Supporting Information for:

Aqueous One-Pot Synthesis of Well-defined Zwitterionic Diblock Copolymers by RAFT Polymerization: An Efficient and Environmentally-friendly Route to a Useful Dispersant for Aqueous Pigments

S. M. North and S. P. Armes*

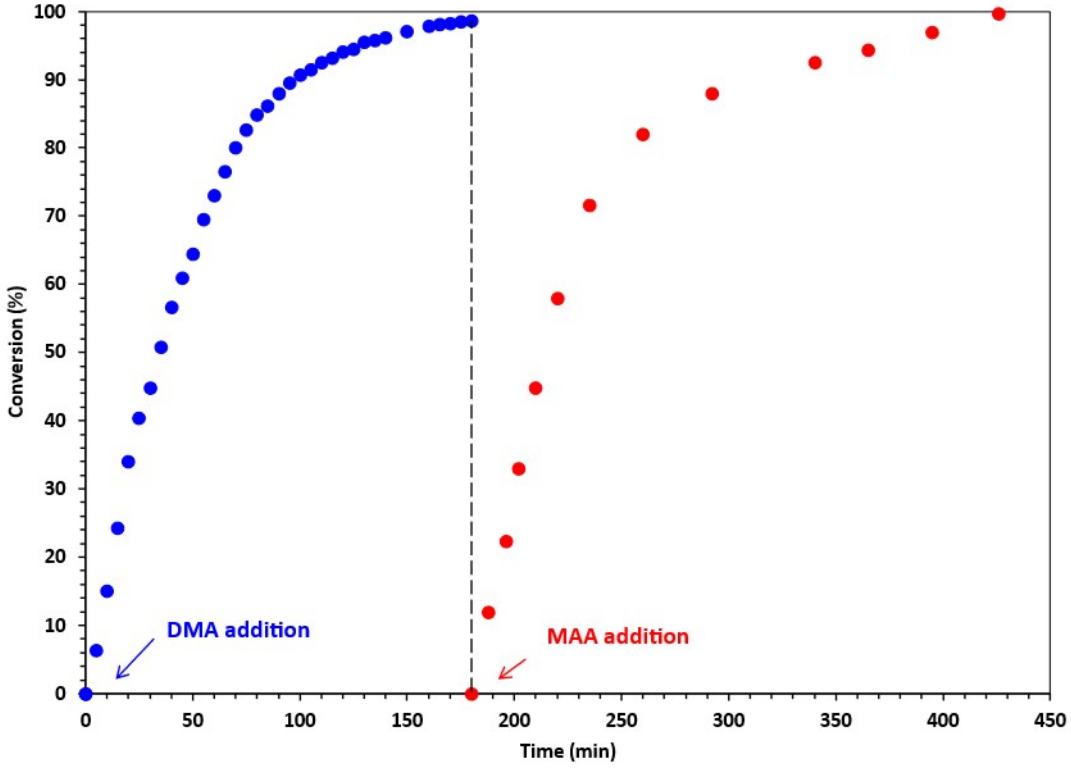


Figure S1. Conversion vs. time curves obtained from *in situ* ^{1}H NMR spectroscopy studies conducted in D_2O for the wholly aqueous one-pot synthesis of a $PDMA_{50}$-$PMAA_{50}$ zwitterionic diblock copolymer. Essentially full DMA conversion is achieved within 3 h at 44 °C for the first block, while the subsequent MAA polymerization requires 4.5 h at the same temperature.

