Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information for:

PISA via Ultrafast RAFT Dispersion Polymerisation in Continuous-flow

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$$Conversion = 1 - \frac{[M]}{[M]_0}$$

Equation S1. Conversion, where [M] is monomer concentration, and $[M]_0$ is concentration at time = 0.

$$Productivity = \frac{1440 * V * \rho * Wt}{t_r}$$

Equation S2. Productivity, where V is the reactor volume (mL), t_r is the residence time (min), ρ is the density of the solution (g mL^{-1}) and Wt is the concentration of the solution (% w/w). For all calculation ρ is assumed to be 1.

Table S1. Summary of reaction temperature, conversion, molecular weight (Mn) and particle size (D_h) data obtained for all polymers synthesised using the flow reactor platform. Polymerizations were conducted at 20 or 30% w/w solids. Monomer conversion was determined by ^{1}H NMR spectroscopy in D_20 or CD_3OD, M_n and Đ were determined by DMF GPC vs. a series of near monodisperse poly(methyl methacrylate) standards, and all size measurements were determined by DLS. *Morphology was unable to be assigned

Targeted Polymer	Reaction Temperature / °C	Conversion (NMR) / %	M_n (GPC) / g mol^{-1}	Đ (GPC)	D_h (DLS) / nm	PDI (DLS)	Assumed Morphology (TEM)
$PDMAm_{46}$	70	99	4400	1.07	-	-	-
$PDMAm_{113}$	70	99	10400	1.11	-	-	-
$PDMAm_{113}$-$PDAAm_{50}$	90	94	18700	1.16	31	0.05	Spheres
$PDMAm_{113}$-$PDAAm_{75}$	90	94	22400	1.15	38	0.03	Spheres
$PDMAm_{113}$-$PDAAm_{100}$	90	94	26400	1.13	40	0.04	Spheres
$PDMAm_{113}$-$PDAAm_{150}$	90	88	30400	1.16	45	0.03	Spheres
$PDMAm_{113}$-$PDAAm_{200}$	90	83	39700	1.09	52	0.03	Spheres
$PDMAm_{46}$-$PDAAm_{50}$	90	98	16600	1.14	33	0.09	Spheres
$PDMAm_{46}$-$PDAAm_{75}$	90	97	18300	1.14	162	0.38	Spheres & Worms
$PDMAm_{46}$-$PDAAm_{100}$	90	96	22500	1.19	508	0.42	Vesicles & Worms
$PDMAm_{46}$-$PDAAm_{150}$	90	86	30800	1.22	165*	0.41*	N/A*
$PDMAm_{46}$-$PDAAm_{200}$	90	79	35500	1.18	246*	0.35*	N/A*
$PDMAm_{46}$-$PDAAm_{150}$	70	94	32000	1.20	1063	0.54	N/A*
$PDMAm_{46}$-$PDAAm_{200}$	70	94	38000	1.36	1630	0.74	N/A*
$PDMAm_{46}$-$PDAAm_{300}$	70	91	55000	1.29	430	0.19	Vesicles
$PDMAm_{46}$-$PDAAm_{400}$	70	92	73600	1.21	386	0.09	Vesicles
$PDMAm_{46}$-$PDAAm_{500}$	70	90	87000	1.19	428	0.08	Vesicles
$PDMAm_{46}$-$PDAAm_{600}$	70	84	95600	1.17	544	0.23	Vesicles
$PDMAm_{46}$-$PDAAm_{1000}$	70	84	155600	1.44	610	0.21	Vesicles

