
Article:
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Supporting Information for:

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

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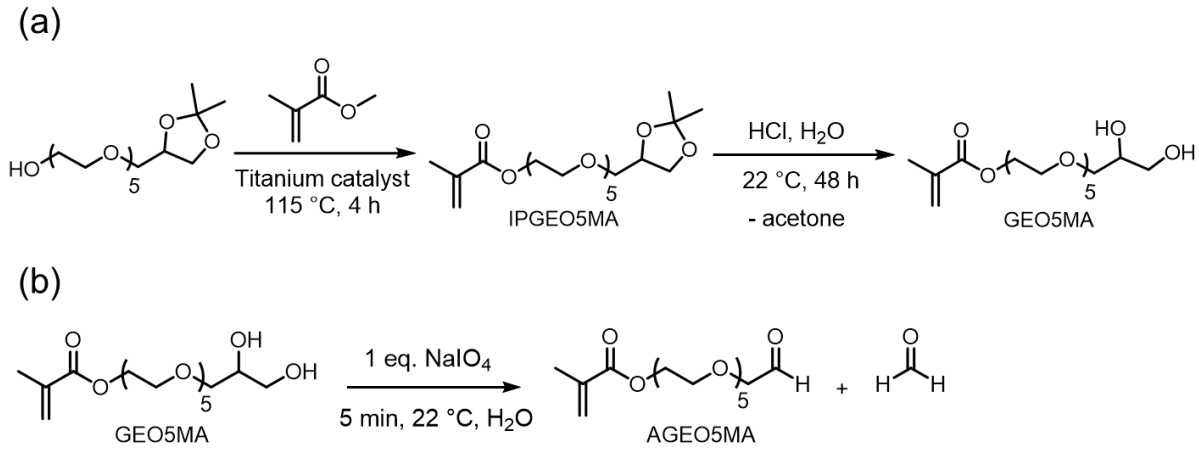


Scheme S1. (a) Two-step synthesis of GEO5MA monomer starting from an isopropylidene glycerol precursor as a hydroxy-functional initiator. This precursor is then transesterified with methyl methacrylate to produce IPGEO5MA, before removing the ketal protecting group with acid to afford GEO5MA monomer. (b) Oxidation of GEO5MA in aqueous solution using sodium periodate at 22°C affords AGEO5MA with formaldehyde as a by-product. The same selective oxidation can be used to convert PGEO5MA homopolymer into PAGEO5MA homopolymer using identical reaction conditions.

