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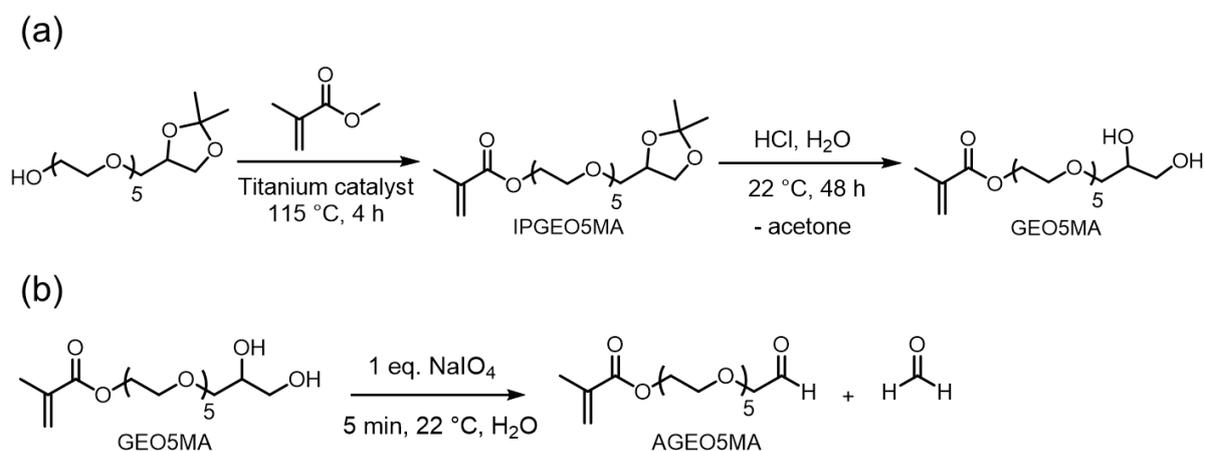


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Supporting Information for:

Aldehyde-functional diblock copolymer nano-objects via RAFT aqueous dispersion polymerization

E. E. Brotherton, M. J. Smallridge and S. P. Armes*



Scheme S1. (a) Two-step synthesis of GEO5MA monomer starting from an isopropylidene glycerol precursor as a hydroxy-functional initiator. This precursor is then transesterified with methyl methacrylate to produce IPGEO5MA, before removing the ketal protecting group with acid to afford GEO5MA monomer. (b) Oxidation of GEO5MA in aqueous solution using sodium periodate at 22 °C affords AGEOSMA with formaldehyde as a by-product. The same selective oxidation can be used to convert PGEO5MA homopolymer into PAGEOSMA homopolymer using identical reaction conditions.

