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Hunter, S.J. orcid.org/0000-0002-9280-1969, Cornel, E.J., Mykhaylyk, O.O. orcid.org/0000-0003-4110-8328 et al. (1 more author) (2020) Effect of salt on the formation and stability of water-in-oil Pickering nanoemulsions stabilized by diblock copolymer nanoparticles. Langmuir, 36 (51). pp. 15523-15535. ISSN 0743-7463

https://doi.org/10.1021/acs.langmuir.0c02742

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Supporting Information for:

Effect of salt on the formation and stability of water-in-oil Pickering nanoemulsions stabilized by diblock copolymer nanoparticles

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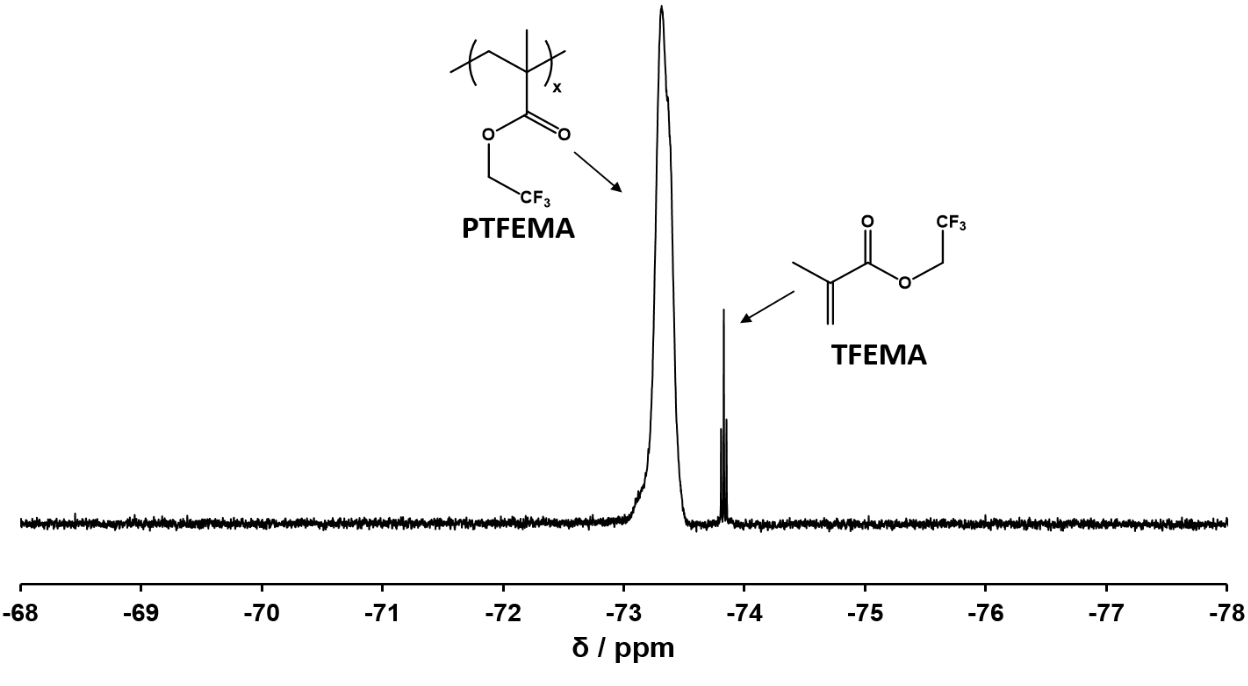

Figure S1. ^{19}F NMR spectrum recorded for PSMA$_{32}$-PTFEMA$_{53}$ diblock copolymer dissolved in CDCl$_3$. From the residual monomer signal observed at -73.8 ppm, a final TFEMA conversion of 97% can be calculated.

