Supporting Information for:

Synthesis of Diblock Copolymer Spheres, Worms and Vesicles *via* RAFT Aqueous Emulsion Polymerization of Hydroxybutyl Methacrylate

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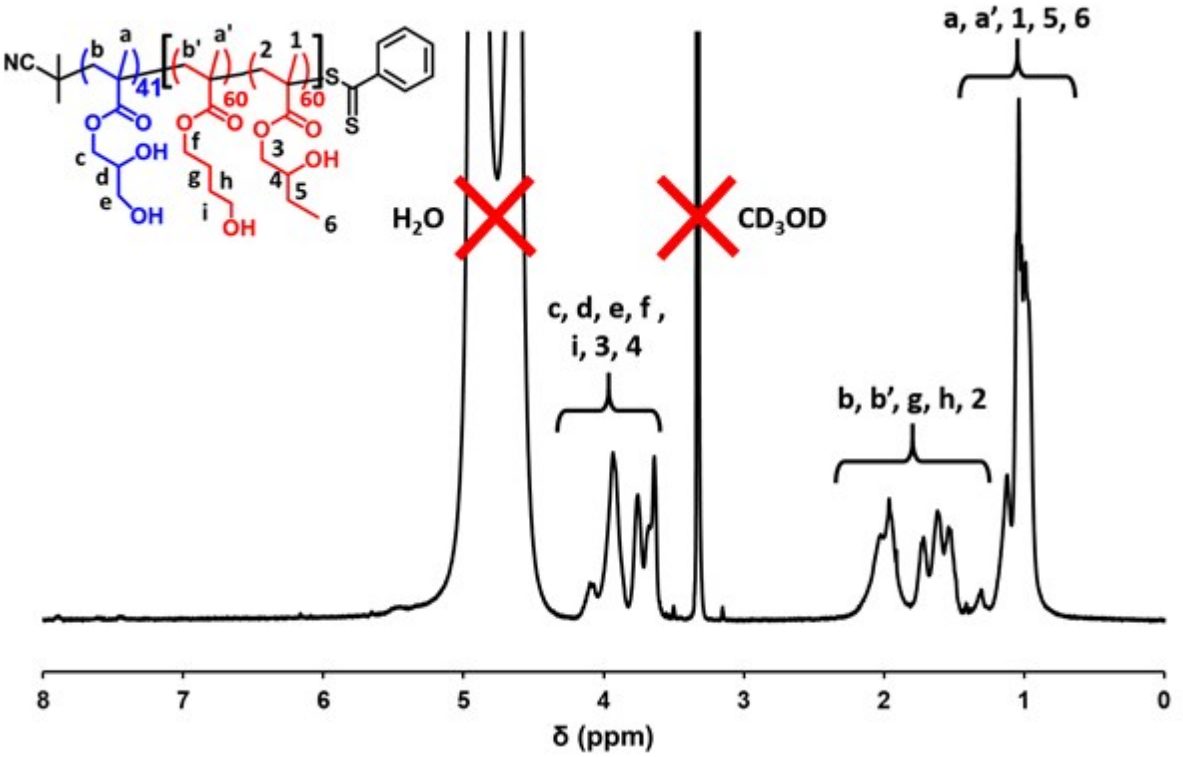


Figure S1. Assigned ^{1}H NMR spectrum (CD_3OD) recorded for a $PGMA_{48}$-$PHBMA_{120}$ diblock copolymer after reaching more than 99 % conversion within 120 min at 50°C. Both isomeric forms of the HBMA monomer, which are present in a 1:1 molar ratio, are depicted in the chemical structure.

Table S1. Summary of target DPs, monomer conversions and molecular weight data for the synthesis of $PGMA_{41}$-$PHBMA_x$ diblock copolymer nano-objects at 5% w/w solids *via* RAFT aqueous emulsion polymerization of HBMA at 50 °C using a $PGMA_{41}$ precursor. (S = spheres, W = worms, V = vesicles).

