Supporting Information for manuscript:

"Synthesis and pH-Responsive Dissociation of Framboidal ABC Triblock Copolymer Vesicles in Aqueous Solution"

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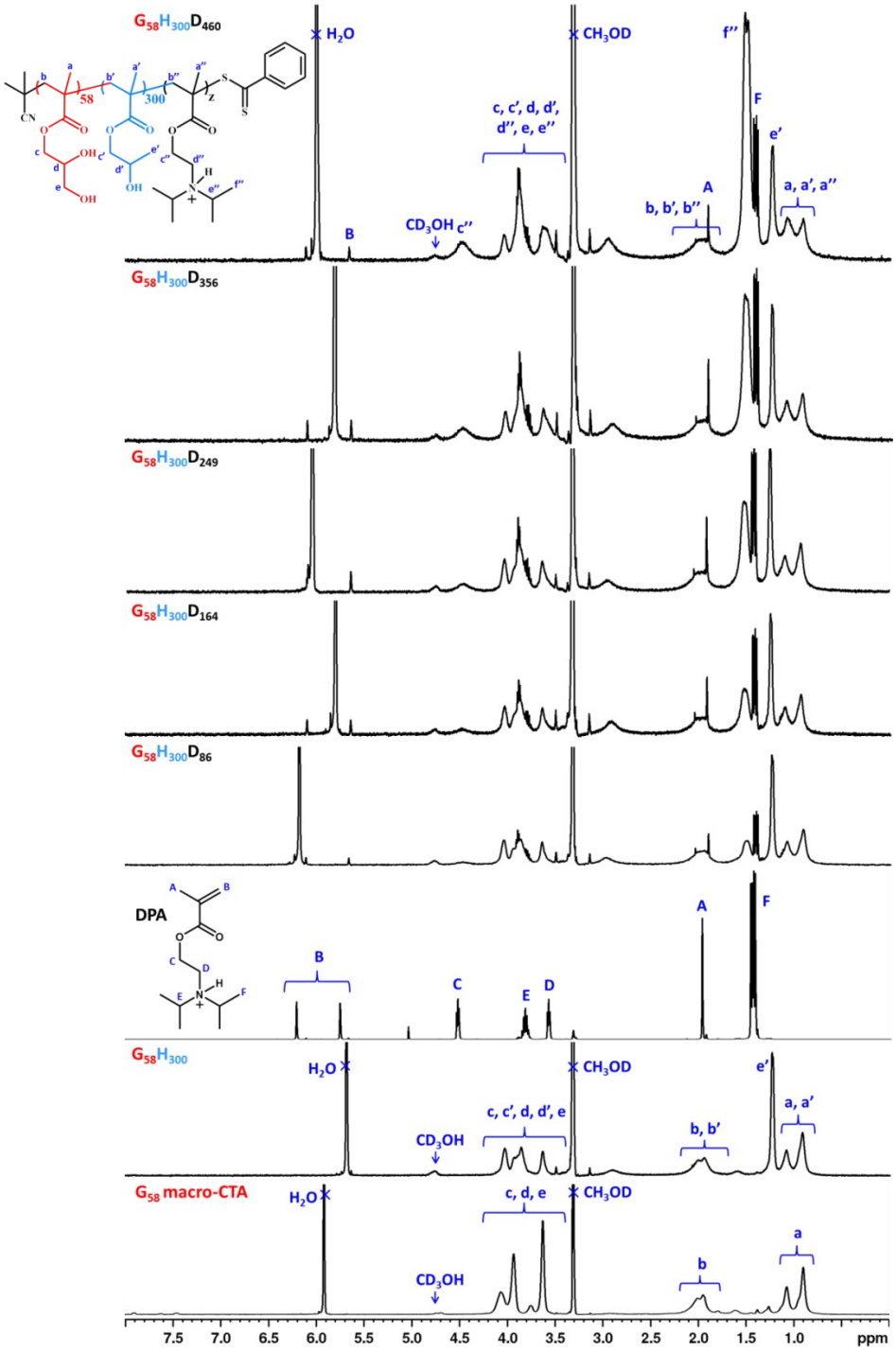

Fig. S1. Assigned ^{1}H NMR spectra in CD_3OD plus 4 % DCl/D_2O (20% w/w DCl) recorded for the G_{58} macro-CTA, $G_{58}H_{300}$ diblock copolymer, DPA monomer and $G_{58}H_{300}D_z$ triblock copolymers (where z = 86, 164, 249, 356 and 460).

