Supporting Information for:

Rational synthesis of epoxy-functional spheres, worms and vesicles by RAFT aqueous emulsion polymerisation of glycidyl methacrylate

Fiona L. Hatton [a†], * *Matthew J. Derry* [a‡] *and Steven P. Armes* [a] *

[a] Dainton Building, Department of Chemistry, University of Sheffield, Brook Hill, Sheffield, South Yorkshire, S3 7HF, UK

[†] Present address: Department of Materials, Loughborough University, Loughborough, LE11 3TU, UK

[‡] Present address: Aston Institute of Materials Research, Aston University, Birmingham, B4 7ET, UK

*Email: f.hatton@lboro.ac.uk (F.L.H.)

*Email: s.p.armes@sheffield.ac.uk (S.P.A.)

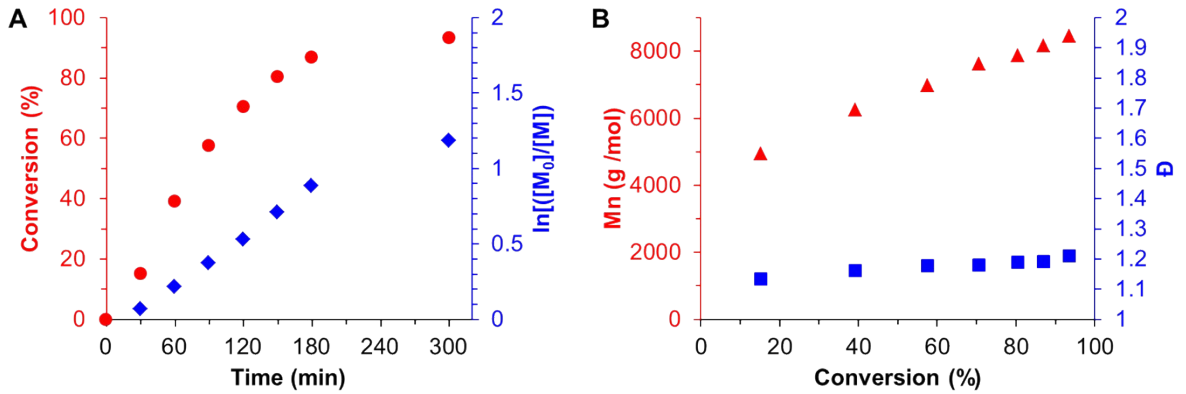

Figure S1. RAFT solution polymerization of glycerol monomethacrylate (GMA) in ethanol at 70 °C using 2-cyano-2-propyl dithiobenzoate (CPDB) and 4,4′-azobis(4-cyanopentanoic acid) (ACVA) when targeting a PGMA DP of 31 and using a CPDB/ACVA molar ratio of 5.0. (A) Conversion vs. time curve and corresponding semilogarithmic plot and (B) evolution in M_n and Đ with monomer conversion.

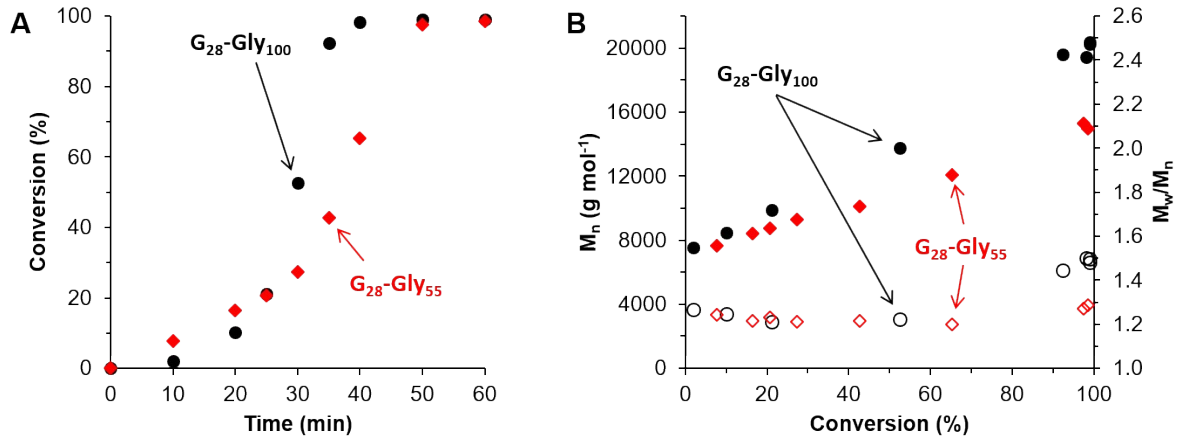

Figure S2. RAFT aqueous emulsion polymerization of glycidyl methacrylate (GlyMA) at 50 °C targeting $PGMA_{28}$-$PGlyMA_{55}$ (red diamonds) and $PGMA_{28}$-$PGlyMA_{100}$ (black circles). Reactions were conducted at 10% w/w solids using a $PGMA_{28}$/VA-044 molar ratio = 4.0. (A) Conversion vs. time curves and corresponding semilogarithmic plots and (B) evolution in M_n (filled symbols) and Đ (open symbols) with monomer conversion.

Table S1. Summary of final conversions, molecular weight data, DLS data (D_z and polydispersity) and TEM-assigned morphologies obtained for a series of $PGMA_{28}$-$PGlyMA_n$ diblock copolymer nano-objects at 5-30% w/w solids prepared via RAFT aqueous emulsion polymerization of GlyMA at 50 °C using a $PGMA_{28}$ macro-CTA using a $PGMA_{28}$/VA-044 molar ratio = 4.0. [N.B. PGMA and PGlyMA blocks are denoted as 'G and 'Gly'].

