Supporting Information

Synthesis and Characterization of Non-ionic AB-diblock Soft Matter Nanoparticles by RAFT PISA

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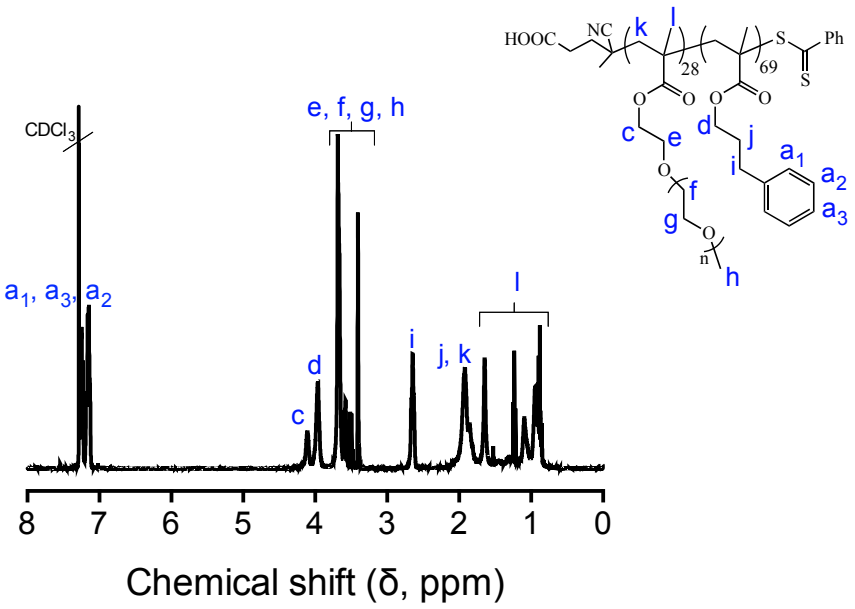
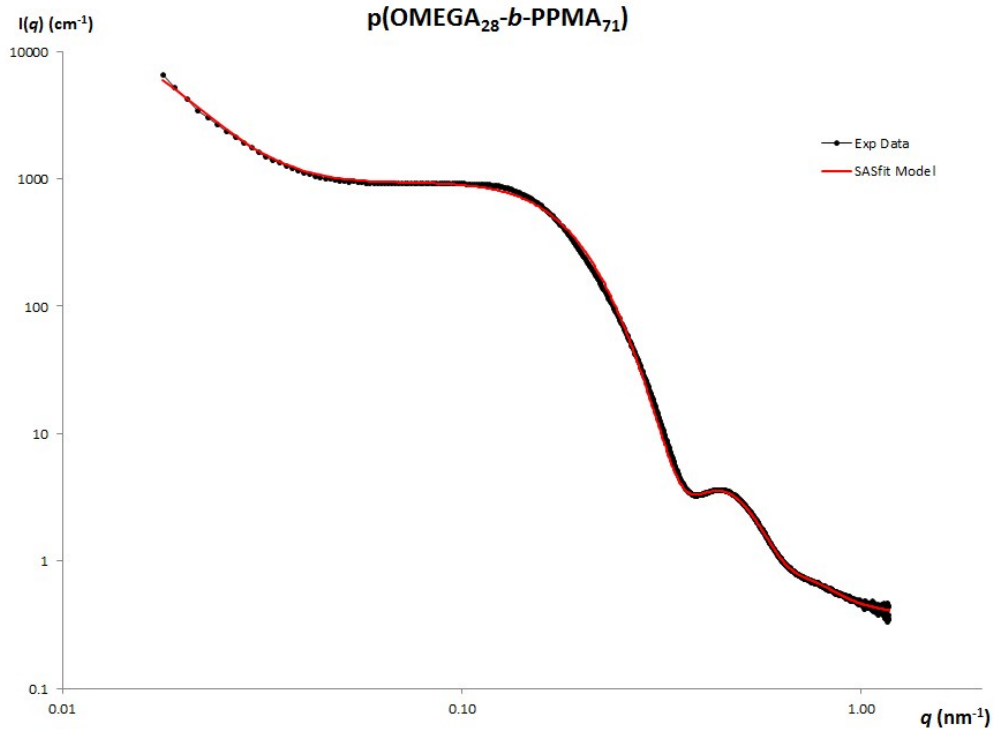


Figure S1. ^{1}H NMR spectrum of p(OEGMA$_{28}$-*b*-PPMA$_{69}$), recorded in $CDCl_3$, with peak assignments.