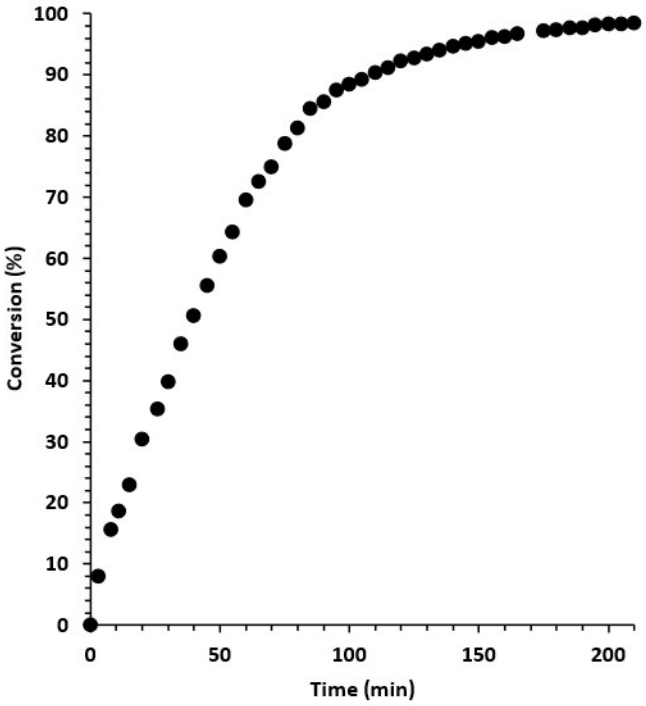


Figure S2. Conversion vs. time curve obtained from in situ ^{1}H NMR spectroscopy studies conducted in D_2O for the wholly aqueous synthesis of a $PDMA_{100}$ precursor. Essentially full DMA conversion is achieved within 3.5 h at 44 °C.

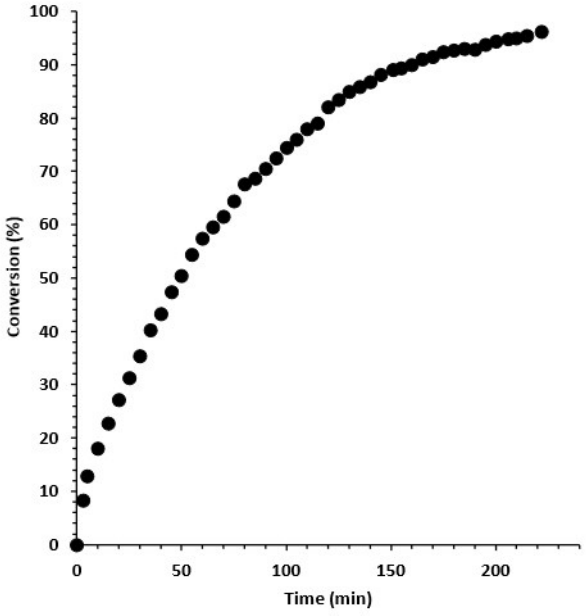


Figure S3. Conversion vs. time curve obtained from *in situ* ^{1}H NMR spectroscopy studies conducted in D_2O for the wholly aqueous synthesis of a $PDMA_{200}$ precursor. Very high (> 95%) DMA conversion is achieved within 4 h at 44 °C.