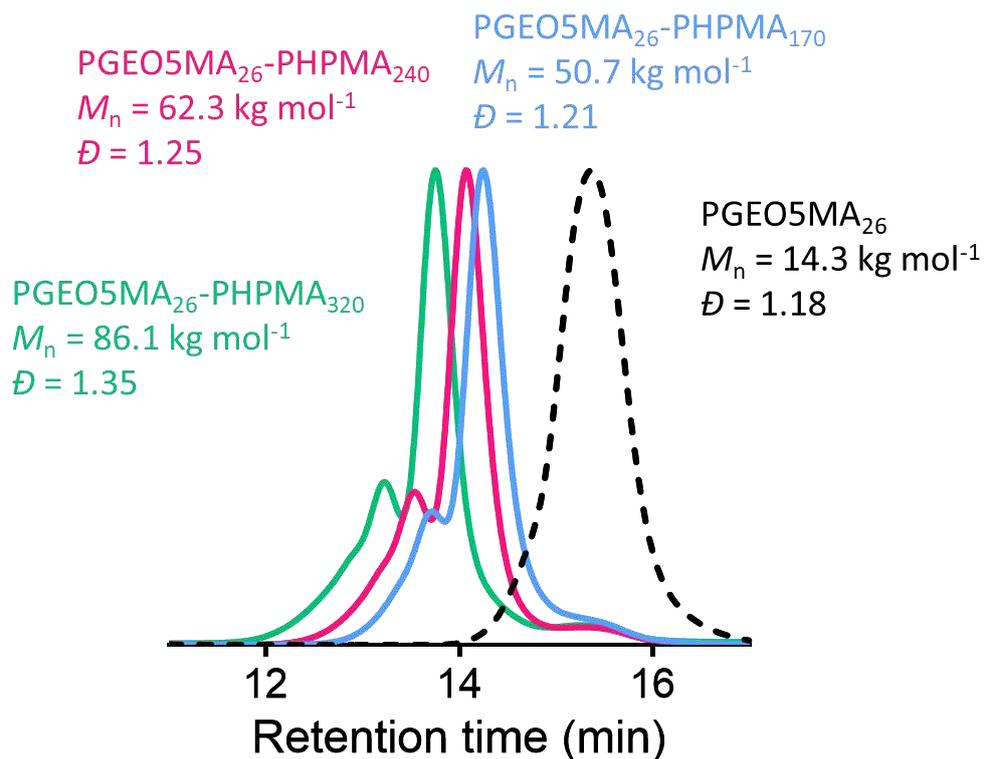


Figure S1. DMF GPC curves recorded for PGE05MA₂₆, PGE05MA₂₆-PHPMA₁₇₀, PGE05MA₂₆-PHPMA₂₄₀ and PGE05MA₂₆-PHPMA₃₂₀ diblock copolymers calibrated against a series of near-monodisperse poly(methyl methacrylate) standards.

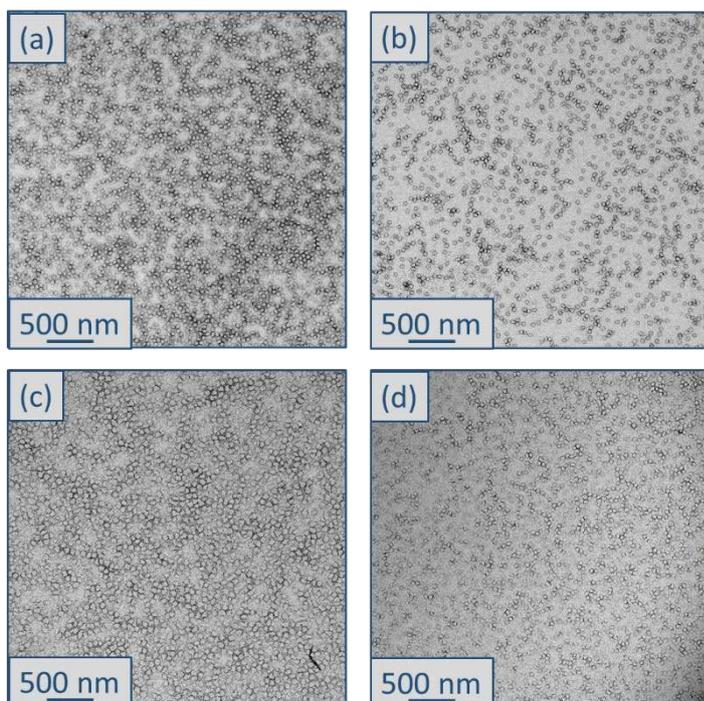


Figure S2. Transmission electron microscopy images recorded for (a) PGE05MA₂₆-PHPMA₁₇₀, (b) PGE05MA₂₆-PHPMA₁₇₀, (c) PGlyGEO5MA₂₆-PHPMA₁₇₀, and (d) PHisGEO5MA₂₆-PHPMA₁₇₀ diblock copolymer spheres.