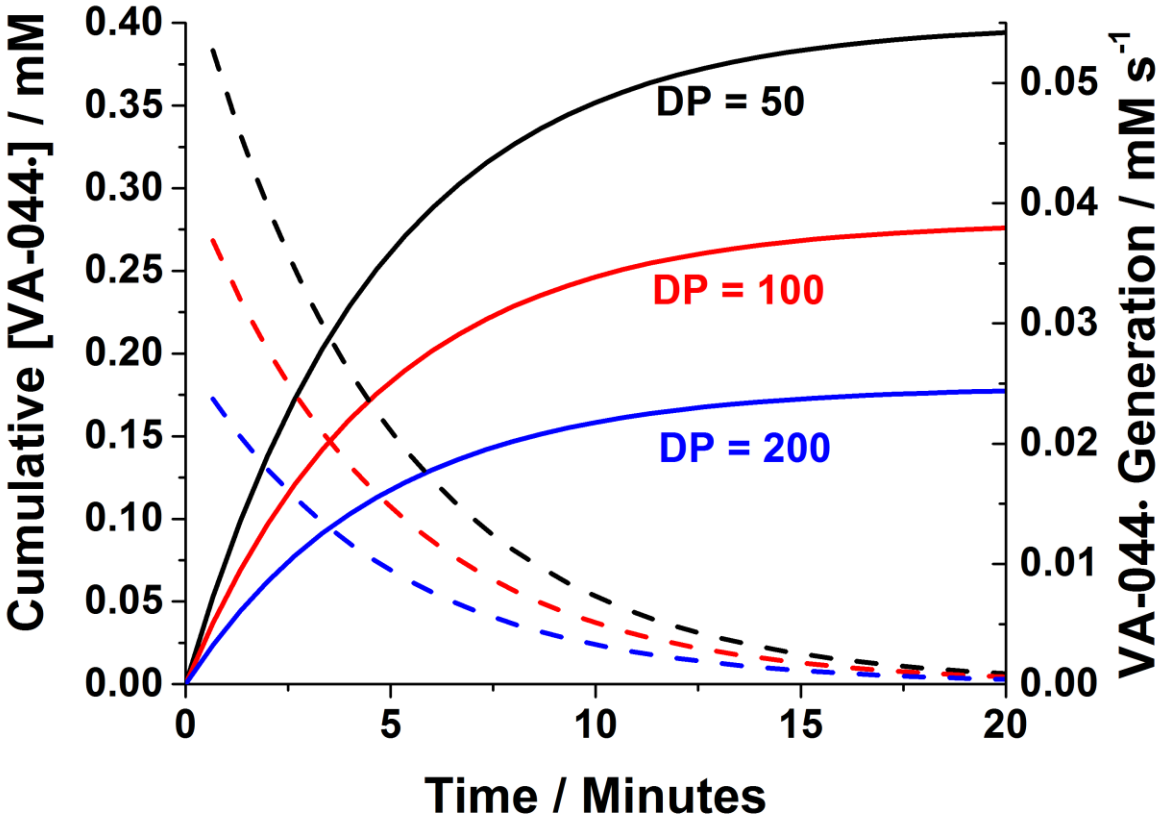

Figure S1. Calculated cumulative (solid) and instantaneous (dash) VA-044 radical generation at various target DPs. Performing polymerisations at a high temperature (90°C) causes a rapid increase in radical concentration. Due to the oxygen permeability of PFA, some radicals will be quenched before participating in the polymerisation.