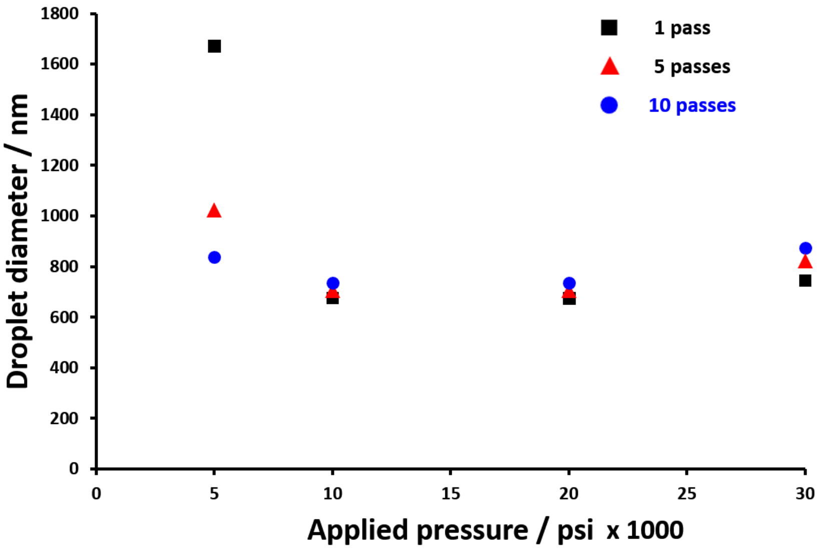

Figure S2. Effect of varying the applied pressure and number of passes during microfluidization on the initial z-average aqueous droplet diameter of w/o Pickering nanoemulsions prepared using 5.0% w/w PSMA$_{32}$-PTFEMA$_{53}$ nanoparticles at a fixed water volume fraction of 0.10, as determined by DLS.

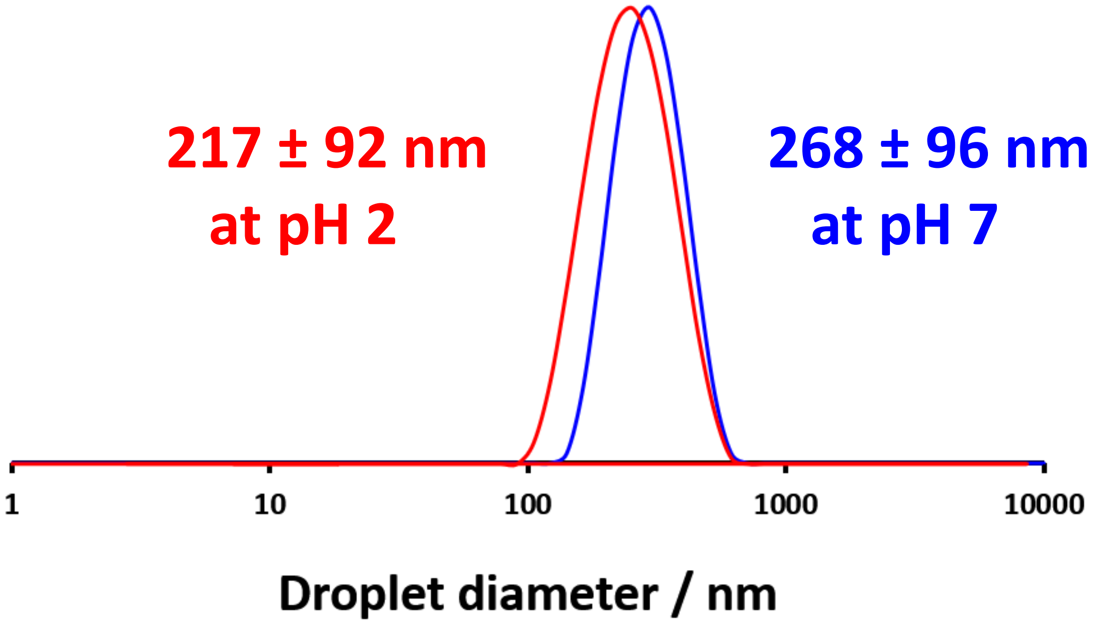

Figure S3. Intensity-average droplet size distributions recorded by DLS for Pickering nanoemulsions prepared using either a neutral (pH 7) or acidic (pH 2) aqueous solution containing 0.11 M NaCl.