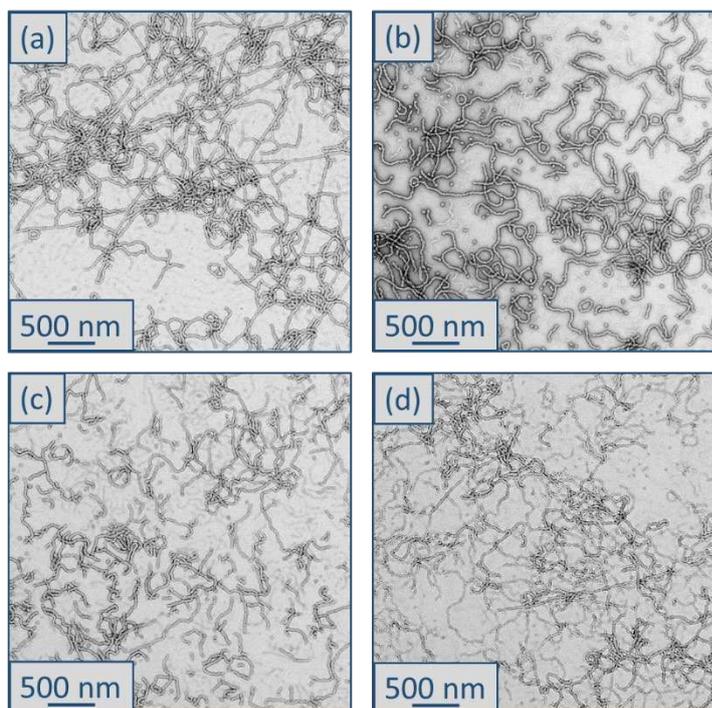


Figure S3. Transmission electron microscopy images recorded for (a) PGEO5MA₂₆-PHPMA₂₅₀, (b) PAGEO5MA₂₆-PHPMA₂₅₀, (c) PGlyGEO5MA₂₆-PHPMA₂₅₀, and (d) PHisGEO5MA₂₆-PHPMA₂₅₀ worms.

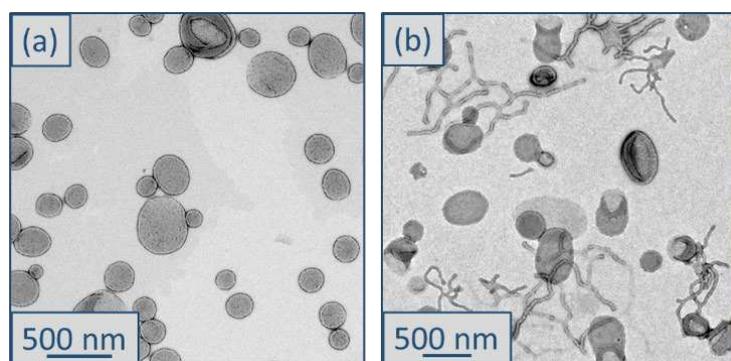


Figure S4. Transmission electron microscopy images recorded for (a) PGEO5MA₂₆-PHPMA₃₅₀ vesicles and (b) a binary mixture of PAGEO5MA₂₆-PHPMA₃₅₀ vesicles and worms.

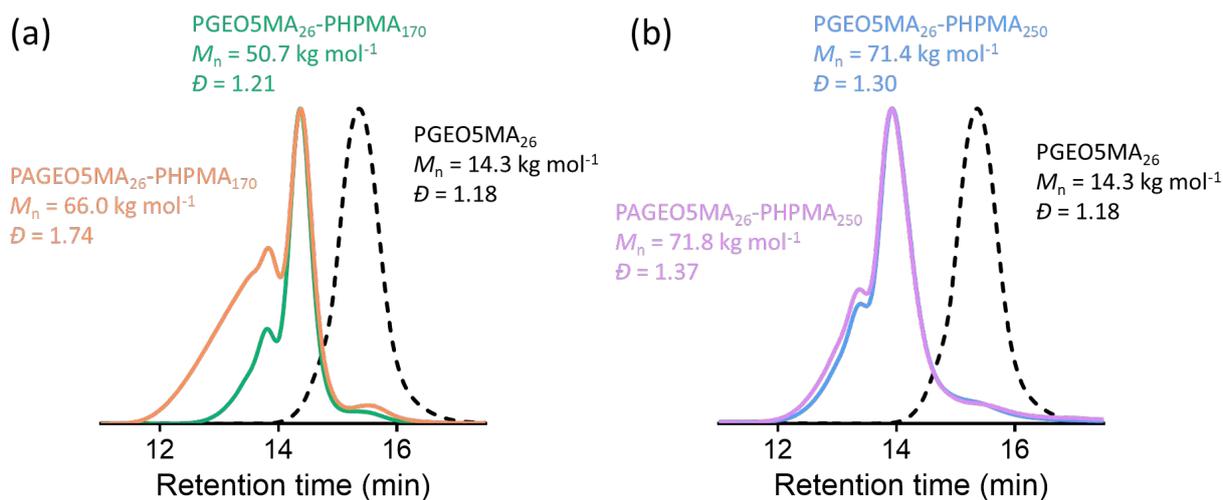
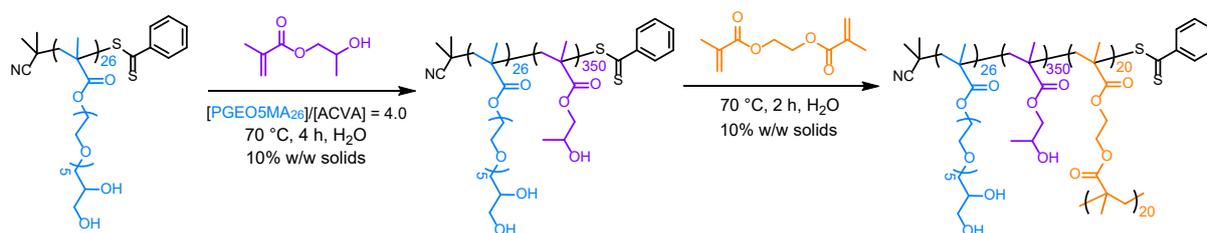