Copolymer concentration / % w/w	Target HBMA DP	Conversion / %	DMF GPC M_n / g mol^{-1}	M_w/M_n	Morphology
5	10	>99	15 400	1.14	C
5	20	>99	17 000	1.14	C
5	30	>99	18 200	1.14	S
5	40	>99	19 000	1.19	S
5	50	>99	21 000	1.19	S
5	60	>99	23 100	1.19	S
5	70	>99	24 900	1.25	S
5	75	>99	26 700	1.24	S
5	80	>99	30 700	1.25	S + W + V
5	85	>99	33 400	1.28	S + W + V
5	90	>99	33 500	1.31	S + W + V
5	100	>99	34 500	1.33	S + W + V
5	110	>99	40 100	1.36	V

Table S2. Summary of target DPs, monomer conversions and molecular weight data for the synthesis of $PGMA_{41}$-$PHBMA_x$ diblock copolymer nano-objects at 10% w/w solids *via* RAFT aqueous emulsion polymerization of HBMA at 50 °C using a $PGMA_{41}$ precursor. (S = spheres, W = worms, V = vesicles).

Copolymer concentration / % w/w	Target HBMA DP	Conversion / %	DMF GPC M_n / g mol^{-1}	M_w/M_n	Morphology
10	10	>99	15 500	1.15	C
10	20	>99	16 300	1.15	C
10	30	>99	17 100	1.18	S
10	35	>99	19 500	1.18	S + W
10	40	>99	20 000	1.18	S + W
10	50	>99	21 300	1.21	S + W
10	55	>99	22 400	1.24	S + W
10	60	>99	26 200	1.24	S + W
10	65	>99	27 800	1.25	W
10	70	>99	28 600	1.24	W
10	75	>99	29 700	1.28	W + V
10	80	>99	31 300	1.29	W + V
10	85	>99	32 900	1.29	W + V
10	90	>99	33 600	1.36	W + V
10	95	>99	34 100	1.30	W + V
10	100	>99	36 100	1.34	V
10	110	>99	40 500	1.37	V

Table S3. Summary of target DPs, monomer conversions and molecular weight data for the synthesis of $PGMA_{41}$-$PHBMA_x$ diblock copolymer nano-objects at 15% w/w solids *via* RAFT aqueous emulsion polymerization of HBMA at 50 °C using a $PGMA_{41}$ precursor. (S = spheres, W = worms, V = vesicles).

Copolymer concentration / % w/w	Target HBMA DP	Conversion / %	DMF GPC M_n / g mol^{-1}	M_w/M_n	Morphology
15	20	>99	15 800	1.17	C
15	30	>99	16 900	1.17	S
15	35	>99	18 100	1.17	S + W
15	40	>99	22 300	1.20	S + W
15	45	>99	24 600	1.20	W
15	50	>99	25 000	1.19	W
15	60	>99	27 100	1.25	W
15	65	>99	26 600	1.26	W + V
15	70	>99	28 900	1.26	W + V
15	80	>99	33 100	1.26	W + V
15	85	>99	33 300	1.27	V
15	90	>99	34 800	1.32	V
15	100	>99	36 200	1.34	V

Table S4. Summary of target DPs, monomer conversions and molecular weight data for the synthesis of $PGMA_{41}$-$PHBMA_x$ diblock copolymer nano-objects at 20% w/w solids *via* RAFT aqueous emulsion polymerization of HBMA at 50 °C using a $PGMA_{41}$ precursor. (S = spheres, W = worms, V = vesicles).

Copolymer concentration / % w/w	Target HBMA DP	Conversion / %	DMF GPC M_n / g mol^{-1}	M_w/M_n	Morphology
20	10	>99	14 700	1.16	C
20	20	>99	15 700	1.16	C
20	30	>99	17 100	1.16	S
20	35	>99	18 100	1.18	S + W
20	40	>99	21 200	1.19	S + W
20	45	>99	23 300	1.22	W
20	50	>99	25 200	1.22	W
20	55	>99	25 800	1.25	W
20	60	>99	26 100	1.24	W + V
20	70	>99	27 600	1.24	W + V
20	80	>99	29 300	1.28	W + V
20	85	>99	33 100	1.28	V
20	90	>99	34 200	1.32	V
20	100	>99	37 100	1.36	V

