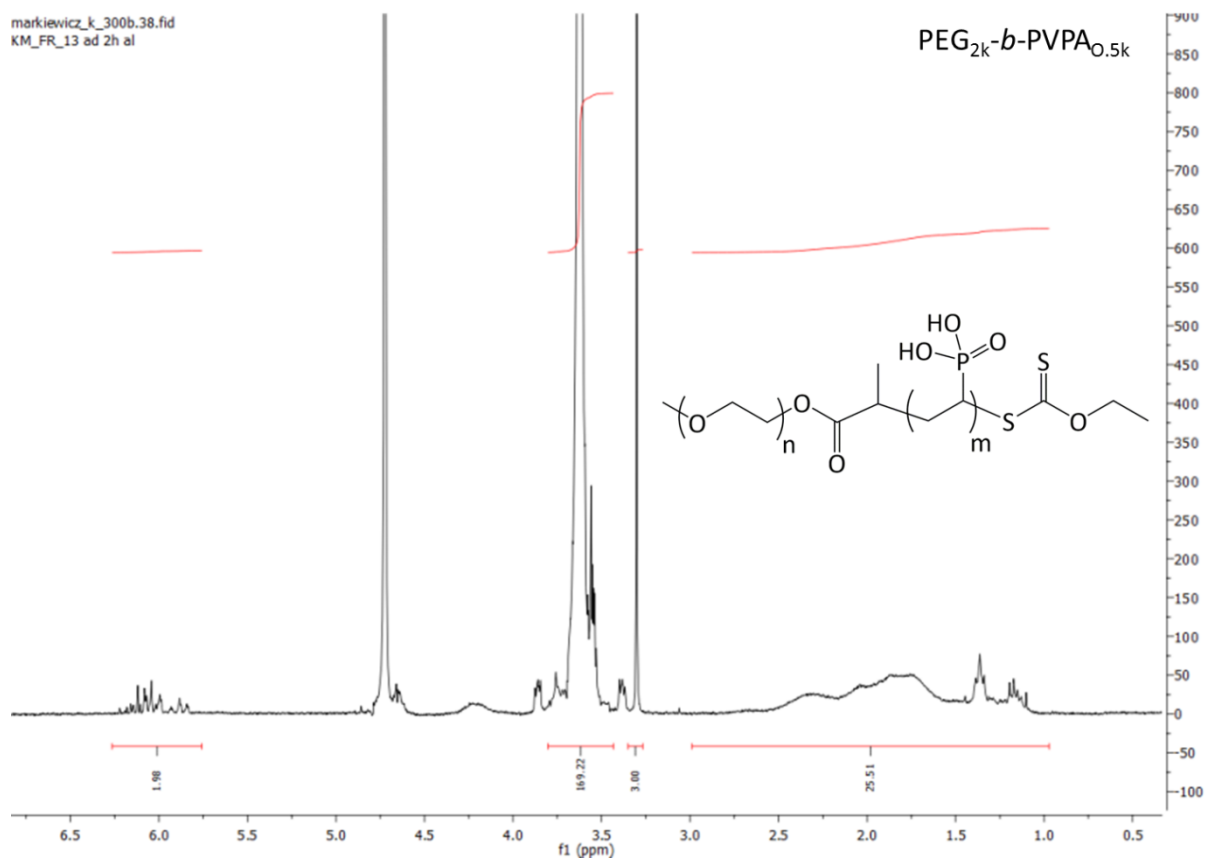


Figure S1B. ^1H NMR and ^{31}P NMR spectra of polymers used in reported study.

markiewicz_k_300b.38.fid
KM_FR_13 ad 2h al

PEG_{2k}-*b*-PVPA_{0.5k}



markiewicz_k_300b.36.fid
KM_FR_26 ad 2h+2h

PEG_{2k}-b-PVPA_{1k}

Chemical structure of the copolymer is shown, with segments labeled n , m , and k .

Integration values: 1.19, 172.96, 3.00, 40.15.

markiewicz_k_300b.59.fid
imrp P3R
KM_FR_47 fd

PEG_{5k}-*b*-PVPA_{0.5k}

Chemical structure of the block copolymer is shown: $(\text{OCH}_2\text{CH}_2)_n\text{O}-\text{C}(=\text{O})-\text{CH}(\text{CH}_3)-\text{CH}_2-\text{CH}_2-\text{P}(\text{O})(\text{OH})_2-\text{S}-\text{C}(=\text{O})-\text{OCH}_2\text{CH}_3$. The structure is labeled with n for the PEG block and m for the PVPA block.