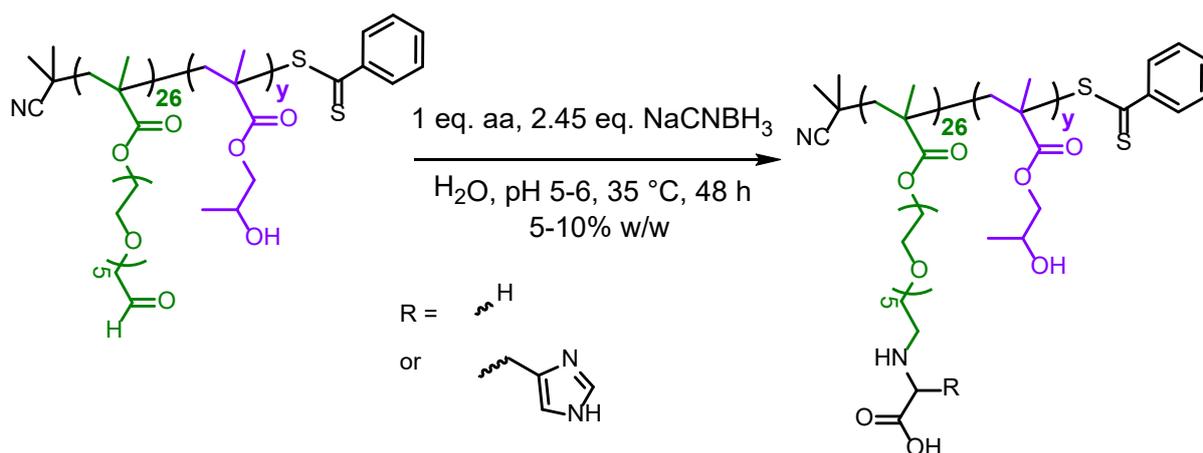
Figure S5. DMF GPC curves recorded for (a) PGE05MA₂₆, PGE05MA₂₆-PPHMA₁₇₀ and PAGE05MA₂₆-PPHMA₁₇₀ and (b) PGE05MA₂₆, PGE05MA₂₆-PPHMA₂₅₀ and PAGE05MA₂₆-PPHMA₂₅₀ diblock copolymers calibrated against a series of near-monodisperse poly(methyl methacrylate) standards.



Scheme S2. Two-step, one-pot synthesis of membrane-crosslinked PGE05MA₂₆-PPHMA₃₅₀-PEGDMA₂₀ diblock copolymer vesicles. The first step involves the chain extension of a PGE05MA₂₆ precursor by RAFT aqueous dispersion polymerization of HPMA. The second step is the addition of EGDMA as a third block to crosslink the vesicle membrane.

Table S1. Summary of DLS data obtained for linear PGE05MA₂₆-PPHMA₃₅₀ and membrane-crosslinked PGE05MA₂₆-PPHMA₃₅₀-PEGDMA₂₀ diblock copolymer vesicles dispersed in either water or ethanol.

Polymer composition	Solvent	DLS diameter (nm)	DLS PDI	Derived count rate (kcps)
PGE05MA ₂₆ -PPHMA ₃₅₀	Water	231	0.04	85976
PGE05MA ₂₆ -PPHMA ₃₅₀ -PEGDMA ₂₀	Water	214	0.11	93896
PGE05MA ₂₆ -PPHMA ₃₅₀	Ethanol	18	0.15	680
PGE05MA ₂₆ -PPHMA ₃₅₀ -PEGDMA ₂₀	Ethanol	549	0.14	41095



Scheme S3. Schiff base reaction of PAGEO5MA₂₆-PPHMA_y with an amino acid (e.g. glycine or histidine) followed by reductive amination using excess aqueous NaCNBH₃ at 35 °C to afford new amino acid-based diblock copolymers *via* a two-step one-pot wholly aqueous protocol.