Solids (% w/w)	Target copolymer composition	Conv. (%)[a]	M_n [b] (g mol^{-1})	M_w [b] (g mol^{-1})	$Đ$ [b]	D_z (nm)	PDI	TEM morphology [c]
40	$PGMA_{28}$ macro-CTA	75	8 300	9 600	1.15	-	-	-
5	G_{28}-Gly_{40}	>99	15 600	17 800	1.14	24	0.16	s
	G_{28}-Gly_{50}	>99	17 100	20 100	1.17	26	0.07	s
	G_{28}-Gly_{55}	>99	18 000	21 400	1.19	29	0.06	s/sw
	G_{28}-Gly_{68}	>99	19 600	23 800	1.21	44	0.12	s/sw
	G_{28}-Gly_{75}	>99	21 700	27 800	1.28	127	0.25	s/sw
	G_{28}-Gly_{85}	>99	22 600	29 800	1.32	398	0.69	s/sw
	G_{28}-Gly_{90}	99	22 200	31 800	1.44	767	0.49	w/v
	G_{28}-Gly_{100}	97	25 600	43 600	1.70	2606	0.31	v
	G_{28}-Gly_{109}	98	25 200	38 100	1.51	513	0.55	v
	G_{28}-Gly_{120}	98	25 900	44 700	1.73	1588	0.97	v
10	G_{28}-Gly_{20}	>99	10 800	13 200	1.22	15	0.05	s
	G_{28}-Gly_{30}	>99	12 500	14 700	1.17	21	0.17	s
	G_{28}-Gly_{40}	>99	14 100	17 000	1.21	28	0.13	s/sw
	G_{28}-Gly_{45}	>99	14 400	17 700	1.23	59	0.16	s/sw
	G_{28}-Gly_{50}	>99	15 000	18 300	1.21	113	0.20	w
	G_{28}-Gly_{55}	98	15 300	18 700	1.22	244	0.68	w
	G_{28}-Gly_{60}	>99	17 000	21 500	1.27	2204	1.00	w/v
	G_{28}-Gly_{65}	98	15 900	20 500	1.29	2050	1.00	w/v
	G_{28}-Gly_{70}	>99	17 000	23 000	1.36	216	0.49	w/v
	G_{28}-Gly_{75}	99	17 700	23 100	1.30	64	0.04	v
	G_{28}-Gly_{80}	>99	18 900	25 700	1.36	72	0.04	v
	G_{28}-Gly_{100}	>99	20 900	29 900	1.43	89	0.17	v
20	G_{28}-Gly_{20}	>99	10 900	13 200	1.21	16	0.05	s
	G_{28}-Gly_{25}	>99	11 500	13 300	1.15	16	0.03	s
	G_{28}-Gly_{30}	>99	12 200	14 000	1.15	24	0.10	s/sw
	G_{28}-Gly_{35}	>99	12 700	15 400	1.21	63	0.18	s/sw
	G_{28}-Gly_{40}	>99	13 500	15 700	1.17	139	0.25	w
	G_{28}-Gly_{45}	99	14 600	17 400	1.20	1079	0.54	w/v
	G_{28}-Gly_{50}	>99	14 800	17 400	1.18	704	0.78	w/v
	G_{28}-Gly_{55}	>99	15 600	19 200	1.23	114	0.06	s/w/v
	G_{28}-Gly_{60}	>99	15 700	18 700	1.19	79	0.04	v
	G_{28}-Gly_{65}	>99	16 900	20 900	1.23	45	0.03	v
	G_{28}-Gly_{70}	>99	17 200	21 200	1.23	44	0.04	v
	G_{28}-Gly_{80}	>99	18 800	23 400	1.25	46	0.06	v
	G_{28}-Gly_{100}	>99	21 100	28 700	1.36	88	0.17	v
30	G_{28}-Gly_{20}	>99	11 000	12 700	1.16	16	0.13	s
	G_{28}-Gly_{30}	>99	12 500	14 300	1.14	42	0.18	s/sw
	G_{28}-Gly_{35}	>99	13 100	16 000	1.22	110	0.22	w
	G_{28}-Gly_{40}	>99	13 800	16 000	1.16	1285	0.84	w
	G_{28}-Gly_{50}	>99	15 100	17 700	1.17	289	0.36	w/mlv
	G_{28}-Gly_{60}	>99	16 100	19 100	1.19	56	0.03	v
	G_{28}-Gly_{80}	>99	18 500	23 000	1.24	45	0.02	v

[a] Calculated from ^{1}H NMR spectroscopy studies conducted in d_6-DMSO after a reaction time of 1 h.,
[b] Determined by GPC analysis with DMF eluent containing 10 mM LiBr and calibrated against PMMA standards.
[c] Morphologies assessed by TEM; s = sphere, sw = short worm, w = worm, v = vesicle, mlv = multilamellar vesicles

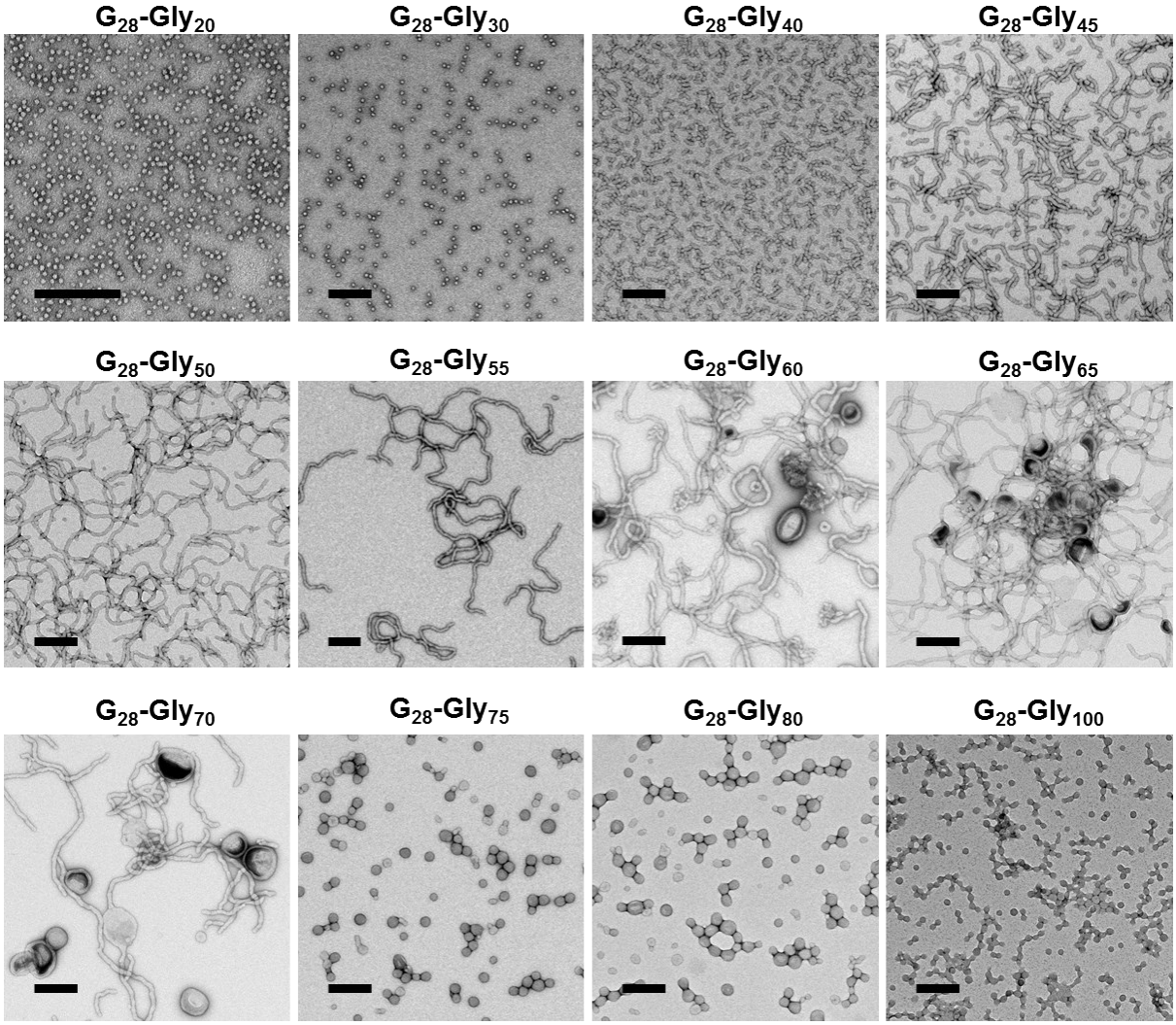

Figure S3. Representative TEM images recorded for $PGMA_{28}$-$PGlyMA_n$ diblock copolymer nano-objects prepared at 10% w/w solids, where n = 20, 30, 40, 45, 50, 55, 60, 65, 70, 75, 80 and 100. Scale bars represent 200 nm. For brevity, the PGMA block is denoted by 'G' and the PGlyMA block is denoted by 'Gly'. Subscripts refer to the mean DP of each block.