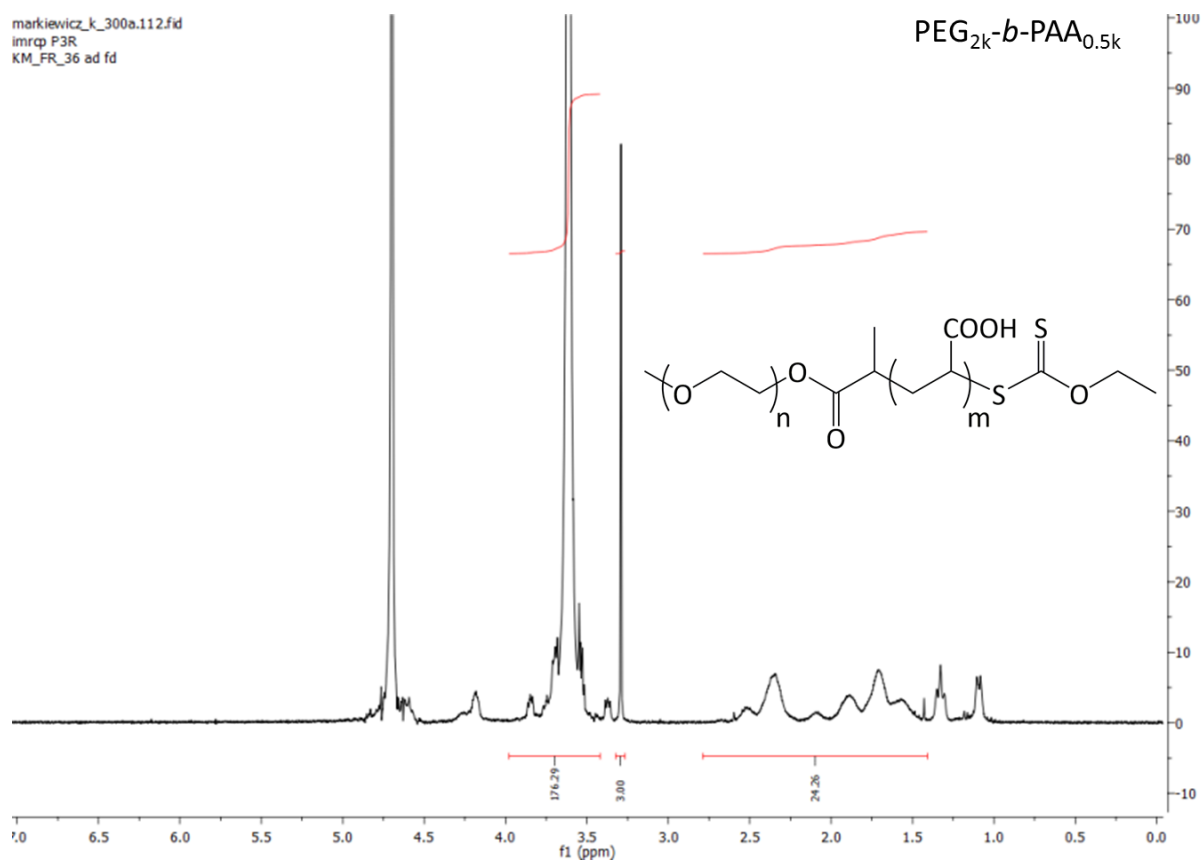