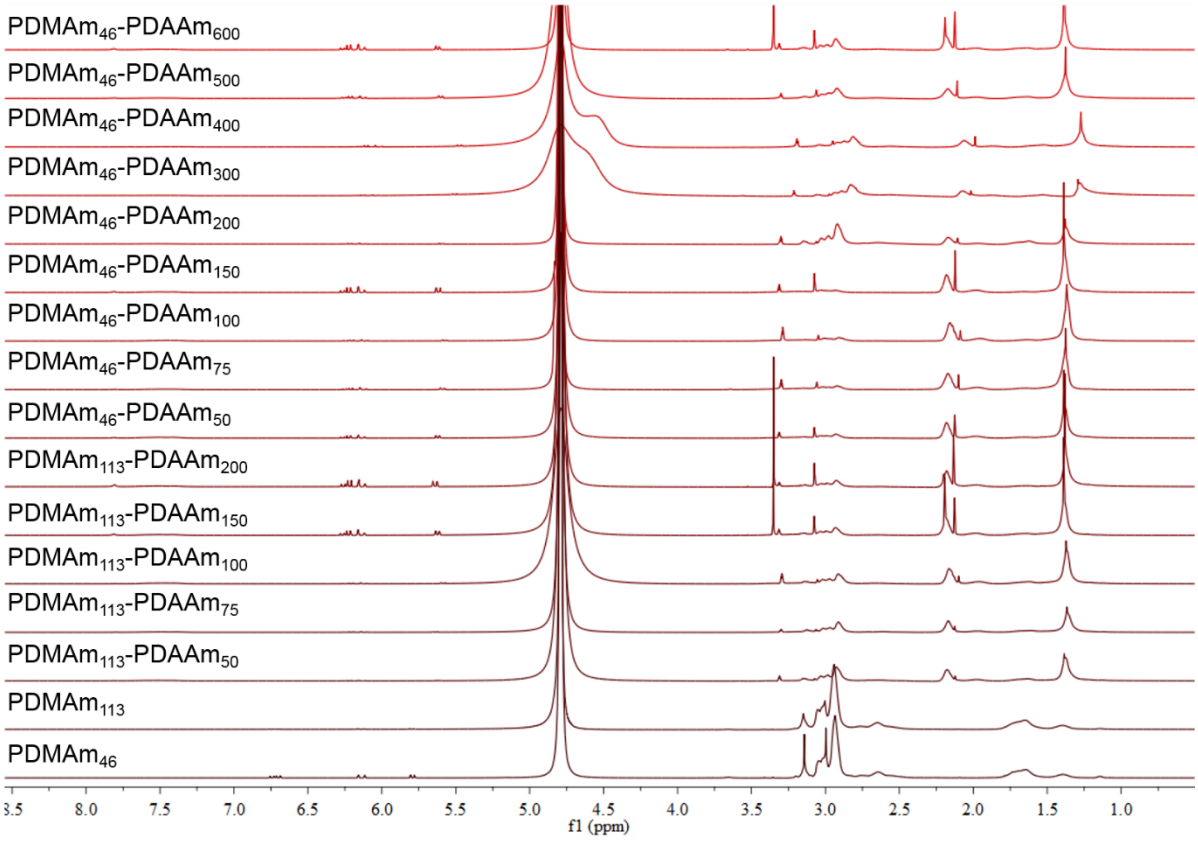

Figure S2. Stacked NMR spectra for all polymers synthesised using the reactor platform. Spectra were recorded using a 500 MHz spectrometer. All homopolymers were dissolved in D_2O and all block copolymers were dissolved in CD_3OD