Small Angle X-Ray Scattering



FigureS1 – The SAXS data and model for p(OMEGA)$_{28}$-*b*-pPPMA$_{71}$. The feature at q = 0.5 nm^{-1} is again prominent in the data.

For the model of p(OMEGA)$_{28}$-*b*-pPPMA$_{71}$ the cross sectional radius is 15.3 ± 0.1 nm, or 30.6 ± 0.2 nm for the average width of the worm like micelles, which is a slightly larger structure than the p(OMEGA)$_{28}$-*b*-pPPMA$_{69}$ micelles. The TEM data for this phase gives a width of 28.8 ± 3.6 nm for these worms which is in agreement with the results from the SAXS model within uncertainty. The correlation peak is located at q = 0.132 ± 0.05 nm^{-1}, which corresponds to a larger distance between interacting micelles of 47.6 ± 0.5 nm when compared to the 36.7 ± 0.5 nm from p(OMEGA)$_{28}$-*b*-pPPMA$_{69}$.

SASfit was used to model the SAXS data obtained from spherical and worm-like polymer micelles[1]. The software package has been developed for the general analysis of scattering data using a variety of shapes (form factors) and models for the interaction of particles (structure factors). The models are implemented with a general equation for the scattering from non-interacting particles (adapted from page 196 of the SASfit manual).

$$I(q)_D = |\Delta\rho|^2 \int_0^\infty |F(q,r)|^2 \cdot V^2(r) \cdot N \cdot P(r) dr$$

The integral is implemented in SASfit with the following; $|\Delta\rho|$ is the scattering contrast, $|F(q,r)|$ is the form factor, $V(r)$ is the volume of the particle, N is the number of particles, and $P(r)$ is the size distribution. If a structure factor is included then

$$I(q) = I(q)_D \cdot S(q)$$

Where S(q) is the structure factor. This calculated value for the intensity is then fit to experimental data using a non-negative least squares method. From the equation for the modelled intensity it can be seen that the correct form factor is a significant choice as it appears squared. So for the simplest cases a sphere is often chosen

$$F_{Sphere}(q,r) = \frac{3 \cdot (\sin(qr) - qr \cdot cos(qr))}{(qr)^3}$$

Where r is the radius of the sphere. This was the form factor incorporated into the model of the p(OMEGA$_{28}$)-*b*-(PPMA$_{36}$) data. In contrast, the form factor of a polymer with a worm-like morphology is more complicated. Kholodenko developed the theoretical framework to describe these semi-felixible chains and they have been incorporated into the SASfit package (see page 94 of the user manual)[2]. The important inputs for this form factor are the cross sectional radius, r, the Kuhn length describing the rigid length of the chain, l, and the contour length describing the total lengh, L.

At larger size scales the polymer aggregates in solution exhibit the self-similar characteristics of mass fractals. This is most prominently displayed in the scattering curves as a sharp gradient at low-q where a dilute solution might be expected to plateau. To account for this feature of the scattering curve an exponential mass fractal term was included in the model as implemented by the SASfit software (page 135 of the user manual)[3].

As these are not dilute samples a structure factor was incorporated into the model. The structure factor used is from the Random Phase Approximation[4].

$$S(q) = \frac{1}{1 + \nu \cdot F(q,r)}$$

Where *F(q,r)* is the form factor being used and ν is a parameter related to the concentration of the polymer in solution.

References for Supplementary Material:

[1] I. Breβler *et. al.* J. Appl. Cryst. (2015) 48, 1587 – 1598.
[2] A.L. Kholodenko Macromolecules (1993) 26, 4179 – 4183.
[3] C.M. Sorensen & G.M. Wang Physical Review E (1999) 60, 7143 – 7148.
[4] J.S. Pedersen, Advances in Colloid and Interface Sciences (1997) 70, 171-210.