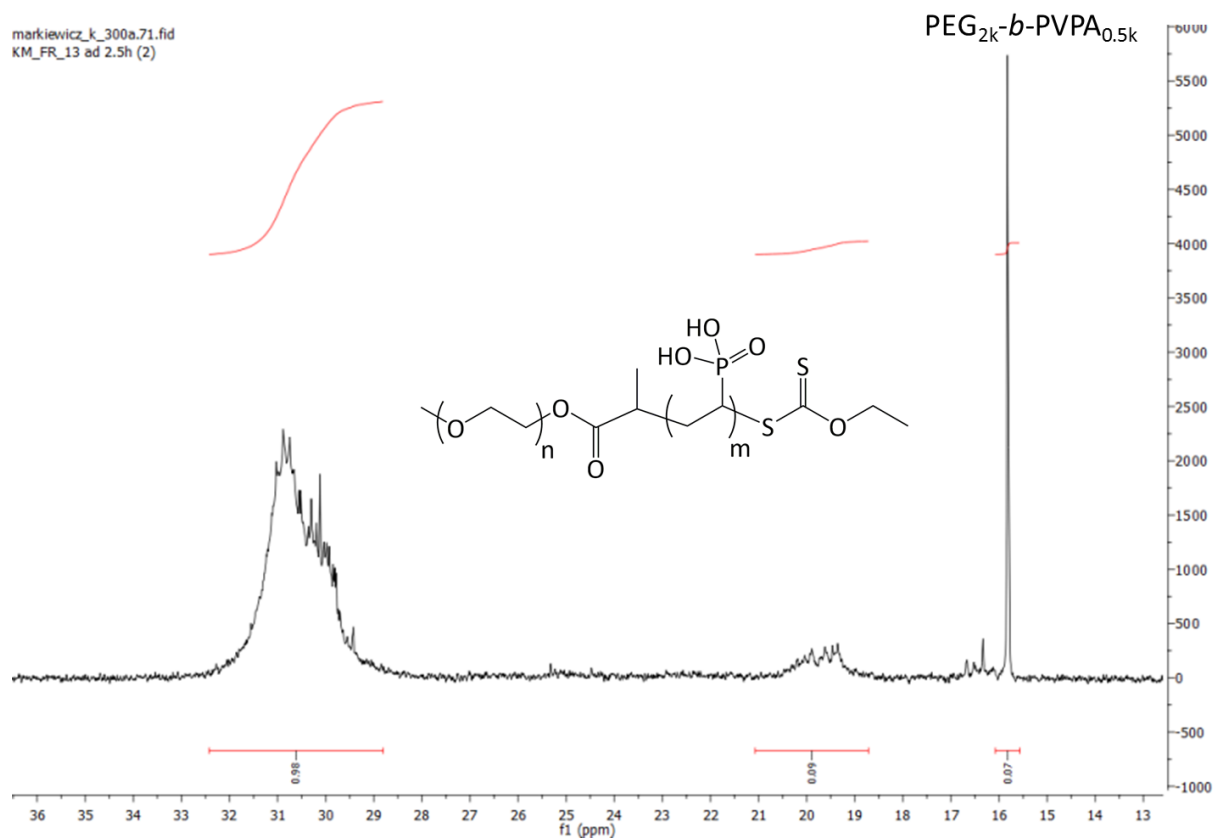


