Supplementary Information

Nanomicellization characteristics of amphiphilic block copolymer tricycles in various topologies

Brian J. Ree

Functional and Structural Polymers Laboratory, Department of Chemistry and Physics, The Dorothy and George Hennings College of Science, Mathematics and Technology, Kean University, 1000 Morris Ave, Union, NJ 07083, USA

Scattering data analysis

Invariant Q. From the obtained 1D scattering intensity profile, the invariant Q could be determined by using the following relation:[S1,S2]

$$Q = \frac{1}{2\pi^2}\int_0^\infty q^2 I(q)dq\,. \tag{S1}$$

where $I(q)$ is the measured scattering intensity and q is the magnitude of the scattering vector defined as $q = (4\pi/\lambda)\sin\theta$ in which 2θ is the scattering angle and λ is the wavelength of the X-ray beam used.

Guinier analysis. The scattering data could be analyzed first in a qualitative manner by using the Guinier scheme,[S1-S7] which is a model independent method but assuming that particles in solution are spherical and possess a uniform density:

$$\ln I(q) = \ln I_{\mathrm{o}}(q) \; - \; \frac{q^2 R_{\mathrm{g,G}}^2}{3} \tag{S2}$$

where $I_{\mathrm{o}}(q)$ is the incident beam intensity and $R_{\mathrm{g,G}}$ is the radius of gyration of micelles or aggregates in solution; $R_{\mathrm{g,G}}$ can be determined from the low q region ($qR_{\mathrm{g,G}} < 1.33$) of the scattering data.

Three phase ellipsoid (3PEL) model. The 3PEL model consists of three phases: a dense core, a dense corona, and a solvated corona.[S3] For this model structure, the scattering intensity can be expressed by the sum of two terms under assumption that the contribution of their cross term is very small or negligible:

$$I(q) = P_{\mathrm{3PEL}}(q) + P_{\mathrm{blob}}(q) \tag{S3}$$

where $P_{\mathrm{3PEL}}(q)$ is the form factor that describes an ellipsoidal particle consisting of three layer phases and $P_{\mathrm{blob}}(q)$ is the scattering contribution from the density fluctuations smaller than the blob radius within the corona regions. $P_{\mathrm{3PEL}}(q)$ can be given by the following:

$$P_{\mathrm{3PEL}}(q) = \int_0^{\frac{\pi}{2}} \left\{ \begin{matrix} [(\rho_{\mathrm{matrix}} - \rho_{\mathrm{s.corona}}) V_{\mathrm{s.corona}} F_{\mathrm{s.corona}}^2] + \\ [(\rho_{\mathrm{s.corona}} - \rho_{\mathrm{d.corona}}) V_{\mathrm{d.corona}} F_{\mathrm{d.corona}}^2] + \\ [(\rho_{\mathrm{d.corona}} - \rho_{\mathrm{core}}) V_{\mathrm{core}} F_{\mathrm{core}}^2] \end{matrix} \right\} \sin\varphi \, d\varphi \tag{S4}$$

where ρ_i, V_i, and F_i are the density, volume, and form factors of phase i, respectively, and ρ_{matrix} is assumed to be 0 due to background subtraction.

Form factor for each phase can be expressed as the following generalized form F_i based on three components, $F[q,r(R_{\mathrm{e.i}},\varepsilon,\varphi)]$, $n(A)$, and $n(t_{\mathrm{f}})$:

$$F_i = F\,[q,r(R_{\mathrm{e.i}},\varepsilon,\varphi)] \cdot n(A) \cdot n(t_{\mathrm{f}}) \tag{S5}$$

with $F[q,r(R_{\mathrm{e.i}},\varepsilon,\varphi)]$ as the scattering amplitude defining the size and shape, $n(\mathrm{A})$ defining the degree of size distribution following Gaussian distribution, and $n(t_{\mathrm{f}})$ defining the degree of fuzziness for each phase.