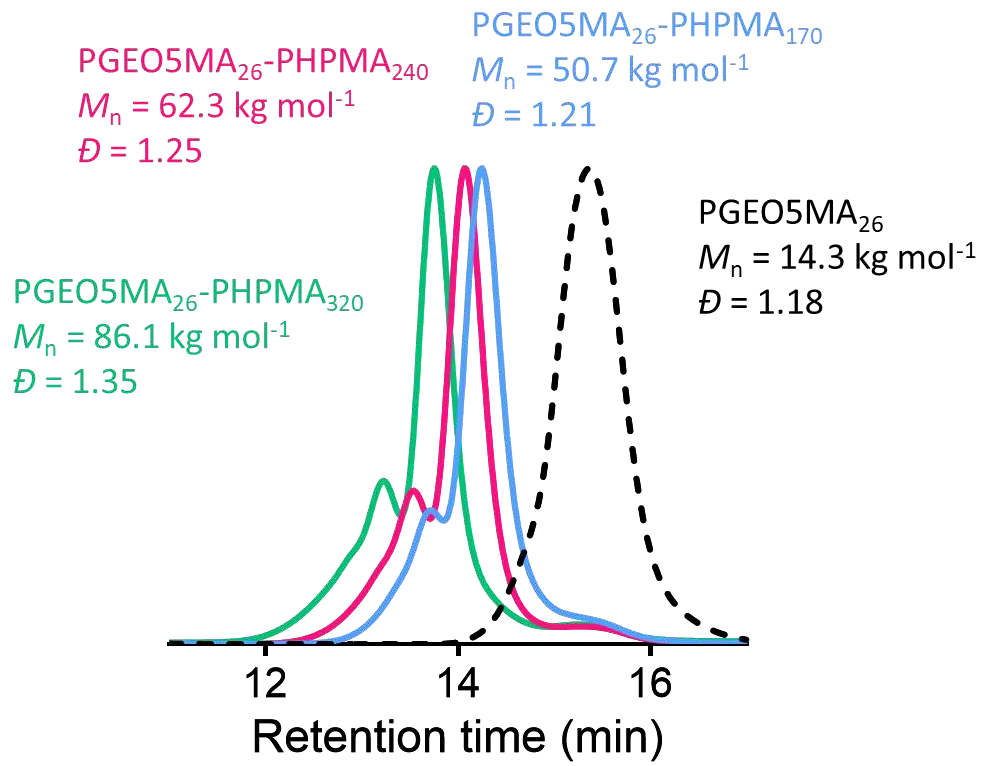


Figure S1. DMF GPC curves recorded for $PGEO5MA_{26}$, $PGEO5MA_{26}$-$PHPMA_{170}$, $PGEO5MA_{26}$-$PHPMA_{240}$ and $PGEO5MA_{26}$-$PHPMA_{320}$ diblock copolymers calibrated against a series of near-monodisperse poly(methyl methacrylate) standards.

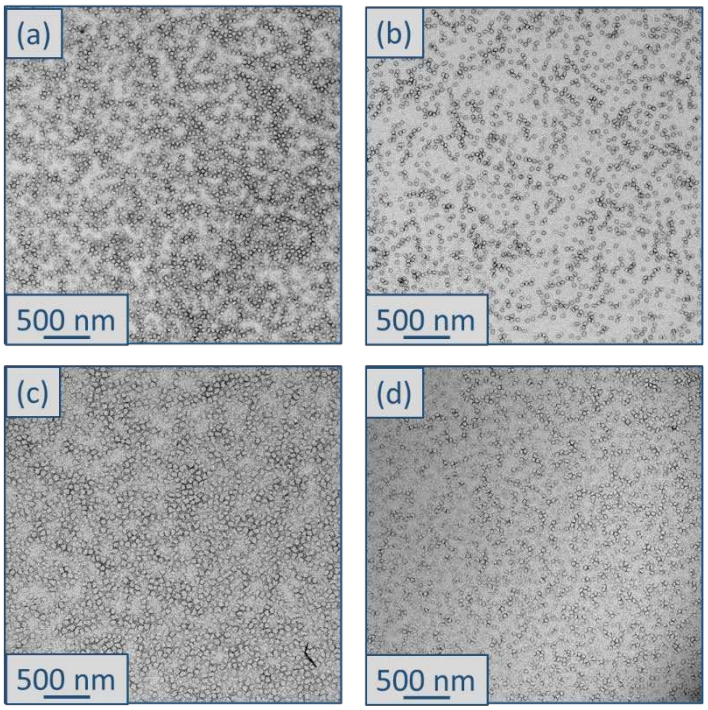


Figure S2. Transmission electron microscopy images recorded for (a) $PGEO5MA_{26}$-$PHPMA_{170}$, (b) $PAGEO5MA_{26}$-$PHPMA_{170}$, (c) $PGlyGEO5MA_{26}$-$PHPMA_{170}$, and (d) $PHisGEO5MA_{26}$-$PHPMA_{170}$ diblock copolymer spheres.

