

Supporting Information for:

Block Copolymer Nanoparticles Prepared via Polymerization-Induced Self-Assembly Provide Excellent Boundary Lubrication Performance for Next-Generation Ultralow Viscosity Automotive Engine Oils

Matthew J. Derry,^{†} Timothy Smith,[‡] Paul S. O'Hora,[‡] and Steven P. Armes^{*†}*

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

[‡] Lubrizol Ltd., The Knowle, Nether Lane, Hazelwood, Derbyshire, DE56 4AN, UK.

*E-mail: m.derry@sheffield.ac.uk; s.p.arnes@sheffield.ac.uk

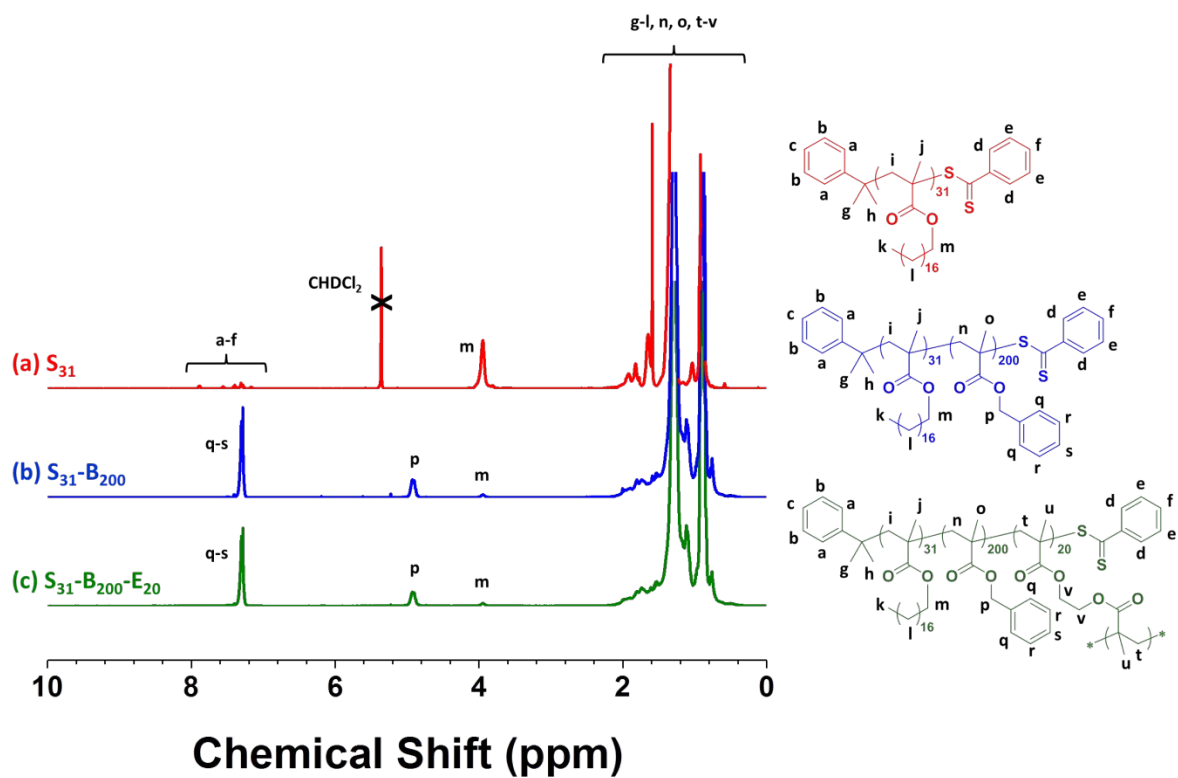


Figure S1. Assigned ^1H NMR spectra for (a) poly(stearyl methacrylate) (S_{31}) macro-CTA in CD_2Cl_2 , (b) poly(stearyl methacrylate)-poly(benzyl methacrylate) ($S_{31}\text{-B}_{200}$) diblock copolymer in CDCl_3 and (c) poly(stearyl methacrylate)-poly(benzyl methacrylate)-poly(ethylene glycol dimethacrylate) ($S_{31}\text{-B}_{200}\text{-E}_{20}$) triblock copolymer in CDCl_3 .