Figure S1C. ¹H NMR spectra of copolymers used in reported study.



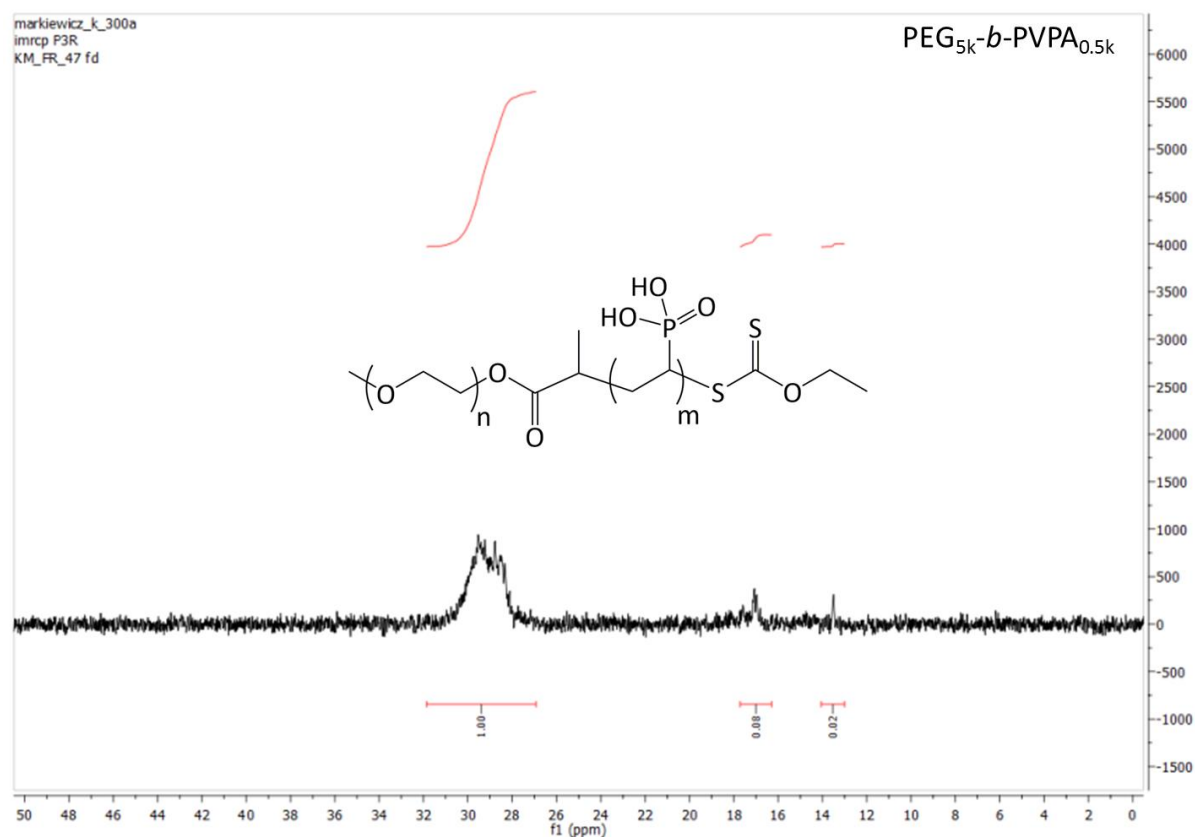
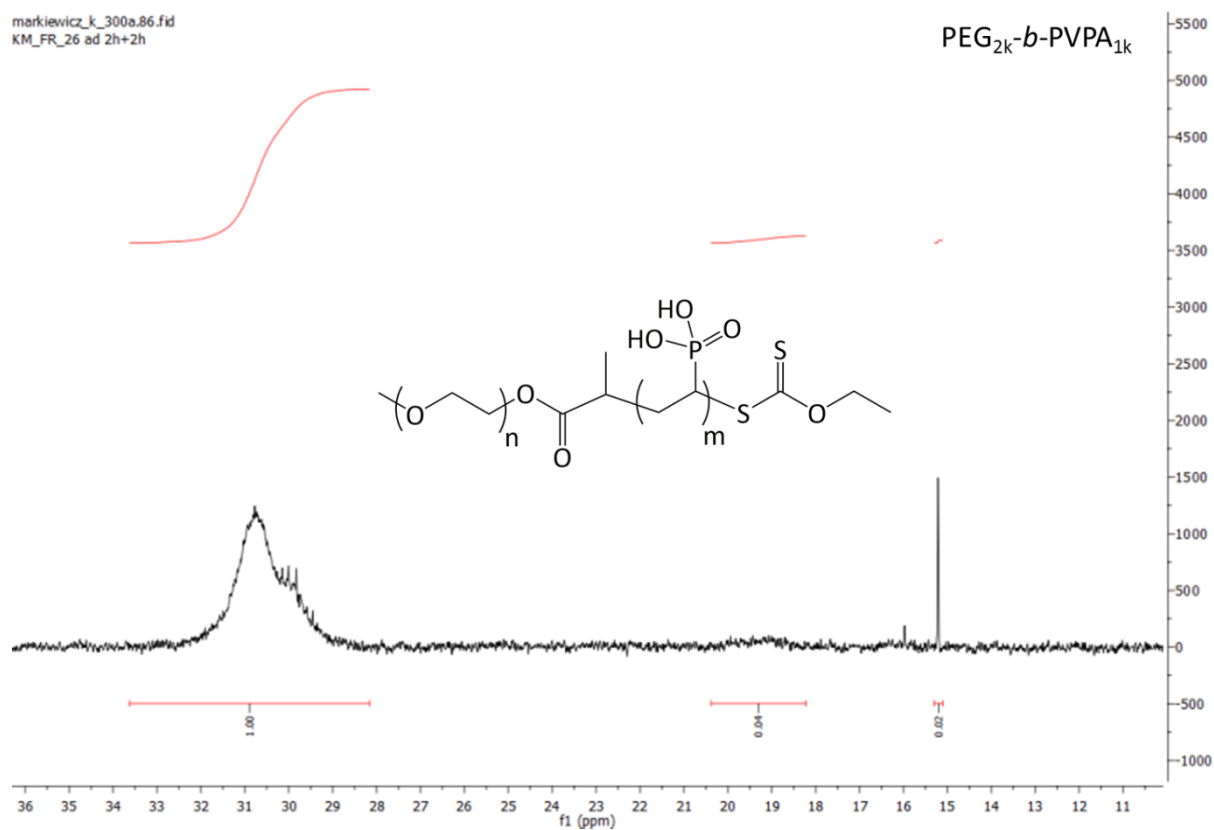


