

Supporting Information

Exploring Precision Polymers to Fine-tune MRI Properties of Iron Oxide Nanoparticles

Aaron M. King,[†] Caroline Bray,[§] Stephen C. L. Hall,[§] Joseph C. Bear,[‡] Lara K. Bogart,^{||} Sebastien Perrier,[§] Gemma-Louise Davies^{*†}

[†]Department of Chemistry, University College London, 20 Gordon Street, London WC1H 0AJ, U.K.

[§]Department of Chemistry, University of Warwick, Gibbet Hill Road, Coventry CV4 7AL, U.K.

[‡]School of Life Science, Pharmacy and Chemistry, Kingston University, Penryhn Road, Kingston-upon-Thames, KT1 2EE, U.K.

^{||}UCL Healthcare Biomagnetics Laboratory, University College London, 21 Albemarle Street, London W1S 4BS, U.K.

CORRESPONDING AUTHOR: Gemma-Louise Davies

E-MAIL: gemma-louise.davies@ucl.ac.uk

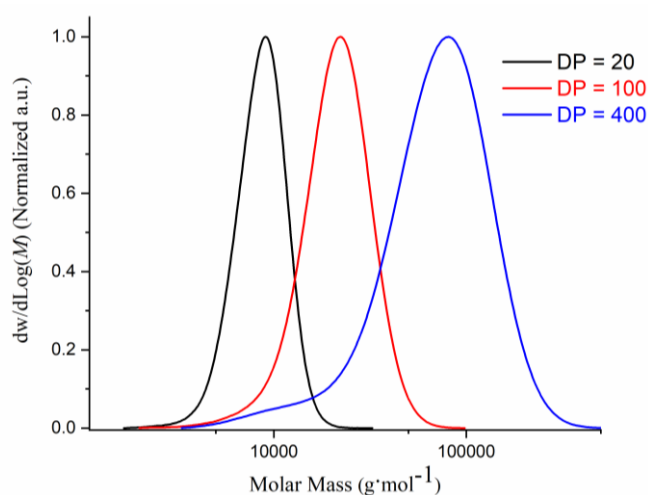


Figure S1. Aqueous size exclusion chromatography (SEC) of P(AMPS) polymers (Degree of polymerisation (DP) of 20, 100 and 400 with $M_{n,SEC}$ values measured to be 8,100, 17,600, and 41,300 g mol⁻¹ respectively as determined by conventional calibration using Agilent GPC/SEC software.)

