

Supplementary Information:

Additive anchored thermoresponsive nanoscale self-assembly generation in normal and reverse Tetronics[®]

Dhruvi Patel,^{1,2} Payal Vaswani,³ Debes Ray,^{4,5} Dhiraj Bhatia,³ Vinod K. Aswal,⁴
Ketan Kuperkar,^{1,*} Pratap Bahadur⁶

¹*Department of Chemistry, Sardar Vallabhbhai National Institute of Technology (SVNIT),
Ichchhanath, Surat-395 007, Gujarat, INDIA.*

²*School of Civil and Environmental Engineering, Cornell University,
Ithaca, 14850, NY, USA.*

³*Biomedical Engineering, Indian Institute of Technology Gandhinagar (IITGn),
Palaj, Gandhinagar-382 355, Gujarat, INDIA.*

⁴*Solid State Physics Division, Bhabha Atomic Research Centre (BARC),
Trombay, Mumbai-400 085, Maharashtra, INDIA.*

⁵*Biomacromolecular Systems and Processes, Institute of Biological Information Processing,
Forschungszentrum Julich, 52428, GERMANY.*

⁶*Department of Chemistry, Veer Narmad South Gujarat University (VNSGU),
Surat-395 007, Gujarat, INDIA.*

***Corresponding author:** E-mail: ketankuperkar@gmail.com

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Neutron Scattering

Small-angle neutron scattering experiments were conducted at the Dhruva reactor, BARC, India. As a function of wave vector transfer Q ($= 4\pi\sin\theta/\lambda$, where λ is the wavelength of the incident neutrons and 2θ is the scattering angle), the coherent differential scattering cross-section ($d\Sigma/d\Omega$) per unit volume is measured in SANS. The monochromatized neutron velocity selection beam has a dispersion of 15% and a mean wavelength of 5.2 Å. Using a 1 m long one-dimensional He³ position sensitive detector, the sample's scattering of neutrons at different angles is measured. The sample slit size of the instrument is 1.3 cm, and the source slit size is 5x3 cm. It has a Q -range of 0.017 to 0.35 Å⁻¹. Data were fitted using the SASFIT tool after the scattering data were adjusted for the background and empty cell contributions were normalized to the absolute cross-sectional unit using the conventional techniques.^{7,8,10-13}

In SANS experiments, the coherent differential scattering cross-section per unit volume ($d\Sigma/d\Omega$) was measured as a function of Q . For monodisperse particles in a medium, it can be written as

$$\frac{d\Sigma}{d\Omega} = I(Q) = NV^2(\Delta\rho)^2 F_{mic}(Q) S(Q) + bkg \quad (1)$$

(where N is the number density of the micelles of volume V , $\Delta\rho$ is the scattering length density difference between micelle and solvent (D₂O), $F_{mic}(Q)$ is the form factor and $S(Q)$ is the inter-particle structure factor. The bkg is a constant term that represents the incoherent background scattering mainly from the hydrogen atoms present in the sample).

The form factor which is a function describing the intra-particle scattering has been calculated for various morphologies. The intermediate range of the profile is the region in which the form factor contains information regarding particle size and shape. In this regime, the scattering results from the dimensionality of the scattered particle were estimated from the calculated slopes. For example, the scattered intensity for unimers/Gaussian coil scales as Q^{-2} , for spherical micelle scales as Q^{-4} , and for ellipsoidal micelle scale as Q^{-3} following the derived analytical expression proposed by Debye:

$$F_G(Q) = \frac{2}{Q^2 R_G^4} [\exp(-Q^2 R_G^2) + Q^2 R_G^2 - 1] \quad (2)$$

(where R_G is the chain radius of gyration and $qR_G < 1$, In the intermediate range

$$F_G(Q) = \frac{2}{Q^2 R_G^2}$$

$F_{mic}(Q)$ for spherical micelles can be written as

$$F_{mic}(Q) = \left[\frac{3(\sin(QR_C)) - QR_C \cos(QR_C)}{(QR_C)^3} \right]^2 \quad (3)$$

where R_C is the hydrophobic core radius which is attributed to the size of the micellar core.

The aggregation number (N_{agg}) is calculated knowing the value of core sizes following the equation:

$$N_{agg} = \frac{4\pi(R_C)_{PO}^3}{3nV_{PO}} \quad (4)$$

where n is the number of propylene oxide monomers in the PO block, $(R_C)_{PO}$ is the radius of the core due to PO only and V_{PO} is the volume of propylene oxide monomer.⁴⁵

$F_{mic}(Q)$ for ellipsoidal micelles can be written as

$$F_{mic}(Q) = \int_0^1 F^2(Q, \mu) d\mu \quad (5)$$

$$F(Q, \mu) = \frac{3(\sin x - x \cos x)}{x^3} \quad (6)$$

$$x = Q[a^2 \mu^2 + b^2(1 - \mu^2)]^{1/2} \quad (7)$$

where a and $b = c$ are semi-major and semi-minor axes of micelles, respectively. The variable μ is the cosine of the angle between the directions of a and Q . The N_{agg} is calculated by following equation:

$$N_{agg} = \frac{4\pi a b^2}{3nV_{PO}} \quad (8)$$

Throughout the data analysis, corrections were made for instrumental smearing. The parameters in the analysis were optimized using a non-linear least-square fitting program.^{18, 38, 46, 47}