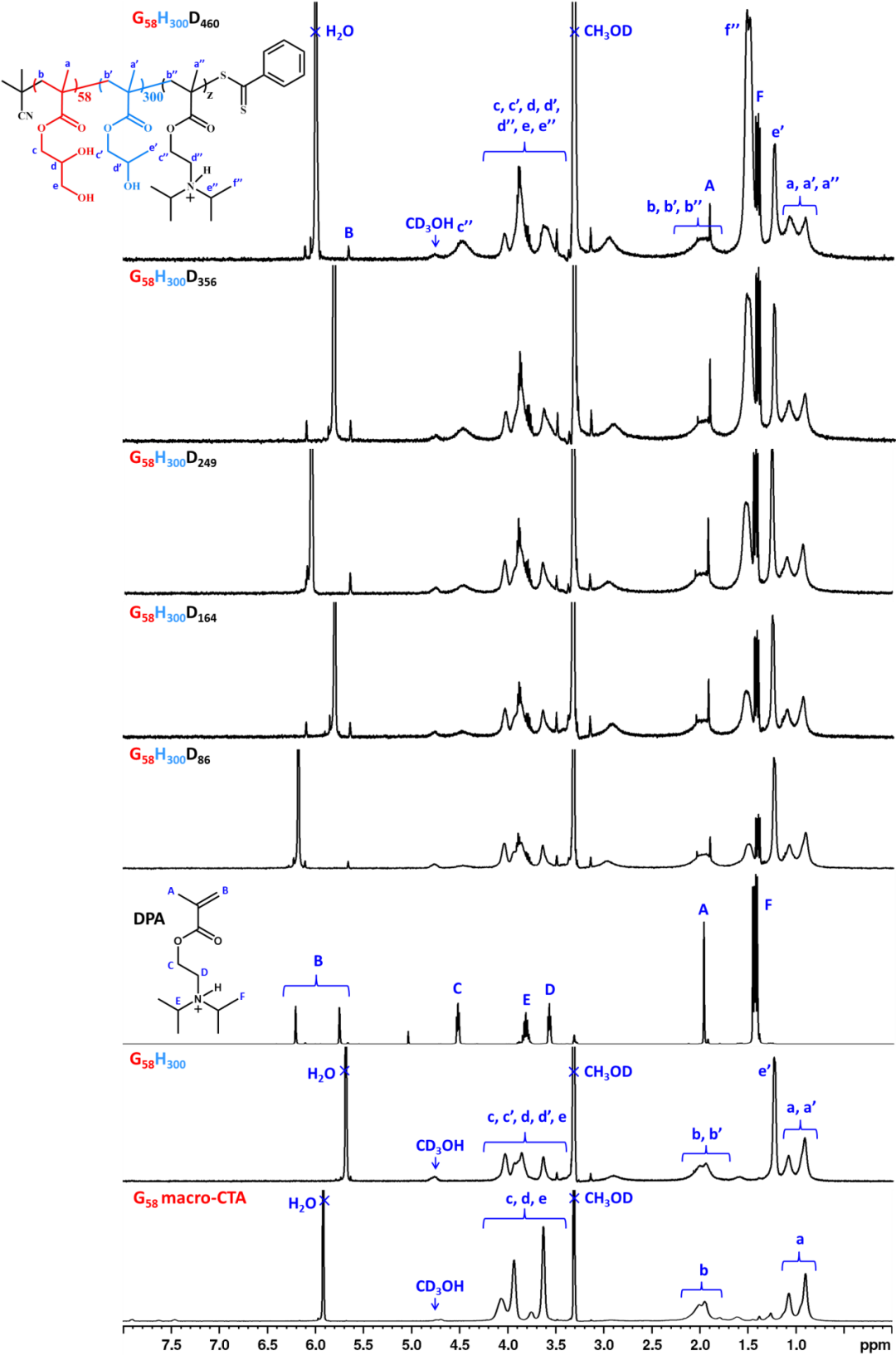
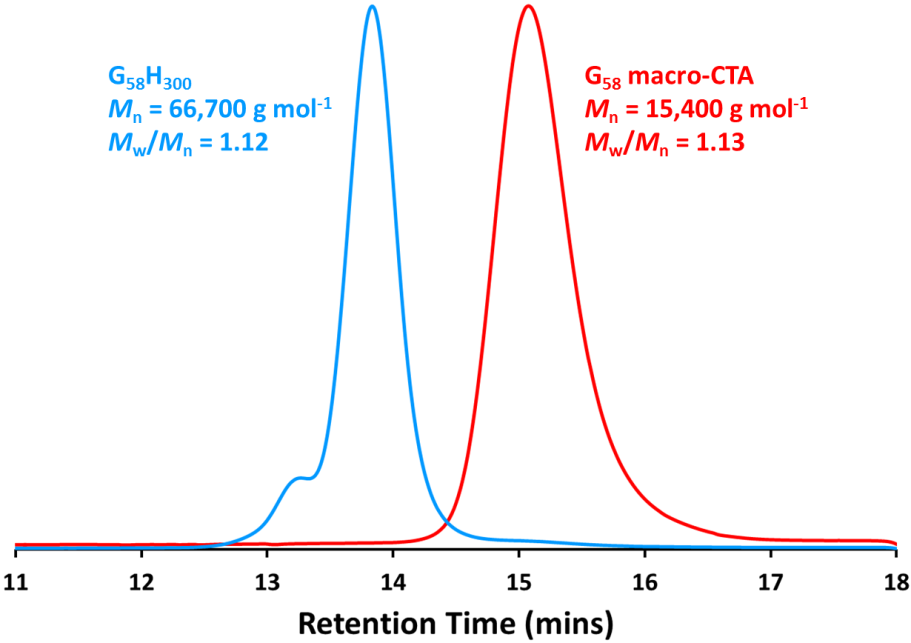
Supporting Information for manuscript:

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

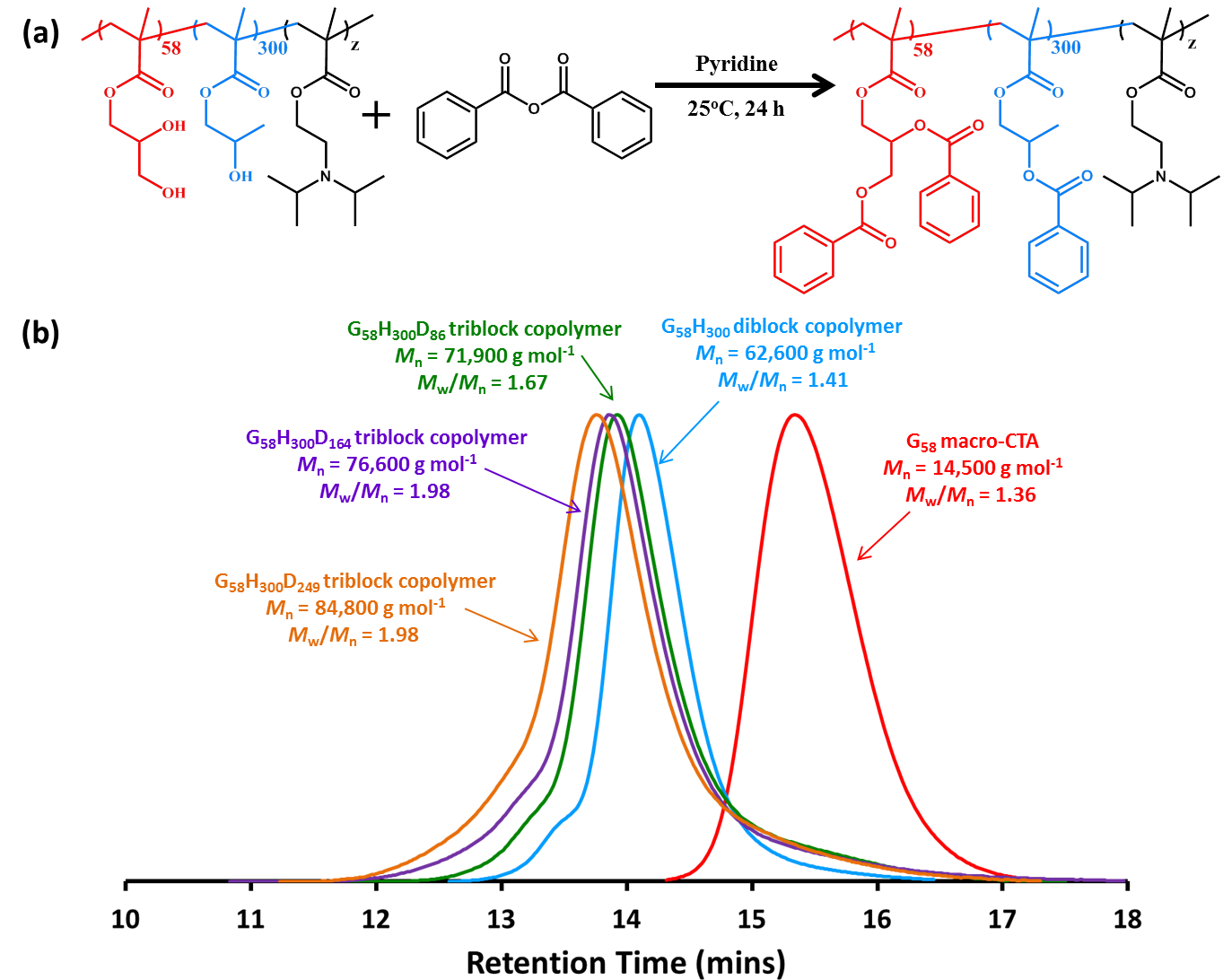