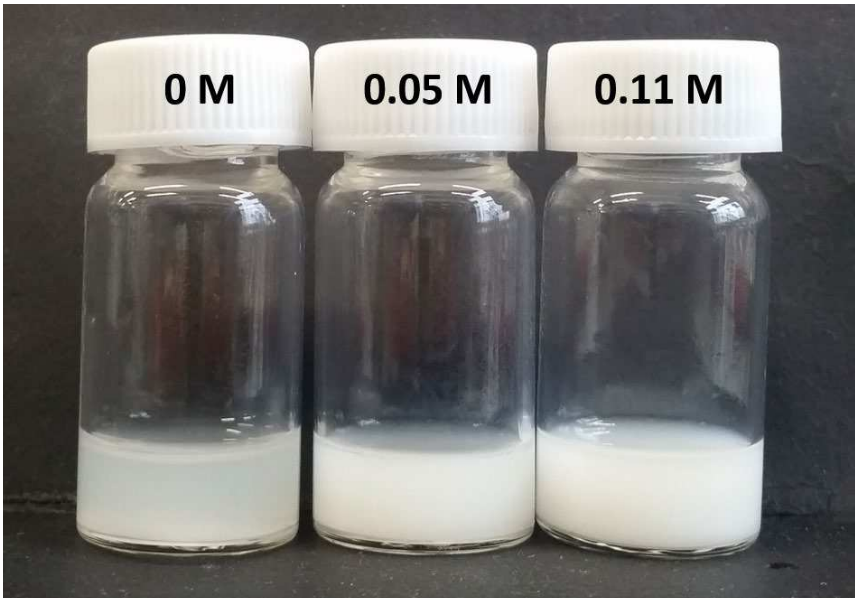

Figure S4. Digital photographs recorded for one-day-old w/o Pickering nanoemulsions prepared using various NaCl concentrations (0, 0.05 or 0.11 M) at a constant nanoparticle concentration of 5.0% w/w and a water volume fraction of 0.10. Microfluidization conditions: applied pressure = 10 000 psi; 5 passes.

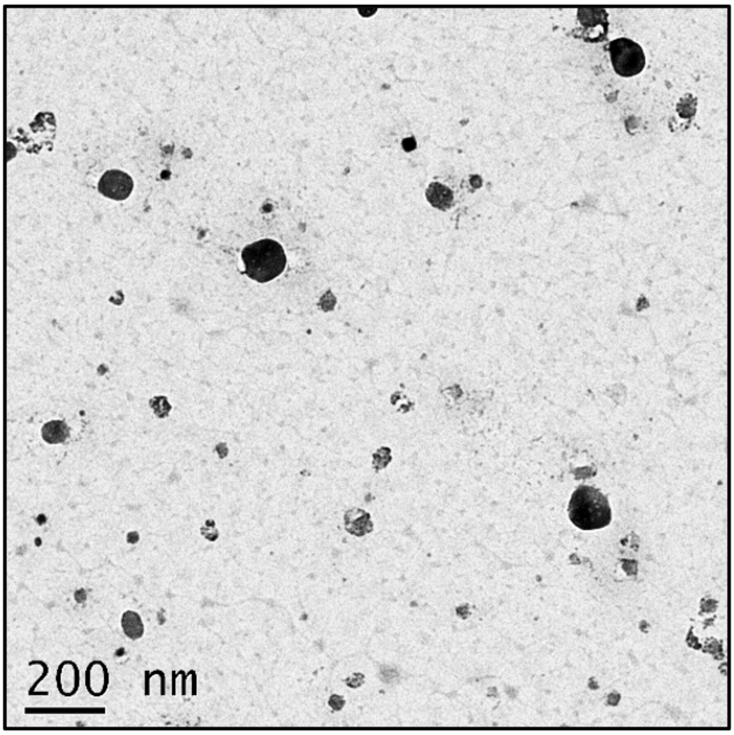

Figure S5. Representative TEM image recorded for dried water-in-*n*-dodecane Pickering nanoemulsions prepared using 5.0% w/w $PSMA_{32}$-$PTFEMA_{53}$ nanoparticles with 0.11 M NaCl dissolved in the aqueous phase. Conditions: microfluidization pressure = 10 000 psi; 5 passes.