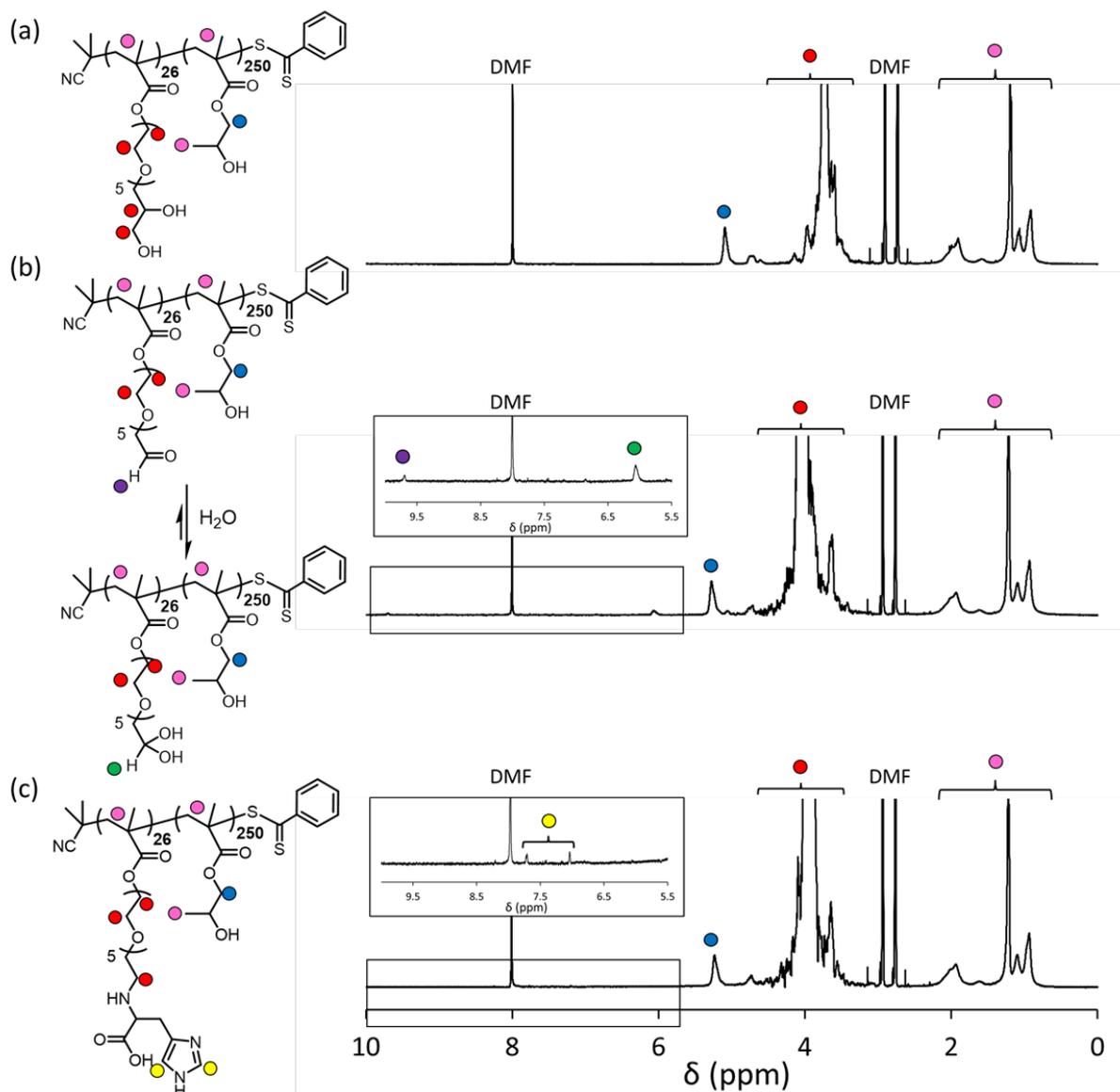


Figure S6. Assigned ¹H NMR spectra (D₂O) recorded for (a) PGE05MA₂₆-PPHMA₂₅₀, (b) PAGE05MA₂₆-PPHMA₂₅₀ and (c) PHisGE05MA₂₆-PPHMA₂₅₀

Table S2. DLS diameters and polydispersities (PDIs) recorded for PGEO5MA₂₆-PHPMA₁₇₀, PAGEO5MA₂₆-PHPMA₁₇₀, PGlyGEO5MA₂₆-PHPMA₁₇₀ and PHisGEO5MA₂₆-PHPMA₁₇₀ spheres.