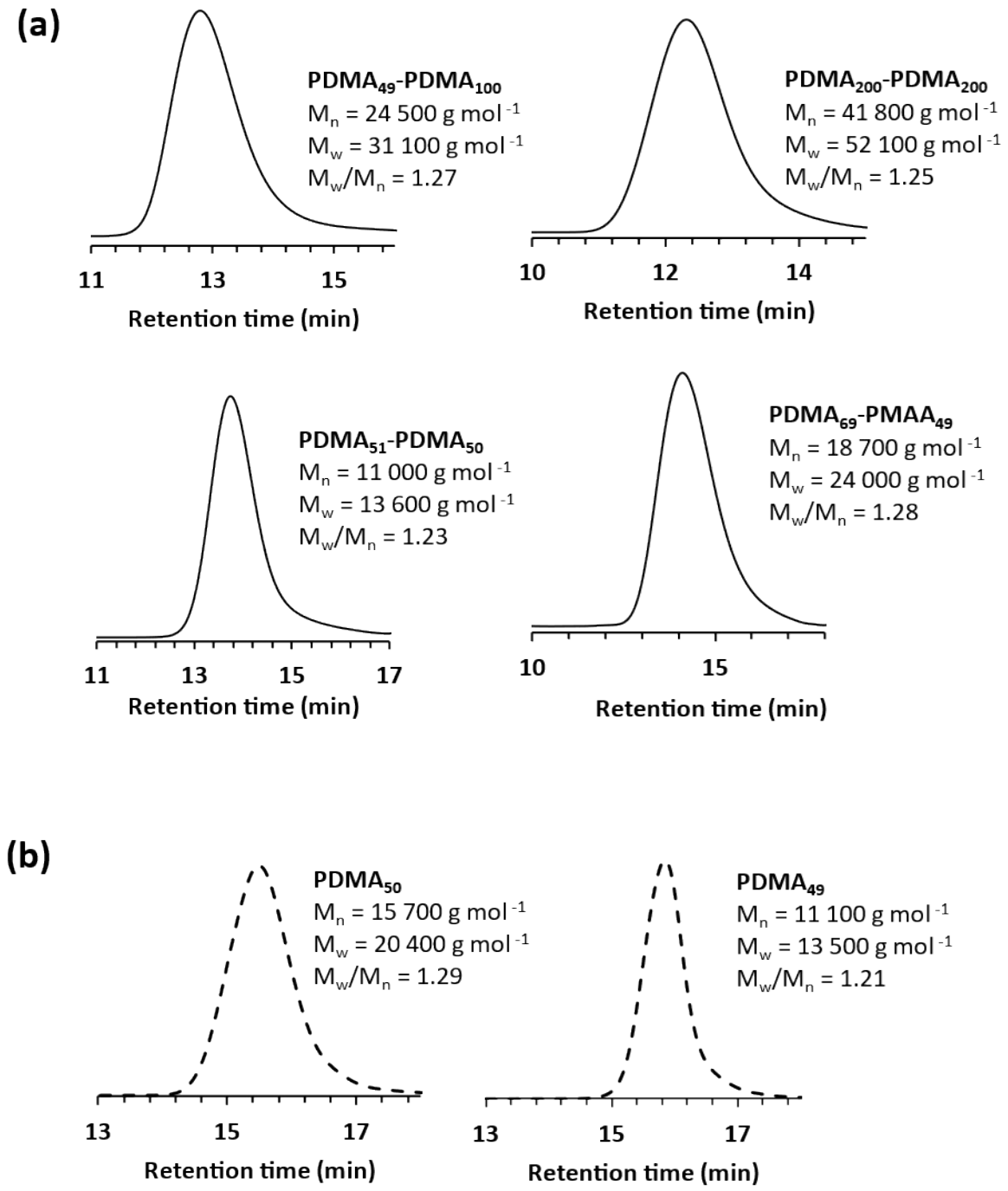
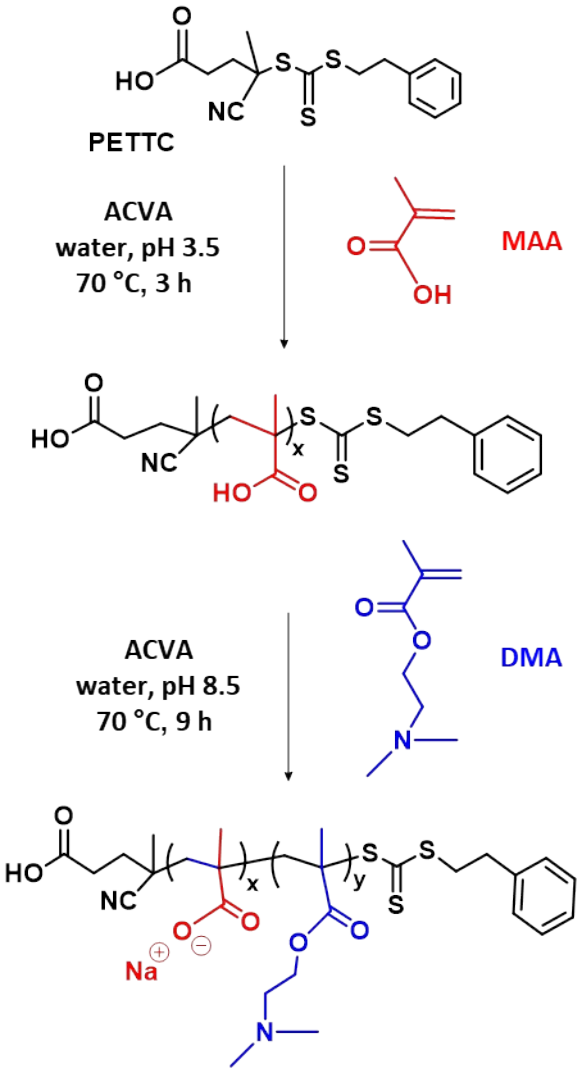