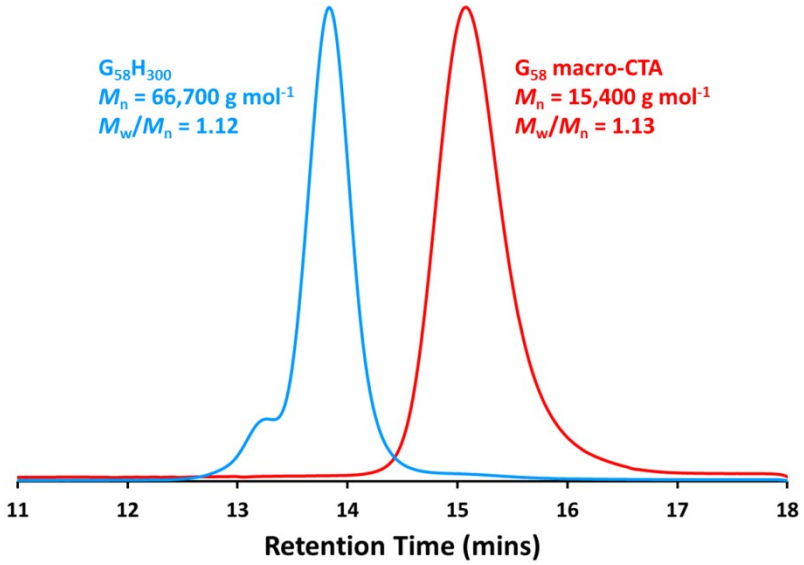

Fig. S2. DMF GPC curves (vs. a series of near-monodisperse PMMA standards) obtained for the G_{58} macro-CTA (red) and the corresponding $G_{58}H_{300}$ diblock copolymer precursor (blue).