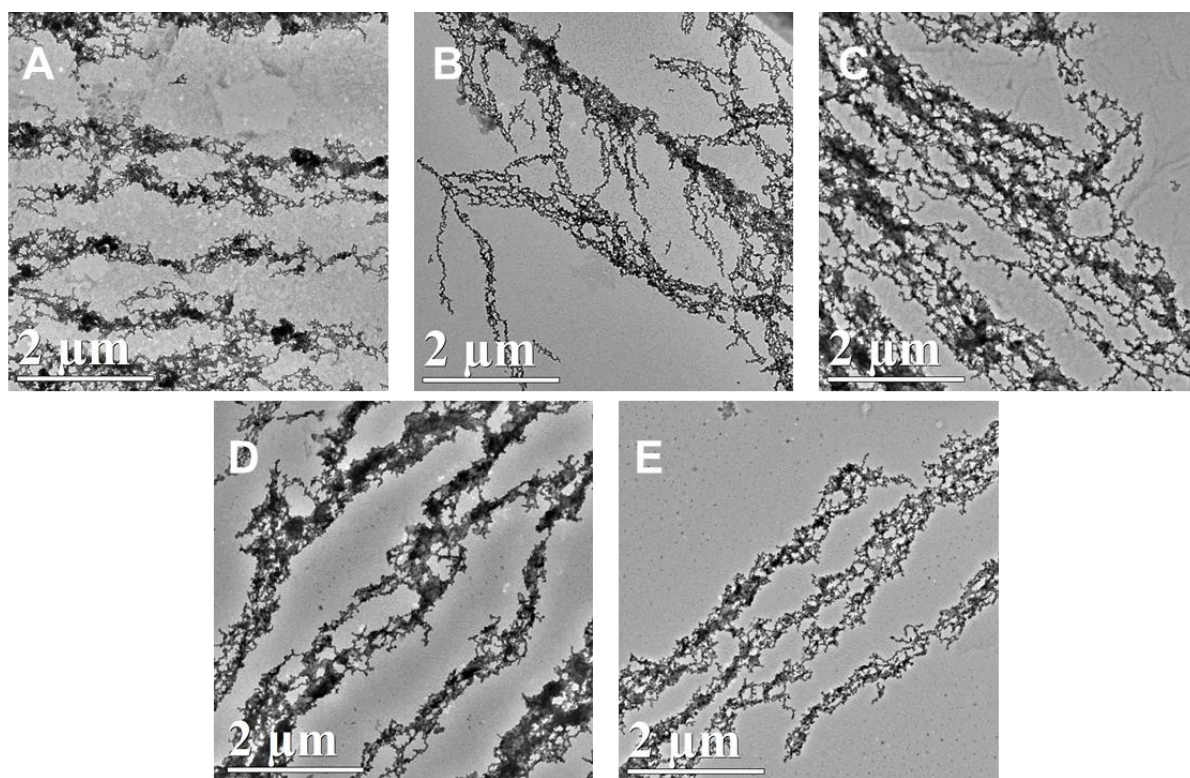


Figure S2. Transmission electron microscope images of P(AMPS) stabilised **iron oxide** nanoparticles, labelled according to Table 1, following drying in an applied parallel magnetic field (2250 Gauss). Scale bar 2 μm .

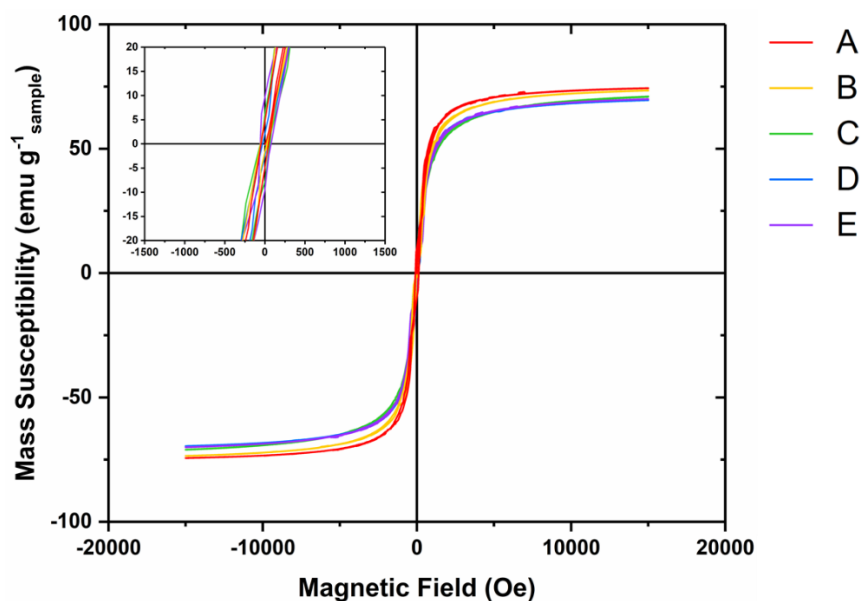


Figure S3. Magnetisation (mass susceptibility) of P(AMPS) stabilised **iron oxide** nanoparticles (A-E) plotted against magnetic field, measured between field strengths of -15 kOe to 15 kOe. Inset showing lack of hysteresis loop indicating superparamagnetic behaviour.

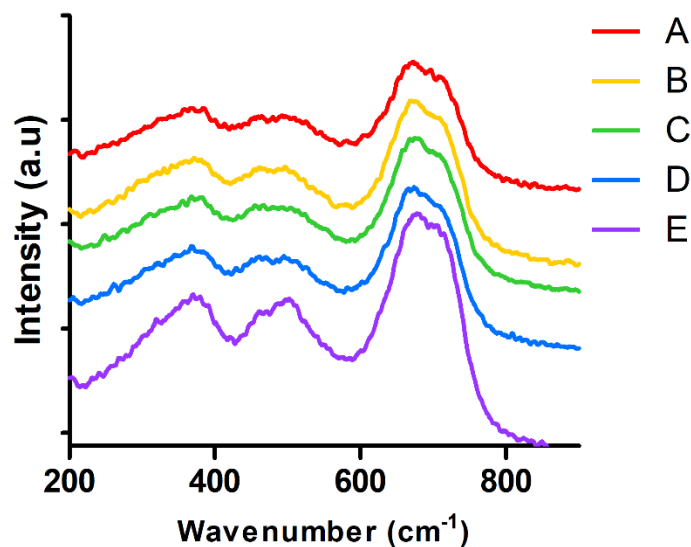


Figure S4. Raman spectra of P(AMPS) stabilised **iron oxide** nanoparticles (A-E) exhibiting a peak at 670 cm^{-1} and shoulder at 702 cm^{-1} indicating the A_{1g} modes of magnetite and maghemite respectively. A broad peak at 368 cm^{-1} represents the T_{2g} mode of maghemite, and another at 494 cm^{-1} , attributed to the E_g mode of maghemite.