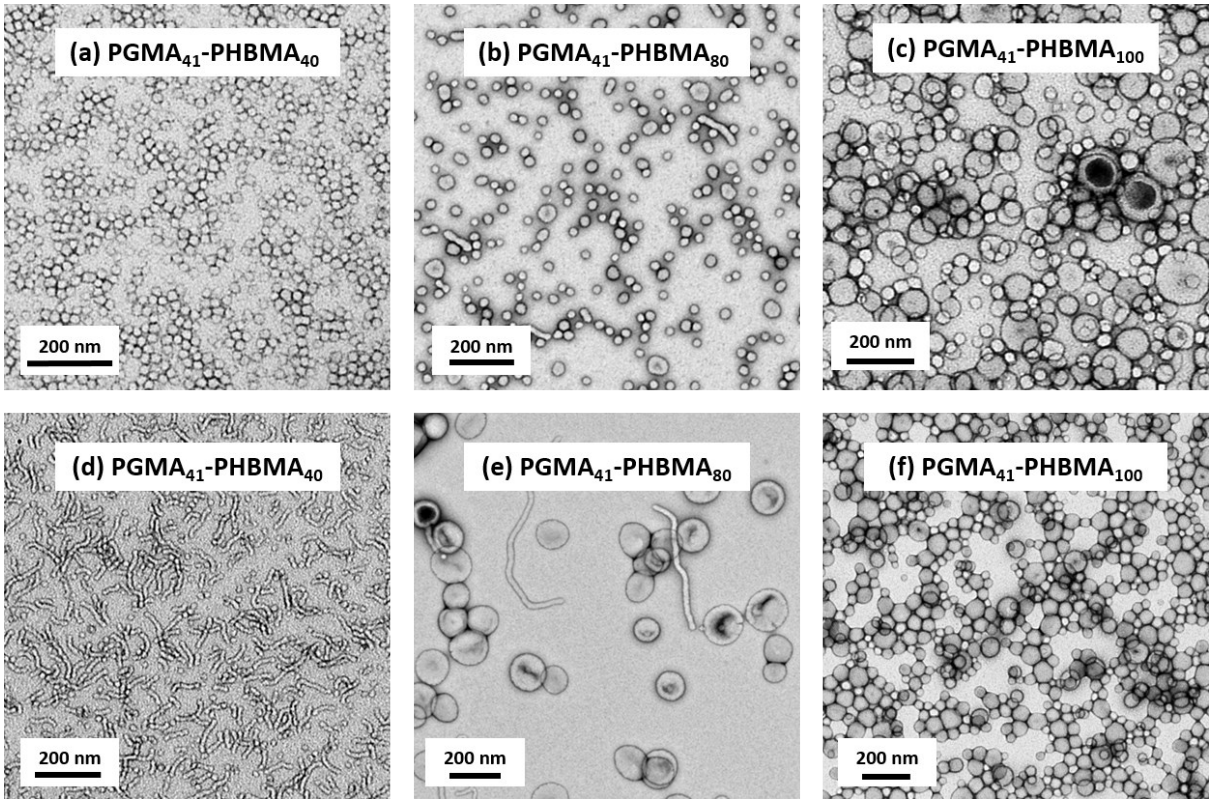


Figure S2. Representative TEM images obtained for various diblock copolymer nano-objects prepared via RAFT aqueous emulsion polymerization of HBMA at 50 °C: (a) $PGMA_{41}$-$PHBMA_{40}$ spheres synthesized at 5% w/w, (b) $PGMA_{41}$-$PHBMA_{80}$ spheres, worms and vesicles synthesized at 5% w/w, (c) $PGMA_{41}$-$PHBMA_{100}$ vesicles synthesized at 5% w/w, (d) $PGMA_{41}$-$PHBMA_{40}$ spheres and worms synthesized at 20% w/w, (e) $PGMA_{41}$-$PHBMA_{80}$ vesicles (plus a few worms) synthesized at 20% w/w and (f) $PGMA_{41}$-$PHBMA_{100}$ vesicles synthesized at 20% w/w.

Table S5. Structural parameters obtained from SAXS analysis of four 1.0% w/w aqueous dispersions of $PGMA_{41}$-$PHBMA_x$ diblock copolymer nanoparticles using sphere, worm or vesicle models, where appropriate. Representative parameters are denoted as follows: V_{PHBMA} is the volume of the PHBMA block, φ is the volume fraction of copolymers forming nanoparticles, R_s represents the mean sphere core volume-average radius, R_w is the mean worm micelle radius, R_m is the mean radius from the centre of the vesicle to the centre of the membrane, $_m$ is the mean vesicle membrane thickness (i.e., the hydrophobic part of the membrane). Here σ_x denotes the standard deviation of the relevant parameter (x = R_s, R_w, R_m or T_m). R_g represents the radius of gyration of the $PGMA_{41}$ stabilizer block, D_s represents the sphere volume-average diameter, D_w is the worm cross-sectional volume-average diameter and D_v represents the vesicle volume-average diameter. x_{sol} is the volume fraction of water within the hydrophobic core/membrane and N_{agg} is the mean aggregation number for each type of nano-object. The volume of the PGMA block, V_{PGMA}, used for fitting these SAXS patterns was 8.23 nm^3 in all cases.