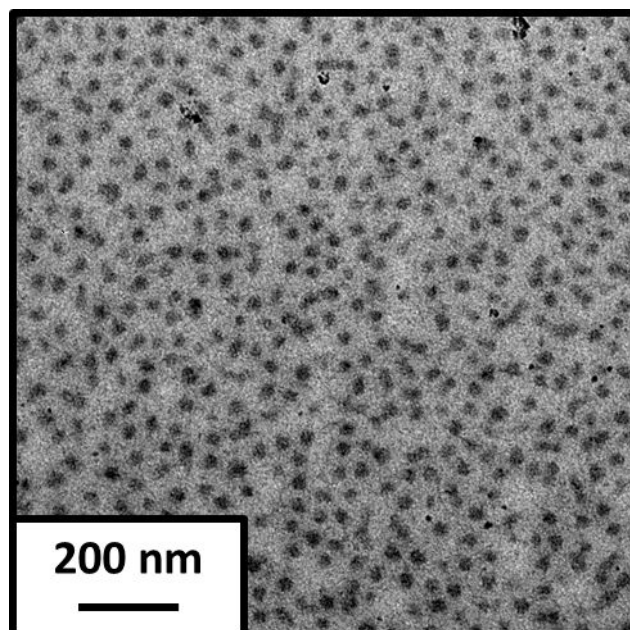


Figure S2. Transmission electron micrograph of cross-linked poly(stearyl methacrylate)-poly(benzyl methacrylate)-poly(ethylene glycol dimethacrylate) (S_{31} - B_{200} - E_{20}) spheres dried from a 0.10% w/w dispersion in THF.