Figure S1D. ³¹P NMR spectra of copolymers used in reported study.

Table S1. Summary of molecular weights of diblock copolymers used for stabilization of IONP based on SEC and ^1H NMR.

	dn/dc (mL/g)	[monomer] ₀ (mol/L)	[X] ₀ (mol/L)	Conv (%)	M _{n th} ^a (g·mol ⁻¹)	M _{n, NMR} ^b (g·mol ⁻¹)	M _{n, SEC} ^c (g·mol ⁻¹)	Đ	DP _n (SEC)
PVPA _{1K}	0.144	7.5	0.65	0.85	1253	-	2926	1.19	-
PVPA _{2K}	0.144	7.5	0.32	0.85	2346	-	4861	1.09	-
PEG _{2K}	0.131	-	-	-	2188	-	2330	1.09	-
PEG _{5K}	0.131	-	-	-	5176	-	5740	1.00	-
PEG _{2K} - <i>b</i> -PVPA _{0.5K}	0.134	4.48	0.24	0.50	3188	2890	2775	1.11	4.1
PEG _{2K} - <i>b</i> -PVPA _{1K}	0.135	4.80	0.16	0.50	3815	3525	3480	1.17	10.6
PEG _{2K} - <i>b</i> -PAA _{0.5K}	0.141	1.55	0.22	0.99	2690	2770	2863	1.03	7.4
PEG _{5K} - <i>b</i> -PVPA _{0.5K}	0.132	2.90	0.25	0.35	5615	5543	6360	1.09	5.7

^aM_{n th} = ([monomer]₀/[X]₀)·Conv·(M_{monomer}) + M(X).

M_{VPA} = 108g/mol M_{AA} = 72g/mol M_X = 194g/mol M_{PEG2K-X} = 2188 g/mol M_{PEG5K-X} = 5176 g/mol

^bDetermined by ^1H NMR taking the weight of the PEG blocks into account.

^cMeasured by SEC-RI-MALS.