Diblock Copolymer Composition	Model used for fitting [a]	V_{PHBMA} / nm^3	φ [b]	R_s / σ_{Rs} / nm or 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]	x_{sol}	N_{agg} [d]
$PGMA_{41}$-$PHBMA_{30}$	S	6.57	0.0004	6.1 / 0.66	-	-	2.20	21.0	0.0008	145
$PGMA_{41}$-$PHBMA_{70}$	W	15.85	0.0010	7.9 / 0.80	-	-	1.98	19.8	0.0003	3828
$PGMA_{41}$-$PHBMA_{100}$	V	22.00	0.0012	-	43.7 / 7.6	13.8 / 2.0	1.76	108.2	0.03	14429
$PGMA_{41}$-$PHBMA_{120}$	V	25.15	0.0046	-	27.3 / 6.2	12.2 / 2.3	2.09	75.2	0.01	4727

[a] Where S denotes a spherical micelle model, W denotes a worm model and V denotes a vesicle model.
[b] When fitted using a spherical micelle model, the sphere volume-average diameter, D_s, was calculated using $D_s = 2R_s + 4R_g$. When fitted using a worm model, the worm cross-sectional volume-average diameter, D_w, was calculated using $D_w = 2R_s + 4R_g$. When fitted using a vesicle model, the vesicle volume-average diameter, D_v, was calculated using $D_v = 2R_m + T_m + 4R_g$.
[c] N_{agg} was calculated using Equation S7 for spheres, Equation S15 for worms, and Equation S18 for vesicles (see following section on SAXS models).

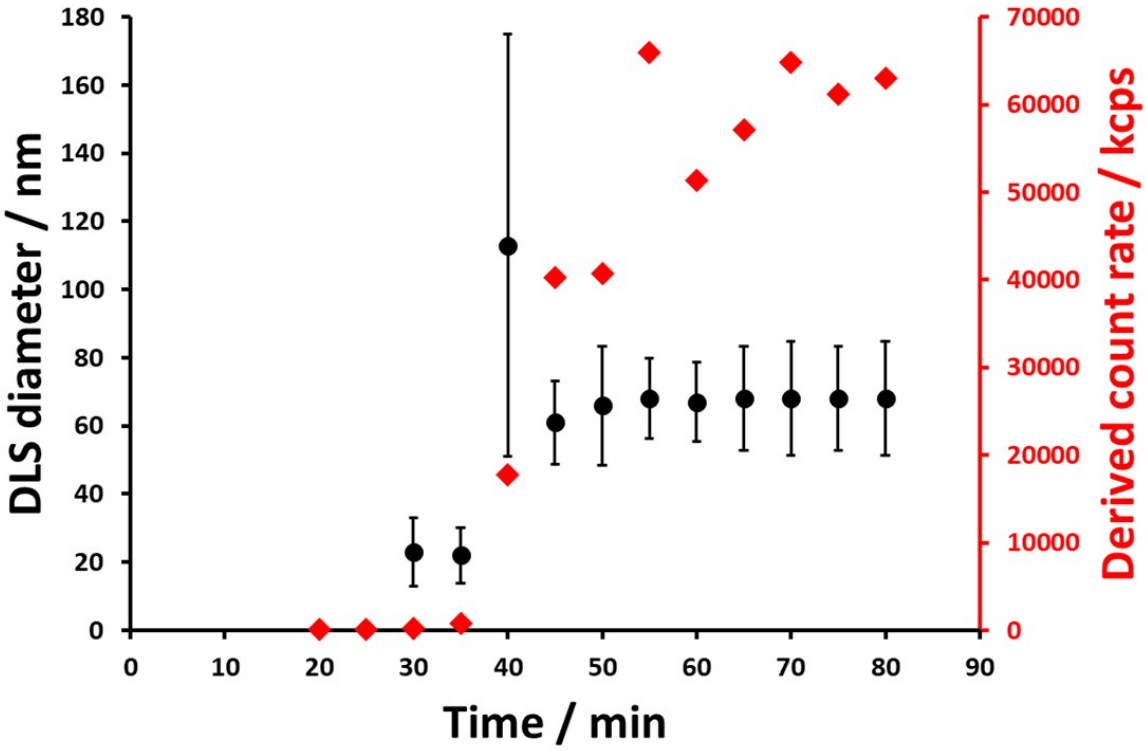
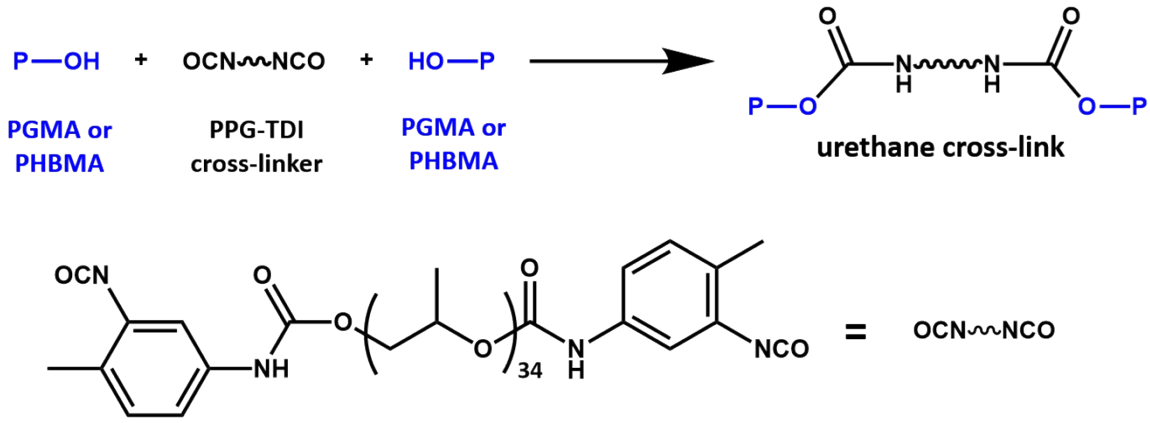