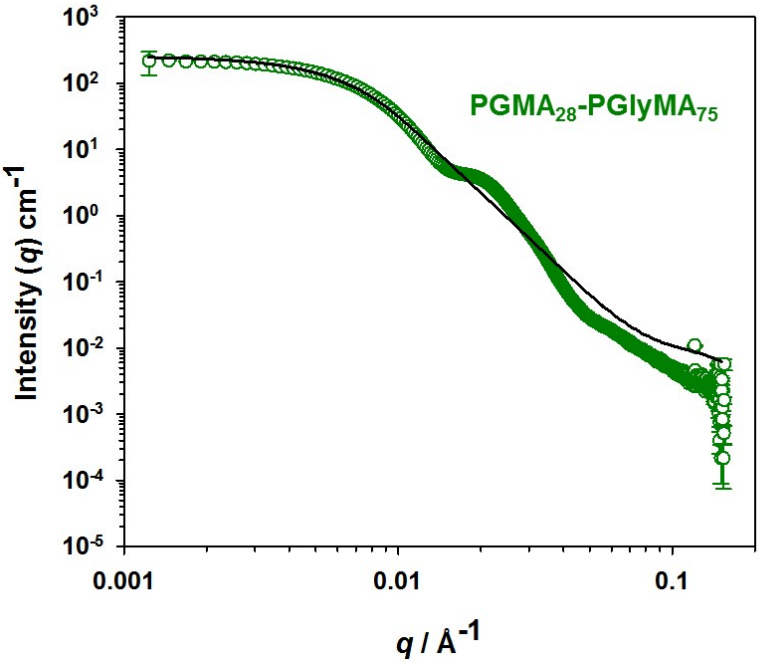

Figure S4. SAXS pattern recorded for a 1.0% w/w aqueous dispersion of $PGMA_{28}$-$PGlyMA_{75}$ diblock copolymer nano-objects originally prepared at 10% w/w solids. The experimental data are denoted by open green circles while the solid black line indicates the unsatisfactory data fit obtained when attempting to use a spherical micelle model. This is because these nanoparticles possess a vesicular (rather than spherical) morphology.

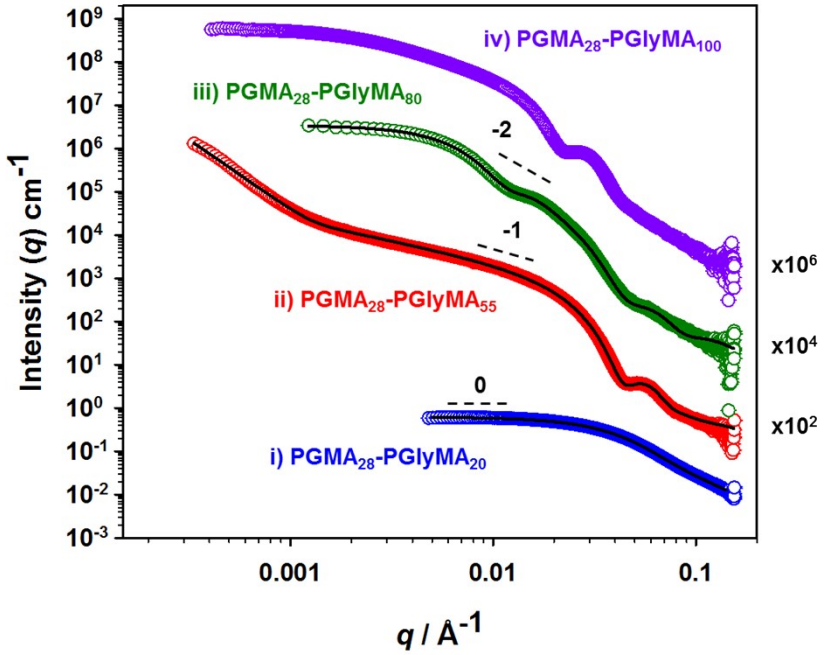

Figure S5. SAXS patterns recorded for 1.0% w/w aqueous dispersions of $PGMA_{28}$-$PGlyMA_n$ diblock copolymer nano-objects originally prepared at 10% w/w solids. (i) $PGMA_{28}$-$PGlyMA_{20}$, (ii) $PGMA_{28}$-$PGlyMA_{55}$, (iii) $PGMA_{28}$-$PGlyMA_{80}$ and (iv) $PGMA_{28}$-$PGlyMA_{100}$. The experimental data are denoted by open circles while the solid black lines indicate the data fits obtained when using (i) a spherical micelle (blue curve), (ii) a worm-like micelle (red curve) or (iii) a vesicle model (green curve). For clarity, the red, green and purple curves are offset by arbitrary factors of 10^2, 10^4 and 10^6 respectively.

Table S2. Structural parameters obtained from SAXS analysis of 1.0% w/w aqueous dispersions of $PGMA_{28}$-$PGlyMA_n$ nano-objects originally prepared at 10% w/w solids using appropriate sphere,[1] worm[1] and vesicle[2] models. Representative parameters are denoted as follows: V_{Gly} is the volume of the PGlyMA block, φ is the volume fraction of the nano-object, R_s represents the volume-average radius of the spherical cores, R_w represents the cross-sectional radius of the worm cores, R_m represents the radius from the centre of the vesicle to the centre of the membrane, T_m is the mean thickness of the hydrophobic component of the vesicle membrane, and σ_x denotes the standard deviation of the relevant parameter (x = R_s, R_w, R_m or T_m). R_g denotes the mean radius of gyration for the $PGMA_{28}$ stabilizer chains. D_s denotes the overall volume-average diameter of the spheres, D_w denotes the cross-sectional volume-average worm diameter, D_v denotes the overall volume-average diameter of the vesicles and D_z is the mean hydrodynamic diameter reported by DLS. The volume of the $PGMA_{28}$ block, V_{PGMA}, used to fit the SAXS patterns was 5.69 nm^3 and x_{sol} was zero in all cases in all cases.