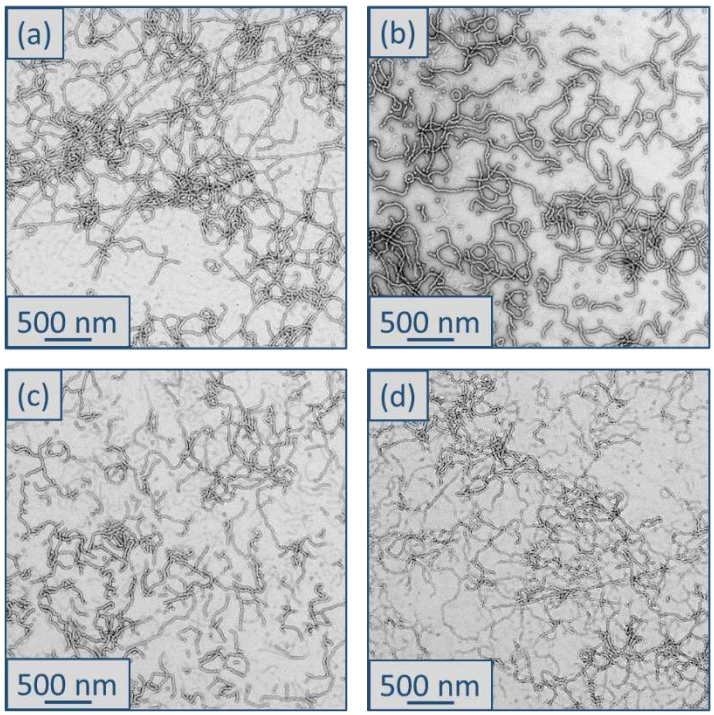


Figure S3. Transmission electron microscopy images recorded for (a) PGEO5MA$_{26}$-PHPMA$_{250}$, (b) PAGEO5MA$_{26}$-PHPMA$_{250}$, (c) PGlyGEO5MA$_{26}$-PHPMA$_{250}$, and (d) PHisGEO5MA$_{26}$-PHPMA$_{250}$ worms.

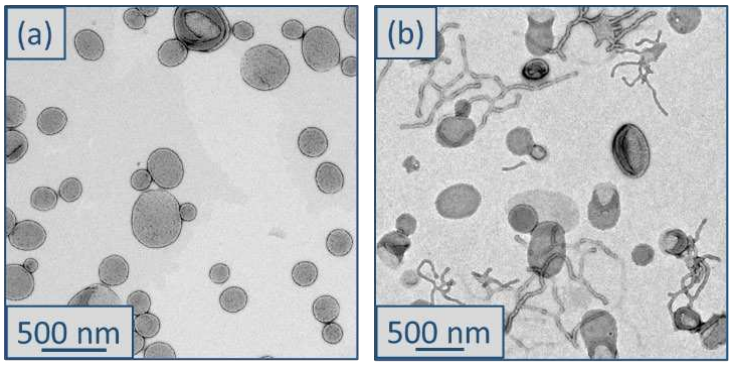


Figure S4. Transmission electron microscopy images recorded for (a) PGEO5MA$_{26}$-PHPMA$_{350}$ vesicles and (b) a binary mixture of PAGEO5MA$_{26}$-PHPMA$_{350}$ vesicles and worms.

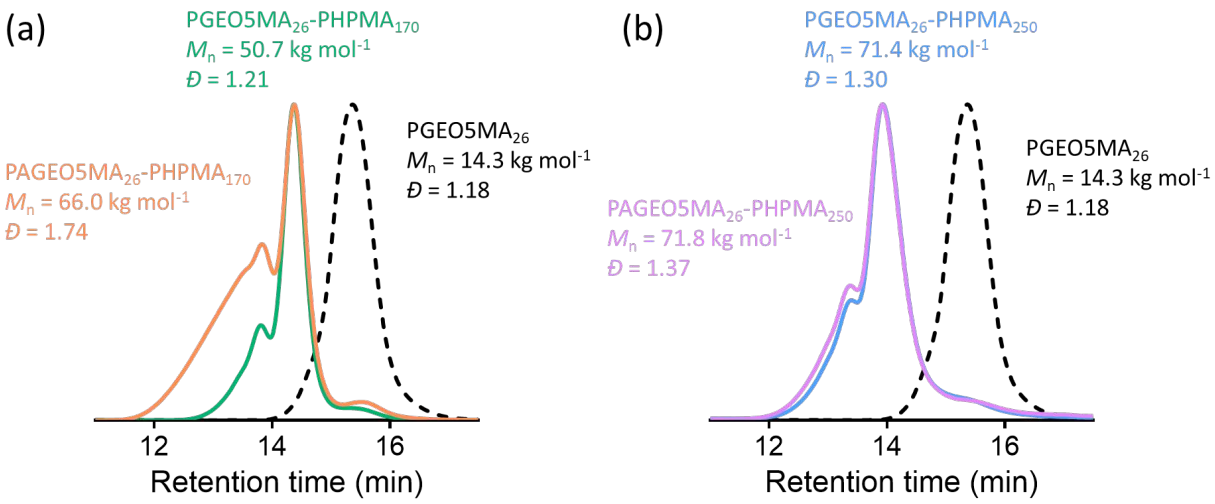
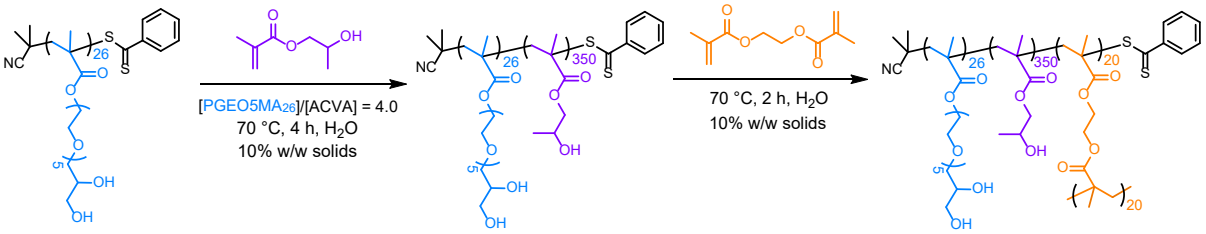


