

Supporting Information for:

Epoxy-Functional Diblock Copolymer Spheres, Worms and Vesicles via Polymerization-Induced Self-Assembly in Mineral Oil

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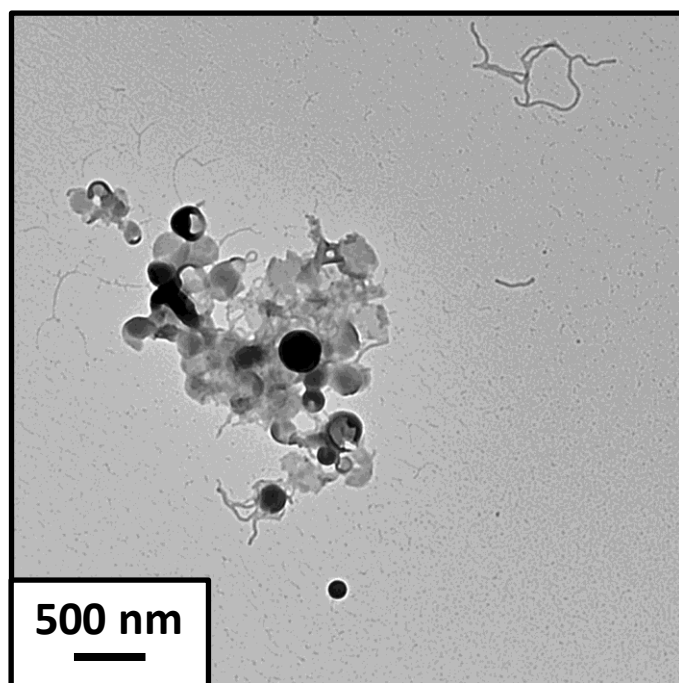


Figure S1. TEM image recorded for PSMA₉-PGlyMA₁₀₀ nano-objects.

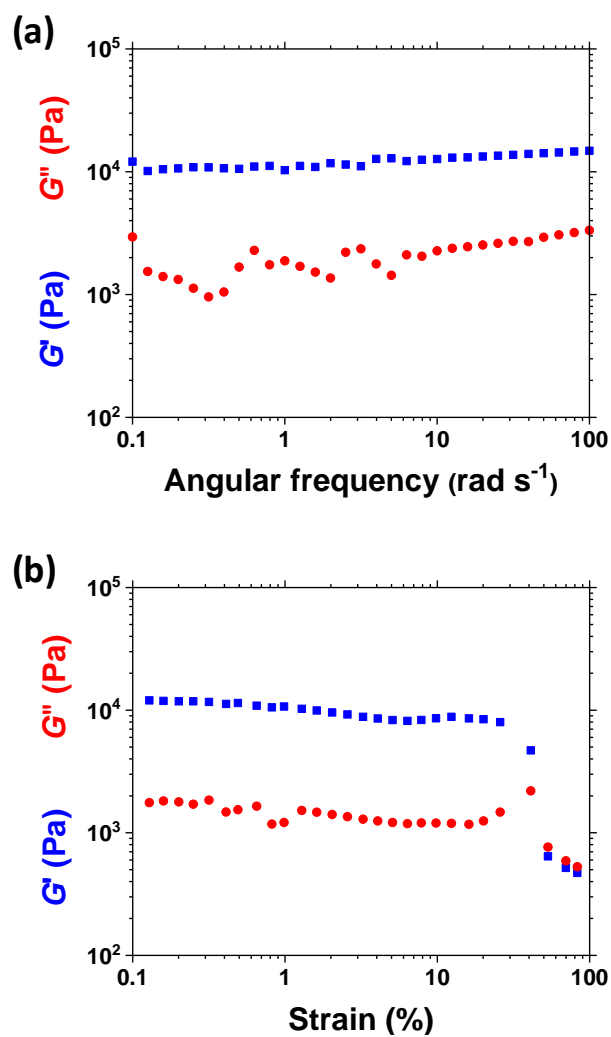


Figure S2. Variation of the storage modulus (G') and loss modulus (G'') for a 30% w/w dispersion of PSMA₉-PGlyMA₇₅ worms in mineral oil during (a) an angular frequency sweep from 0.1 rad s⁻¹ to 100 rad s⁻¹ at 1.0% strain amplitude and (b) a strain sweep from 0.1% to 100% at an angular frequency of 10 rad s⁻¹.