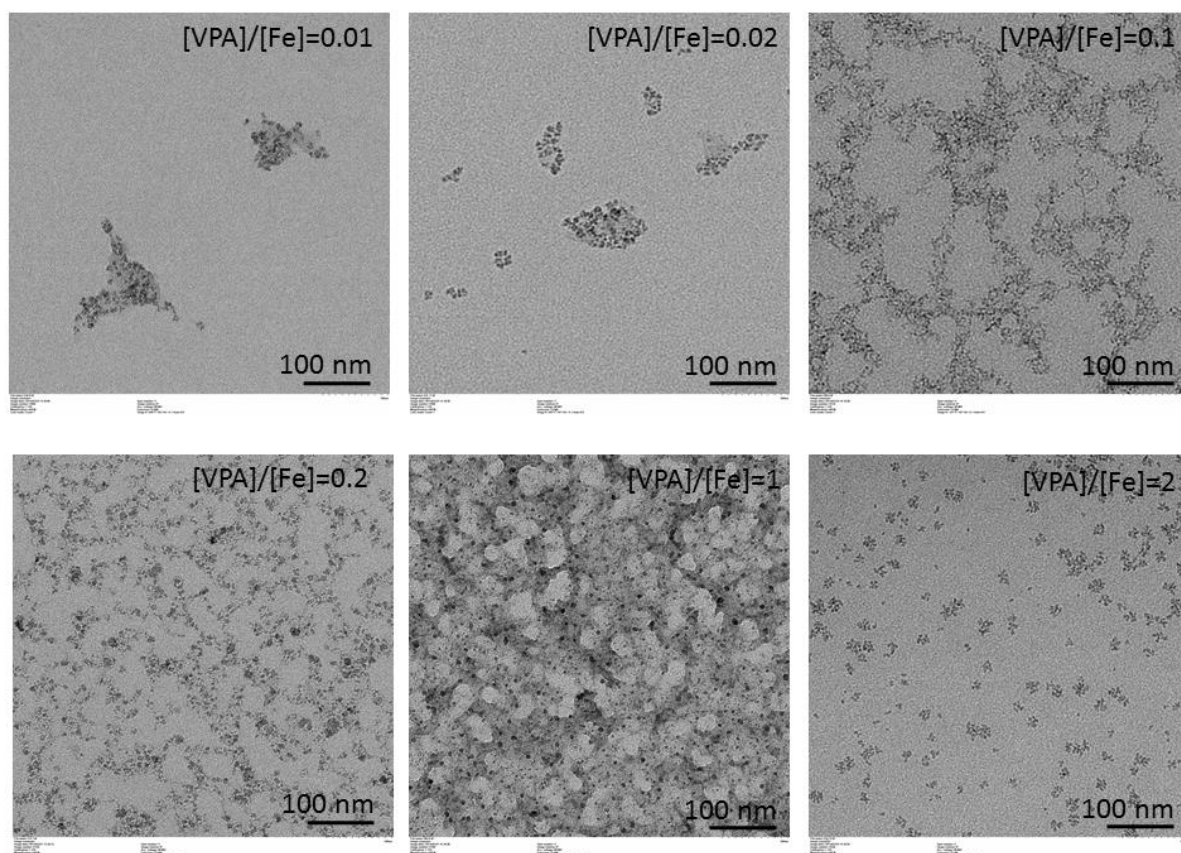


Figure S2. Effect of block copolymer concentration on NP growth for constant Fe concentration. TEM photographs of IONP@PVPA_{0.5K}-*b*-PEG_{2K} samples of different [VPA]:[Fe] molar ratio.

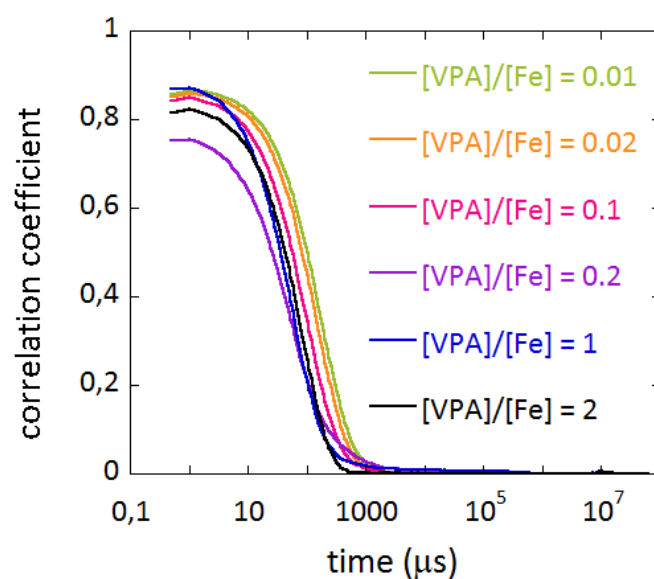


Figure S3. Effect of block copolymer concentration on NP growth for constant Fe concentration. Correlation coefficient graphs of IONP@PVPA_{0.5K}-*b*-PEG_{2K} samples of different [VPA]:[Fe] molar ratio.