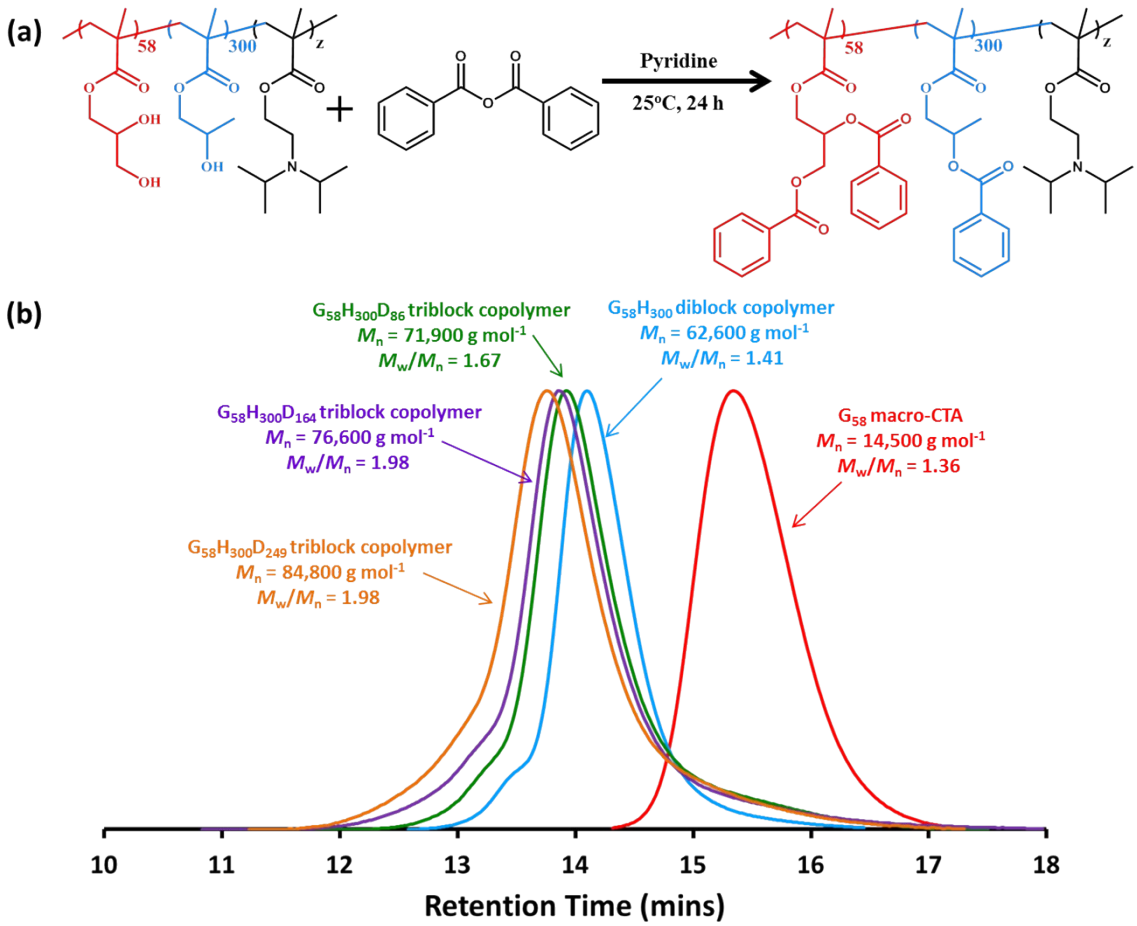

Fig. S3. (a) Reaction scheme for the esterification of GMA and HPMA residues of the triblock copolymers using excess benzoic anhydride. (b) THF GPC curves (vs. a series of near-monodisperse PMMA standards) obtained for the benzoate-modified G_{58} macro-CTA, $G_{58}H_{300}$ diblock copolymer precursor and four $G_{58}H_{300}D_z$ triblock copolymers (where z = 86, 164, 249 or 460).

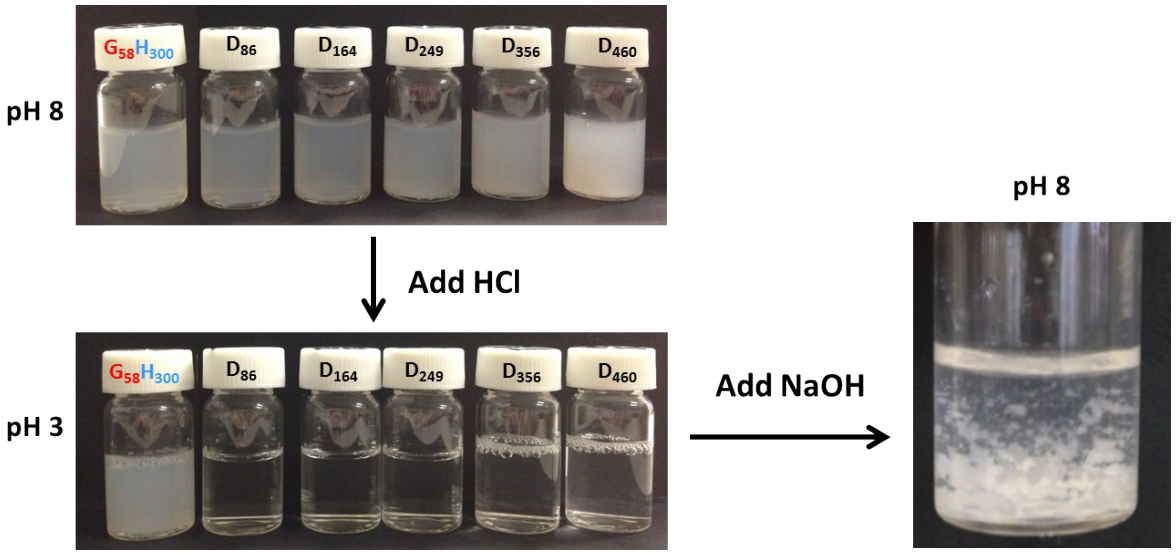

Fig. S4. Digital photographs recorded for $G_{58}H_{300}D_z$ triblock copolymer vesicle dispersions (where z is 86, 164, 249, 356 or 460) at pH 8 and the resulting change in turbidity after switching to pH 3.