Figure S4. Example GPC curves obtained by (a) aqueous GPC of PDMA-PMAA diblock copolymers and (b) THF GPC of PDMA homopolymer (first block).



Scheme S1. Wholly aqueous one-pot synthetic route to zwitterionic diblock copolymers via RAFT solution polymerisation, where the first block comprises poly(methacrylic acid) (PMAA) and the second block is poly(2-(dimethylamino)ethyl methacrylate) (PDMA).

Entry	Diblock copolymer composition	CTA	PMAA ^{1}H NMR conversion (%)	PDMA ^{1}H NMR conversion (%)	Aqueous GPC (g mol^{-1})	
					M_n	M_w/M_n
1	$PMAA_{45}$-$PDMA_{48}$	PETTC	89	95	13 800 g mol^{-1}	1.35
2	$PMAA_{50}$-$PDMA_{95}$	PETTC	99	95	14 700 g mol^{-1}	1.47
3	$PMAA_{97}$-$PDMA_{49}$	PETTC	97	97	17 700 g mol^{-1}	1.23

Table S1. Summary of the characterization data obtained for six PMAA-PDMA zwitterionic diblock copolymers prepared according to **Scheme S1**. In each case, the second stage polymerization of DMA was conducted in aqueous solution at pH 8.5. ^{1}H NMR spectroscopy was used to calculate the final comonomer conversion achieved for each block.

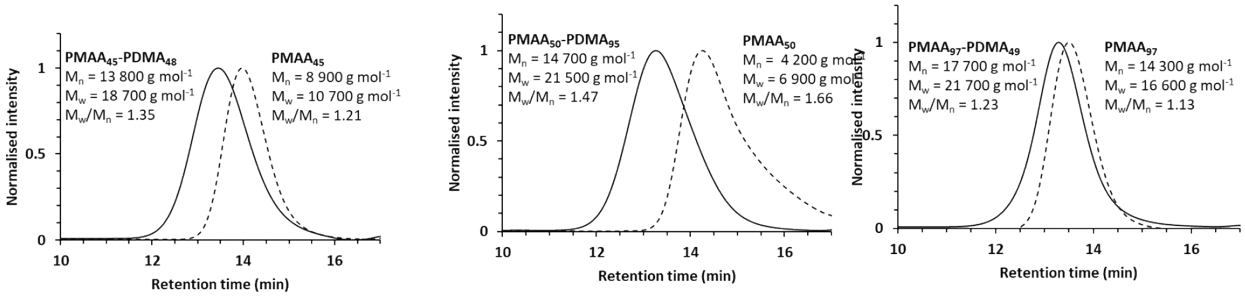


Figure S5. Example aqueous GPC traces of PMAA precursors and PMAA-PDMA diblock copolymers listed in **Table S1** to show blocking efficiency and to determine molecular weight distribution.