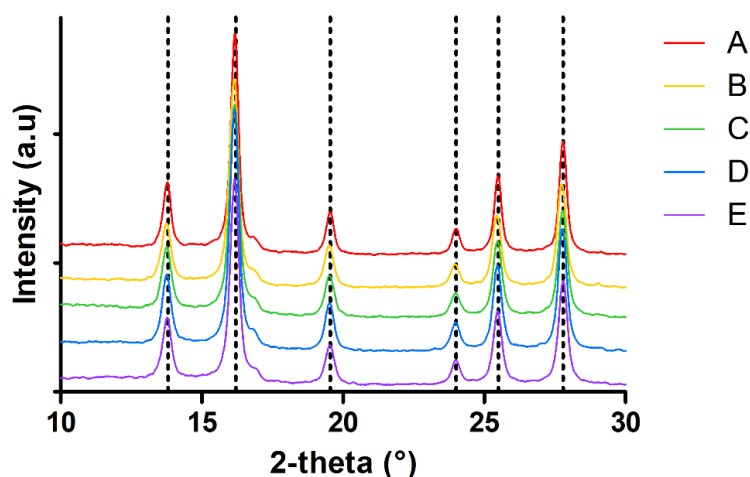


Figure S5. Powder X-ray diffraction patterns of P(AMPS) stabilised **iron oxide** nanoparticles (A-E). Dashed lines represent the expected peaks positions at 13.8° , 16.2° , 19.6° , 25.5° , and 27.8° readily indexed to the (220), (311), (400), (511), and (440) planes for cubic inverse spinel type iron oxides according to JCPDS database card number 39-1346.

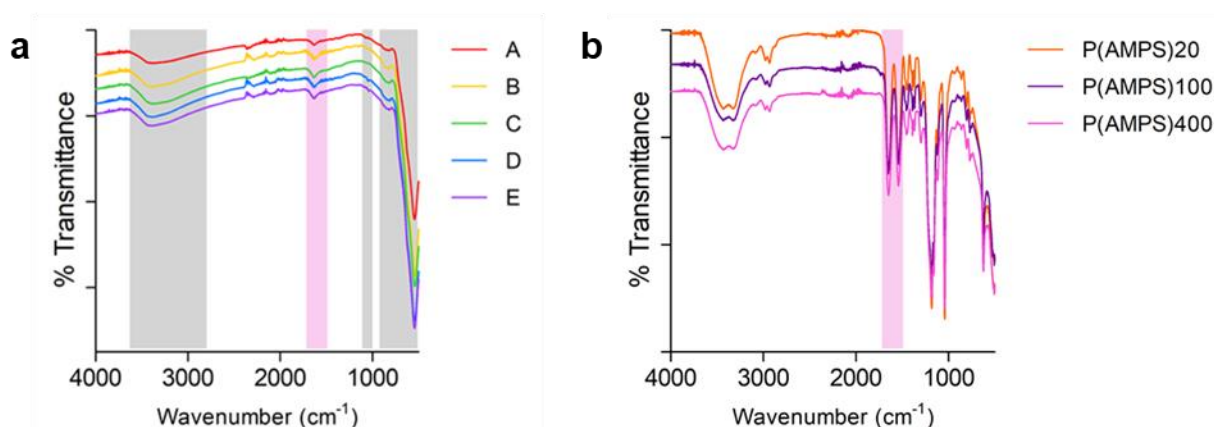


Figure S6. Fourier transform infrared (FT-IR) spectra of a) P(AMPS) stabilised **iron oxide** nanoparticles (A-E), and b) P(AMPS) ((P(AMPS)20, P(AMPS)100), and P(AMPS)400, with respective $M_{n,SEC}$ of 8,100, 17,600, and 41,300 g mol^{-1}). The stretches between $3600\text{--}3000\text{ cm}^{-1}$ (representing OH stretching vibrations from surface hydroxyl groups and physisorbed water groups), and the stretch at $650\text{--}500\text{ cm}^{-1}$ (correlating to the Fe-O stretch) are observed for the 5 P(AMPS) stabilised nanoparticles, with stretches at $1370\text{--}1340\text{ cm}^{-1}$ and $1080\text{--}1030\text{ cm}^{-1}$, indicative of O=S=O and C=S stretching vibrations, respectively, of functional groups on the P(AMPS) chains.