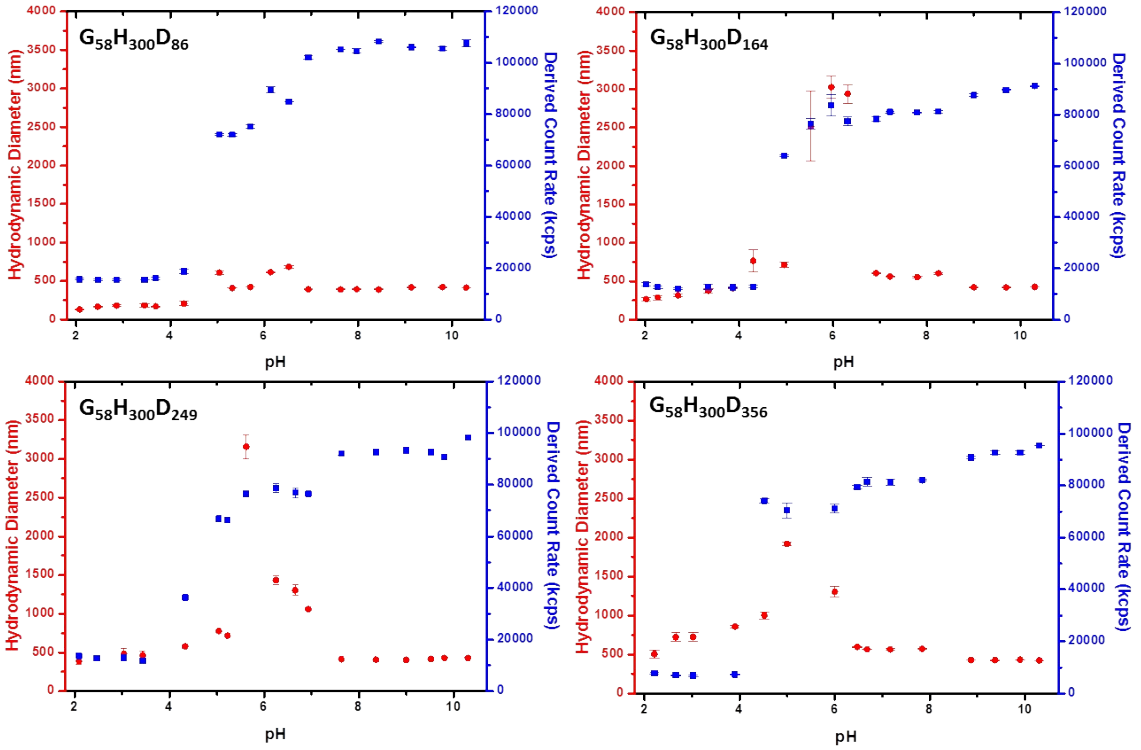

Fig. S5. Variation of the hydrodynamic diameter (red ●) and count rate (blue ■) with solution pH for (top left) $G_{58}H_{300}D_{86}$ triblock copolymer vesicles, (top right) $G_{58}H_{300}D_{164}$ triblock copolymer vesicles, (bottom left) $G_{58}H_{300}D_{249}$ triblock copolymer vesicles and (bottom right) $G_{58}H_{300}D_{356}$ triblock copolymer vesicles.