Target copolymer composition	Scattering model	V_{Gly} (nm^3)	*Volume fraction (φ)*	R_s /σ_{Rs} (nm)	R_w /σ_{Rw} (nm)	R_m /σ_{Rm} (nm)	T_m /σ_{Tm} (nm)	R_g (nm)	D_s, D_w or D_v (nm) [a]	D_z (nm)
$PGMA_{28}$-$PGlyMA_{20}$	sphere	3.78	0.0094	2.60 / 0.97	-	-	-	1.97	13.1	15
$PGMA_{28}$-$PGlyMA_{30}$	sphere	5.67	0.0018	4.09 / 0.92	-	-	-	1.84	15.5	21
$PGMA_{28}$-$PGlyMA_{50}$	worm	9.44	0.0080	-	6.17 / 0.86	-	-	1.37	17.8	16.6*
$PGMA_{28}$-$PGlyMA_{55}$	worm	10.39	0.0074	-	6.69 / 0.81	-	-	1.41	19.0	19.1*
$PGMA_{28}$-$PGlyMA_{75}$	vesicle	14.16	0.0082	-	-	20.63 / 4.81	8.24 / 1.57	1.75	53.0	64
$PGMA_{28}$-$PGlyMA_{80}$	vesicle	15.11	0.0083	-	-	24.61 / 6.58	9.00 / 1.53	1.75	61.7	72

*Worm cross-sectional diameter estimated by TEM (since this parameter is not accessible using DLS).

[a] When fitted using a spherical micelle model, the overall volume-average sphere diameter, D_s, was calculated using $D_s = 2R_s + 4R_g$. When fitted using a worm model, the cross-sectional volume-average worm diameter, D_w, was calculated using $D_w = 2R_s + 4R_g$. When fitted using a vesicle model, the overall volume-average vesicle diameter, D_v, was calculated using $D_v = 2R_m + T_m + 2R_g$.

Table S3. Nitrogen and sulfur microanalyses obtained before and after L-cysteine derivatization of 5% w/w aqueous dispersions of $PGMA_{28}$-$PGlyMA_{25}$, $PGMA_{28}$-$PGlyMA_{40}$ and $PGMA_{28}$-$PGlyMA_{80}$ nano-objects originally prepared at 20% w/w solids.

Target polymer composition	N content (%)		S content (%)		Degree of Derivatization (%) [a]	
	theory	exp	theory	exp	N	S
$PGMA_{28}$-$PGlyMA_{25}$	0.17	0.23[b]	0.78	1.04	-	-
$PGMA_{28}$-$P(GlyMA\text{-}cys)_{25}$	3.23	2.94	7.67	6.98	91	91
$PGMA_{28}$-$PGlyMA_{40}$	0.13	0.16[b]	0.62	0.70	-	-
$PGMA_{28}$-$P(GlyMA\text{-}cys)_{40}$	3.77	3.42	8.84	8.02	91	91
$PGMA_{28}$-$PGlyMA_{80}$	0.09	0.06[b]	0.40	0.48	-	-
$PGMA_{28}$-$P(GlyMA\text{-}cys)_{80}$	4.40	1.89	10.20	4.68	43	46
$PGMA_{28}$-$P(GlyMA\text{-}cys)_{80}$-50 °C	4.40	3.86	10.20	9.13	88	90

[a] calculated using the equation: Degree of derivatization = (exp N or S content / theory N or S content) x 100, where the theoretical values assume quantitative reaction.
[b] Below the instrument detection limit of 0.3%.

Table S4. DLS diameters, D_z, polydispersities, PDI, and zeta potentials (ZP) obtained for dilute aqueous dispersions of $PGMA_{28}$-$PGlyMA_n$ nano-objects originally prepared at 20% w/w solids and also for the corresponding L-cysteine-derivatized $PGMA_{28}$-$P(Gly\text{-}cys)_n$ nano-objects.

Target polymer composition	D_z (nm)	PDI	ZP (mV) at pH 7
$PGMA_{28}$-$PGlyMA_{25}$	18	0.12	-
$PGMA_{28}$-$P(GlyMA\text{-}cys)_{25}$	14	0.36	-
$PGMA_{28}$-$PGlyMA_{40}$	186	0.42	-4.11
$PGMA_{28}$-$P(GlyMA\text{-}cys)_{40}$	126	0.28	-21.1
$PGMA_{28}$-$PGlyMA_{80}$	49	0.03	-
$PGMA_{28}$-$P(GlyMA\text{-}cys)_{80}$	59	0.09	-
$PGMA_{28}$-$P(GlyMA\text{-}cys)_{80}$-50 °C	81	0.10	-30.1

Table S5. Structural parameters obtained from SAXS analysis of 1.0% w/w aqueous dispersions of $PGMA_{28}$-$PGlyMA_n$ nano-objects originally prepared at 20% w/w solids and corresponding $PGMA_{28}$-$P(GlyMA\text{-}cys)_n$ nano-objects following derivatization with L-cysteine, using Guassian coil,[3] sphere,[1] worm[1] or vesicle[2] models. Representative parameters are denoted as follows: V_{PGlyMA} is the volume of the PGlyMA block, φ is the volume fraction of the nano-object, R_s represents the volume-average radius of the spherical cores, R_w represents the cross-sectional radius of the worm cores, R_m represents the radius from the centre of the vesicle to the centre of the membrane, T_m is the mean thickness of the hydrophobic component of the vesicle membrane, and σ_y denotes the standard deviation of the relevant parameter (y = R_s, R_w, R_m or T_m). R_g denotes the mean radius of gyration for the $PGMA_{28}$ stabilizer chains (or dissolved copolymer chains when fitting to the Gaussian coil model). D_s denotes the overall volume-average diameter of the spheres, D_w denotes the cross-sectional volume-average worm diameter, D_v denotes the overall volume-average diameter of the vesicles and D_z is the mean hydrodynamic diameter reported by DLS. From the Hayter-Penfold approximation,[4] R_{HP} is an interparticle correlation radius, f_{HP} is an effective volume fraction and Q denotes the particle charge (expressed in electrons). The volume of the $PGMA_{28}$ block, V_{PGMA}, used to fit the SAXS patterns was 5.69 nm^3 and x_{sol} was zero in all cases.