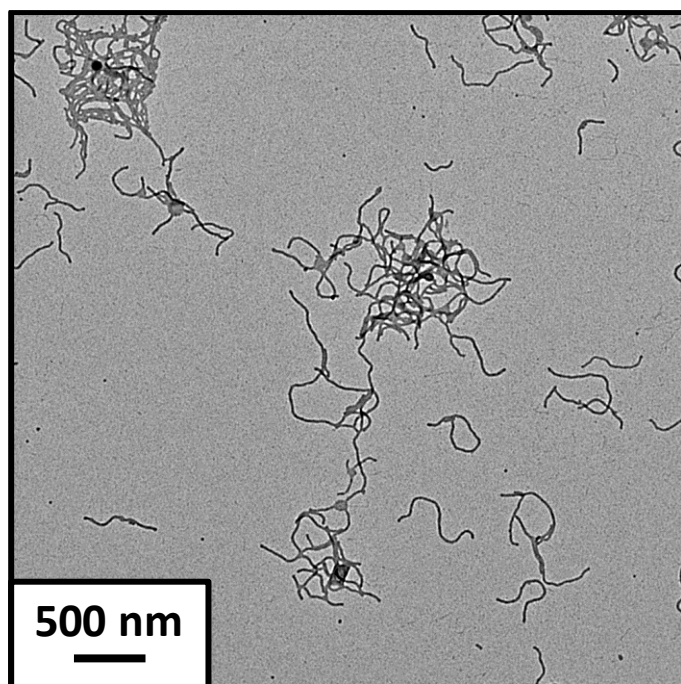


Figure S3. TEM image recorded for PSMA₉-PGlyMA₇₅ nano-objects obtained at room temperature after an oscillatory rheology temperature sweep (from 25 °C to 100 °C at 2 °C min⁻¹).

SAXS Models

The SAXS models used in this study (for spheres, dimers and trimers,¹ worm-like micelles,² and vesicles³) have been reported in detail elsewhere.^{1,4} The scattering length densities used for the coronal PSMA (ζ_{PSMA}) and core PGlyMA (ζ_{PGlyMA}) blocks were $9.24 \times 10^{10} \text{ cm}^{-2}$ and $11.34 \times 10^{10} \text{ cm}^{-2}$, respectively, and that for the mineral oil solvent (ζ_{sol}) was $7.63 \times 10^{10} \text{ cm}^{-2}$.

Throughout the manuscript, the following terms are used and are defined as follows:

φ_{spheres}	-	volume fraction of spheres
φ_{dimers}	-	volume fraction of dimers
φ_{trimers}	-	volume fraction of trimers
D_{sphere}	-	overall diameter of a sphere (equal to $2 \times [\text{spherical core radius}] + 4 \times [\text{stabilizer radius of gyration}]$)
T_{worm}	-	overall worm thickness (equal to $2 \times [\text{worm core radius}] + 4 \times [\text{stabilizer radius of gyration}]$)
L_{worm}	-	worm length
T_{membrane}	-	vesicle membrane thickness
D_{vesicle}	-	overall vesicle diameter (equal to $2 \times [\text{distance from the centre of the vesicle to the centre of the membrane}] + 4 \times [\text{stabilizer radius of gyration}]$)
N_{agg}	-	aggregation number (or number of copolymer chains per nanoparticle)

Table S1. Summary of fitting parameters and dimensions determined by fitting SAXS patterns recorded for 1.0% w/w dispersions of PSMA₉-PGlyMA_x (S₉-Gly_x) diblock copolymer nanoparticles in mineral oil. Standard deviations for the value of D_{sphere} , T_{worm} , T_{membrane} and D_{vesicle} are also indicated.

Copolymer composition	Sphere, dimer, trimer model ¹				Worm-like micelle model ²		Vesicle model ³		N_{agg}
	D_{sphere} (nm)	ϕ_{spheres}	ϕ_{dimers}	ϕ_{trimers}	T_{worm} (nm)	L_{worm} (nm)	T_{membrane} (nm)	D_{vesicle} (nm)	
S ₉ -Gly ₅₀ spheres	17.0 ± 1.3	0.62	0.29	0.09	-	-	-	-	321
S ₉ -Gly ₇₅ worms	-	-	-	-	18.0 ± 1.6	262.4	-	-	4085
S ₉ -Gly ₁₅₀ vesicles	-	-	-	-	-	-	16.1 ± 1.8	136.6 ± 21.5	25524
S ₉ -Gly ₂₀₀ vesicles	-	-	-	-	-	-	19.6 ± 1.8	156.5 ± 36.6	30237

References

1. N. J. Warren, O. O. Mykhaylyk, D. Mahmood, A. J. Ryan and S. P. Armes, *Journal of the American Chemical Society*, 2014, **136**, 1023-1033.
2. J. S. Pedersen, *Journal of Applied Crystallography*, 2000, **33**, 637-640.
3. J. Bang, S. M. Jain, Z. B. Li, T. P. Lodge, J. S. Pedersen, E. Kesselman and Y. Talmon, *Macromolecules*, 2006, **39**, 1199-1208.
4. M. J. Derry, L. A. Fielding, N. J. Warren, C. J. Mable, A. J. Smith, O. O. Mykhaylyk and S. P. Armes, *Chemical Science*, 2016, **7**, 5078-5090.