*C. J. Mable, L. A. Fielding, M. J. Derry, O. O. Mykhaylyk, P. Chambon and S. P. Armes*

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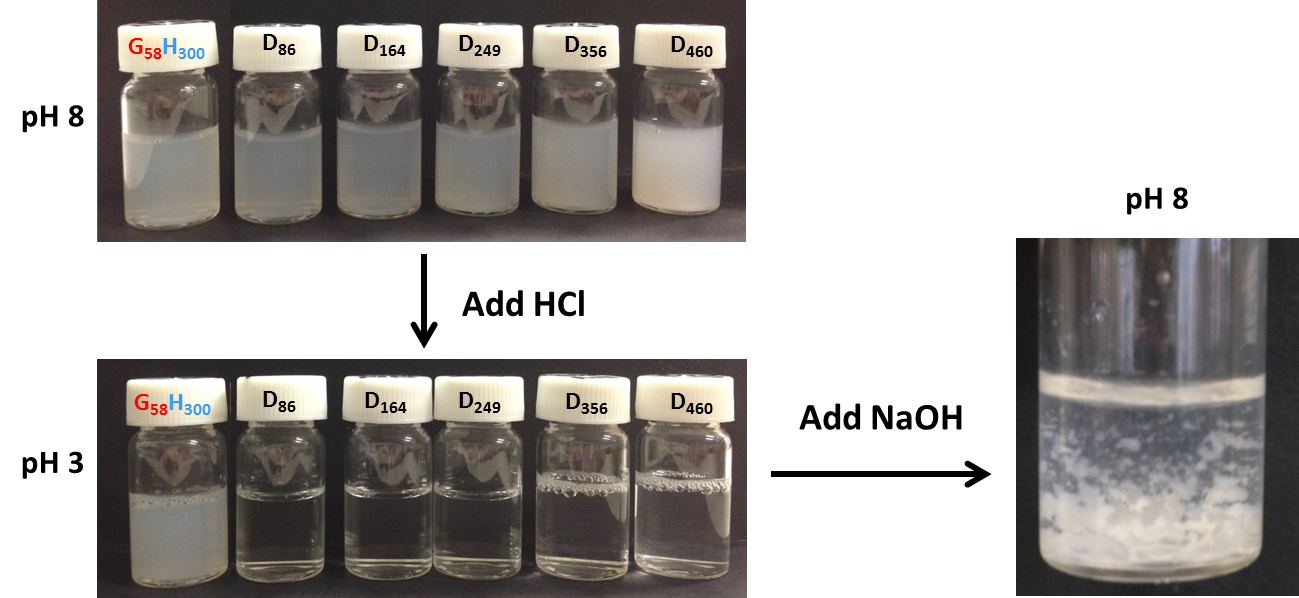
**Fig. S1.** Assigned 1H NMR spectra in CD3OD plus 4 % DCl/D2O (20% w/w DCl) recorded for the G58 macro-CTA, G58H300 diblock copolymer, DPA monomer and G58H300Dz triblock copolymers (where z = 86, 164, 249, 356 and 460).



