Adsorption of small cationic nanoparticles onto large anionic particles from aqueous solution: a model system for understanding pigment dispersion and the problem of effective particle density

S. M. North[a], E. R. Jones[a,*], G. N. Smith[a], O. O. Mykhaylyk[a], T. Annable[b] and S. P. Armes[a,*]

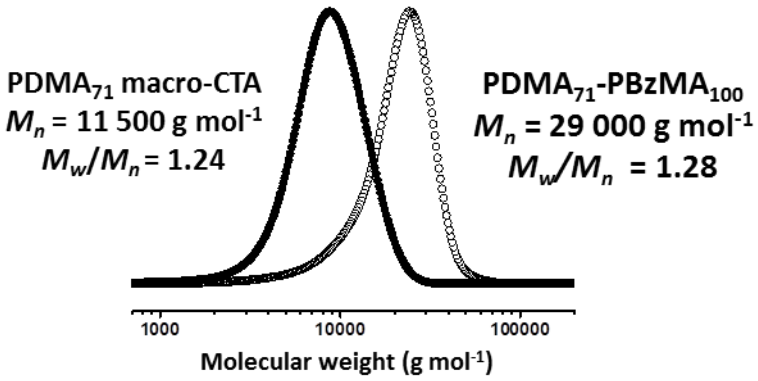

Figure S1. THF gel permeation chromatography traces obtained for the $PDMA_{71}$ macro-CTA and $PDMA_{71}$-$PBzMA_{100}$ diblock copolymer (refractive index detector; calibration using a series of ten near-monodisperse poly(methyl methacrylate) standards. A clear shift to higher molecular weight is observed following chain extension of the $PDMA_{71}$ macro CTA via RAFT alcoholic dispersion polymerization of BzMA.

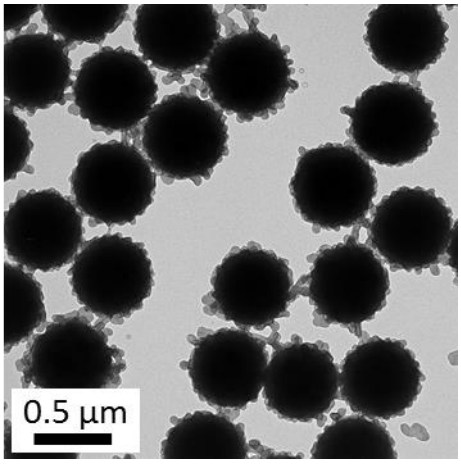

Figure S2. Representative TEM image showing $PDMA_{71}$-$PBzMA_{500}$ diblock copolymer nanoparticles adsorbed onto 470 nm silica particles.

Spherical micelle model used for SAXS analysis

In general, the scattering intensity of a system comprising one type of non-interacting polydisperse objects can be expressed as

$$I(q) = K\int_0^\infty ...\int_0^\infty F(q, r_1, ..., r_k)^2 \Psi(r_1, ..., r_k) dr_1 ... dr_k \quad \text{(S1)}$$

where $F(q, r_1, ..., r_k)$ is the form factor for the scattering objects, $\Psi(r_1, ..., r_k)$ is the distribution function, K is the number density per unit volume of the objects and $r_1, ..., r_k$ is a set of k parameters describing their structural morphology. The $PDMA_{71}$-$PBzMA_x$ diblock copolymer chains studied in this work self-assemble in water/ethanol mixtures to form sterically stabilized spherical nanoparticles (or micelles). Thus, the form factor in equation S1 is given by an analytical expression previously reported for spherical copolymer micelles:[1]

$$F(q) = [N_{agg}\beta_{mc}A_{mc}(q)]^2 + N_{agg}\beta_c^2 F_c(qR_g) + N_{agg}(N_{agg}-1)\beta_c^2 A_c^2(q) + 2N_{agg}^2\beta_{mc}\beta_c A_{mc}(q)A_c(q) \quad \text{(S2)}$$