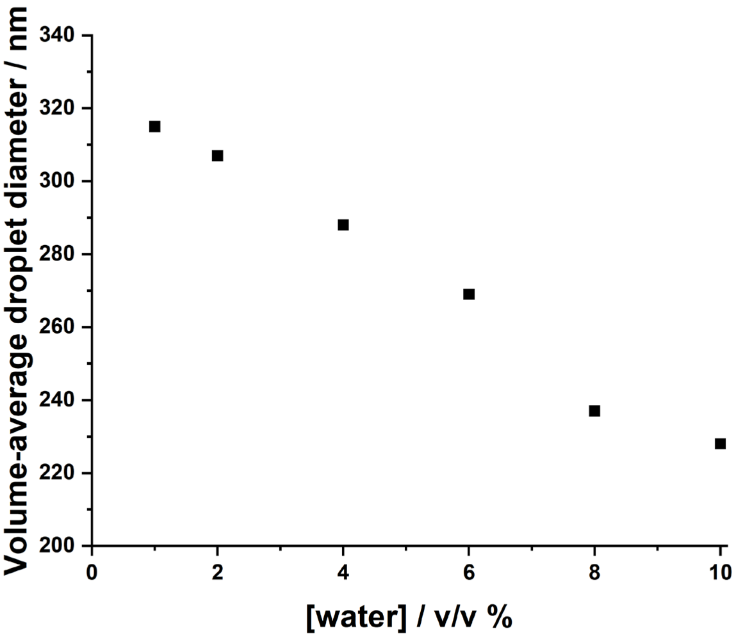

Figure S6. Effect of varying the aqueous droplet concentration on the apparent droplet diameter of a water-in-*n*-dodecane Pickering nanoemulsion as determined by analytical centrifugation (LUMiSizer instrument). This so-called 'hindrance' function indicates that the optimum droplet concentration for such analyses is approximately 1.0% v/v, with higher concentrations leading to hindered creaming and hence undersizing.

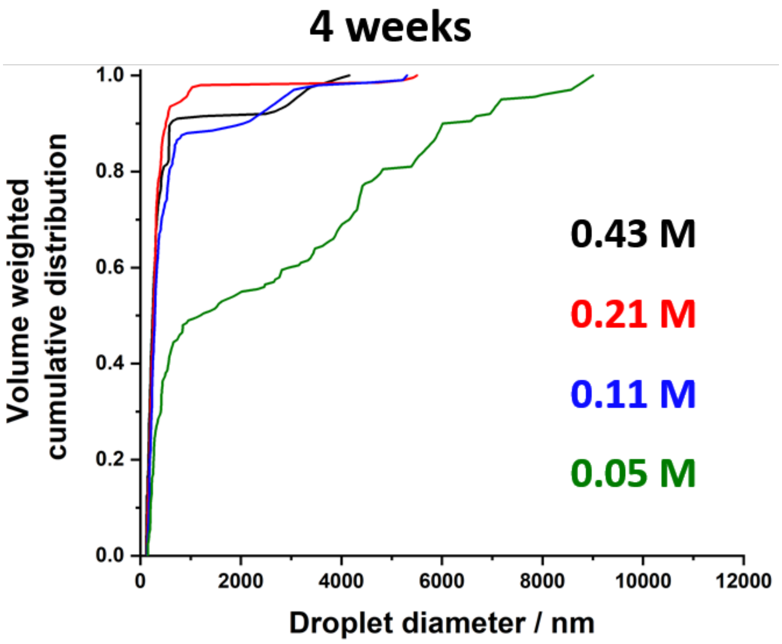

Figure S7. Volume-weighted cumulative distributions determined by analytical centrifugation (LUMiSizer instrument) for *n*-dodecane-in-water Pickering nanoemulsions prepared using various amounts of NaCl dissolved in the aqueous phase) after ageing for 4 weeks at 20 °C.

Structural models for SAXS analysis

In general, the X-ray intensity scattered by a system composed of *n* different (non-interacting) populations of polydisperse objects [usually described by the differential scattering cross-section per unit sample volume, $d\Sigma(\mathrm{q})/d\Omega$] can be expressed as:[1]

$$\frac{d\Sigma(q)}{d\Omega}=\sum_{l=1}^{n}S_l(q)N_l\int_0^\infty\ldots\int_0^\infty F_l(q,r_{l1},\ldots,r_{lk})^2\Psi_l(r_{l1},\ldots,r_{lk})dr_{l1}\ldots dr_{lk}\quad S1$$

where $F_l(q,r_{l1},...,r_{lk})$ is the form factor, $\Psi_l(r_{l1},...,r_{lk})$ is the distribution function, N_l is the number density per unit volume and $S_l(q)$ is the structure factor of the l^{th} population in the system. Here, $r_{l1},...,r_{lk}$ is a set of *k* parameters describing the structural morphology of the l^{th} population.