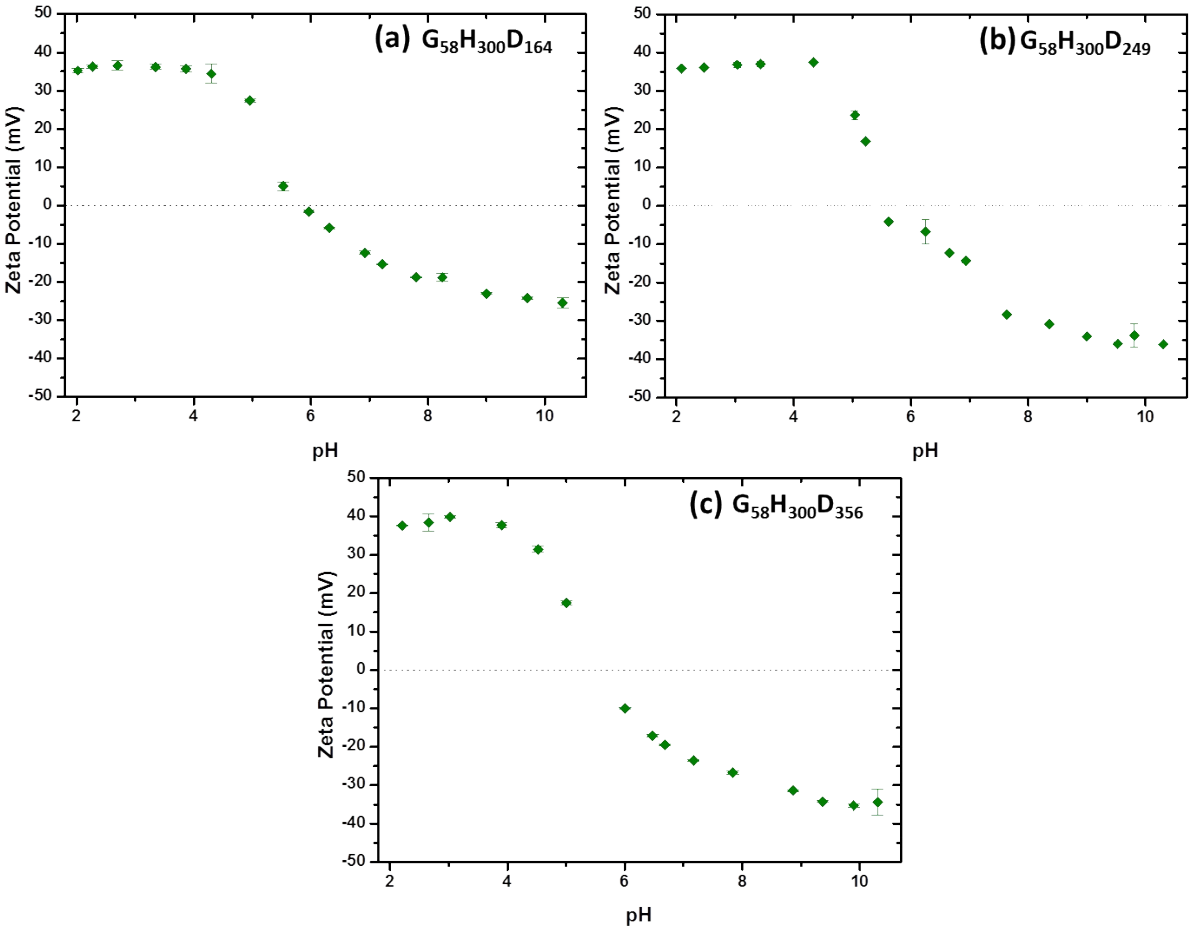

Fig. S6. Variation in zeta potential with solution pH for (a) $G_{58}H_{300}D_{164}$ triblock copolymer vesicles, (b) $G_{58}H_{300}D_{249}$ triblock copolymer vesicles and (c) $G_{58}H_{300}D_{356}$ triblock copolymer vesicles.

Table S1. Structural parameters obtained for a series of $G_{58}H_{300}D_z$ (z = 0 to 249) aqueous copolymer dispersions from SAXS analysis. The volume and scattering length density of the brush/corona block (V_{brush} and ξ_{brush}, respectively) and the core block (V_{core} and ξ_{core}, respectively) were fixed parameters for fitting, based on theoretical calculations. Representative parameters for **population 1** corresponding to vesicles: R_{mc} is the radius from the centre of the vesicle to the centre of the membrane and σ_{Rmc} is the associated standard deviation, T_{mc} is the thickness of the hydrophobic part of the vesicle membrane and σ_{Tmc} is the associated standard deviation, D_{SAXS} is the vesicle diameter: $D_{SAXS} = 2(R_{mc} + \frac{1}{2}T_{mc} + 2R_g)$, where R_g is the radius of gyration of the brush/corona block. Representative parameters for **population 2** corresponding to spherical micelles: R_s is the core radius, σ_{Rs} is the standard deviation of the core radius, R_{PY} is the Percus-Yevick correlation radius of densely-packed spherical micelles (this parameter should be doubled for the inter-particle correlation distance) and F_{PY} is the Percus-Yevick effective volume fraction of the packed micelles. c_2/c_1 is the ratio of the copolymer volume fraction forming spherical micelles (**population 2**) to that forming vesicles (**population 1**). Finally, D is the mass fractal dimensions for the mass fractal model (**population 3**).