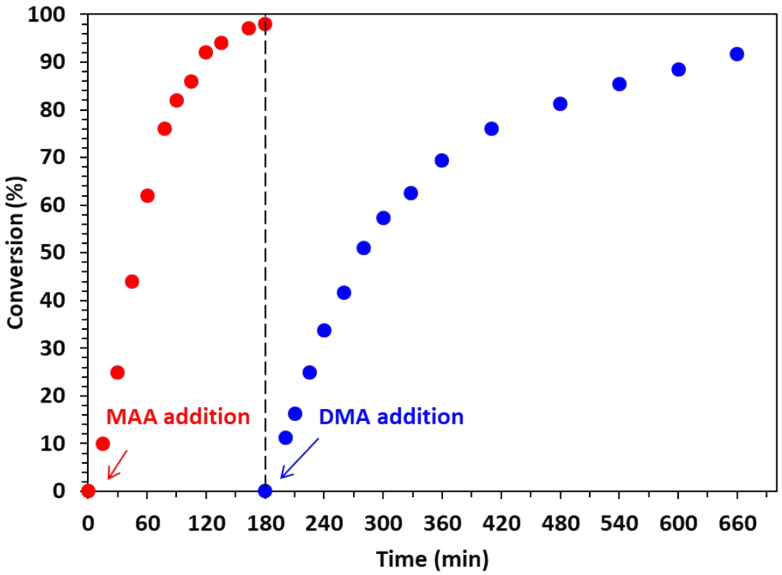


Figure S6. Conversion vs. time curves obtained by periodic reaction sampling, determined by ^{1}H NMR spectroscopy studies conducted in D_2O for the wholly aqueous one-pot synthesis of a $PMAA_{50}$-$PDMA_{100}$ zwitterionic diblock copolymer (target composition). Full MAA conversion is achieved within 3 h at 44 °C for the first block in this case, while the subsequent MAA polymerization requires 4.5 h at the same temperature.

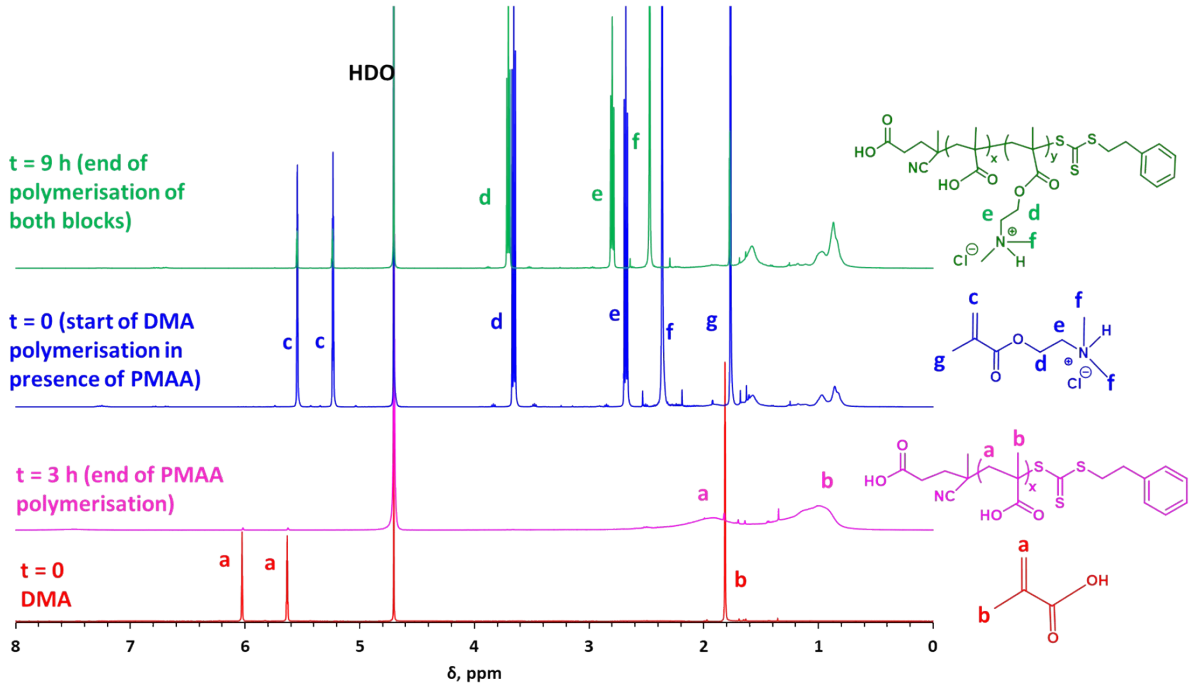


Figure S7. Selected ^{1}H NMR spectra recorded in D_2O at the start (red) and end (pink) of the RAFT aqueous solution polymerization of MAA and the start (blue) and end (green) of the subsequent DMA polymerization (see **Scheme S1**).