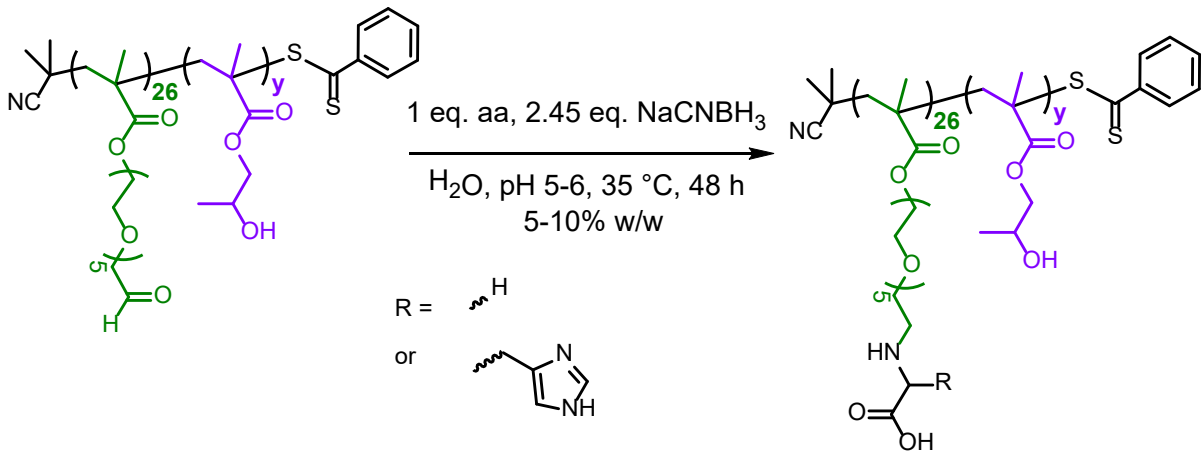
Figure S5. DMF GPC curves recorded for (a) $PGEO5MA_{26}$, $PGEO5MA_{26}$-$PHPMA_{170}$ and $PAGEO5MA_{26}$-$PHPMA_{170}$ and (b) $PGEO5MA_{26}$, $PGEO5MA_{26}$-$PHPMA_{250}$ and $PAGEO5MA_{26}$-$PHPMA_{250}$ diblock copolymers calibrated against a series of near-monodisperse poly(methyl methacrylate) standards.



Scheme S2. Two-step, one-pot synthesis of membrane-crosslinked $PGEO5MA_{26}$-$PHPMA_{350}$-$PEGDMA_{20}$ diblock copolymer vesicles. The first step involves the chain extension of a $PGEO5MA_{26}$ 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 $PGEO5MA_{26}$-$PHPMA_{350}$ and membrane-crosslinked $PGEO5MA_{26}$-$PHPMA_{350}$-$PEGDMA_{20}$ diblock copolymer vesicles dispersed in either water or ethanol.

