Supporting Information for:

Rationally designed anionic diblock copolymer worm gels are useful model systems for calcite occlusion studies

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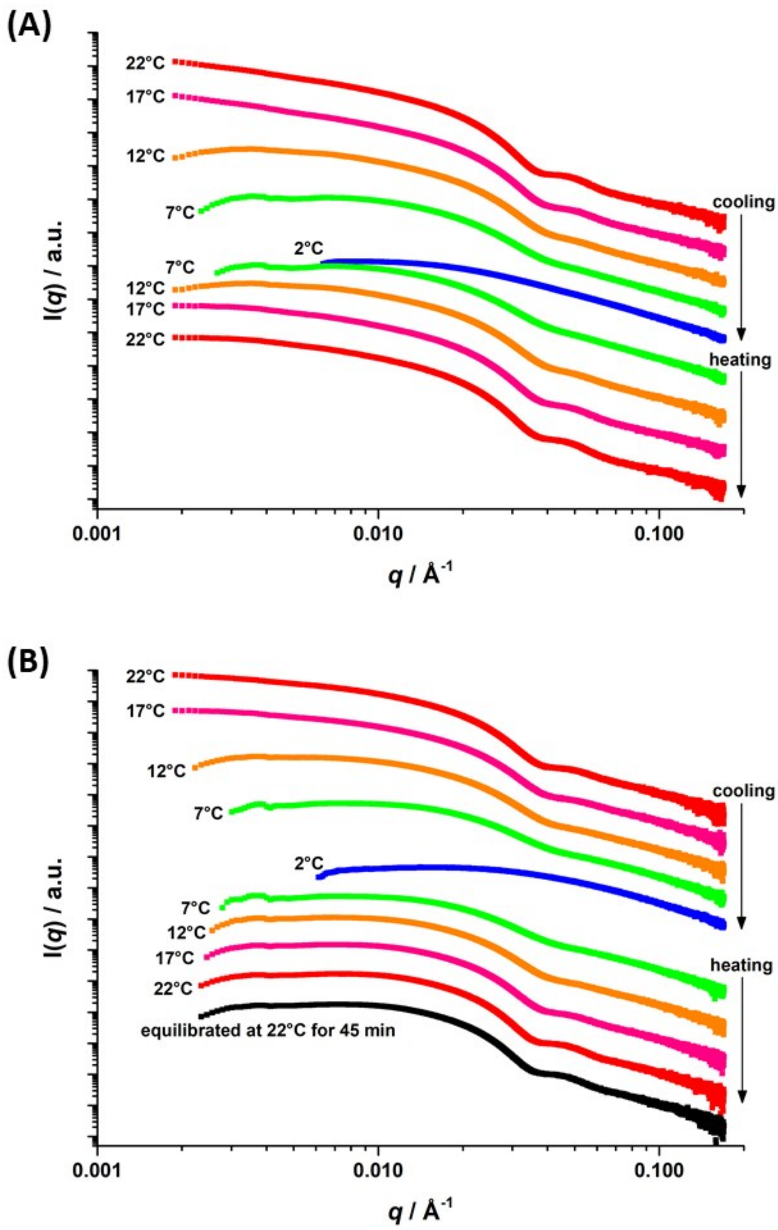

Figure S1. Small-angle X-ray scattering patterns recorded for [n$PMAA_{85}$ + (1-n)$PGMA_{48}$]-$PHPMA_{140}$ 5.0 % w/w worm gels where (A) n = 0 and (B) n = 0.15. The temperature was cycled between 22 and 2 °C in the steps indicated on the plots and the sample was allowed to equilibrate for 5 minutes at each step.

Table S1. Summary of models[a] and various structural parameters obtained from fitting SAXS patterns recorded for 1.0 % w/w aqueous dispersions of copolymer nano-objects from Figure 4.