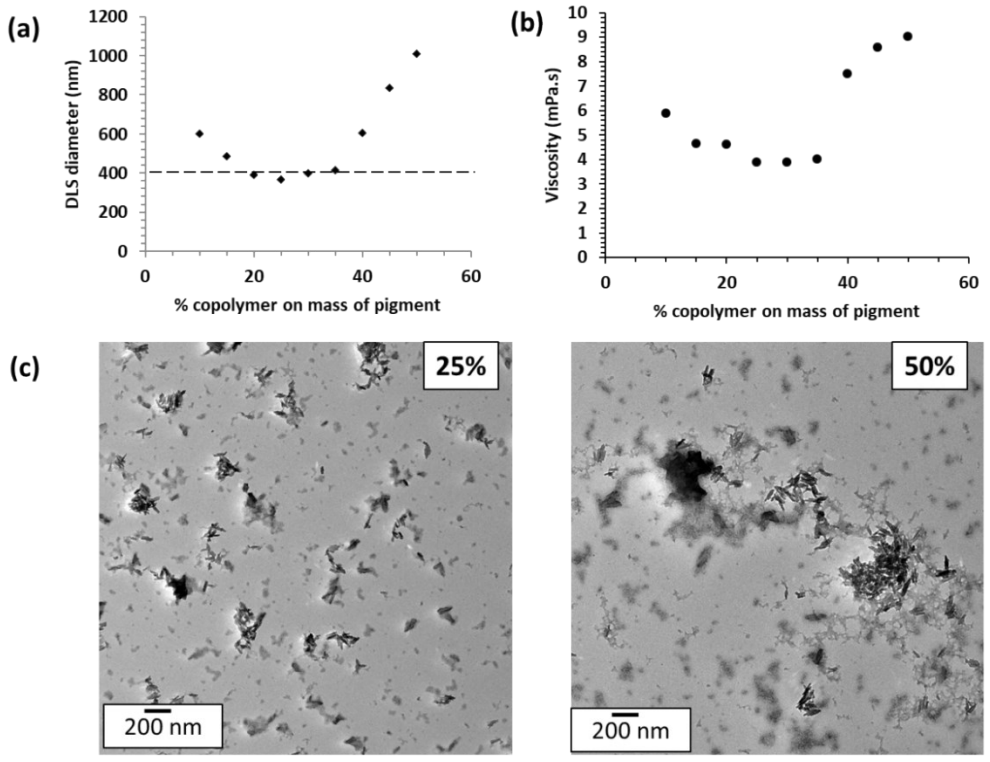


Figure S8. Dispersion of transparent yellow iron oxide with $PDMA_{49}$-$PMAA_{100}$ at pH 7.5, above the copolymer IEP (a) DLS diameter at varying copolymer concentration, (b) viscosity at varying copolymer concentration and (c) TEM images at 25% and 50% copolymer with respect to pigment.