Polymer composition	Solvent	DLS diameter (nm)	DLS PDI	Derived count rate (kcps)
$PGEO5MA_{26}$-$PHPMA_{350}$	Water	231	0.04	85976
$PGEO5MA_{26}$-$PHPMA_{350}$-$PEGDMA_{20}$	Water	214	0.11	93896
$PGEO5MA_{26}$-$PHPMA_{350}$	Ethanol	18	0.15	680
$PGEO5MA_{26}$-$PHPMA_{350}$-$PEGDMA_{20}$	Ethanol	549	0.14	41095



Scheme S3. Schiff base reaction of PAGEO5MA$_{26}$-PHPMA$_y$ with an amino acid (e.g. glycine or histidine) followed by reductive amination using excess aqueous $NaCNBH_3$ at 35 °C to afford new amino acid-based diblock copolymers *via* a two-step one-pot wholly aqueous protocol.

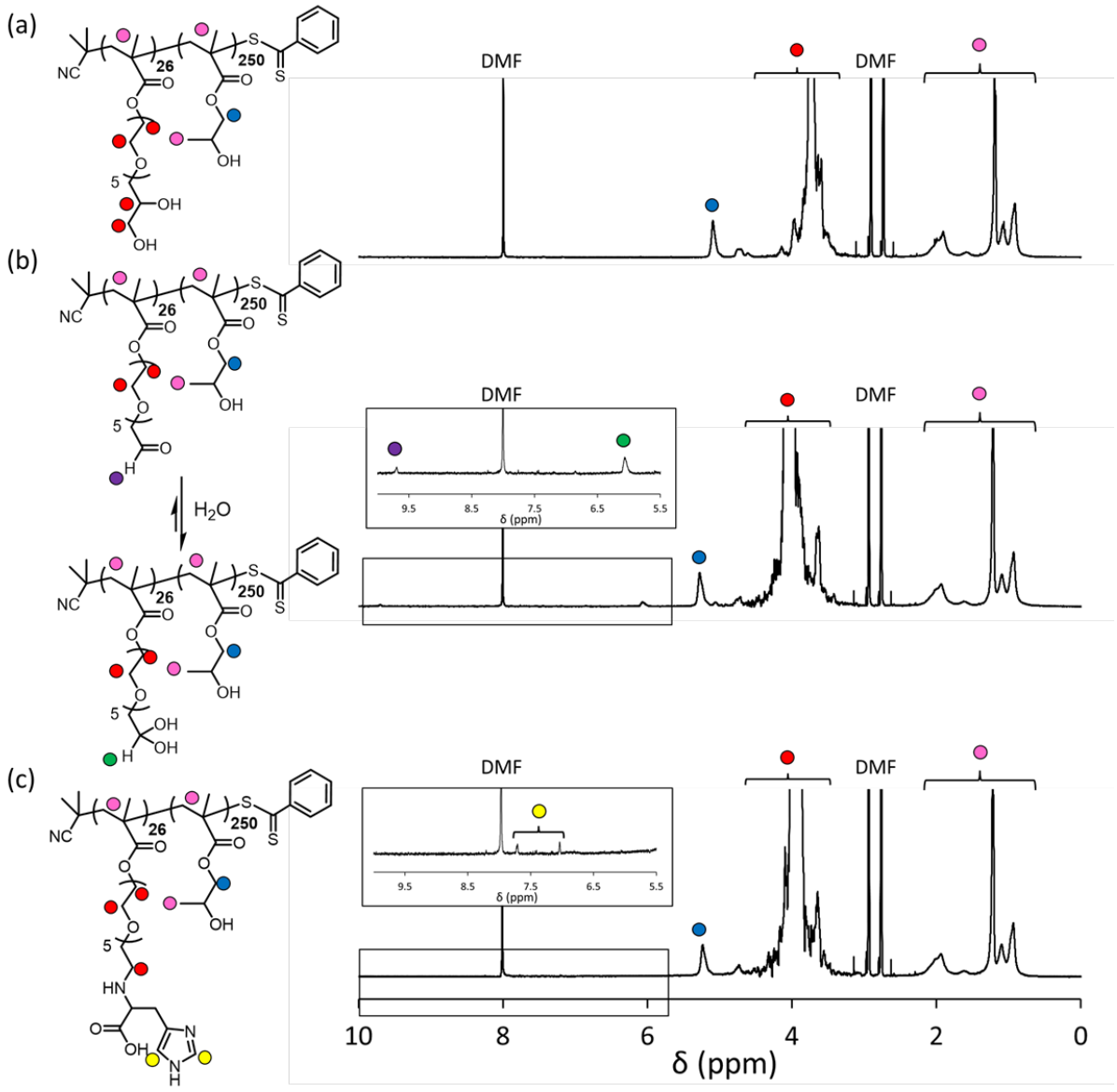


Figure S6. Assigned ^{1}H NMR spectra (D_2O) recorded for (a) PGEO5MA$_{26}$-PHPMA$_{250}$, (b) PAGEO5MA$_{26}$-PHPMA$_{250}$ and (c) PHisGEO5MA$_{26}$-PHPMA$_{250}$