Target copolymer composition	Scattering model[a]	V_{PGlyMA} (nm^3)	*Volume fraction (φ)*	R_s / σ_{Rs} (nm)	R_w / σ_{Rw} (nm)	R_m / σ_{Rm} (nm)	T_m / σ_{Tm} (nm)	R_g (nm)	D_s, D_w or D_v (nm) [c]	D_z (nm)	R_{HP} (nm)	f_{HP}	*Q (e)*
G_{28}-Gly_{25}	S+bkg	4.72	0.0028	3.96 / 0.77	-	-	-	1.68	14.6	18	-	-	-
G_{28}-$(Gly\text{-}cys)_{25}$	GC,HP	10.41 [b]	0.0030	-	-	-	-	7.18	-	14	22.2	0.0610	1.7
G_{28}-Gly_{40}	W	7.55	0.0096	-	4.81 / 0.64	-	-	1.41	15.3	13.4*	-	-	-
G_{28}-$(Gly\text{-}cys)_{40}$	P1 = W	7.55	0.0072	-	6.44 / 1.31	-	-	1.23	17.8	16.4*	-	-	-
	P2 = GC,HP	13.24 [b]	0.0027	-	-	-	-	1.52	-	-	2.46	0.0042	2.0
G_{28}-Gly_{80}	V+Unified level	15.11	0.0080	-	-	15.1 / 2.79	7.46 / 1.38	1.89	45.3	49	-	-	-
G_{28}-$(Gly\text{-}cys)_{80}$-50 °C	V-HP	15.11	0.0072	-	-	22.1 / 4.60	9.74 / 2.29	0.96	57.8	81	91.1	0.2018	2.0

*Worm cross-section not obtainable by DLS. Therefore, the worm cross-section is reported as determined by TEM

[a] Models used were; S = spherical micelle, W = worm, V = vesicle, GC = Gaussian coil, HP = Hayter-Penfold, where P1 and P2, denote different populations modelled.

[b] For the Gaussian coil model, the total molecular volume of the copolymer, V_{mol}, was used in the fitting parameters ($V_{mol} = V_{PGMA} + V_{PGlyMA}$).

[c] When fitted using a spherical micelle model, the overall volume-average sphere diameter, D_s, was calculated using $D_s = 2R_s + 4R_g$. When fitted using a worm model, the volume-average cross-sectional worm diameter, D_w, was calculated using $D_w = 2R_s + 4R_g$. When fitted using a vesicle model, the overall volume-average vesicle diameter, D_v, was calculated using $D_v = 2R_m + T_m + 2R_g$.

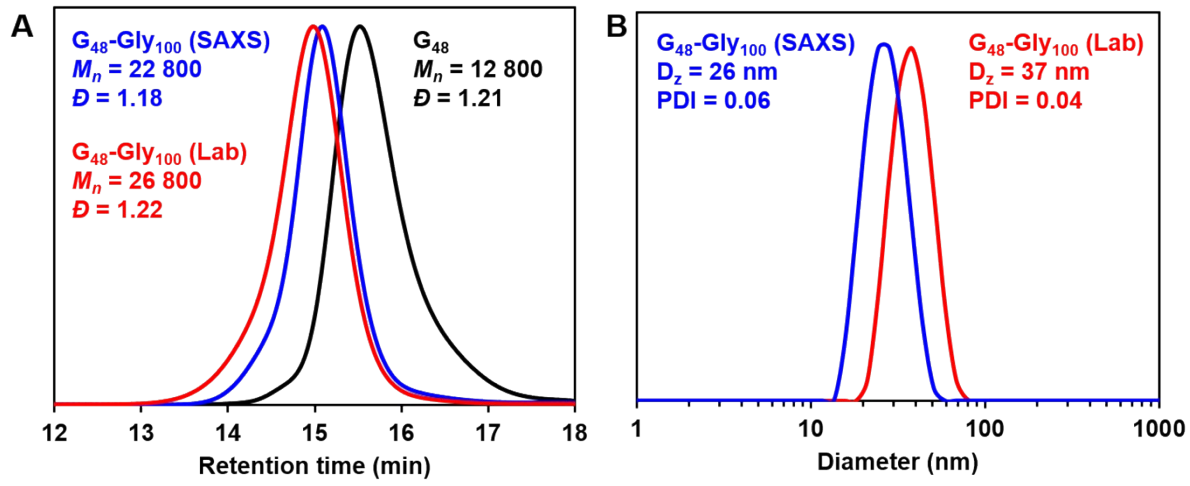

Figure S6. *Postmortem* analysis of the $PGMA_{48}$-$PGlyMA_{100}$ diblock copolymer spheres prepared at 10% w/w solids for both a laboratory-scale synthesis (red data) and the corresponding *in situ* SAXS experiment conducted using a stirrable reaction cell (blue data): (A) overlaid DMF GPC chromatograms, with the $PGMA_{48}$ precursor also shown as a reference (black curve), and (B) overlaid DLS traces.

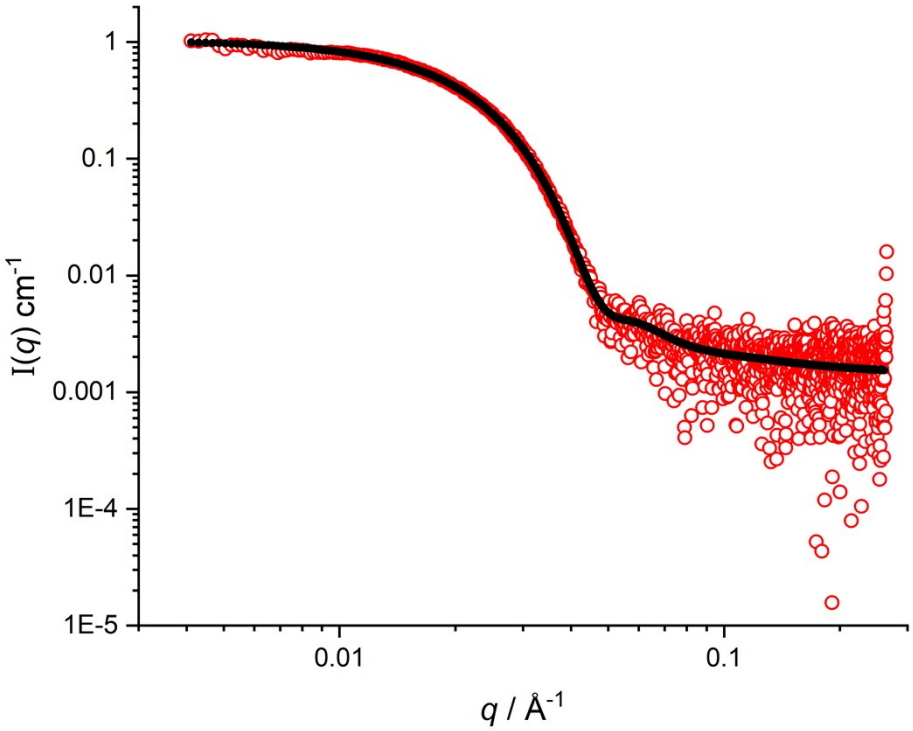

Figure S7. SAXS pattern recorded for a 1.0% w/w aqueous dispersion of $PGMA_{48}$-$PGlyMA_{100}$ originally prepared during the *in situ* SAXS experiment at 10% w/w solids using the bespoke stirrable reaction cell. The experimental data are denoted by open circles while the solid black line indicates the data fit obtained when using a spherical micelle model.