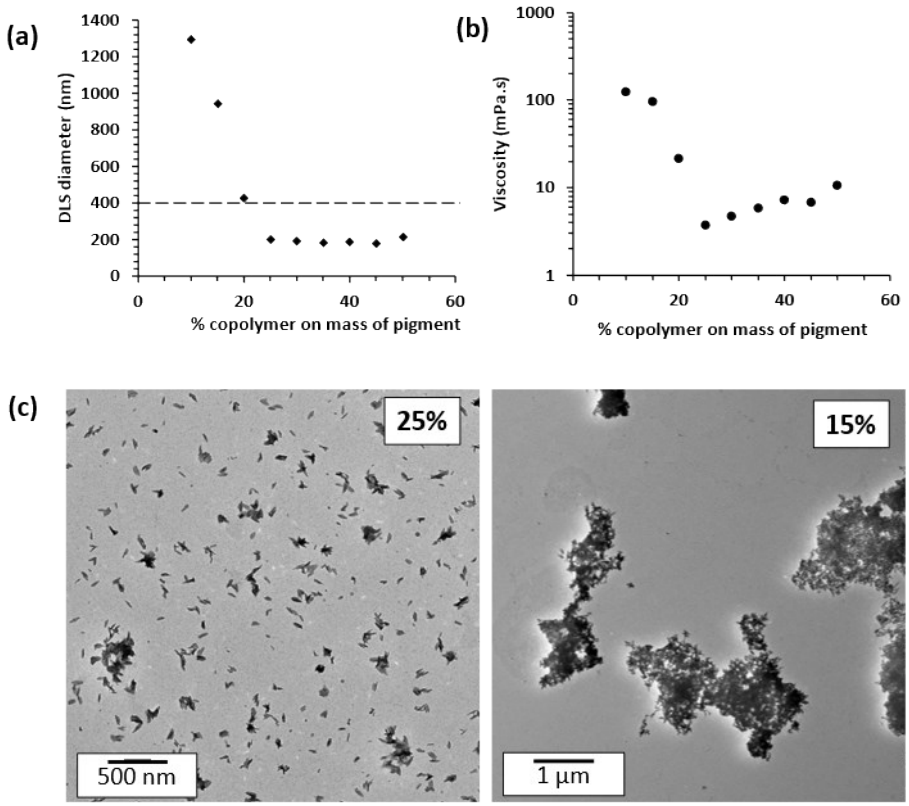


Figure S9. Dispersion of transparent yellow iron oxide with $PDMA_{49}$-$PMAA_{100}$ at pH 3.5, below the copolymer IEP (a) DLS diameter at varying copolymer concentration, (b) viscosity at varying copolymer concentration and (c) TEM images at 25% and 15% copolymer with respect to pigment.

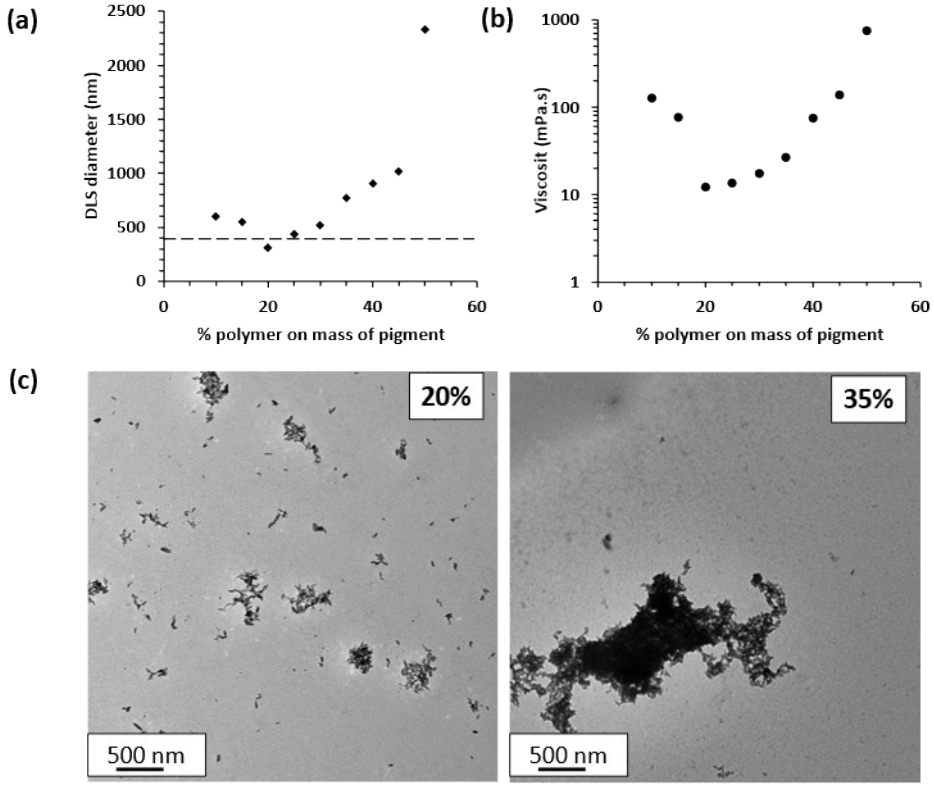


Figure S10. Dispersion of transparent yellow iron oxide with $PDMA_{100}$-$PMAA_{50}$ at pH 10.5, above the copolymer IEP (a) DLS diameter at varying copolymer concentration, (b) viscosity at varying copolymer concentration and (c) TEM images at 20% and 35% copolymer with respect to pigment.