Here the X-ray scattering length contrast for the core block and the corona block is given by $\beta_{mc} = V_{mc}(\xi_{mc} - \xi_{sol})$ and $\beta_c = V_c(\xi_c - \xi_{sol})$, where ξ_{mc}, ξ_c, and ξ_{sol} are the X-ray scattering lengths of the core block (ξ_{PBzMA} = 10.42 × 10^{10} cm^{-2}), the corona block (ξ_{PDMA} = 10.12 × 10^{10} cm^{-2}) and the solvent ($\xi_{water/ethanol}$ = 9.35 × 10^{10} cm^{-2}, where the water-to-ethanol ratio is 95/5 w/w) respectively. V_{mc} and V_c denote the volumes of the core block (V_{PBzMA} = 25.4 nm^3) and the corona block (V_{PDMA} = 17.0 nm^3), respectively. These volumes were obtained from $V = \frac{M_n}{N_A\rho}$ using the molecular weight (M_w) of the corresponding block and the solid-state homopolymer densities determined by helium pycnometry (ρ_{PBzMA} = 1.16 g cm^{-3} and ρ_{PDMA} = 1.09 g cm^{-3}). The spherical form factor amplitude is used for the amplitude of the micelle core self-term

$$A_{mc}(q) = \frac{3[\sin(qR_s) - qR_s\cos(qR_s)]}{(qR_s)^3} \quad \text{(S3)}$$

where R_s is the radius of the spherical micelle core. The mean aggregation number for the spherical micelles is given by $N_{agg} = (1 - x_{sol})\frac{4\pi R_s^3}{3V_{mc}}$, where x_{sol} is the solvent fraction in the micelle core. The self-correlation term of the corona block is described by the Debye function:

$$F_c(qR_g) = \frac{2[\exp(-q^2R_g^2) - 1 + q^2R_g^2]}{q^4R_g^4} \quad \text{(S4)}$$

where R_g is the radius of gyration of the corona block. For diblock copolymers with a relatively short PBzMA block DP, the corona contribution to the scattering, β_c, is comparable to the scattering from the micelle core, β_{mc}, i.e. $PDMA_{71}$-$PBzMA_{100}$ with $(\beta_c/\beta_{mc})^2 \approx 0.20$. Thus, in accordance with previous

work,[2] the amplitude of the corona self-term was calculated from a normalized Fourier transform of the radial density distribution function of the $PDMA_{71}$ coronal chains in the micelle:.

$$A_c(q) = \frac{\int_{R_s}^{R_s+2s} \mu_c(r) \frac{\sin(qr)}{qr} r^2 dr}{\int_{R_s}^{R_s+2s} \mu_c(r) r^2 dr} \quad \text{(S5)}$$

The radial profile, $\mu_c(r)$, is 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.[3] The precise analytical expression of the integration applied in the SAXS analysis is not given in ref. 3 but it can be obtained by using a mathematical software package such as Maple or MatLab. An approximate integration can also be found elsewhere.[4] In accordance with previous studies,[3-5] the confinement $s = 2R_g$ was introduced into the model. It has to be noted that *a* tended to zero for this condition. For the form factor given by equation S2, a sharp, non-sigmoidal interface between the blocks with no penetration of the corona blocks into the micelle cores was assumed. It was considered for the model (equation S1) that a polydispersity of the spherical micelle core radius (R_s) is expressed as a Gaussian distribution:

$$\Psi(r_1) = \frac{1}{\sqrt{2\pi\sigma_{Rs}^2}} e^{-\frac{(r_1 - R_s)^2}{2\sigma_{Rs}^2}} \quad \text{(S6)}$$

where σ_{Rs} is the standard deviation for R_s. The number density per unit volume in equation S1 is expressed as:

$$K = \frac{c}{\int_0^\infty V(r_1)\Psi(r_1) dr_1} \quad \text{(S7)}$$

where *c* is the total copolymer volume fraction in the spherical micelles and $V(r_1)$ is the total copolymer volume in a spherical micelle [$V(r_1) = (V_{mc} + V_c) N_{agg}(r_1)$]. Thus, the overall number of structural parameters required for the spherical micelle model described by equations S1 and S2 is six (namely R_s, σ_{Rs}, x_{sol}, R_g, *a* and *c*).

References

1. Pedersen, J. S. Form factors of block copolymer micelles with spherical, ellipsoidal and cylindrical cores. *J. Appl. Crystallogr.* **2000,** *33*, 637-640.
2. Jones, E. R.; Mykhaylyk, O. O.; Semsarilar, M.; Boerakker, M.; Wyman, P.; Armes, S. P. How Do Spherical Diblock Copolymer Nanoparticles Grow during RAFT Alcoholic Dispersion Polymerization? *Macromolecules* **2016,** *49*, 172-181.

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.
5. Warren, N. J.; Mykhaylyk, O. O.; Ryan, A. J.; Williams, M.; Doussineau, T.; Dugourd, P.; Antoine, R.; Portale, G.; Armes, S. P. Testing the Vesicular Morphology to Destruction: Birth and Death of Diblock Copolymer Vesicles Prepared via Polymerization-Induced Self-Assembly. *J. Am. Chem. Soc.* **2015,** *137*, 1929-1937.