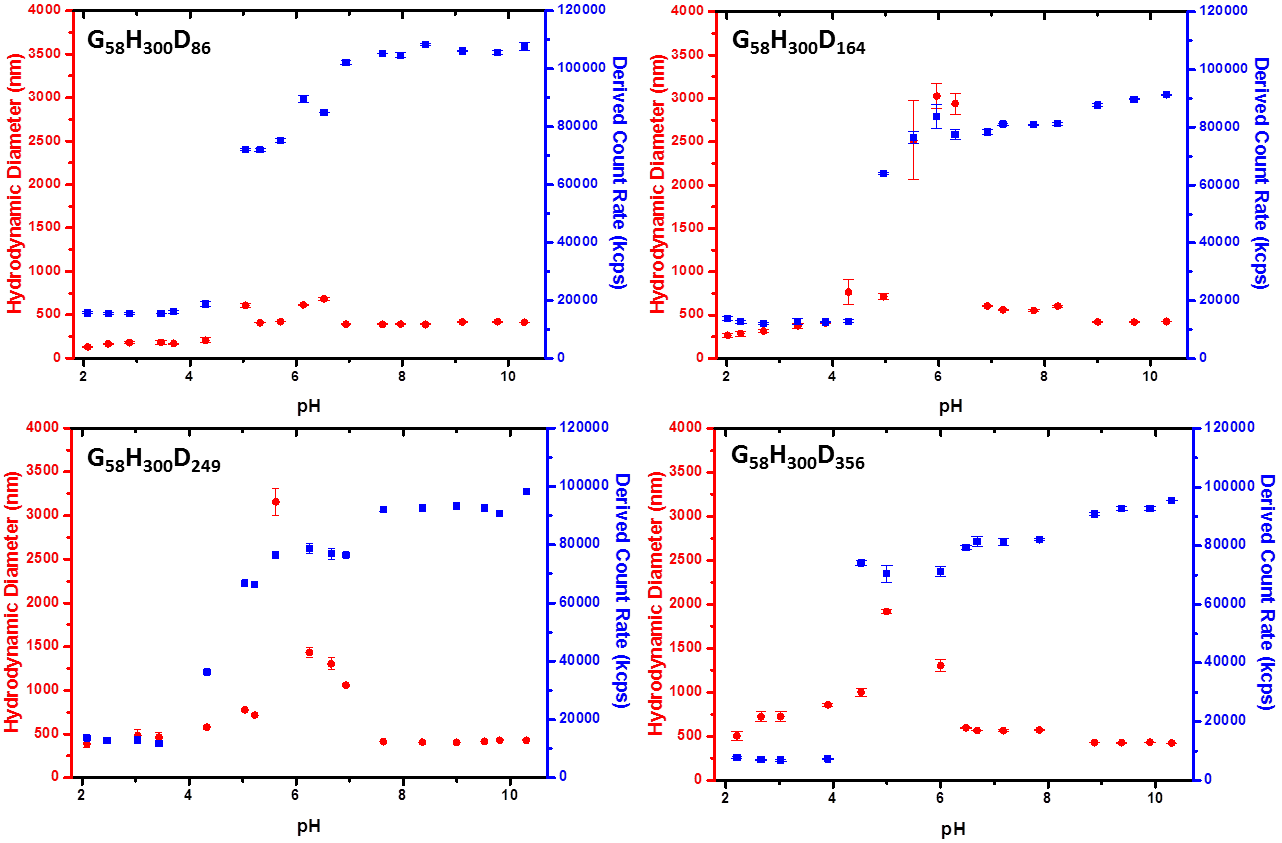
**Fig. S2.** DMF GPC curves (vs. a series of near-monodisperse PMMA standards) obtained for the G58 macro-CTA (red) and the corresponding G58H300 diblock copolymer precursor (blue).