Polymer composition	DLS diameter (nm)	DLS PDI
PGEO5MA ₂₆ -PHPMA ₁₇₀	31	0.02
PAGEO5MA ₂₆ -PHPMA ₁₇₀	32	0.08
PGlyGEO5MA ₂₆ -PHPMA ₁₇₀	26	0.08
PHisGEO5MA ₂₆ -PHPMA ₁₇₀	32	0.08

Table S3. DLS diameters and polydispersities (PDIs) recorded for PGEO5MA₂₆-PHPMA₂₅₀, PAGEO5MA₂₆-PHPMA₂₅₀, PGlyGEO5MA₂₆-PHPMA₂₅₀ and PHisGEO5MA₂₆-PHPMA₂₅₀ worms.

Polymer composition	DLS diameter (nm)	DLS PDI
PGEO5MA ₂₆ -PHPMA ₂₅₀	409	0.44
PAGEO5MA ₂₆ -PHPMA ₂₅₀	242	0.26
PGlyGEO5MA ₂₆ -PHPMA ₂₅₀	146	0.26
PHisGEO5MA ₂₆ -PHPMA ₂₅₀	320	0.48

Table S4. DLS diameters and polydispersities (PDIs) recorded for PGEO5MA₂₆-PHPMA₃₅₀-PEGDMA₂₀, PAGEO5MA₂₆-PHPMA₃₅₀-PEGDMA₂₀, PGlyGEO5MA₂₆-PHPMA₃₅₀-PEGDMA₂₀ and PHisGEO5MA₂₆-PHPMA₃₅₀-PEGDMA₂₀ vesicles.

Polymer composition	DLS diameter (nm)	DLS PDI
PGEO5MA ₂₆ -PHPMA ₃₅₀ -PEGDMA ₂₀	214	0.11
PAGEO5MA ₂₆ -PHPMA ₃₅₀ -PEGDMA ₂₀	210	0.10
PGlyGEO5MA ₂₆ -PHPMA ₃₅₀ -PEGDMA ₂₀	216	0.08
PHisGEO5MA ₂₆ -PHPMA ₃₅₀ -PEGDMA ₂₀	212	0.10