Copolymer Composition	pH	V_{brush}[a] /nm^3	V_{core}[b] /nm^3	ξ_{brush}[a] $\times 10^{10}$ /cm^{-2}	ξ_{core}[b] $\times 10^{10}$ /cm^{-2}	Population 1 - Vesicles			c_2/c_1	Population 2 – Spherical Micelles			Population 3 - Mass Fractals
						R_{mc} (σ_{Rmc})[c] /nm	T_{mc} (σ_{Tmc})/ nm	D_{SAXS}[c]/ nm		R_s (σ_{Rs})/ nm	R_{PY} /nm	F_{PY} /nm	D
$G_{58}H_{300}$	8.0 and 3.0	11.8	59.4	11.94	11.11	178 (40)	16.8 (1.8)	383					
$G_{58}H_{300}D_{86}$	8.0	11.8	88.3	11.94	10.71	178 (49)	24.9 (1.3)	391	0.273	8.5 (1.2)	11.9	0.34	
	3.0	40.7	59.4	10.48	11.11					11.9 (1.6)	12.0	0.05	
$G_{58}H_{300}D_{164}$	8.0	11.8	114	11.94	10.52	178 (50)	36.3 (1.5)	402	0.701	13.7 (2.6)	15.3	0.45	
	3.0	66.9	59.4	10.25	11.11					10.5 (1.4)	10.8	0.08	1.61
$G_{58}H_{300}D_{249}$	8.0	11.8	143	11.94	10.40	178 (45)	46.4 (1.3)	412	0.997	17.0 (4.1)	20.7	0.53	
	3.0	95.5	59.4	10.14	11.11					8.5 (1.3)	10.0	0.12	1.88

[a] At pH 8.0, $V_{brush} = \frac{M_{n,PGMA}}{N_A \rho_{PGMA}}$ and $\xi_{brush} = \xi_{PGMA}$. At pH 3.0, $V_{brush} = \frac{M_{n,PGMA}}{N_A \rho_{PGMA}} + \frac{M_{n,PDPA}}{N_A \rho_{PDPA}}$ and $\xi_{brush} = \varphi_{PGMA}\xi_{PGMA} + (1 - \varphi_{PGMA})\xi_{PDPA}$ where φ_{PGMA} is the volume fraction of PGMA in the corona.

[b] At pH 8.0, $V_{core} = \frac{M_{n,PHPMA}}{N_A \rho_{PHPMA}} + \frac{M_{n,PDPA}}{N_A \rho_{PDPA}}$ and $\xi_{core} = \varphi_{PHPMA}\xi_{PHPMA} + (1 - \varphi_{PHPMA})\xi_{PDPA}$ where φ_{PHPMA} is the volume fraction of PHPMA in the core-forming block. At pH 3.0, $V_{core} = \frac{M_{n,PHPMA}}{N_A \rho_{PHPMA}}$ and $\xi_{core} = \xi_{PHPMA}$.

[c]These data are considered less reliable because the camera length used to obtain the SAXS data was not long enough to give accurate overall vesicle diameters.