Spherical Micelle SAXS Model

In terms of Equation *S1*, a dispersion of spherical micelles formed by an amphiphilic diblock copolymer can be described as a single population system ($n = 1$). Assuming that only the micelle core radius is polydisperse, Equation S1 for this system can be rewritten as:

$$\frac{d\Sigma(q)}{d\Omega}=S_1(q)N_1\int_0^\infty F_1(q,r_{11})^2\Psi_1(r_{11})dr_{11}\quad S2$$

The spherical micelle form factor for Equation *S2* is given by:[1]

$$\begin{aligned}F_1(q,r_{11}) &= N_\mathrm{s}^2\beta_\mathrm{s}^2A_\mathrm{s}^2(q,r_{11})+N_\mathrm{s}\beta_\mathrm{c}^2F_\mathrm{c}(q,R_\mathrm{g})+N_\mathrm{s}(N_\mathrm{s}-1)\beta_\mathrm{c}^2A_\mathrm{c}^2(q)\\&\quad+2N_\mathrm{s}^2\beta_\mathrm{s}\beta_\mathrm{c}A_\mathrm{s}(q,r_{11})A_\mathrm{c}(q)\end{aligned}\qquad S3$$

where r_1 is the spherical micelle core radius, R_g is the radius of gyration of the PSMA coronal block, and the X-ray scattering length contrast for the core and corona blocks is given by $\beta_\mathrm{s}=V_\mathrm{s}(\xi_\mathrm{s}-\xi_\mathrm{sol})$ and $\beta_\mathrm{c}=V_\mathrm{c}(\xi_\mathrm{c}-\xi_\mathrm{sol})$, respectively. Here ξ_s, ξ_c and ξ_sol are the X-ray scattering length densities of the core block ($\xi_\mathrm{PTFEMA} = 12.76 \times 10^{10}$ cm^{-2}), the corona block ($\xi_\mathrm{PSMA} = 9.24 \times 10^{10}$ cm^{-2}) and the solvent ($\xi_\mathrm{sol} = 7.63 \times 10^{10}$ cm^{-2}), respectively. V_s and V_c are volumes of the core block (V_PTFEMA) and the corona block (V_SMA), respectively. The volumes were calculated from $V=\frac{M_\mathrm{n,pol}}{N_\mathrm{A}\rho}$ using the solid-state homopolymer densities of PTFEMA (ρ_PTFEMA = 1.47 g cm^{-3})[2] and PSMA (ρ_PSMA = 0.97 g cm^{-3})[3] determined by helium pycnometry, where $M_\mathrm{n,pol}$ corresponds to the number-average molecular weight of the block. The mean aggregation number of the spherical micelle is expressed as $N_\mathrm{s}=\frac{\frac{4}{3}\pi r_{11}^3}{V_\mathrm{s}}$ where it is assumed that the solvent is absent in the micelle core. The sphere form factor amplitude is used for the amplitude of the core self-term:

$$A_{\mathrm{c}}(q, r_{11}) = \Phi(qr_{11})\exp\left(-\frac{q^2\sigma^2}{2}\right) \quad S4$$

where

$$\Phi(x) = \frac{3[\sin(x) - x\cos(x)]}{x^3} \quad S5$$

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 2.5 during fitting.

The form factor amplitude of the spherical micelle corona in Equation *S3* is given by:

$$A_{\mathrm{c}}(q) = \frac{\int_{R_{\mathrm{s}}}^{R_{\mathrm{s}}+2s} \mu_{\mathrm{c}}(r)\frac{\sin(qr)}{qr} r^2 dr}{\int_{R_{\mathrm{s}}}^{R_{\mathrm{s}}+2s} \mu_{\mathrm{c}}(r) r^2 dr}\exp\left(-\frac{q^2\sigma^2}{2}\right) \quad S6$$