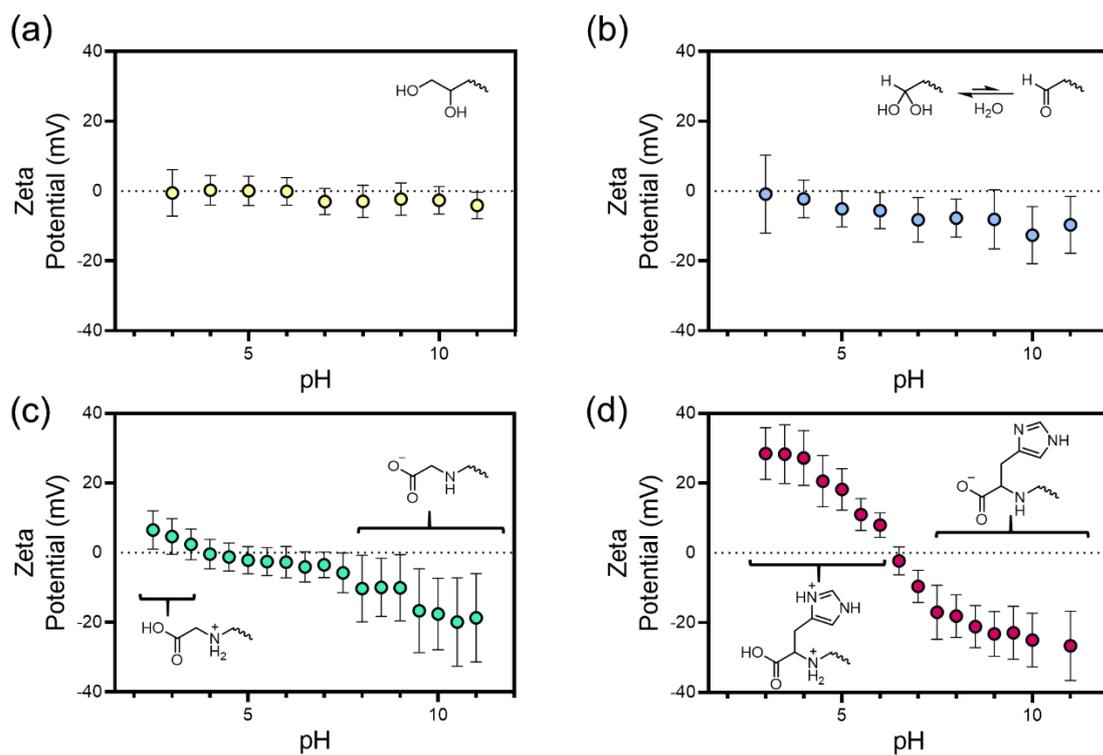


Figure S8. Zeta potential vs. pH curves obtained for (a) PGE05MA₂₆-PPHMA₁₇₀, (b) PAGE05MA₂₆-PPHMA₁₇₀, (c) PGlyGEO5MA₂₆-PPHMA₁₇₀, and (d) PHisGEO5MA₂₆-PPHMA₁₇₀ spheres.

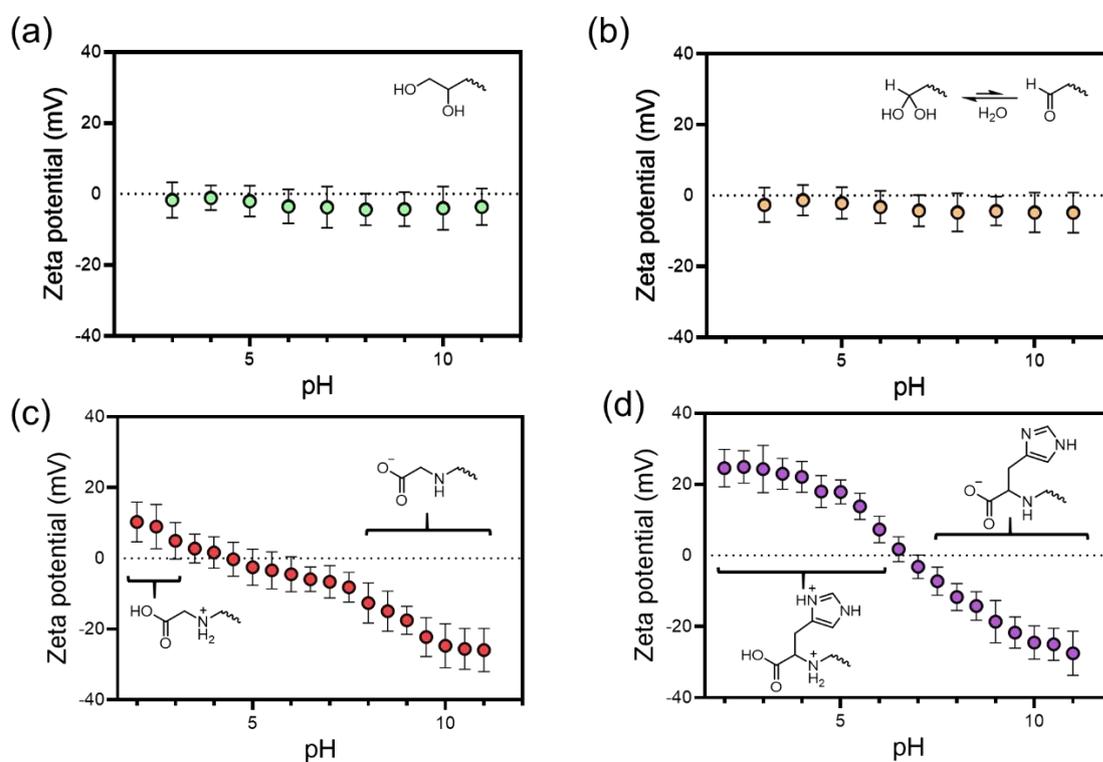


Figure S7. Zeta potential vs. pH curves obtained for (a) PGE05MA₂₆-PPHMA₂₅₀, (b) PAGE05MA₂₆-PPHMA₂₅₀, (c) PGlyGEO5MA₂₆-PPHMA₂₅₀, and (d) PHisGEO5MA₂₆-PPHMA₂₅₀ worms.