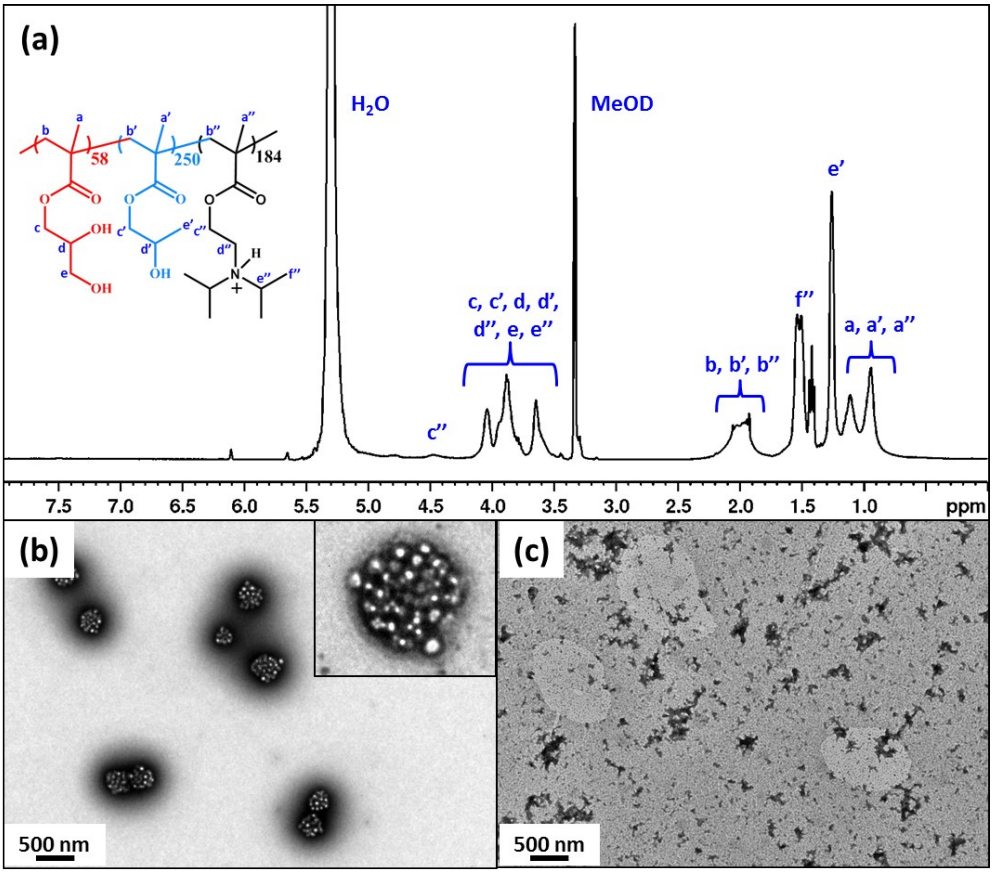

Fig. S7. (a) Assigned ^{1}H NMR spectrum of the $G_{58}H_{250}D_{184}$ triblock copolymer recorded in CD_3OD plus 4 % DCl/D_2O (20% w/w DCl). Representative TEM images obtained for (b) $G_{58}H_{250}D_{184}$ framboidal triblock vesicles at pH 8 and (c) fractal aggregates of cationic spheres formed by the same copolymer at pH 3.

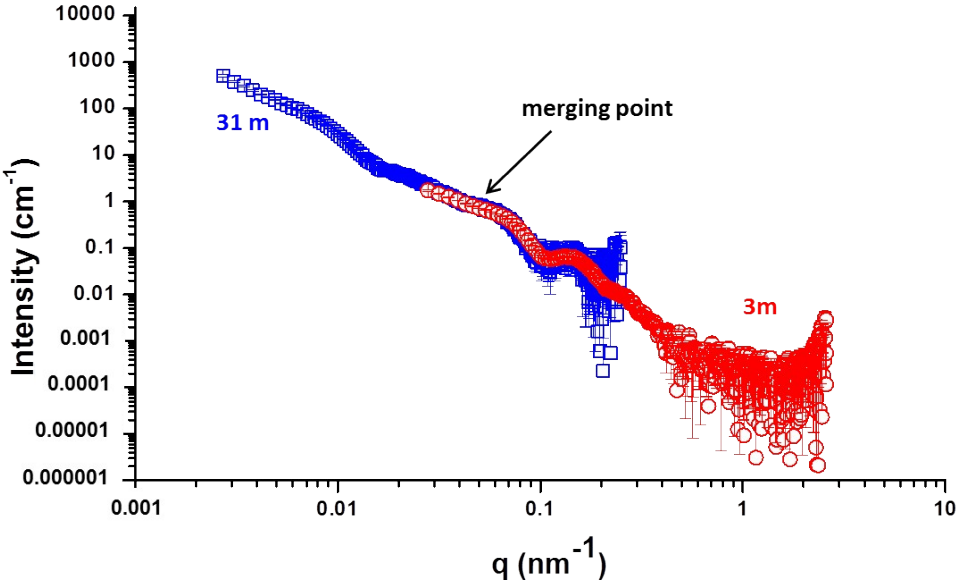

Fig. S8. Two SAXS patterns recorded for $G_{58}H_{250}D_{184}$ framboidal vesicles 100 ms after HCl addition. These patterns were obtained from two identical experiments run using a camera length of 3 m (red data) or 31 m (blue data). The overlap between the two data sets indicates excellent data reproducibility.

References

1. J. Ilavsky and P. R. Jemian, *J. Appl. Crystallogr.*, **2009**, *42*, 347-353