Sample Composition	Model[a]	Φ_1[b]	R[c] / Å	σ_R / Å	L_c[d] / Å	L_k[d] / Å	T_m[e] / Å	σ_{Tm} / Å	Φ_2[b]
$[0.5M_{37}+0.5G_{68}]-H_{250}$	Vesicle	0.0103	804	259			182	25	0.0027
$[0.1M_{37}+0.9G_{68}]-H_{200}$	Vesicle	0.0122	1012	312			126	22	0.0007
$[0.2M_{37}+0.8G_{68}]-H_{150}$	Worm	0.0022	97	15	784	25			0.0024
$[0.6M_{37}+0.4G_{68}]-H_{200}$	Sphere	0.0054	292	47					0.0030
$[0.6M_{37}+0.4G_{68}]-H_{100}$	Sphere	0.0044	207	34					0.0040
$M_{37}-H_{300}$	Sphere	0.0047	252	36					0.0054
$[0.2M_{85}+0.8G_{62}]-H_{300}$	Vesicle	0.0117	1415	531			358	67	0.0011
$[0.05M_{85}+0.95G_{62}]-H_{200}$	Vesicle	0.0200	1135	360			140	20	0.0014
$[0.2M_{85}+0.8G_{62}]-H_{150}$	Worm	0.0043	100	9	500	108			0.0029
$[0.05M_{85}+0.95G_{62}]-H_{150}$	Worm	0.0054	94	13	1298	170			0.0029
$[0.3M_{85}+0.7G_{62}]-H_{200}$	Sphere	0.0064	406	48					0.0014
$[0.05M_{85}+0.95G_{62}]-H_{75}$	Sphere	0.0047	87	8					0.0048

[a] Data collected for 1.0 % w/w aqueous dispersions of nano-objects were fitted to a two-population model of either spherical micelles (Sphere), worm-like micelles (Worm) or copolymer vesicles (Vesicle) plus Gaussian polymer chains. The total scattering intensity, $I(q)$, is represented by: $I(q) = \frac{d\Sigma}{d\Omega}(q)_s + \frac{d\Sigma}{d\Omega}(q)_c$ where $\frac{d\Sigma}{d\Omega}(q)_s$ is the scattering cross-section per unit sample volume of the first population and $\frac{d\Sigma}{d\Omega}(q)_c$ is the scattering cross-section per unit sample volume of Gaussian polymer chains. Additional descriptions of these models are given below.

[b] Φ_1 and Φ_2 represent the volume fraction of the 1st population and Gaussian polymer chains, respectively.

[c] R represents either the radius of the spherical core, worm-cross section or outer vesicle radius.

[d] L_c and L_k are the worm contour length and Kuhn length, respectively.

[e] T_m represents the vesicle wall thickness.

SAXS models

Programming tools within Irena SAS Igor Pro macros[1] were used to implement model fitting.

The SAXS models used in this work have been described in detail before and can be found at the following sources:

Model	**Location**	**DOI**
Gaussian polymer chains[2]	Supporting information, page S10	10.1021/acs.macromol.6b00987
Spherical micelles[2]	Supporting information, page S11	10.1021/acs.macromol.6b00987
Worm-like micelles[3]	Supporting information, page S3	10.1021/ja501756h
Copolymer vesicles[4]	Supporting information, page S14	10.1039/C6SC01243D

All X-ray scattering length densities (ξ) were calculated using Irena SAS Igor Pro macros[1] using homopolymer densities measured by helium pycnometry, where appropriate. Specifically: ξ_{PHPMA} = 11.11 x 10^{10} cm^{-2}; ξ_{PGMA}= 11.94 ×10^{10} cm^{-2}; ξ_{PMAA}= 10.88 ×10^{10} cm^{-2} and the solvent, ξ_{H2O} = 9.42 × 10^{10} cm^{-2}. Calculated volumes of the core and the corona block used in model fitting were obtained from V = $M_w/(N_A \rho)$, using homopolymer densities determined by helium pycnometry.

References

1. Ilavsky, J.; Jemian, P. R. Irena: tool suite for modeling and analysis of small-angle scattering. *J. Appl. Crystallogr.* **2009,** *42*, 347-353.
2. Akpinar, B.; Fielding, L. A.; Cunningham, V. J.; Ning, Y.; Mykhaylyk, O. O.; Fowler, P. W.; Armes, S. P. Determining the Effective Density and Stabilizer Layer Thickness of Sterically Stabilized Nanoparticles. *Macromolecules* **2016,** *49*, (14), 5160-5171.
3. Fielding, L. A.; Lane, J. A.; Derry, M. J.; Mykhaylyk, O. O.; Armes, S. P. Thermo-responsive diblock copolymer worm gels in non-polar solvents. *J. Am. Chem. Soc.* **2014,** *136*, (15), 5790-5798.
4. Derry, M. J.; Fielding, L. A.; Warren, N. J.; Mable, C. J.; Smith, A. J.; Mykhaylyk, O. O.; Armes, S. P. In situ small-angle X-ray scattering studies of sterically-stabilized diblock copolymer nanoparticles formed during polymerization-induced self-assembly in non-polar media. *Chemical Science* **2016,** *7*, (8), 5078-5090.