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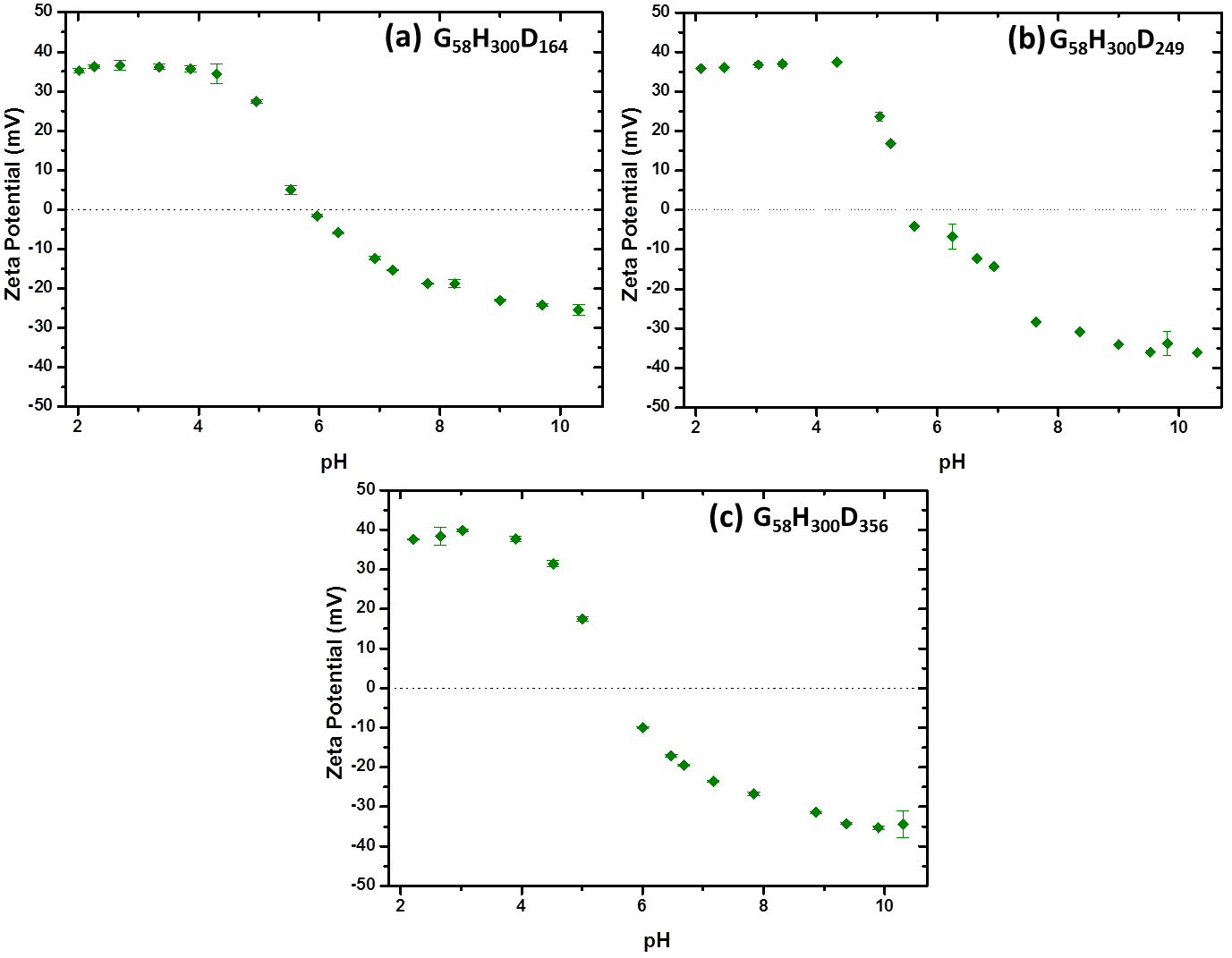
**Fig. S3.** (a) Reaction scheme for the esterification of GMA and HPMA residues of the triblock copolymers using excess benzoic anhydride. (b) THF GPC curves (vs. a series of near-monodisperse PMMA standards) obtained for the benzoate-modified G58 macro-CTA, G58H300 diblock copolymer precursor and four G58H300Dz triblock copolymers (where z = 86, 164, 249 or 460).