Figure S3. DLS studies of the evolution in particle diameter during the synthesis of $PGMA_{41}$-$PHBMA_{120}$ vesicles via RAFT aqueous emulsion polymerization targeting 10% w/w solids. DLS diameter data are indicated by black circles while the corresponding derived count rate data are indicated by red diamonds.



Tolylene 2,4-diisocyanate-terminated poly(propylene glycol) (PPG-TDI)

Figure S4. Chemical structure of the oil-soluble polymeric cross-linker (PPG-TDI) used in this study (top). Schematic representation of the reaction between the terminal isocyanate groups on this PPD-TDI crosslinker with the pendent hydroxyl groups (P–OH) on either the PGMA or PHBMA chains to form urethane cross-links

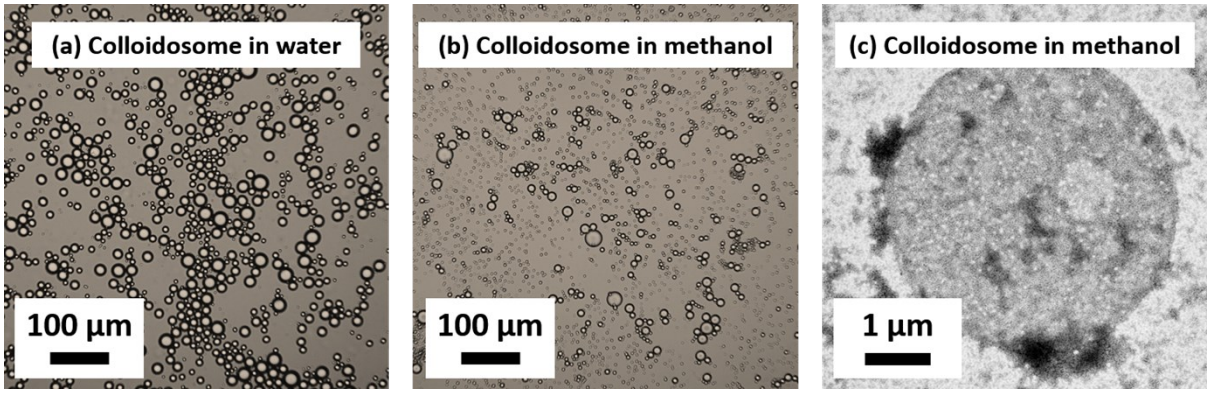


Figure S5. Representative optical microscopy images recorded for PPG-TDI cross-linked colloidosomes prepared via high-shear homogenization (12 000 rpm for 2 min at 20 °C) of a 0.25% w/w aqueous dispersion of $PGMA_{41}$-$PHBMA_{110}$ vesicles with *n*-dodecane followed by dilution using either (a) water or (b) methanol. (c) TEM image recorded for a single colloidosome after dilution using methanol.