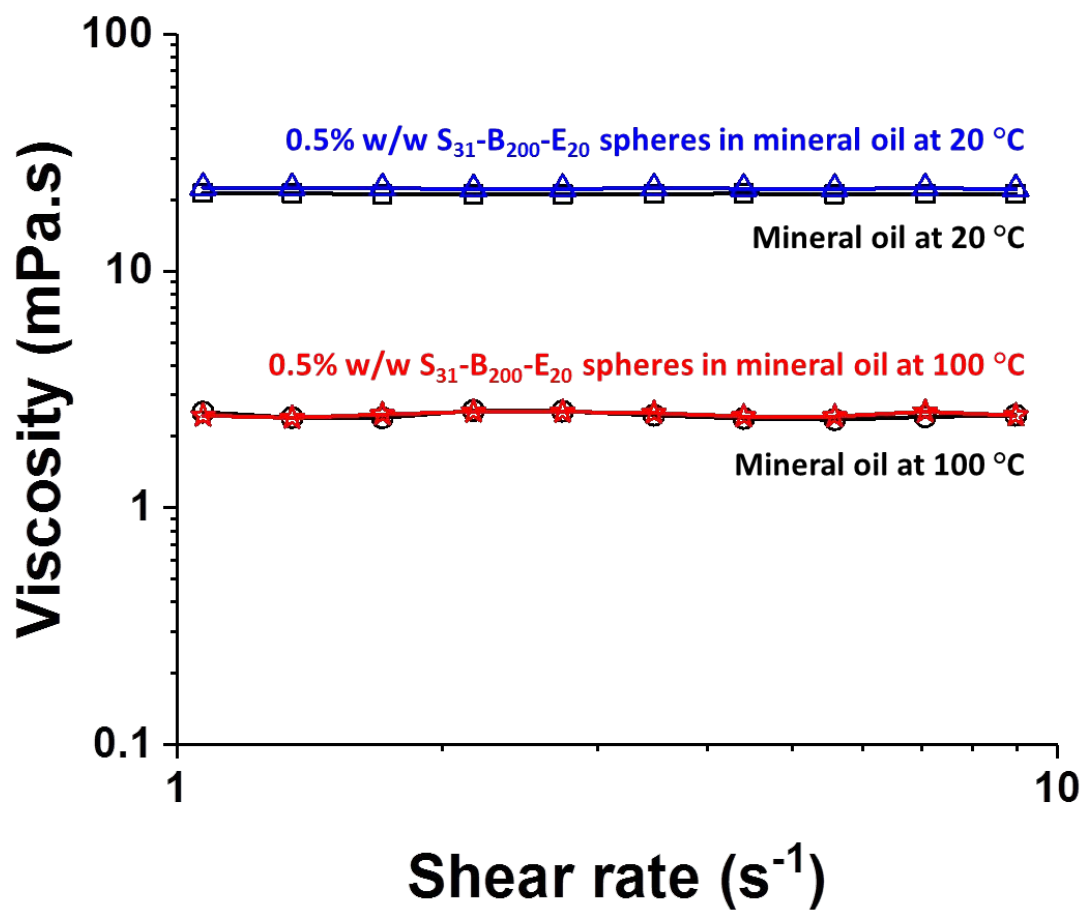


Figure S3. Shear rate vs. viscosity for mineral oil alone at 20 °C (open black squares) and 100 °C (open black circles), and a 0.5% w/w dispersion of S₃₁-B₂₀₀-E₂₀ spheres in mineral oil at 20 °C (open blue triangles) and 100 °C (open red stars).

SAXS Models

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

$$\frac{d\Sigma}{d\Omega}(q) = NS(q) \prod_0^{\infty} \dots \prod_0^{\infty} F(q, r_1, \dots, r_k)^2 \Psi(r_1, \dots, r_k) dr_1 \dots dr_k \quad S1$$

where $F(q, r_1, \dots, r_k)$ is their form factor, r_1, \dots, r_k is a set of k parameters describing the particle structural morphology, $\Psi(r_1, \dots, r_k)$ is the distribution function, $S(q)$ is the structure factor (for 1.0% w/w dispersions it can be assumed that there are no inter-particle interactions and thus $S(q) = 1$) and N is the particle number density per unit sample volume expressed as:

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

where $V(r_1, \dots, r_k)$ is volume of the particle and φ is their volume fraction in the dispersion.

The spherical micelle form factor for Equation *S1* can be expressed as:¹

$$F_{s_mic}(q) = N_s^2 \beta_s^2 A_s^2(q, R_s) + N_s \beta_c^2 F_c(q, R_g) + N_s (N_s - 1) \beta_c^2 A_c^2(q) + 2N_s^2 \beta_s \beta_c A_s(q) A_c(q) \quad S3$$

where R_s is the radius of the spherical micelle core, R_g is the radius of gyration of the PSMA coronal block. The core block and the corona block X-ray scattering length contrast is 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 ($\xi_{PBzMA_{200}} = 10.38 \times 10^{10} \text{ cm}^{-2}$ or $\xi_{PBzMA_{200} - PEGDMA_{20}} = 10.36 \times 10^{10} \text{ cm}^{-2}$), the corona block ($\xi_{PSMA_{31}} = 9.26 \times 10^{10} \text{ cm}^{-2}$) and the mineral oil solvent ($\xi_{sol} = 7.63 \times 10^{10} \text{ cm}^{-2}$), respectively. V_s and V_c are volumes of the core block ($V_{PBzMA_{200}}$ or $V_{PBzMA_{200} - PEGDMA_{20}}$) and the corona block ($V_{PSMA_{31}}$), respectively.