**Fig. S4.** Digital photographs recorded for G58H300Dz 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) G58H300D86 triblock copolymer vesicles, (top right) G58H300D164 triblock copolymer vesicles, (bottom left) G58H300D249 triblock copolymer vesicles and (bottom right) G58H300D356 triblock copolymer vesicles.



**Fig. S6.** Variation in zeta potential with solution pH for (a) G58H300D164 triblock copolymer vesicles, (b) G58H300D249 triblock copolymer vesicles and (c) G58H300D356 triblock copolymer vesicles.

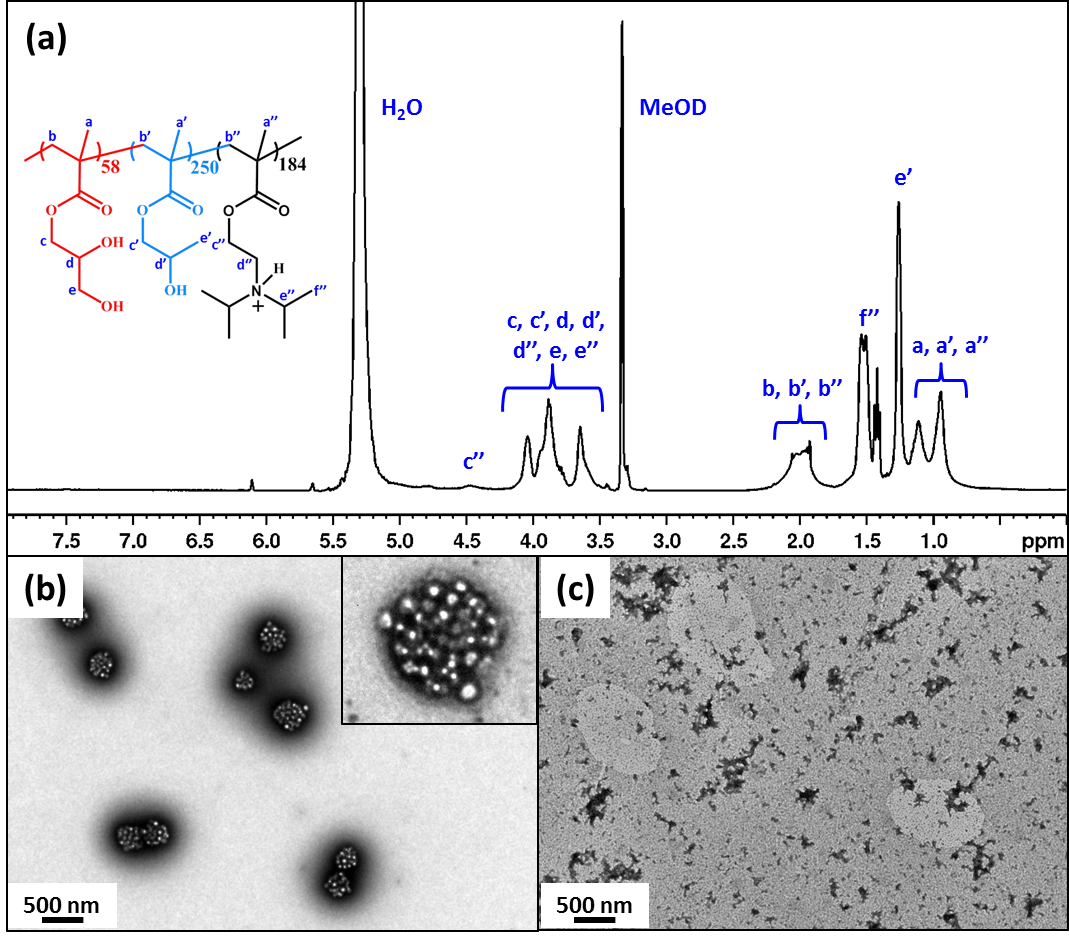
**Table S1.** Structural parameters obtained for a series of G58H300Dz (z = 0 to 249)aqueous copolymer dispersions from SAXS analysis. The volume and scattering length density of the brush/corona block (*V*brush and ***ξ***brush, respectively) and the core block (*V*core and ***ξ***core, respectively) 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 *σR*mc is the associated standard deviation, *T*mc is the thickness of the hydrophobic part of the vesicle membrane and *σT*mc is the associated standard deviation, *D*SAXS is the vesicle diameter: ), 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, *σR*s 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*brusha/nm3** | ***V*coreb/nm3** | ***ξ*brusha ×1010 /cm-2** | ***ξ*coreb ×1010 /cm-2** | **Population 1 - Vesicles** | | | ***c*2*/c*1** | **Population 2 – Spherical Micelles** | | | **Population 3 - Mass Fractals** |
| ***R*mc (*σR*mc)c /nm** | ***T*mc (*σT*mc)/ nm** | ***D*SAXSc/ nm** | ***R*s (*σR*s)/ nm** | ***R*PY /nm** | ***F*PY /nm** | ***D*** |
| G58H300 | 8.0 and 3.0 | 11.8 | 59.4 | 11.94 | 11.11 | 178 (40) | 16.8 (1.8) | 383 |  |  |  |  |  |
| G58H300D86 | 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 |  |
| G58H300D164 | 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 |
| G58H300D249 | 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 |

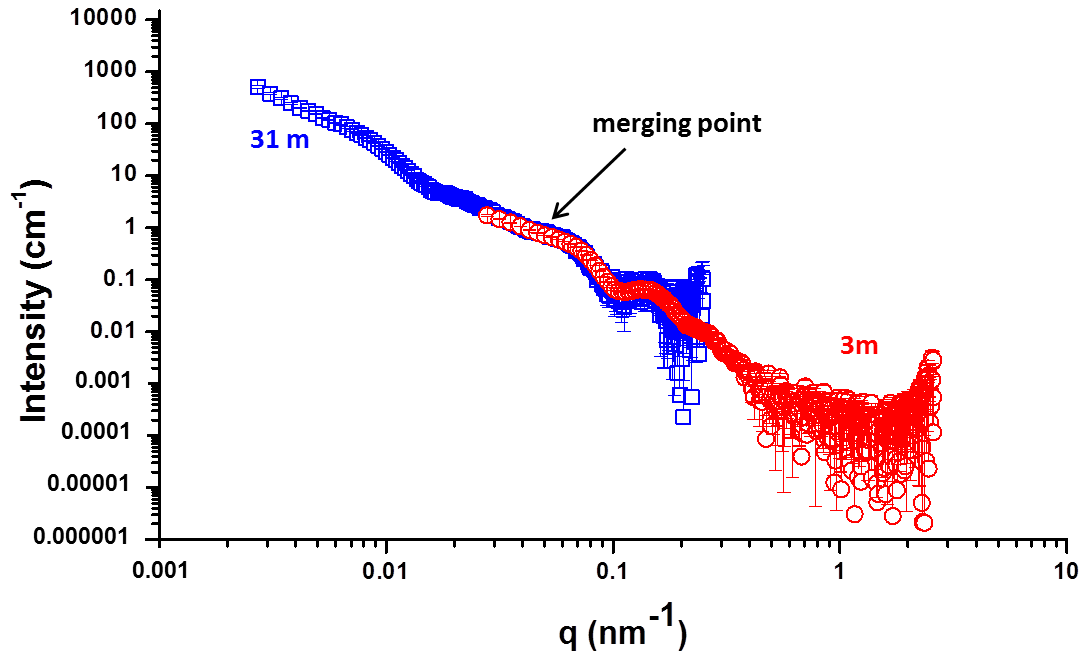
aAt pH 8.0, and . At pH 3.0, and where is the volume fraction of PGMA in the corona.

bAt pH 8.0, and where is the volume fraction of PHPMA in the core-forming block. At pH 3.0, and .

cThese 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 1H NMR spectrum of the G58H250D184 triblock copolymer recorded in CD3OD plus 4 % DCl/D2O (20% w/w DCl). Representative TEM images obtained for (b) G58H250D184 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 G58H250D184 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