SAXS models

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

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

Equation S1

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

$$N = \frac{\varphi}{\int_0^\infty \ldots \int_0^\infty V(r_{1,\ldots,}r_k)\Psi(r_{1,\ldots,}r_k) dr_{1,\ldots,}dr_k}$$

Equation S2

where $V(r_{1,\ldots,}r_k)$ is the volume of the nanoparticle and φ is the volume fraction of nanoparticles.

Given the relatively low nanoparticle concentration, the structure factor term in Equation S1 was assumed to be unity [$S(q) = 1$].

Spherical micelle model

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

$$F_{s_{mic}}(q,r_1) = N_s^2(r_1)\beta_s^2 A_s^2(q,r_1) + N_s(r_1)\beta_c^2 F_c(q,R_g) + N_s(r_1)[N_s(r_1)-1]\beta_c^2 A_c^2(q) + 2N_s(r_1)A_c(q)$$

Equation S3

where r_1 is the radius of the sphere core and R_g is the radius of gyration of the coronal steric stabilizer block (in this case, $PGMA_{41}$). 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_{PHBMA}= 10.61 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_{PHBMA}) and the corona block (V_{PGMA}), respectively. These volumes were calculated using $V = \frac{M_{n,pol}}{N_A \rho}$ where the mass density of a PHBMA homopolymer was previously reported (ρ_{PHBMA} = 1.15 g cm^{-3})[2] and the density of PGMA was taken to be 1.31 g cm^{-3}.[3] $M_{n,pol}$ corresponds to the number-average molecular weight of the diblock copolymer chains determined by ^{1}H NMR spectroscopy. The sphere form factor amplitude is used for the amplitude of the core self-term:

$$A_c(q,r_1) = \Phi(qr_1)exp\left(-\frac{q^2\sigma^2}{2}\right)$$

Equation S4

where $\Phi(qr_1) = \frac{3[\sin(qr_1) - qr_1\cos(qr_1)]}{(qr_1)^3}$. A sigmoidal interface between the two blocks was assumed for the spherical micelle form factor (Equation S4). 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 0.25 nm during fitting.

The form factor amplitude of the spherical micelle corona is:

$$A_c(q) = \frac{\int_{r_1}^{r_1+2s} \mu_c(r)\frac{\sin(qr)}{qr}r^2 dr}{\int_{r_1}^{r_1+2s} \mu_c(r)r^2 dr} exp\left(-\frac{q^2\sigma^2}{2}\right)$$

Equation S5

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,[4-5] as can the approximate integrated form of Equation S5. The self-correlation term for the coronal block is given by the Debye function:

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

Equation S6

The aggregation number, N_s, of the spherical micelle is given by:

$$N_s(r_1) = (1 - x_{sol})\frac{\frac{4}{3}\pi {r_1}^3}{V_s}$$

Equation S7

where x_{sol} is the volume fraction of solvent within the PHBMA micelle core.

A polydispersity for one parameter (r_1) is assumed for the micelle model, which is described by a Gaussian distribution. Thus, the polydispersity function in Equation S1 can be represented as:

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

Equation S8

where R_s is the mean spherical micelle core radius and σ_{R_s} is its standard deviation. In accordance with Equation S2, the number density per unit volume for the micelle model is expressed as:

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

Equation S9

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

Worm-like micelle model

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

$$F_{w_{mic}}(q,r_1) = {N_w}^2(r_1){\beta_s}^2 F_w(q,r_1) + N_w(r_1){\beta_c}^2 F_c(q,R_g) + N_w(r_1)[N_w(r_1) - 1]{\beta_c}^2 S_{cc}(q) + 2I$$
$$(q,r_1)$$

Equation S10

where all the parameters are the same as in the spherical micelles model (Equation S3) unless stated otherwise.