Table S2. DLS diameters and polydispersities (PDIs) recorded for $PGEO5MA_{26}$-$PHPMA_{170}$, $PAGEO5MA_{26}$-$PHPMA_{170}$, $PGlyGEO5MA_{26}$-$PHPMA_{170}$ and $PHisGEO5MA_{26}$-$PHPMA_{170}$ 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 $PGEO5MA_{26}$-$PHPMA_{250}$, $PAGEO5MA_{26}$-$PHPMA_{250}$, $PGlyGEO5MA_{26}$-$PHPMA_{250}$ and $PHisGEO5MA_{26}$-$PHPMA_{250}$ 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 $PGEO5MA_{26}$-$PHPMA_{350}$-$PEGDMA_{20}$, $PAGEO5MA_{26}$-$PHPMA_{350}$-$PEGDMA_{20}$, $PGlyGEO5MA_{26}$-$PHPMA_{350}$-$PEGDMA_{20}$ and $PHisGEO5MA_{26}$-$PHPMA_{350}$-$PEGDMA_{20}$ 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

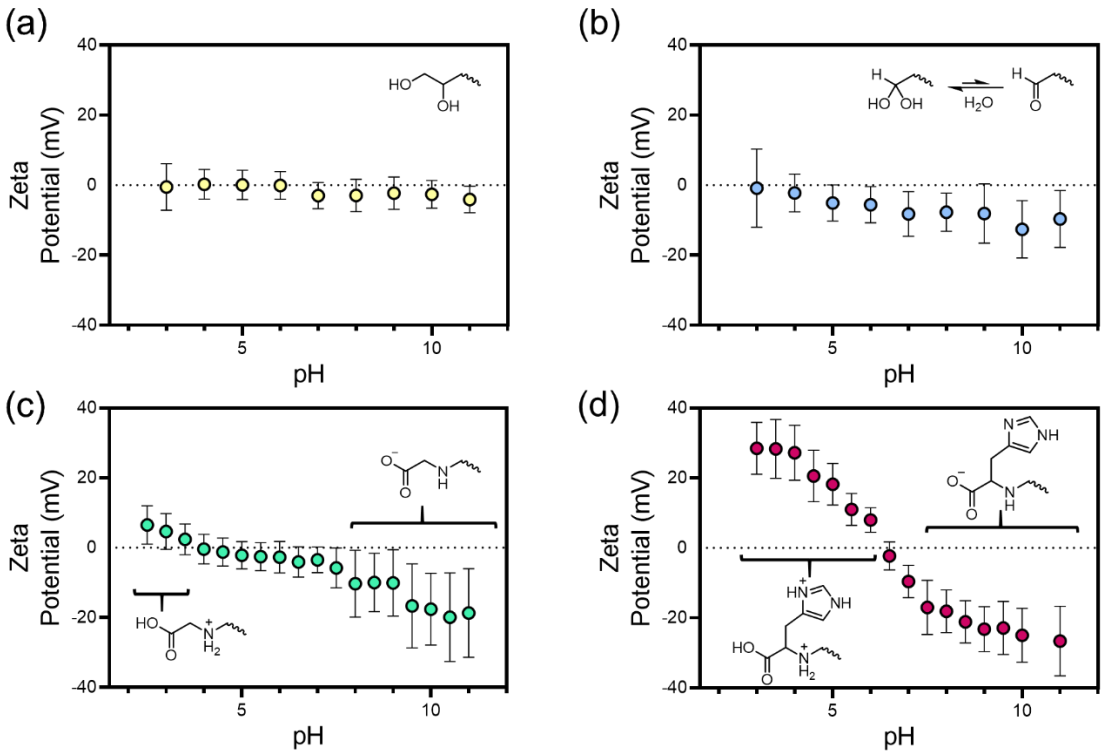


Figure S8. Zeta potential vs. pH curves obtained for (a) PGEO5MA$_{26}$-PHPMA$_{170}$, (b) PAGEO5MA$_{26}$-PHPMA$_{170}$, (c) PGlyGEO5MA$_{26}$-PHPMA$_{170}$, and (d) PHisGEO5MA$_{26}$-PHPMA$_{170}$ spheres.