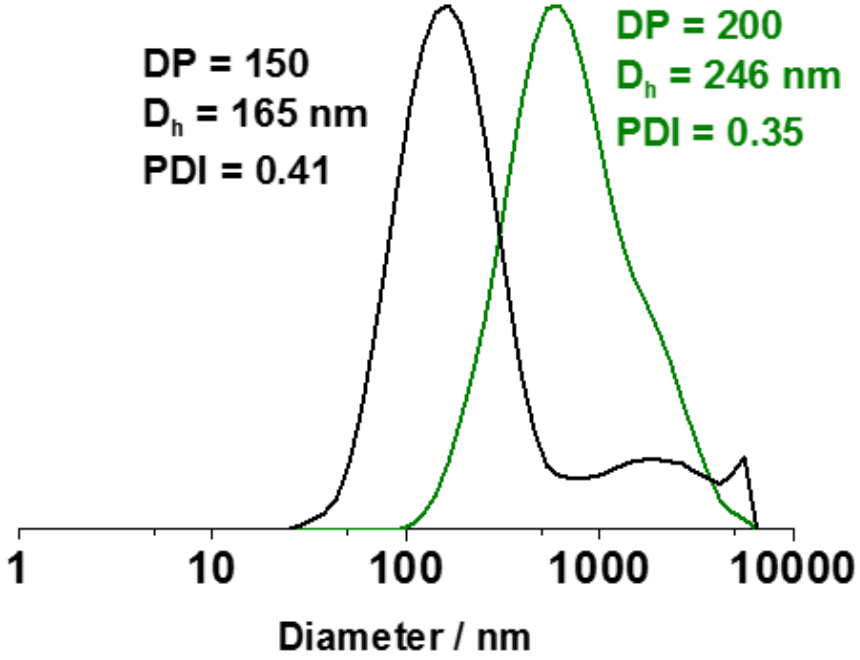

Figure S3. DLS traces for $PDMAm_{46}$-$PDAAm_X$ block copolymers synthesised using the flow platform. X = 150 (black) or 200 (green). Samples were filtered through a 1 µm membrane to remove large particulates