The self-correlation term for the worm core with cross-sectional radius r_1 is:

$$F_w(q,r_1) = F_{worm}(q,L_w,b_w){A_{csworm}}^2(q,r_1)$$

Equation S11

where

$$A_{csworm}{}^2(q,r_1) = \left[2\frac{J_1(qr_1)}{qr_1}\right]^2$$

Equation S12

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.[6]

The mean aggregation number of the worm-like micelle, $N_w(r_1)$, is given by:

$$N_w(r_1) = (1 - x_{sol})\frac{\pi r_1{}^2 L_w}{V_s}$$

Equation S13

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

A polydispersity for one parameter (r_1) is assumed for the micelle model, which is described by a Gaussian distribution. Thus, the polydispersity function in Equation S1 can be represented as:

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

Equation S14

where R_w is the volume-average cross-sectional radius and σ_{R_w} is its standard deviation. In accordance with Equation S2, the number density per unit volume for the micelle model is expressed as:

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

Equation S15

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 $\left[V(r_1) = (V_s + V_c)N_w(r_1)\right]$.

Vesicle model

The vesicle form factor in Equation S1 is expressed as:[7]

$$F_{ves}(q,r_1,r_2) = N_v{}^2(r_1,r_2)\beta_s{}^2 A_m{}^2(q,r_1,r_2) + N_v(r_1,r_2)\beta_c{}^2 F_c(q,R_g) + N_v(r_1,r_2)[N_v(r_1,r_2) - 1]\beta$$
$$N_v{}^2(r_1,r_2)\beta_s\beta_c A_m(q,r_1,r_2)A_{vc}(q)$$

Equation S16

where all the parameters are the same as in the spherical micelles model (Equation S3) unless stated otherwise.

The amplitude of the membrane self-term is:

$$A_m(q,r_1,r_2) = \frac{V_{out}\Phi(qR_{out}) - V_{in}\Phi(qR_{in})}{V_{out} - V_{in}} exp\left(-\frac{q^2{\sigma_{in}}^2}{2}\right)$$

Equation S17

where $R_{in} = r_1 - \frac{1}{2}r_2$ is the inner radius of the membrane and $R_{out} = r_1 + \frac{1}{2}r_2$ is the outer radius of the membrane (r_1 is the radius from the centre of the vesicle to the centre of the membrane and r_2 is the membrane thickness), and $V_{in} = \frac{4}{3}\pi{R_{in}}^3$ and $V_{out} = \frac{4}{3}\pi{R_{out}}^3$. It should be noted that Equation S17 differs from the original work in which they were first described.[7] The exponent term in Equation S18 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 0.25 nm during fitting. The mean vesicle aggregation number, $N_v(r_1,r_2)$, is given by:

$$N_v(r_1,r_2) = (1 - x_{sol})\frac{V_{out} - V_{in}}{V_s}$$

Equation S18

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:

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

Equation S19

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

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

Equation S20

The R_g values of the PGMA coronal block from all data fitting (1.76-2.20 nm) are comparable to the estimated value. The latter can be calculated from the total contour length of the $PGMA_{41}$ block, $L_{PGMA_{41}}$= 41 x 0.255 nm = 10.45 nm (since the projected contour length per GMA monomer repeat

unit is defined by two carbon bonds in an all-trans conformation, or 0.255 nm) and the Kuhn length of 1.53 nm [based on the known literature value for poly(methyl methacrylate)] result in an approximate R_g of (10.45 x 1.53/6)$^{1/2}$ = 1.63 nm.

For the vesicle model, it was assumed that two parameters are polydisperse: the radius from the centre of the vesicle to the centre of the membrane and the membrane thickness (r_1 and r_2, respectively). Each parameter is considered to have a Gaussian distribution of values, hence the polydispersity function in Equation S1 can be expressed in each case as:

$$\frac{}{\sqrt{}}\left(-\right)\frac{}{\sqrt{}}\left(-\right)$$

Equation S21

where R_m is the mean radius from the centre of the vesicle to the centre of the membrane and T_m is the mean membrane thickness. σ_{R_m} and σ_{T_m} 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:

$$N = \frac{\varphi}{\int_0^\infty \int_0^\infty V(r_1,r_2)\Psi(r_1,r_2)dr_1dr_2}$$

Equation S22

where φ is the total *volume fraction* of copolymer in the vesicles and $V(r_1,r_2)$ is the total *volume* of copolymer in a vesicle $\left[V(r_1,r_2) = (V_s + V_c)N_v(r_1,r_2)\right]$.

Programming tools within the Irena SAS Igor Pro macros[8] were used to implement the scattering models.

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