The radial profile, $\mu_{\mathrm{c}}(r)$, 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 corona block is given by the Debye function:

$$F_{\mathrm{c}}(q, R_{\mathrm{g}}) = \frac{2\left[\exp\left(-q^2{R_{\mathrm{g}}}^2\right) - 1 + q^2{R_{\mathrm{g}}}^2\right]}{q^4{R_{\mathrm{g}}}^4} \quad S7$$

The structure factor in Equation *S2*, $S_1(q)$, is usually expressed for interacting spherical micelles as:[6]

$$S_1(q) = 1 + \frac{A_1^{\mathrm{av}}(q, r_{11})^2[S_{\mathrm{PY}}(q, R_{\mathrm{PY}}, f_{\mathrm{PY}}) - 1]}{F_1(q, r_{11})} \quad S8$$

Herein the form factor of the average radial scattering length density distribution of micelles is expressed as $A_1^{\mathrm{av}}(q, r_1) = N_{\mathrm{s}}[\beta_{\mathrm{s}}A_{\mathrm{s}}(q, r_{11}) + \beta_{\mathrm{c}}A_{\mathrm{c}}(q)]$ and $S_{\mathrm{PY}}(q, R_{\mathrm{PY}}, f_{\mathrm{PY}})$ is a hard-sphere interaction structure factor solved using the Percus-Yevick closure relation,[1, 7] where R_{PY} is the interaction radius and f_{PY} is the hard-sphere volume fraction. For dilute dispersions of micelles it is assumed that $S_{\mathrm{PY}}(q, R_{\mathrm{PY}}, f_{\mathrm{PY}}) = 1$.

A polydispersity of the micelle radius in Equation *S2* can be described by a Gaussian distribution:

$$\Psi_1(r_{11}) = \frac{1}{\sqrt{2\pi{\sigma_{Rs}}^2}}\exp\left(-\frac{(r_{11} - R_{\mathrm{s}})^2}{2{\sigma_{Rs}}^2}\right) \quad S9$$

where R_{s} is the mean of the micelle core radius and σ_{Rs} is its standard deviation. The number density per unit volume for the micelle model is expressed as:

$$N_1 = \frac{\varphi_1}{\int_0^{\infty} V(r_{11})\Psi(r_{11})dr_{11}} \qquad S10$$

where φ_1 is the total volume fraction of copolymer in the spherical micelles and $V(r_{11})$ is the total *volume* of copolymer in a spherical micelle $[V(r_{11}) = (V_s + V_c)N_s]$.

Assuming that the projected contour length of a PSMA monomer is 0.255 nm (two C-C bonds in *all-trans* conformation), the total contour length of a $PSMA_{32}$ block, L_{PSMA32} = 32 x 0.255 nm = 8.16 nm. Given a mean Kuhn length of 1.53 nm (based on the known literature value for PMMA[8]) an estimated unperturbed radius of gyration, $R_g = (8.16 \times 1.53/6)^{0.5} = 1.44$ nm is calculated. The data fit to the SAXS pattern recorded for $PSMA_{32}$-$PTFEMA_{53}$ spheres using the spherical micelle suggested that the experimental R_g for the corona PSMA block (1.72 nm) is physically reasonable, since it is close to this theoretical estimate.

Two-population SAXS Model

In order to construct a structural model for the SAXS analysis of water-in-oil emulsion droplets stabilised by $PSMA_{32}$-$PTFEMA_{53}$ spherical micelles, a previously used formalism for core-particulate shell spherical particles was employed.[9] It was assumed that the differential cross-section per unit sample volume for the studied system patterns can be represented as a sum of two terms corresponding to scattering signals generated by two populations ($n = 2$ in Equation *S1*): spherical micelles forming the particulate shell (the first population, $l = 1$ in Equation *S1*) and core-shell particles (the second population, $l = 2$ in Equation *S1*). The contribution to the scattering signal from the first population can be described by the same term used for the spherical micelle dispersion (Equation *S2*). By expressing the scattering signal from the second population in a similar manner to that of the first population, the differential scattering cross-section per unit sample volume of the whole system could be written as:

$$\frac{d\Sigma(q)}{d\Omega} = S_1(q)N_1\int_0^{\infty} F_1(q,r_{11})^2\Psi_1(r_{11})dr_{11} + S_2(q)N_2\int_0^{\infty} F_2(q,r_{21})^2\Psi_2(r_{21})dr_{21} \qquad S11$$