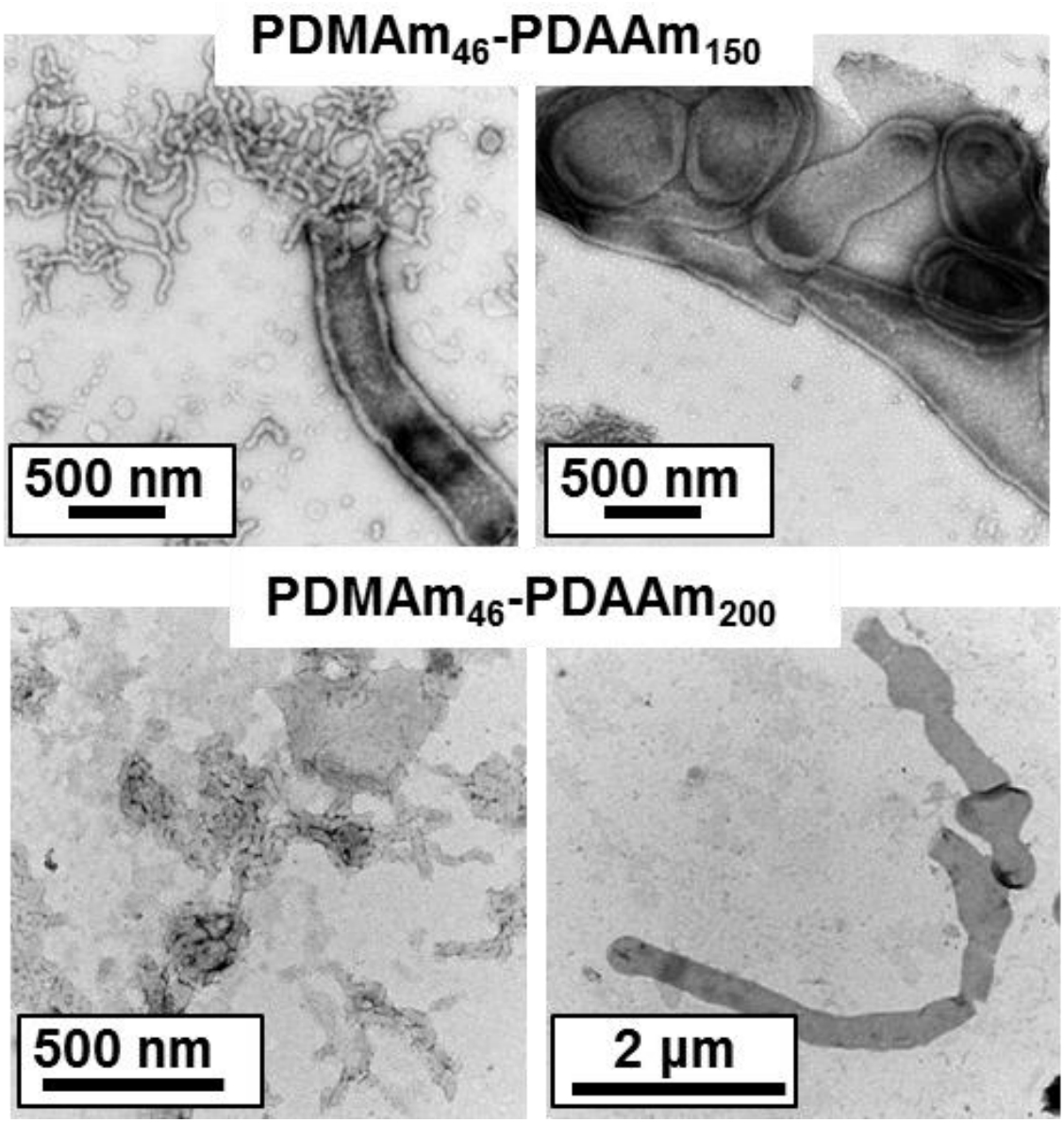

Figure S4. TEM images of $PDMAm_{46}$-$PDAAm_{150/200}$ block copolymers synthesised using the platform indicating no clear morphology. All images were obtained using 0.1% w/w of diblock copolymer at pH 3 filtered through a 1 µm membrane.

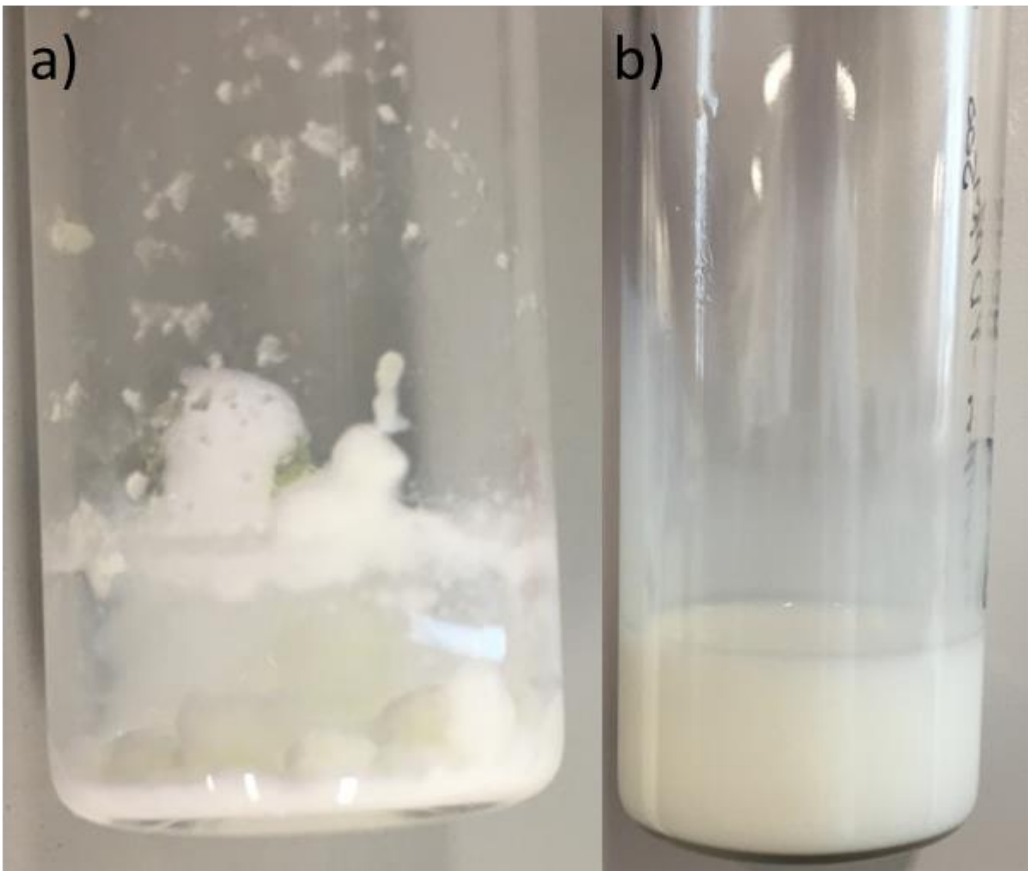

Figure S5. $PDMAm_{46}$-$PDAAm_{500}$ vesicle batch synthesis using RAFT-PISA at a) 90°C and b) 70°C after 20 minutes. Polymer vesicles seem to aggregate and phase separate when the polymerization is performed at 90°C. Polymerisations were performed at 20% w/w solids with [PDMAm46]:[VA-044] = 50:1.