Scattering amplitudes of the core, dense corona, and solvated corona, take a spheroid shape with a pair of equal semi-axes (R, R) and a distinct third semi-axis (εR) (*i.e.*, an ellipsoid of gyration). The ellipsoidicity ratio ε is defined as $\varepsilon = R_p/R_e$ and therefore the complete scattering amplitude can be defined as:

$$F[q,r(R_{e.i},\varepsilon,\varphi)] = \frac{3\{\sin[qr(R_{e.i},\varepsilon,\varphi)] - qr(R_{e.i},\varepsilon,\varphi)\cos[qr(R_{e.i},\varepsilon,\varphi)]\}}{[qr(R_{e.i},\varepsilon,\varphi)]^3} \tag{S6}$$

with

$$r(R_{e.i},\varepsilon,\varphi) = R_{e.i}(\sin^2\varphi + \varepsilon^2\cos^2\varphi)^{\frac{1}{2}} \tag{S7}$$

where φ is the modular angle of ellipsoid. $R_{e.i}$ corresponds to: the core radius $r_{e.\mathrm{core}}$, the sum of core radius $r_{e.\mathrm{core}}$ and dense corona thickness $t_{\mathrm{d.corona}}$, and the sum of core radius $r_{e.\mathrm{core}}$, dense corona thickness $t_{\mathrm{d.corona}}$ and solvated corona thickness $t_{\mathrm{s.corona}}$, for the three phases respectively:

$$R_{\mathrm{e,core}} = r_{\mathrm{e.core}} \tag{S8}$$

$$R_{\mathrm{e,d.corona}} = r_{\mathrm{e.core}} + t_{\mathrm{d.corona}} \tag{S9}$$

$$R_{\mathrm{e,d.corona}} = r_{\mathrm{e.core}} + t_{\mathrm{d.corona}} + t_{\mathrm{s.corona}}. \tag{S10}$$

Size distribution for core radius, dense corona thickness, and solvated corona thickness is expressed in the following form:

$$n(A) = \frac{1}{\sqrt{2\pi}\sigma_A} \cdot e^{-\frac{(A-\bar{A})^2}{2\sigma_A^2}} \tag{S11}$$

where A corresponds to the magnitude of core radius or the dense corona thickness or the solvated corona thickness, $\bar{A}$ is the mean value of A, and σ_A is the standard deviation of A from $\bar{A}$.

The degrees of fuzziness of the core, dense corona, and solvated corona, which describe the gradual change in density amongst the three phases, are defined as:

$$n(t_{\mathrm{f}}) = \mathrm{e}^{-\frac{q^2 t_{\mathrm{f}}^2}{4}} \tag{S12}$$

where $2t_{\mathrm{f}}$ is the width (*i.e.*, thickness) of the fuzzy interface at the surface of each phase (core, dense corona, and solvated corona).

On the other hand, $P_{\mathrm{blob}}(q)$ can be expressed by the following relation:[S3,S8]

$$P_{\mathrm{blob}}(q) = \frac{\alpha'}{\mu q^{*}_{blob}} \frac{\sin[\mu \tan^{-1}(q^{*}_{blob})]}{[1+(q^{*}_{blob})^{2}]^{\mu/2}} \tag{S13}$$

where $q^{*}_{\mathrm{blob}} = q^{*}\xi$, $\mu = \chi^{-1} - 1$, and $\alpha' = \alpha 4\pi\mu\xi^{\mu+1}\Gamma(\mu)$; here, $q^{*} = q/[erf(qR_{\mathrm{g,3PEL}}/\sqrt{6})]^{3}$ where *erf* indicates the error function, ξ is the average correlation length (i.e., mean blob size), χ is the Flory-Huggins parameter ($\chi = 3/5$ for the good solvent condition and 1/2 for the Θ solvent condition), α is the amplitude of the blob scattering relative to the shape contribution, and $\Gamma(\mu)$ indicates the gamma function.

Pair distribution function. The pair distance distribution function $p(r)$ can provide information on the probability of finding two scatterers separated by a distance r inside a micelle. The $p(r)$ profile could be obtained from the results of the scattering data fits with the 3PEL models by Fourier transformation using the following relation:[S3-S5,S9,S10]

$$p(r) = \frac{1}{2\pi}\int_{0}^{\infty} I(q)qr\,sin(qr)dq\,. \tag{S14}$$

From the $p(r)$ profiles, the radii of gyration $R_{\mathrm{g,IFT}}$ of the micelles could be further estimated by using the following equation:

$$R_{\mathrm{g},p(r)} = \frac{\int_{0}^{\infty} p(r)r^{2}dr}{2\int_{0}^{\infty} p(r)dr}\,. \tag{S15}$$

Radial density profile. Furthermore, a radial scattering length density profile $\Delta\rho(r)$ (*i.e.*, radial density profile) of micelle could be estimated from the scattering amplitude determined by the 3PEL model analysis. The $\Delta\rho(r)$ can be obtained from F_i in equation S5 through the following numerical Fourier transformation:[S4,S11]

$$\Delta\rho(r) = \frac{1}{2\pi^{2}}\int F_{i}\frac{\sin(qr)}{qr}dq. \tag{S16}$$

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