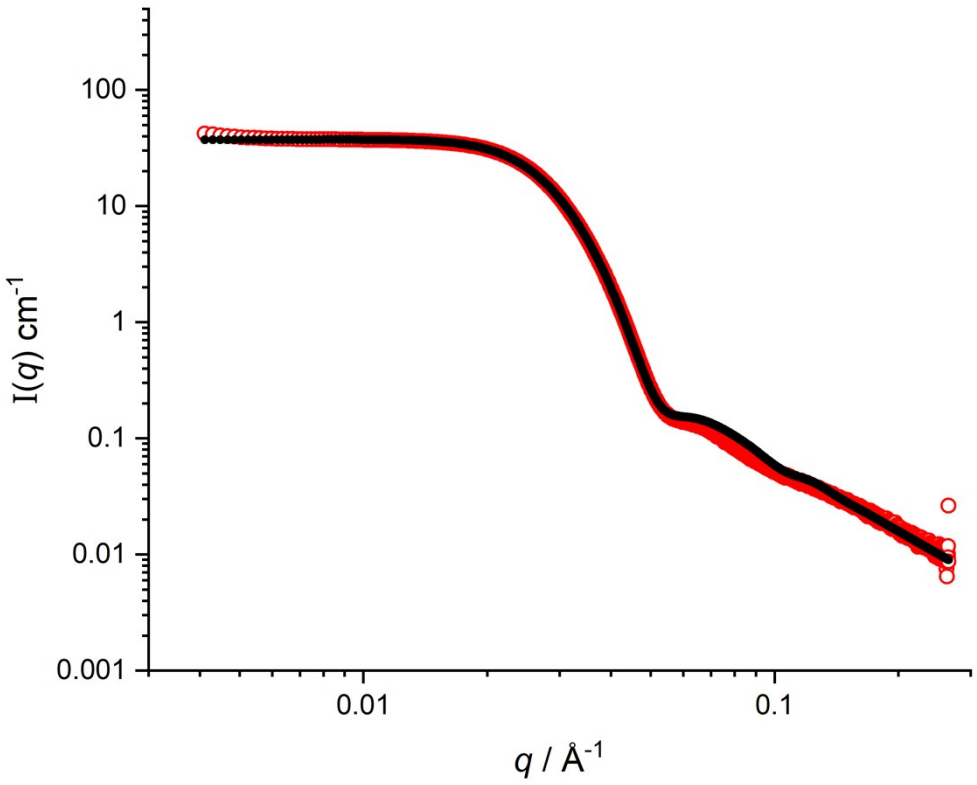

Figure S8. SAXS pattern recorded for the concentrated aqueous dispersion of $PGMA_{48}$-$PGlyMA_{100}$ prepared during the *in situ* SAXS experiment at 10% w/w solids using the bespoke stirrable reaction cell. Data were collected immediately following the polymerization. The experimental data are denoted by red open circles while the solid black line indicates the data fit obtained when using a spherical micelle model with a hard-sphere interaction structure factor incorporated due to the higher concentration of dispersed nano-objects.

Table S6. Structural parameters obtained from SAXS analysis of aqueous dispersions of $PGMA_{48}$-$PGlyMA_{100}$ nano-objects originally prepared at 10% w/w solids during an *in situ* SAXS experiment using a stirrable reaction cell; the final reaction mixture at 10% w/w and also after dilution to 1.0% w/w, fitted using an appropriate spherical micelle model.[1] Representative parameters are denoted as follows: φ is the volume fraction of the nano-object, R_s represents the volume-average radius of the spherical core, σ_{Rs} denotes the standard deviation of R_s. R_g is the mean radius of gyration for the $PGMA_{48}$ stabilizer chains and D_s denotes the overall volume-average diameter of the spheres. From the hard-sphere interaction structure factor[5] based on the Percus-Yevick approximation,[6] R_{PY} is the interaction radius and f_{PY} is the hard-sphere volume fraction. The volumes of the $PGMA_{48}$ block, V_{PGMA}, and $PGlyMA_{100}$ stabilizer block, V_{PGlyMA}, used to fit the SAXS patterns were 9.75 nm^3 and 18.9 nm^3 respectively, and x_{sol} was zero in both cases.

Target copolymer composition	Copolymer concentration for analysis (% w/w)	Scattering model	*Volume fraction (φ)*	R_s / σ_{Rs} (nm)	R_g (nm)	D_s (nm) [a]	R_{PY} (nm)	f_{PY}	*background*
$PGMA_{48}$-$GlyMA_{100}$	1.0	Spherical micelle	0.000341	7.9 / 0.96	1.83	23.1	-	-	0.00141
$PGMA_{48}$-$GlyMA_{100}$	10	Spherical micelle + structure factor	0.0255	7.5 / 0.73	2.08	23.3	10.5	0.095	-

[a] The overall volume-average sphere diameter, D_s, was calculated using $D_s = 2R_s + 4R_g$.

SAXS Models

In general, the intensity of X-rays scattered by a dispersion of nano-objects [as represented by the scattering cross-section per unit sample volume, $\frac{d\Sigma}{d\Omega}(q)$] can be expressed as:

$$\frac{d\Sigma}{d\Omega}(q) = NS(q)\int_0^\infty \dots \int_0^\infty F(q,r_{1,\dots,}r_k)^2\Psi(r_{1,\dots,}r_k)dr_{1,\dots,}dr_k \quad \text{(S1)}$$

where $F(q,r_1,\dots,r_k)$ is the form factor, $r_{1,\dots,}r_k$ is a set of *k* parameters describing the structural morphology, $\Psi(r_{1,\dots,}r_k)$ is the distribution function, *S*(*q*) is the structure factor and *N* is the number density of nano-objects per unit volume expressed as:

$$N = \frac{\varphi}{\int_0^\infty \dots \int_0^\infty V(r_1,\dots,r_k)\Psi(r_1,\dots,r_k)dr_1,\dots,dr_k} \quad \text{(S2)}$$

where $V(r_1,\dots,r_k)$ is the volume of the nano-object and φ is its volume fraction within the dispersion. Unless stated otherwise, it is assumed that *S*(*q*) = 1 at sufficiently low copolymer concentrations (e.g. 1.0% w/w).