where it is assumed that only the particle core radius is polydisperse. The form factor for the second population, corresponding to the core-shell particles, is given by:

$$F_2(q,r_{21}) = V_{\mathrm{total}}(\xi_{\mathrm{shell}} - \xi_{\mathrm{sol}})\Phi[q(r_{21} + T_{\mathrm{shell}})] + V_{\mathrm{core}}(\xi_{\mathrm{core}} - \xi_{\mathrm{shell}})\Phi(qr_{21}) \qquad S12$$

where r_{21} is the core radius and T_{shell} is the shell thickness. $V_{\mathrm{total}} = \frac{4}{3}\pi(r_{21} + T_{\mathrm{shell}})^3$ and $V_{\mathrm{core}} = \frac{4}{3}\pi r_{21}^3$ are volumetric parameters for the core-shell particles, while ξ_{core}, ξ_{shell} and ξ_{sol} are the scattering length densities for the aqueous droplets [$\xi_{\mathrm{H2O}} = 9.42 \times 10^{10}$ cm^{-2}], the particulate worm shell [volume-averaged scattering length density of the spherical micelles $\bar{\xi}_{\mathrm{mic}} = (\xi_{\mathrm{PSMA}} V_{\mathrm{s}} + \xi_{\mathrm{PTFEMA}} V_{\mathrm{c}}) / (V_{\mathrm{s}} + V_{\mathrm{c}})$] and the solvent ($\xi_{n\text{-dodecane}} = 7.63 \times 10^{10}$ cm^{-2}), respectively. As for population 1, a Gaussian distribution is assumed for the particle core radius (with a mean radius R_{c} and its standard deviation σ_{Rc}):

$$\Psi_2(r_{21}) = \frac{1}{\sqrt{2\pi\sigma_{Rc}^2}} e^{-\frac{(r_{21} - R_{\mathrm{c}})^2}{2\sigma_{Rc}^2}} \qquad S13$$

Thus, the number density, N_2, of the second population in Equation S11 is expressed as

$$N_2 = \frac{\varphi_2}{\int_0^{\infty} V(r_{21})\Psi_2(r_{21})dr_{21}} \qquad S14$$

where φ_2 is the volume fraction of core-shell particles (i.e., nanoparticle-stabilized aqueous droplets) within the w/o nanoemulsion. Since the φ_2 used for the SAXS measurements is relatively low (0.01) and the q range resolved in the SAXS experiment (Figure 7) is virtually unaffected by the inter-droplet interactions, it was assumed that the structure factor was equal to unity [$S_2(q) = 1$]. However, since the nanoparticles (a.k.a. spherical micelles) are expected to form reasonably close-packed layer at the surface of the aqueous droplets (Figure 6b), a structure factor for the first population [$S_1(q)$], as represented by Equation *S8*, had to be used in the analysis.

References

1. Pedersen, J. S.; Gerstenberg, M. C., Scattering Form Factor of Block Copolymer Micelles. *Macromolecules* **1996,** *29*, 1363-1365.
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*, 5160-5171.
3. 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. *Chem. Sci.* **2016,** *7*, 5078-5090.
4. Pedersen, J. S.; Gerstenberg, M. C., The structure of P85 Pluronic block copolymer micelles determined by small-angle neutron scattering. *Colloids Surf., A* **2003,** *213*, 175-187.
5. 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.
6. Pedersen, J. S., Structure factors effects in small-angle scattering from block copolymer micelles and star polymers. *The Journal of Chemical Physics* **2001,** *114*, 2839-2846.
7. Percus, J. K.; Yevick, G. J., Analysis of Classical Statistical Mechanics by Means of Collective Coordinates. *Physical Review* **1958,** *110*, 1-13.
8. Fetters, L. J.; Lohsey, D. J.; Colby, R. H., *Physical Properties of Polymers Handbook.* 2nd ed.; Springer: New York: 2007.
9. Thompson, K. L.; Fielding, L. A.; Mykhaylyk, O. O.; Lane, J. A.; Derry, M. J.; Armes, S. P., Vermicious thermo-responsive Pickering emulsifiers. *Chem. Sci.* **2015,** *6*, 4207-4214.