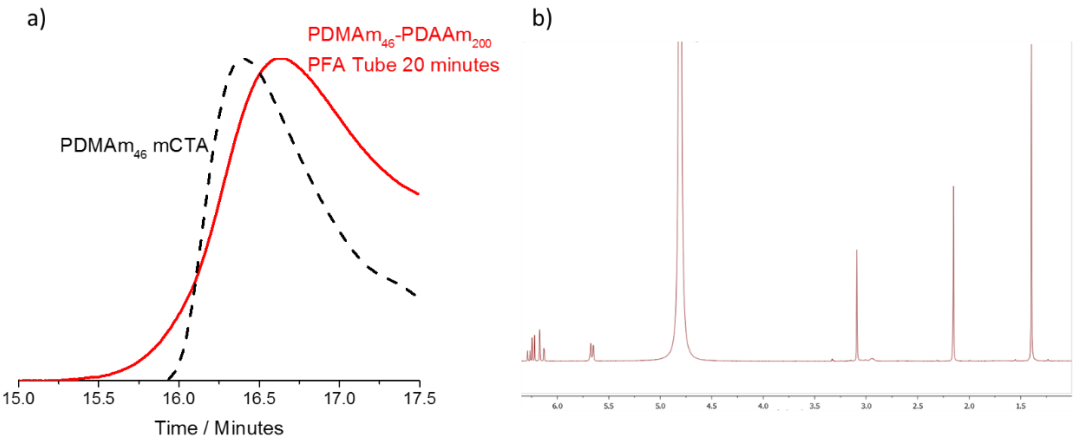

Figure S6. a) GPC chromatograms and b) NMR spectra for the polymerization of $PDMAm_{46}$-$PDAAm_{200}$ performed using the continuous reactor platform indicating no polymerization has taken place. Polymerizations were conducted at 70°C using RAFT aqueous dispersion polymerization at 20% w/w solids and [$PDMAm_{46}$]:[VA-044] = 50:1.

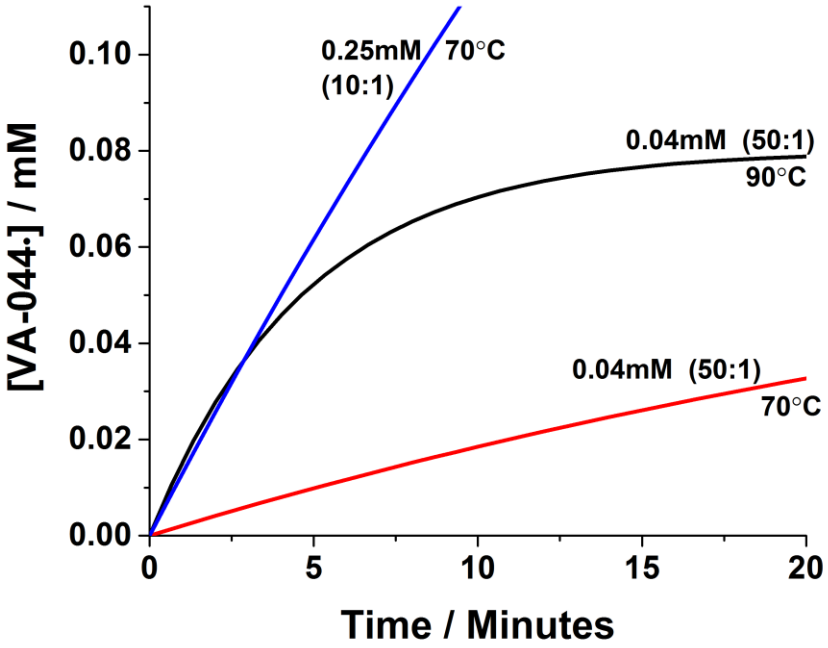

Figure S7. Calculated temperature dependence on VA-044 initiator radical generation at various concentrations. Performing polymerisations at different temperatures has a pronounced effect on the radical concentration. Using the continuous flow platform, due to the oxygen permeability of PFA, synthesising $PDMAm_{46}$-$PDAAm_{500}$ at 70°C with [$PDMAm_{46}$]:[VA-044] = 50:1 is not possible as the radical flux (red) is insufficient to quench oxygen. Whilst performing the reaction at higher temperature (black) or higher [VA-044]0 (blue) allows for a successful polymerisation.