Gaussian chain model

Generally, the scattering cross-section per unit sample volume for an individual Gaussian polymer chain can be expressed as:

$$\frac{d\Sigma}{d\Omega}(q) = \varphi(\Delta\xi)^2 V_{mol} F_{mol}(q) \quad \text{(S3)}$$

where V_{mol} is the total molecular volume and $\Delta\xi$ is the excess scattering length density of the copolymer [$\Delta\xi = \xi_{PGMA-PGlyMA} - \xi_{H_2O}$]. The scattering length density of water is ξ_{H_2O} = 9.42 x 10^{10} cm^{-2}, while $\xi_{PGMA-PGlyMA}$ is the mean scattering length density of the copolymer, which is calculated as:

$$\xi_{PGMA-PGlyMA} = \xi_{PGMA}v_{PGMA} + \xi_{PGlyMA}v_{PGlyMA} \quad \text{(S4)}$$

where v_{PGMA} and v_{PGlyMA} represent the respective volume fractions of the PGMA and PGlyMA blocks in the copolymer, and ξ_{PGMA} and ξ_{PGlyMA} are the respective scattering length densities of PGMA (11.94 x 10^{10} cm^{-2}) and PGlyMA (11.34 x 10^{10} cm^{-2}). The respective volume fractions, v, were calculated using:

$$v = \frac{V}{V_{mol}} \tag{S5}$$

where V is the volume of the PGMA block (V_{PGMA}) or PGlyMA block (V_{PGlyMA}) respectively, and V_{mol} is the total molecular volume of the copolymer ($V_{mol} = V_{PGMA} + V_{PGlyMA}$). The volume of each block was obtained using $V = \frac{M_{n,pol}}{N_A \rho}$, where the solid-state density of a PGlyMA homopolymer was determined by helium pycnometry (ρ_{PGlyMA} = 1.25 g cm^{-3}) and the density of PGMA, ρ_{PGMA} was taken to be 1.31 g cm^{-3}.[7] $M_{n,pol}$ corresponds to the number-average molecular weight of each block as determined by end-group analysis using ^{1}H NMR spectroscopy.

The generalized form factor for a Gaussian polymer chain is given by[3]:

$$F_{mol}(q) = \left[\frac{1}{\nu U^{1/(2\nu)}}\gamma\left(\frac{1}{2\nu}, U\right) - \frac{1}{\nu U^{1/\nu}}\left(\frac{1}{\nu}, U\right)\right] \tag{S6}$$

where the lower incomplete gamma function is $\gamma(s,x) = \int_0^x t^{s-1}\exp(-t)dt$ and U is the modified variable:

$$U = (2\nu + 1)(2\nu + 2)\frac{q^2 R_{g,cop}^{\ 2}}{6} \tag{S7}$$

Here, ν is the extended volume parameter (here theta conditions are assumed and thus v is fixed at 0.50) and $R_{g,cop}$ is the radius of gyration of the copolymer chain.

Spherical micelle model

The spherical micelle form factor for Equation S1 is given by[1]:

$$F_{s_{mic}}(q) = N_s{}^2\beta_s{}^2A_s{}^2(q,R_s) + N_s\beta_c{}^2F_c(q,R_g) + N_s(N_s-1)\beta_c{}^2A_c{}^2(q) + 2N_s{}^2\beta_s\beta_cA_s(q \quad \text{(S8)}$$

where R_s is the volume-average sphere core radius and R_g is the radius of gyration of the coronal steric stabilizer block (in this case, $PGMA_{28}$). The X-ray scattering length contrasts for the core and corona blocks are given by $\beta_s = V_s(\xi_s - \xi_{sol})$ and $\beta_c = V_c(\xi_c - \xi_{sol})$ respectively. Here, ξ_s, ξ_c and ξ_{sol} are the X-ray scattering length densities of the core block (ξ_{PGlyMA}= 11.34 x 10^{10} cm^{-2}), corona block (ξ_{PGMA}= 11.94 x 10^{10} cm^{-2}) and solvent (water) (ξ_{sol}= 9.42 x 10^{10} cm^{-2}), respectively. V_s and V_c are the volumes of the core block (V_{PGlyMA}) and the corona block (V_{PGMA}) respectively. These volumes were obtained as described previously for the Gaussian coil model. The sphere form factor amplitude is used for the amplitude of the core self-term:

$$A_c(q,R_s) = \Phi(qR_s)exp\left(-\frac{q^2\sigma^2}{2}\right) \quad \text{(S9)}$$

where $\Phi(qR_s) = \frac{3\left[\sin(qR_s) - qR_s\cos(qR_s)\right]}{(qR_s)^3}$. A sigmoidal interface between the two blocks was assumed for the spherical micelle form factor (Equation S8). This is described by the exponent term with a width σ accounting for a decaying scattering length density at the micellar interface. This σ value was fixed at 2.2 during fitting.

The form factor amplitude of the spherical micelle corona is:

$$A_c(q) = \frac{\int_{R_s}^{R_s+2s} \mu_c(r)\frac{\sin(qr)}{qr}r^2dr}{\int_{R_s}^{R_s+2s} \mu_c(r)r^2dr}exp\left(-\frac{q^2\sigma^2}{2}\right) \quad \text{(S10)}$$

The radial profile, $\mu_c(r)$, can be expressed by a linear combination of two cubic b splines, with two fitting parameters s and a corresponding to the width of the profile and the weight coefficient respectively. This information can be found elsewhere,[8,9] as can the approximate integrated form of Equation S10. The self-correlation term for the coronal block is given by the Debye function:

$$F_c(q,R_g) = \frac{2\left[\exp\left(-q^2R_g{}^2\right) - 1 + q^2R_g{}^2\right]}{q^4R_g{}^4} \quad \text{(S11)}$$

where R_g is the radius of gyration of the PGMA coronal block. The aggregation number, N_s, of the spherical micelle is given by:

$$N_s = (1 - x_{sol})\frac{\frac{4}{3}\pi {R_s}^3}{V_s} \quad \text{(S12)}$$

where x_{sol} is the volume fraction of solvent within the PGlyMA micelle cores.

An effective structure factor proposed for interacting spherical micelles[5] has been used in Equation S1:

$$S_s(q) = 1 + \frac{{A_s}_{mic}^{av}(q)^2\left[S_{PY}(q,R_{PY},f_{PY}) - 1\right]}{{F_s}_{mic}(q)} \quad \text{(S13)}$$

Herein the form factor of the average radial scattering length density distribution of micelles is used such that ${A_s}_{mic}^{av}(q) = N_s\left[\beta_s A_s(q,R_s) + \beta_c A_c(q)\right]$ and $S_{PY}(q,R_{PY},f_{PY})$ is a structure factor based on the Percus-Yevick approximation for hard spheres,[6] where R_{PY} is the interaction radius and f_{PY} is the hard-sphere volume fraction. A polydispersity for one parameter (R_s) is assumed for the micelle model, which is described by a Gaussian distribution. Thus, the polydispersity function in Equation S1 can be represented as:

$$\Psi(r_1) = \frac{1}{\sqrt{2\pi {\sigma_{Rs}}^2}} exp\left(-\frac{(r_1 - R_s)^2}{2{\sigma_{Rs}}^2}\right) \quad \text{(S14)}$$

where σ_{Rs} is the standard deviation for R_s. In accordance with Equation S2, the number density per unit volume for the micelle model is expressed as:

$$N = \frac{\varphi}{\int_0^\infty V(r_1)\Psi(r_1)dr_1} \quad \text{(S15)}$$

where φ is the total volume fraction of copolymer in the spherical micelles and $V(r_1)$ is the total volume of copolymer within a spherical micelle $\left[V(r_1) = (V_s + V_c)N_s(r_1)\right]$.

