[Electronic Supplementary Information]

Monodisperse micelles composed of poly(ethylene glycol) attached surfactants: Platonic nature in a macromolecular aggregate

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Experimental section

Materials and synthesis of PEG-attached surfactant (C_m -PEG_{1k}). All chemical reagents were purchased from Tokyo Chemical Industry Co., Sigma-Aldrich Co., or Wako and were used without further purification. All reactions were carried out under a nitrogen atmosphere and all solvents were dehydrated by standard methods. We monitored the progress of the reactions using thin-layer chromatography (TLC), in which the reactions were detected using ultraviolet (UV; 254 nm) irradiation and staining with a basic solution of potassium permanganate. Products were purified by column chromatography with silica gel 60 (240–400 mesh).

Compound I. 4-Hydroxybenzaldehyde (1.00 g, 1.0 equiv.), 1-bromodecane (2.17 g, 1.2 equiv.), and potassium carbonate (3.34 g, 3.0 equiv.) were dissolved in dimethylformaldehyde; DMF (10 mL). The reaction mixture was refluxed for 2 h at 60 °C. After cooling to room temperature, water and ethyl acetate were added for extraction. The organic solvent layer was washed with saturated NaCl aqueous solution (10 mL) and MgSO₄ was added to remove the remaining water. The crude product was purified by flash column chromatography on silica gel, by elution with CH₂Cl₂:hexane at a 1:1 (v/v) ratio to afford white solids (m=9: 1.626 g, 6.55×10^{-3} mol, 80.1%, m=10: 1.98 g, 7.50×10^{-3} mol, 91.6%, m=11: 1.99 g, 7.23×10^{-3} mol, 88.2%). m=9 (500 MHz, NMR CDCl₃), δ (ppm)=9.88 (s, 1H), 7.82 (d, 2H), 6.99 (d, 2H), 4.05 (t, 2H), 1.82 (m, 2H), 1.46 (m, 2H), 1.28 (m, 12H), 0.87 (t, 3H); m=11 (500 MHz, NMR CDCl₃), δ (ppm)=9.88 (s, 1H), 7.82 (m, 2H), 1.46 (m, 2H), 1.46 (m, 2H), 1.46 (m, 2H), 1.28 (m, 14H), 0.87 (t, 3H):

Compound II. Compound I (1.97 g, 1.0 equiv.) and sodium borohydride (1.43 g, 5.0 equiv.) were dissolved in ethanol (12 mL) and stirred for 2 h at room temperature. Then, 1 M HCl_{aq} (20 mL) and saturated NaHCO₃ aqueous solution were added to the reaction mixture. The crude product was purified by flash column chromatography on silica gel, by elution with CH₂Cl₂:MeOH at a 20:1 (v/v) ratio to afford white solids (m=9: 1.40 g, 5.59×10^{-3} mol, 85.0%, m=10: 1.76 g, 7.43×10^{-3} mol, 99.7%, m=11: 1.46 g, 5.81×10^{-3} mol, 85.0%). m=9 (500 MHz, NMR CDCl₃), δ (ppm)=7.27 (d, 2H), 6.89 (d, 2H), 4.62 (s, 2H), 3.97 (t, 2H), 1.76 (m, 2H), 1.33 (m, 2H), 1.28 (m, 10H), 0.87 (t, 3H); m=10: (500 MHz, NMR CDCl₃), δ (ppm)=7.26 (d,

2H), 6.87 (d, 2H), 4.61 (s, 2H), 3.96 (t, 2H), 1.76 (m, 2H), 1.55 (s, 1H), 1.45 (m, 2H), 1.27 (m, 12H), 0.88 (t, 3H); m=11: (500 MHz, NMR CDCl₃), δ (ppm)=7.27 (d, 2H), 6.89 (d, 2H), 4.62 (d, 2H), 3.97 (t, 2H), 1.76 (m, 2H), 1.55 (t, 1H), 1.45 (m, 2H), 1.27 (m, 14H), 0.88 (t, 3H).

