## Electronic Supplementary Information for *Soft Matter* manuscript: New Non-spherical Morphologies from Cross-Linked Biomimetic Diblock Copolymers Using RAFT Aqueous Dispersion Polymerization

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Figures in Supporting Information



**Fig. S1** Conversion vs. time curves for the aqueous RAFT polymerization of MPC at target degrees of polymerization of 50 and 150 in the presence of NaHCO<sub>3</sub> at 70 °C. For more detailed polymerization conditions, see Experimental Section.



**Fig. S2** Evolution of  $M_n$  and  $M_w/M_n$  with conversion for the aqueous RAFT polymerization of MPC at target degrees of polymerization of either 50 or 150 in the presence of NaHCO<sub>3</sub> at 70 °C. For more detailed polymerization conditions, see Experimental Section.



**Fig. S3** Typical <sup>1</sup>H NMR spectra recorded for (a) PMPC<sub>50</sub> macro-CTA in D<sub>2</sub>O and (b) CDAB in CDCl<sub>3</sub> at 25°C as a reference. The inset shows the chemical structures of PMPC<sub>50</sub> macro-CTA and CADB with full peak assignments (a - j for PMPC and 1-6 for CDAB).



**Fig. S4** Typical GPC curves obtained for the RAFT aqueous dispersion polymerization of HPMA at 70 °C using the PMPC<sub>50</sub> macro-CTA targeting mean degrees of polymerization for the PHPMA block of 100 to 400. There is a prominent high molecular weight shoulder, particularly when targeting higher DP PHPMA chains. This is due to a small amount (< 0.20 mol %) dimethacrylate impurity that is known to be present in HPMA monomer due to its propensity to undergo slow transesterification on storage at ambient temperature.<sup>3</sup> However, this impurity only causes relatively light branching rather than cross-linking, since DLS studies confirm complete dissolution of these linear PMPC<sub>50</sub>-PHPMA<sub>m</sub> nanolatex particles in methanol, which is a good solvent for both the PMPC and PHPMA blocks.



**Fig. S5** Tapping-mode AFM image obtained for the PMPC<sub>50</sub>-(PHPMA<sub>400</sub>-*stat*-EGDMA<sub>6</sub>) 'lumpy rod' particles. (a) Height image (10.0  $\mu$ m × 10.0  $\mu$ m), (b) amplitude image, (c) cross-sectional image. The dilute aqueous dispersion was deposited onto freshly-cleaved mica and allowed to dry at 20 °C for 24 h prior to analysis.



PMPC<sub>150</sub>-PHPMA<sub>200</sub>

**Fig. S6** TEM image of the linear PMPC<sub>150</sub>-PHPMA<sub>200</sub> spherical nanolatex prepared by RAFT aqueous dispersion polymerization of HPMA at 70 °C using PMPC<sub>50</sub> macro-CTA at 10 w/w % solids.