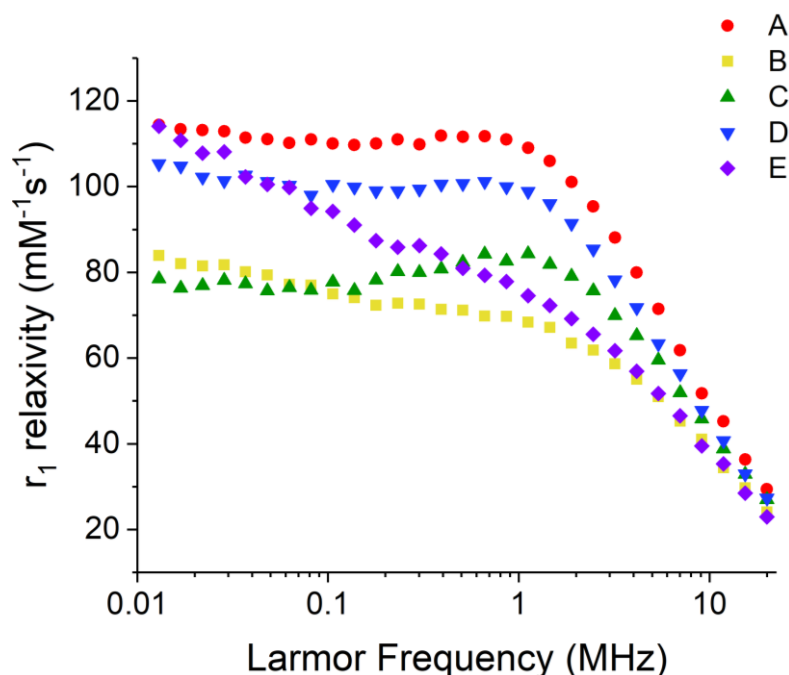


Figure S7. ^1H NMRD profiles, measured at 25 °C, of P(AMPS) stabilised **iron oxide** suspended in 0.1% Xanthan Gum. The r_1 values have been calculated in terms of total mM [Fe] content of the samples, as measured by ICP-OES.

Table S1. Theoretical and experimental molecular weight of the P(AMPS) used in this study.

Degree of Polymerisation	[AMPS] ₀ : [CTA] ₀ : [VA-086] ₀ (mol L ⁻¹)	$M_{n,\text{th}}^{\text{a}}$ (g mol ⁻¹)	$M_{n,\text{SEC}}^{\text{b}}$ (g mol ⁻¹)	\bar{D}^{b}
20	20 : 1 : 0.033	4,800	8,100	1.10
100	100 : 1 : 0.167	23,000	17,600	1.16
400	400 : 1 : 0.667	91,000	41,300	1.51

^a Theoretical M_n values were calculated using the following equation; $M_{n,\text{th}} = ([M]_0 \cdot p \cdot M_M / [CTA]_0) + M_{CTA}$; ^b Experimental $M_{n,\text{SEC}}$ and \bar{D} values were determined by size exclusion chromatography in 20% methanol / 80 % of 0.1 M NaNO₃ in milli-Q water eluent using a conventional calibration obtained with PEG/PEO standards. The dispersity, \bar{D} , was calculated according to $\bar{D} = M_w / M_n$, where M_w is the weight-average molar mass and M_n is the number-average molar mass.

Table S2. Total initial concentrations of iron salts and P(AMPS) used in the preparation of P(AMPS) stabilised iron oxide nanoparticles.

Sample	[Fe] (mM)	[P(AMPS)] (mM)	Total [Fe]:[P(AMPS)] ratio
A	30	0.300	100:1
B	50	0.020	2,500:1
C	50	0.008	6,250:1
D	50	0.008	6,250:1
E	50	0.008	6,250:1

Table S3. Room temperature ^{57}Fe Mössbauer parameters as deduced from best fits to the data presented in Figure 4a, obtained using the "centre of gravity" model, with fitting to spectra performed using Recoil.

Sample	α^a	Linewidth (mm/s)	$\langle H \rangle^b$ (kOe)	$\sigma_{\langle H \rangle}^b$ (kOe)	FWHM ^d (kOe)
A	0.06 ± 0.15	0.27	408.6	20.1	45
B	0.13 ± 0.06	0.31	400.5	28.5	63
C	0.10 ± 0.07	0.34	375.3	20.8	50
D	0.14 ± 0.05	0.30	390.8	36.2	60
E	0.13 ± 0.06	0.32	392.0	25.6	54

^a α is the numerical proportion of Fe atoms in the magnetite environment as determined by the 'centre of gravity' method with the corresponding uncertainty given as error bars; ^b The mean static hyperfine field, $\langle H \rangle$, and the standard deviation of the mean, $\sigma_{\langle H \rangle}$. ^d FWHM is the full width at half maximum.