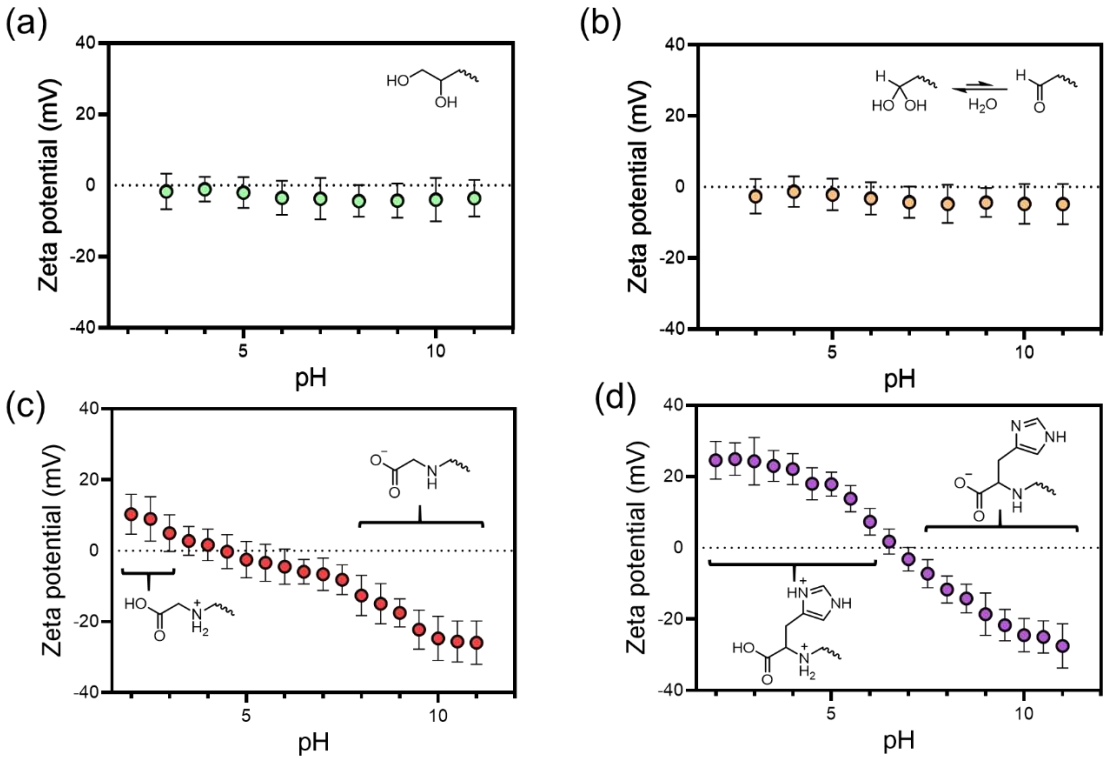


Figure S7. Zeta potential vs. pH curves obtained for (a) PGEO5MA$_{26}$-PHPMA$_{250}$, (b) PAGEO5MA$_{26}$-PHPMA$_{250}$, (c) PGlyGEO5MA$_{26}$-PHPMA$_{250}$, and (d) PHisGEO5MA$_{26}$-PHPMA$_{250}$ worms.