Worm-like micelle model

The worm-like micelle form factor for Equation S1 is given by:

$$F_{w\_mic}(q) = N_w{}^2\beta_s{}^2F_{sw}(q) + N_w\beta_c{}^2F_c(q,R_g) + N_w(N_w-1)\beta_c{}^2S_{cc}(q) + 2N_w{}^2\beta_s\beta_cS_{sc}(\quad \text{(S16)}$$

where all the parameters are the same as those described in the spherical micelle model (Equation S8), unless stated otherwise.

The self-correlation term for the worm core cross-sectional volume-average radius R_w is:

$$F_{sw}(q) = F_{worm}(q,L_w,b_w)A_{CSworm}{}^2(q,R_{sw}) \quad \text{(S17)}$$

where

$$A_{CSworm}{}^2(q,R_{sw}) = \left[2\frac{J_1(qR_{sw})}{qR_{sw}}\right]^2 \quad \text{(S18)}$$

and J_1 is the first-order Bessel function of the first kind, and a form factor $F_{worm}(q,L_w,b_w)$ for self-avoiding semi-flexible chains represents the worm-like micelles, where b_w is the Kuhn length and L_w is the mean contour length. A complete expression for the chain form factor can be found elsewhere.[10]

The mean aggregation number of the worm-like micelle, N_w, is given by:

$$N_w = (1-x_{sol})\frac{\pi R_{sw}{}^2L_w}{V_s} \quad \text{(S19)}$$

where x_{sol} is the volume fraction of solvent within the worm-like micelle cores. The possible presence of semi-spherical caps at both ends of each worm is neglected in this form factor.

A polydispersity for one parameter (R_w) is assumed for the micelle model, which is described by a Gaussian distribution. Thus, the polydispersity function in Equation S1 can be represented as:

$$\Psi(r_1) = \frac{1}{\sqrt{2\pi\sigma_{R_w}{}^2}}exp\left(-\frac{(r_1-R_w)^2}{2\sigma_{R_w}{}^2}\right) \quad \text{(S20)}$$

where σ_{R_w} is the standard deviation for R_w. In accordance with Equation S2, the number density per unit volume for the worm-like micelle model is expressed as:

$$N = \frac{\varphi}{\int_0^\infty V(r_1)\Psi(r_1)dr_1} \quad \text{(S21)}$$

where φ is the total volume fraction of copolymer in the worm-like micelles and $V(r_1)$ is the total volume of copolymer in a worm-like micelle $[V(r_1) = (V_s + V_c)N_w(r_1)]$.

Vesicle model

The vesicle form factor in Equation S1 is expressed as[2]:

$$F_{ves}(q) = N_v{}^2\beta_m{}^2A_m{}^2(q) + N_v\beta_{vc}{}^2F_c(q,R_g) + N_v(N_v-1)\beta_{vc}{}^2A_{vc}{}^2(q) + 2N_v{}^2\beta_m\beta_{vc}A \quad \text{(S22)}$$

where all the parameters are the same as in the spherical micelle model (see Equation S8) unless stated otherwise.

The amplitude of the membrane self-term is:

$$A_m(q) = \frac{V_{out}\varphi(qR_{out}) - V_{in}\varphi(qR_{in})}{V_{out} - V_{in}} exp\left(-\frac{q^2\sigma_{in}{}^2}{2}\right) \quad \text{(S23)}$$

where $R_{in} = R_m - \frac{1}{2}T_m$ is the inner radius of the membrane, $R_{out} = R_m + \frac{1}{2}T_m$ is the outer radius of the membrane (R_m is the radius from the centre of the vesicle to the centre of the membrane), $V_{in} = \frac{4}{3}\pi R_{in}{}^3$ and $V_{out} = \frac{4}{3}\pi R_{out}{}^3$. It should be noted that Equation S22 differs subtly from the original work in which it was first described.[2] The exponent term in Equation S23 represents a sigmoidal interface between the blocks, with a width σ_{in} accounting for a decaying scattering length density at the membrane surface. The value of σ_{in} was fixed at 2.5 during fitting. The mean vesicle aggregation number, N_v, is given by:

$$N_v = (1 - x_{sol})\frac{V_{out} - V_{in}}{V_m} \quad \text{(S24)}$$

where x_{sol} is the volume fraction of solvent within the vesicle membrane. Assuming that there is no penetration of the hydrophilic coronal blocks into the hydrophobic membrane, the amplitude of the vesicle corona self-term is expressed as:

$$A_{vc}(q) = \Psi(qR_g)\frac{1}{2}\left[\frac{sin[q(R_{out} + R_g)]}{q(R_{out} + R_g)} + \frac{sin[q(R_{in} - R_g)]}{q(R_{in} - R_g)}\right] \quad \text{(S25)}$$

where the term outside the square brackets is the factor amplitude of the corona block polymer chain such that:

$$\Psi(qR_g) = \frac{1 - exp(-qR_g)}{(qR_g)^2} \quad \text{(S26)}$$

For the vesicle model, it was assumed that two parameters are polydisperse: the radius from the centre of the vesicles to the centre of the membrane and the membrane thickness (denoted R_m and T_m, respectively). Each parameter is considered to have a Gaussian distribution of values, so the polydispersity function in Equation S1 can be expressed in each case as:

$$\Psi(r_1 r_2) = \frac{1}{\sqrt{2\pi\sigma_{Rs}{}^2}}exp\left(-\frac{(r_1 - R_m)^2}{2\sigma_{Rm}{}^2}\right)\frac{1}{\sqrt{2\pi\sigma_{Tm}{}^2}}exp\left(-\frac{(r_1 - T_m)^2}{2\sigma_{Tm}{}^2}\right) \quad \text{(S27)}$$

where σ_{Rm} and σ_{Tm} are the standard deviations for R_m and T_m, respectively. Following Equation S2, the number density per unit volume for the vesicle model is expressed as:

$$N = \frac{\varphi}{\int_0^\infty \int_0^\infty V(r_1,r_2)\Psi(r_1,r_2)dr_1 dr_2} \quad \text{(S28)}$$

where φ is the total volume fraction of copolymer in the vesicles and $V(r_1,r_2)$ is the total volume of copolymers in a vesicle $[V(r_1,r_2) = (V_m + V_{vc})N_v(r_1,r_2)]$.

Hayter-Penfold Approximation

An effective structure factor expression for interactions between charged spheres in a dielectric medium[4,11] was used in Equation S1:

$$S(q) = S_{HP}(q, R_{HP}, f_{HP}, M, T, \varepsilon, Q) \quad \text{(S29)}$$

where R_{HP} is an interparticle correlation radius, f_{HP} is an effective volume fraction, M is the ionic strength of the aqueous solution, T is the absolute temperature, ε is the solvent dielectric constant, and Q is the particle charge expressed in electrons.

Programming tools within the Irena SAS Igor Pro macros[12] were used to implement the scattering models.

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