The volumes were obtained from $V = \frac{M_{n,pol}}{N_A \rho}$ using the densities of PBzMA ($\rho_{PBzMA} = 1.15 \text{ g cm}^{-3}$),² PEGDMA ($\rho_{PEGDMA} = 1.10 \text{ g cm}^{-3}$) and the solid-state homopolymer density of PSMA

determined by helium pycnometry ($\rho_{\text{PSMA}} = 0.97 \text{ g cm}^{-3}$), where $M_{n,\text{pol}}$ corresponds to the number-average molecular weight of the block determined by ^1H NMR spectroscopy. The scattering amplitude of the micelle core is expressed via sphere form factor amplitude:

$$A_c(q, R_s) = \Phi(qR_s) \exp\left(-\frac{q^2\sigma^2}{2}\right) \quad S4$$

where $\Phi(qR_s) = \frac{3[\sin(qR_s) - qR_s\cos(qR_s)]}{(qR_s)^3}$. 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 membrane surface. This σ value was fixed at 0.22 nm during fitting.

The scattering amplitude of the spherical micelle corona is:

$$A_c(q) = \frac{\int_{R_s}^{R_s+2s} \mu_c(r) \frac{\sin(qr)}{qr} r^2 dr}{\int_{R_s}^{R_s+2s} \mu_c(r) r^2 dr} \exp\left(-\frac{q^2\sigma^2}{2}\right) \quad S5$$

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 electron density corona profile and the function weight coefficient, respectively. This information can be found elsewhere,³⁻⁴ as can the approximate integrated form of Equation S5. The self-correlation term for the corona block is given by the Debye function:

$$F_c(q, R_g) = \frac{2[\exp(-q^2R_g^2) - 1 + q^2R_g^2]}{q^4R_g^4} \quad S6$$

where R_g is the radius of gyration of the PSMA coronal block. The aggregation number of the spherical micelle is:

$$N_s = (1 - x_{\text{sol}}) \frac{\frac{4}{3}\pi R_s^3}{V_s} \quad S7$$

where x_{sol} is the volume fraction of solvent in the PBzMA or PBzMA-PEGDMA micelle core. A polydispersity of the micelle core radius (R_s) was incorporated in the structural model (Equation S1) assuming a Gaussian distribution:

$$\Psi(r_1) = \frac{1}{\sqrt{2\pi\sigma_{R_s}^2}} \exp\left(-\frac{(r_1 - R_s)^2}{2\sigma_{R_s}^2}\right) \quad S8$$

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

$$N = \frac{\varphi}{\int_0^\infty V(r_1)\Psi(r_1)dr_1} \quad S9$$

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

Table S1. Summary of parameters after fitting SAXS patterns obtained for 1.0% w/w dispersions in mineral oil using a spherical micelle model.¹ φ is the volume fraction of copolymers obtained from the fitting, D_s is the spherical micelle core diameter (equal to $2R_s$, where R_s is the spherical micelle core radius), R_g is the radius of gyration of the PSMA stabilizer block, x_{sol} is the volume fraction of solvent within the core domain and N_s is the mean aggregation number.

Sample	φ	$D_s (= 2R_s) / \text{nm}$	R_g / nm	x_{sol}	N_s
S ₃₁ -B ₂₀₀ , 20 °C	0.00594	27.6 ± 2.1	1.4	0	218
S ₃₁ -B ₂₀₀ -E ₂₀ , 20 °C	0.00742	29.4 ± 2.4	1.4	0	234
S ₃₁ -B ₂₀₀ -E ₂₀ , 100 °C	0.00630	29.5 ± 2.3	1.4	0	237

References

1. Pedersen, J. S. Form factors of block copolymer micelles with spherical, ellipsoidal and cylindrical cores. *Journal of Applied Crystallography* **2000**, *33*, 637-640.
2. 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. *Journal of the American Chemical Society* **2014**, *136*, 5790-5798.

3. Pedersen, J. S.; Gerstenberg, M. C. The structure of P85 Pluronic block copolymer micelles determined by small-angle neutron scattering. *Colloids and Surfaces a-Physicochemical and Engineering Aspects* **2003**, *213*, 175-187.
4. Pedersen, J. S.; Svaneborg, C.; Almdal, K.; Hamley, I. W.; Young, R. N. A small-angle neutron and X-ray contrast variation scattering study of the structure of block copolymer micelles: Corona shape and excluded volume interactions. *Macromolecules* **2003**, *36*, 416-433.