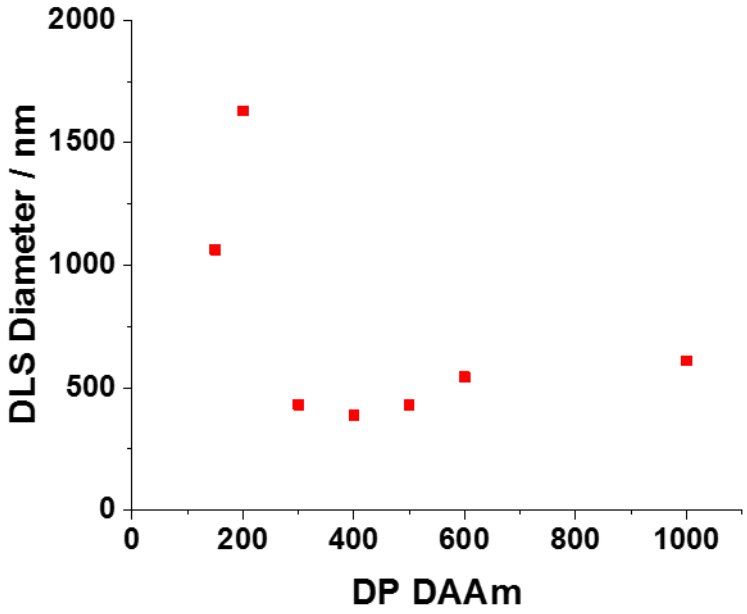

Figure S8. Particle diameter obtained by DLS for $PDMAm_{46}$-$PDAAm_X$ block copolymers synthesised using the flow platform.

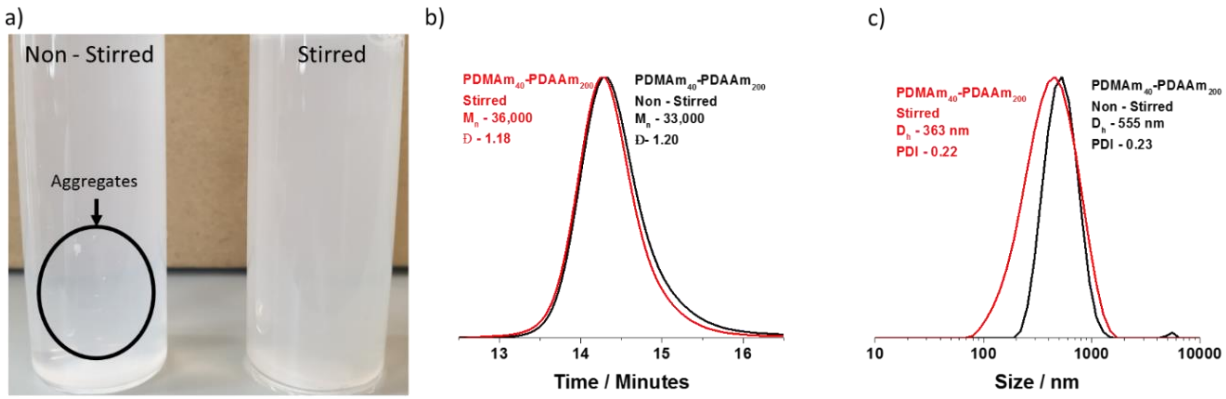

Figure S9. Batch polymerizations of $PDMAm_{46}$-$PDAAm_{200}$ with or without stirring indicating a) aggregate formation b) comparable molecular mass and c) increased particle size for non-stirred polymerizations.