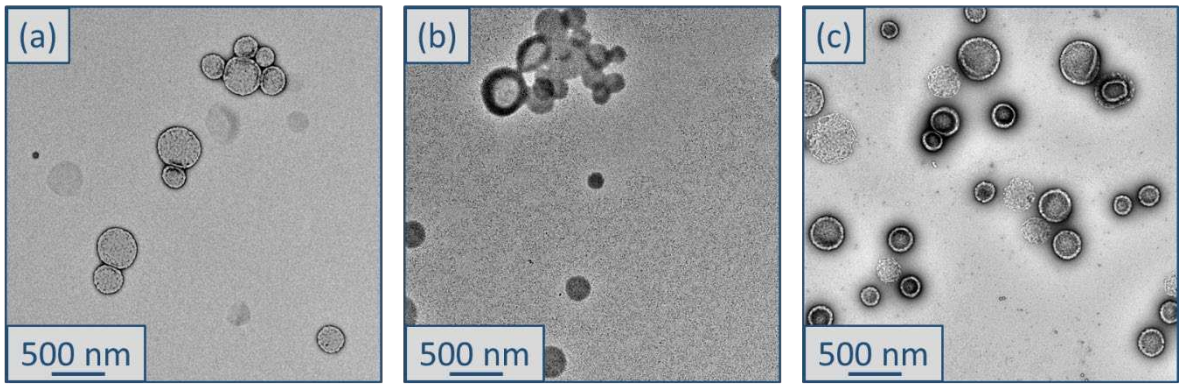


Figure S9. Transmission electron microscopy images obtained for (a) PGEO5MA$_{26}$-PHPMA$_{350}$-PEGDMA$_{20}$ vesicles before attempted reaction with BSA, (b) PGEO5MA$_{26}$-PHPMA$_{350}$-PEGDMA$_{20}$ vesicles directly after attempted reaction with BSA and (c) PGEO5MA$_{26}$-PHPMA$_{350}$-PEGDMA$_{20}$ vesicles after attempted reaction with BSA and subsequent purification via five centrifugation and redispersion cycles.

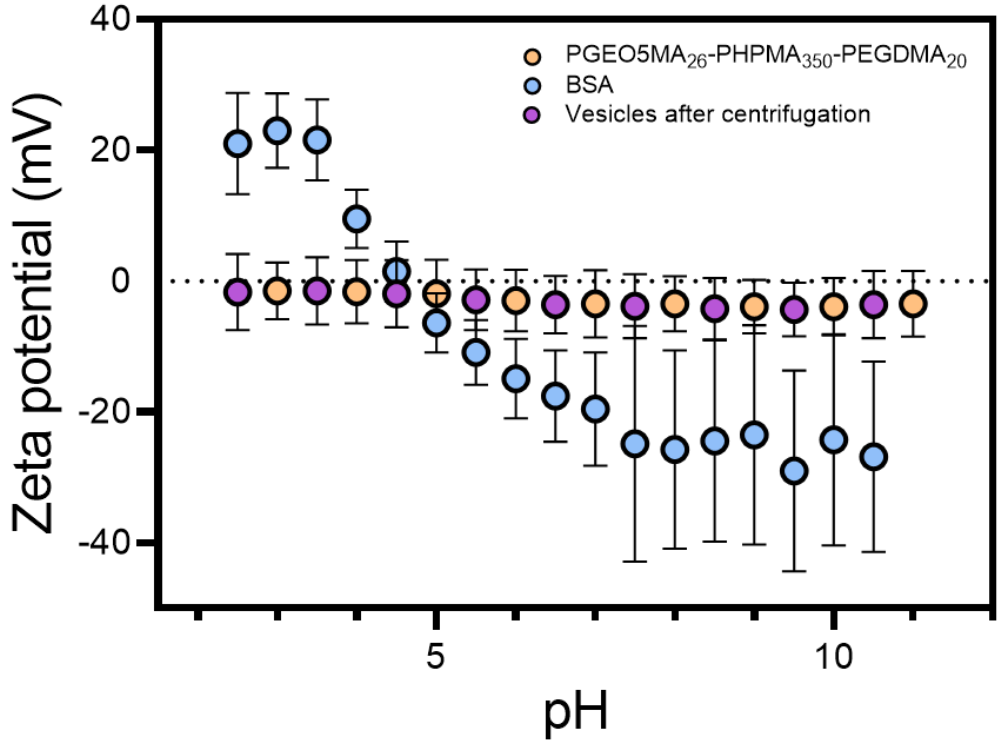


Figure S10. Zeta potential vs. pH curves obtained for membrane-crosslinked PGEO5MA$_{26}$-PHPMA$_{350}$-PEGDMA$_{20}$ vesicles, BSA protein alone and membrane-crosslinked PGEO5MA$_{26}$-PHPMA$_{350}$-PEGDMA$_{20}$ vesicles after exposure to BSA followed by six centrifugation and redispersion cycles. The unchanged electrophoretic data observed for the vesicles confirms that there is no BSA adsorption in this case.