Compound III. Compound II (1.60 g, 1.0 equiv.) and sodium hydride (1.68 g, 6.2 equiv.) were dissolved in DMF (15 mL), to which propargyl bromide (4.02 g, 5.0 equiv.) was added slowly. The reaction mixture was stirred for 24 h at room temperature. After that, ethyl acetate was added to the reaction mixture for extraction and MgSO₄ was added to remove the remaining water. The crude product was purified by flash column chromatography on silica gel, by elution with ethylacetate:hexane at a 1:4 (v/v) ratio to afford white solids (m=9: 0.139 g, 4.40×10^{-4} mol, 36.3%, m=10: 0.700 g, 2.55×10^{-3} mol, 37.8%, m=11: 0.281 g, 8.88×10^{-4} mol, 35.1%). m=9 (500 MHz, NMR CD₃OD), δ (ppm)=7.27 (d, 2H), 6.89 (d, 2H), 4.57 (s, 2H), 4.13 (d, 2H), 3.95 (t, 2H), 2.45 (t, 1H), 1.76 (m, 2H), 1.43 (m, 2H), 1.28 (m, 10H), 0.88 (t, 3H); m=10 (500 MHz, NMR CD₃OD), δ (ppm)=7.26 (d, 2H), 6.88 (d, 2H), 5.47 (d, 1H), 4.53 (d, 2H), 4.14 (d, 1H), 3.92 (t, 2H), 1.77 (m, 2H), 1.44 (m, 2H), 1.26 (m, 12H), 0.89 (t, 3H); m=11 (500 MHz, NMR CD₃OD), δ (ppm)=7.27 (d, 2H), 4.54 (s, 2H), 4.14 (d, 2H), 3.95 (t, 2H), 1.27 (m, 14H), 0.89 (t, 3H).

Compound IV: C_m-PEG_{1k}. O-(2-Azidoethyl)-O'-methyl-undecaethylene glycol (0.150 g, 0.273 mmol, 0.83 equiv.), copper (II) sulfate pentahydrate (14.6 mg, 5.83×10^{-2} mmol, 0.17 equiv.), and sodium L-ascorbate (5.07 mg, 2.56×10^{-2} mmol, 0.08 equiv.) were dissolved in dry DMF. Then, compound III (92.0 mg, 0.336 mmol, 1.0 equiv.) in DMF was added to the reaction mixture and refluxed for 24 h at 90 °C. The crude product was purified by reprecipitation, by elution with CH₂Cl₂:hexane at a 3:500 (v/v) ratio to afford compound IV (C₉-PEG_{1k}: 0.169 g, 1.39×10^{-4} mol, 54.9%, C₁₀-PEG_{1k}: 0.119 g, 9.68×10^{-5} mol, 72.2%, C₁₁-PEG_{1k}: 0.177 g, 1.42×10^{-4} mol, 58.9%). C₉-PEG_{1k} (500 MHz, CDCl₃), δ (ppm)=7.74 (s, 1H), 6.87 (d, 2H), 4.64 (s, 2H), 4.53 (t, 2H), 3.94 (t, 2H), 3.87 (t, 2H), 3.64 (m, 95H), 3.38 (s, 3H), 1.77 (m, 2H), 1.44 (m, 2H), 1.27 (m, 10H), 0.882 (t, 3H); C₁₀-PEG_{1k}: ¹H-NMR (500 MHz, CDCl₃), δ (ppm)=7.75 (s, 1H), 6.87 (d, 2H), 4.64 (s, 2H), 4.53 (t, 2H), 3.464 (s, 2H), 4.53 (t, 2H), 3.39 (t, 3H), 1.77 (m, 2H), 1.27 (m, 12H), 0.880 (t, 3H); C₁₁-PEG_{1k} (500 MHz, CDCl₃), δ (ppm)=7.74 (s, 1H), 6.87 (d, 2H), 3.64 (m, 2H), 3.87 (t, 2H), 3.87 (t, 2H), 3.94 (t, 2H), 3.87 (t, 2H), 3.64 (m, 2H), 1.27 (m, 12H), 1.27 (m, 12H), 1.27 (m, 12H), 0.880 (t, 3H); C₁₁-PEG_{1k} (500 MHz, CDCl₃), δ (ppm)=7.74 (s, 1H), 6.87 (d, 2H), 4.64 (s, 2H), 4.53 (t, 2H), 3.94 (t, 2H), 3.87 (t, 2H), 3.84 (t, 2H), 3.87 (t, 2H), 3.84 (t, 2H), 3.87 (t, 2H), 3.94 (t, 2H), 3.87 (t, 2H), 3.84 (t, 2H), 3.87 (t, 2H), 3.84 (t, 2H), 3.87 (t, 2H), 3.87 (t, 2H), 3.87 (t, 2H), 3.84 (t, 2H), 4.64 (s, 2H), 4.53 (t, 2H), 3.87 (t, 2H), 3.87 (t, 2H), 3.87 (t, 2H), 3.84 (t, 2H), 3.87 (t, 2H), 3.87 (t, 2H), 3.87 (t, 2H), 3.84 (t, 2H), 4.64 (s, 2H), 4.53 (t, 2H), 4.64 (s, 2H), 4.53 (t, 2H), 4.64 (s, 2H), 4.53 (t, 2H), 3.87 (t, 2H), 3.87 (t, 2H), 3.86 (m, 95H), 3.38 (s, 3H), 1.77 (m, 2