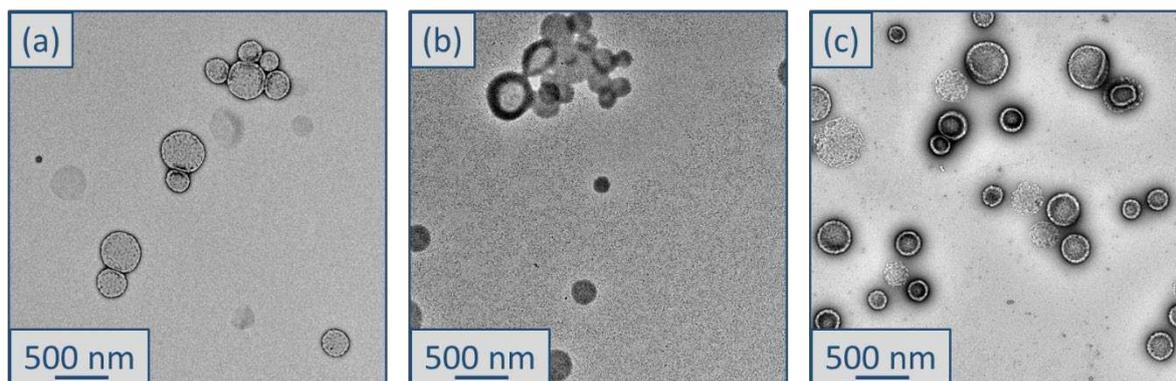


Figure S9. Transmission electron microscopy images obtained for (a) PGE05MA₂₆-PHPMA₃₅₀-PEGDMA₂₀ vesicles before attempted reaction with BSA, (b) PGE05MA₂₆-PHPMA₃₅₀-PEGDMA₂₀ vesicles directly after attempted reaction with BSA and (c) PGE05MA₂₆-PHPMA₃₅₀-PEGDMA₂₀ vesicles after attempted reaction with BSA and subsequent purification via five centrifugation and redispersion cycles.

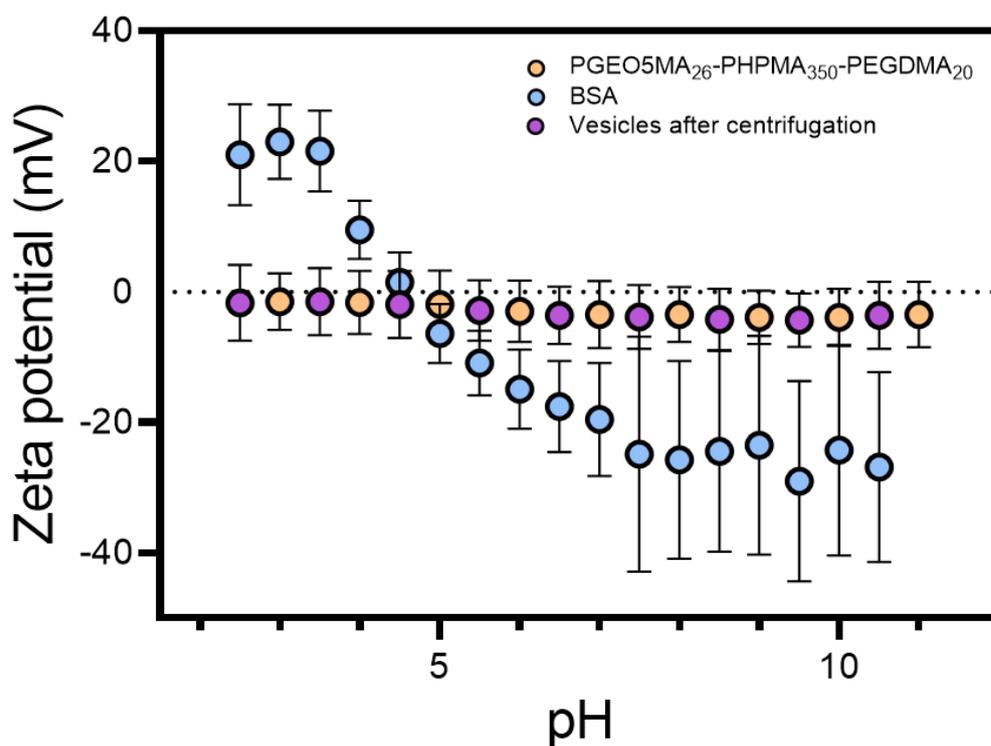


Figure S10. Zeta potential vs. pH curves obtained for membrane-crosslinked PGE05MA₂₆-PHPMA₃₅₀-PEGDMA₂₀ vesicles, BSA protein alone and membrane-crosslinked PGE05MA₂₆-PHPMA₃₅₀-PEGDMA₂₀ vesicles after exposure to BSA followed by six centrifugation and redispersion cycles. The unchanged electrophoretic data observed for the vesicles confirms that there is no BSA adsorption in this case.