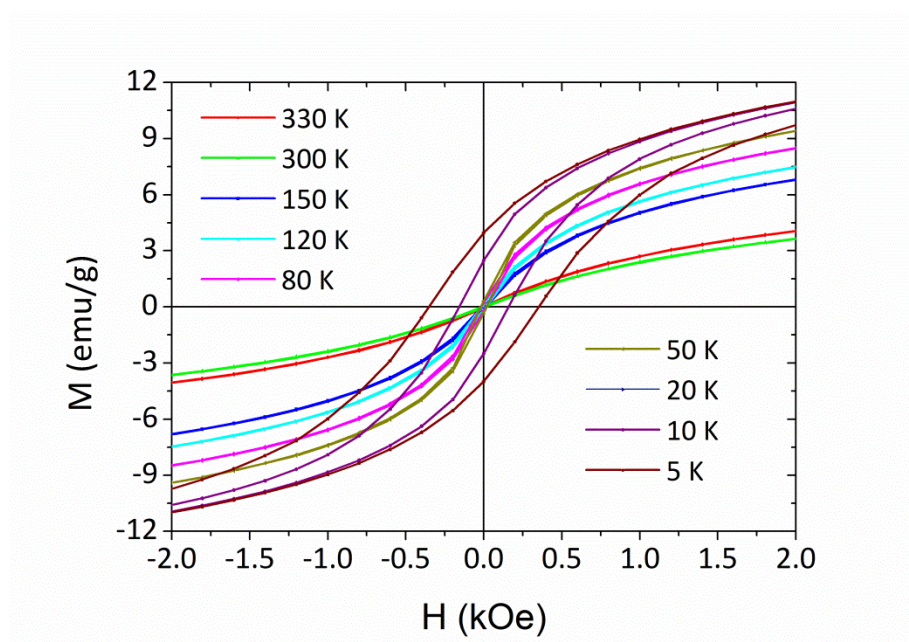


Figure S4. Magnetisation as a function of external magnetic field measured for IONP@PVPA_{0.5K}-*b*-PEG_{2K} at various temperatures.

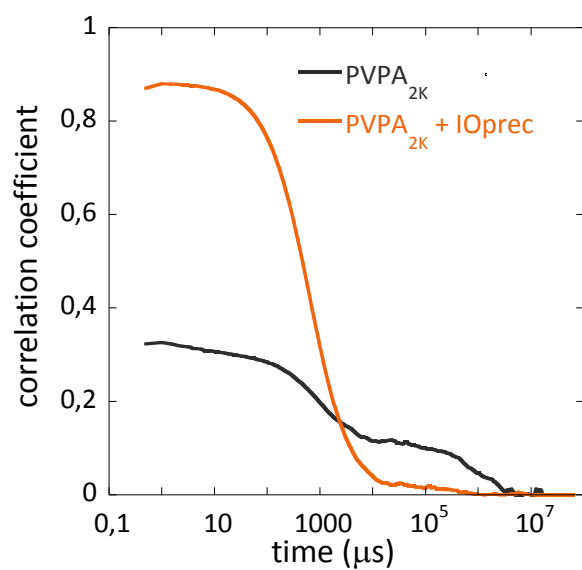


Figure S5. Correlation coefficient graphs of polymer PVPA_{2K} solution (0.1wt%) and its mixture with iron oxide precursors ([VPA]/[Fe] = 1).

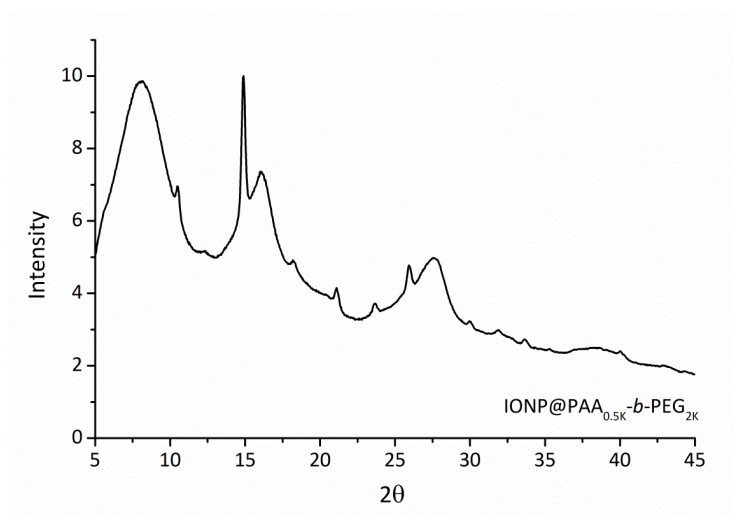


Figure S6. XRD pattern of IONP@PAA_{0.5K}-b-PEG_{2K} (P:Fe mass ratio 10:1).