Small-angle X-ray scattering (SAXS) measurements. The SAXS measurements were performed at BL-40B2 at SPring-8, Hyogo Prefecture, Japan. The distances between the sample and detector were 0.7, 1, and 4 m (C_9 -PEG_{1k}: 1.0 m, 4.0 m; C_{10} -PEG_{1k}: 0.7 m, 4.0 m; C_{11} -PEG_{1k}: 1.0 m, 4.0 m). The wavelength was 0.10 nm. The detailed experimental procedures are reported elsewhere¹⁸. The samples were prepared in aqueous solution. For the fitting of the micellar SAXS profiles, we employed the model of a core-corona spherical model [eq. (1)] described by the following expression ¹⁸:

$$\frac{\binom{I(q)}{c}_{c\to0}}{=\rho(Rc)\frac{N_A}{M_W}} \left\{ (\rho_c - \rho_s) V_c \frac{3[\sin(qRc) - qRc\cos(qRc)]}{(qRc)^3} + 4\pi \int_{R_c}^{R_s} \frac{(\rho_s(r))}{(qRc)^3} \right\}$$

Here, $R_{\rm C}$ and $R_{\rm S}$ are the outer radii of the core and micelle; $\rho_{\rm C}$, $\rho_{\rm S}(r)$, and ρ_0 are the scattering lengths (cm⁻¹) of the core, shell, and solvent, respectively; and $N_{\rm A}$ is Avogadro's number. $\rho(R_{\rm C})$ gives smearing due to the size distribution, and we assumed that the core size has a Gaussian distribution with the standard deviation of σ . At the low-q region of the SAXS profiles, the Guinier law is given by the following equation:

$$R_{g}^{2} = \frac{3\left[V_{s}R_{c}^{2}(\rho_{c}-\rho_{s})+V_{s}R_{s}^{2}\rho_{s}\right]}{5\left[V_{c}(\rho_{c}-\rho_{s})+V_{s}\rho_{s}\right]}$$

The Guinier plot of $\ln(I(q))$ vs. q^2 provides the I(0) and R_g determined from the intercept and the slope, respectively. Since the effect of sample concentration including inter-particle interference affects the values of I(0) and R_g , the contribution of the concentration was eliminated by extrapolating to a zero concentration (an infinitely diluted state).

Analytical ultracentrifugation (AUC) measurements. To evaluate the molar mass and distribution of the micelles under several conditions, we performed analytical ultracentrifugation for the samples using a Beckman Optima XL^{-1} ultracentrifuge¹². The rotor speeds were set at 2.8 x 10⁴ rpm. The concentration profile was determined from analyzing the Rayleigh fringe at the sedimentation equilibrium state, which provided the apparent weight-averaged molecular weight *M*w, App, and *Q* (=*M*w, App/*Mz*, App) of the micelle at each sample concentration. By extrapolating the concentration to zero, the micellar mass and the value of *Q* could be determined.



Figure S1. NMR spectrum of compound I. Figure S2. NMR spectrum of compound II.



trum of C_{10} -PEG_{1k}.



Figure S5. NMR spectrum of C_9 -PEG_{1k}.



Figure S6. NMR spectrum of C_{11} -PEG_{1k}.



Figure S7. CMC values of surfactant.