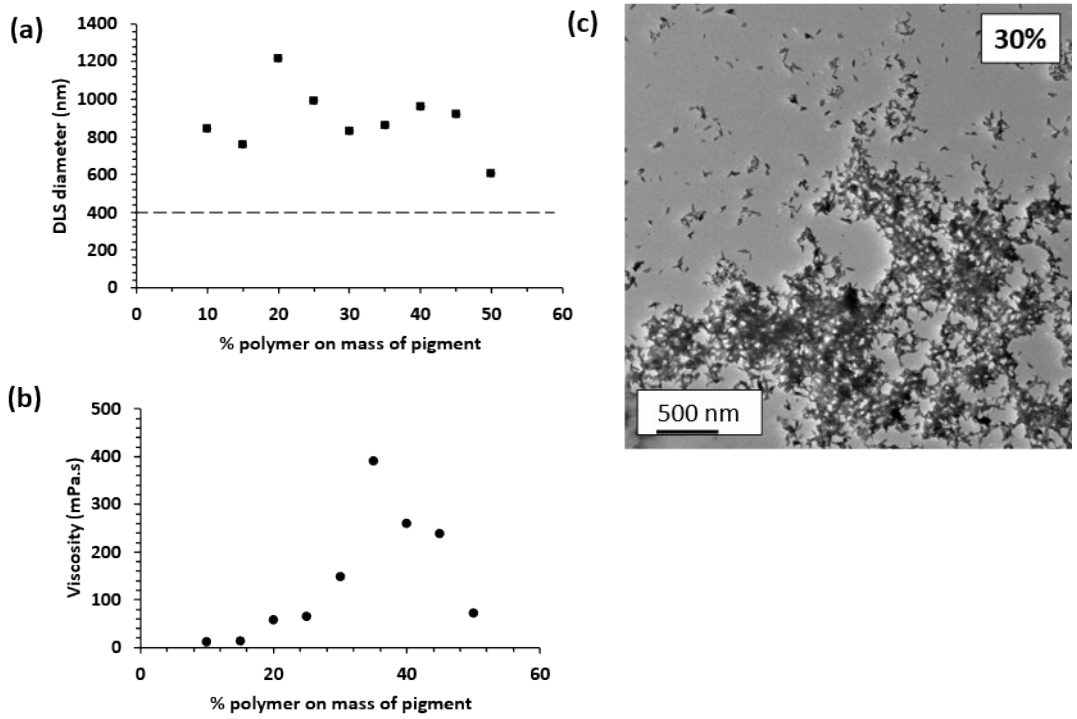


Figure S11. Dispersion of transparent yellow iron oxide with $PDMA_{100}$-$PMAA_{50}$ at pH 5.0, below the copolymer IEP (a) DLS diameter at varying copolymer concentration, (b) viscosity at varying copolymer concentration and (c) TEM image at 30% copolymer with respect to pigment.

Table S2. Summary of the optimal concentration, minimum apparent pigment diameter and dispersion viscosity of aqueous dispersions of transparent yellow iron oxide particles prepared using three different $PDMA_x$-$PMAA_y$ diblock copolymers at a solution pH either above or below their IEP.

Copolymer	pH	Optimal concentration	Minimum pigment size at optimal [copolymer] (nm)	Minimum dispersion viscosity at optimal [copolymer] (mPa.s)
$PDMA_{51}$-$PMAA_{50}$	8.5	25%	118	3.21
	4.0	20%	165	3.30
$PDMA_{49}$-$PMAA_{100}$	7.5	25%	369	3.88
	3.5	25%	201	3.75
$PDMA_{100}$-$PMAA_{50}$	10.5	20%	305	12.03
	5.0	-	606	13.2