Electronic Supplementary Material (ESI) for Soft Matter.

Supplementary Information

Dendrimer-mediated Columnar Mesophase of Surfactant

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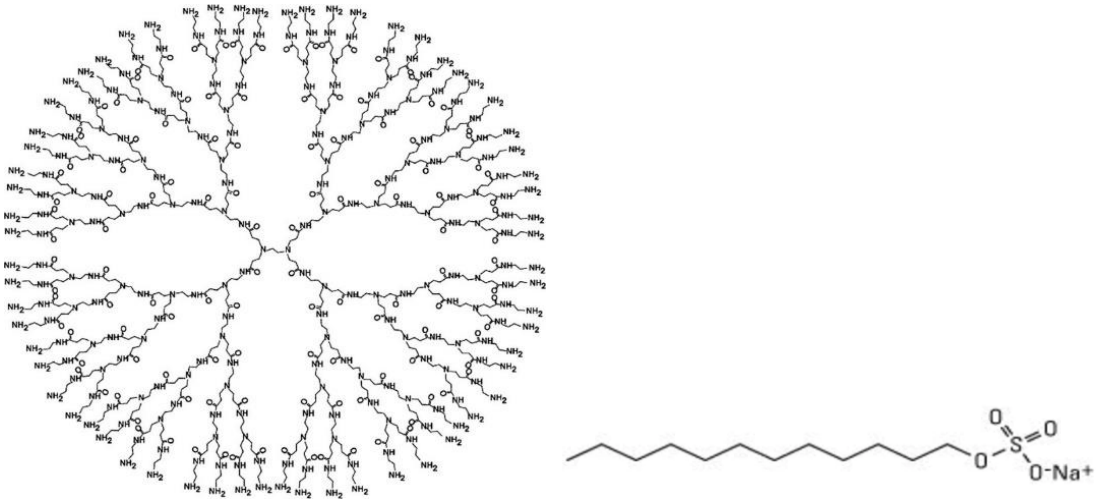

Scheme S1. Chemical structures of PAMAM G4 dendrimer and SDS

1. Observation of Columnar Mesophase using Polarized Optical Microscope (POM)

The mesomorphic phase of the PAMAM G4 dendrimer-SDS complexes were observed by an Olympus BX51 polarized optical microscope (POM) at room temperature. The samples were prepared by sandwiching the white precipitates suspended in water between the microscope slides.

Optically birefringent patterns clearly recognized in the representative polarized optical micrographs displayed in Figure S1 attested that Type I pattern was associated with the distorted 2D columnar phase, since disordered sphere phase with neither positional nor orientation order does not have optical anisotropy.

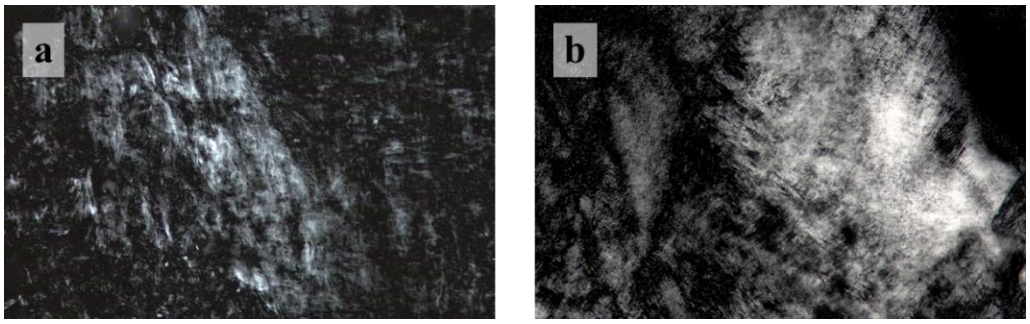

Figure S1. Representative polarized optical micrographs of PAMAM G4 dendrimer-SDS complexes with (a) d_p = 0.4, X_n= 0.8 and (b) d_p =0.5, X_n = 0.5. The presence of birefringent patterns in the micrographs manifests the formation of mesophases in the complexes.

2. Identification of Distorted Hexagonal Columnar Phase by Paracrystalline Model Fitting

Due to the optically birefringent patterns clearly recognized in the representative polarized optical micrographs displayed in Figure S1, Type I pattern was attributed to the distorted hexagonal columnar phase. This structural assignment was confirmed by fitting the observed SAXS profile by the paracrystalline model of hexagonally packed cylinders. As shown in Figure S2, the red solid line represents the scattering profile calculated from the model using the parameters of: lattice parameter = 4.98 nm, grain size = 25 nm, and average lattice displacement = 1.2 nm. The calculated SAXS profile matched with the experimental SAXS result very well. Therefore, Type I SAXS scattering pattern can be identified as distorted hexagonal columnar phase, where Type I is denoted as "Col_{dh}" herein.

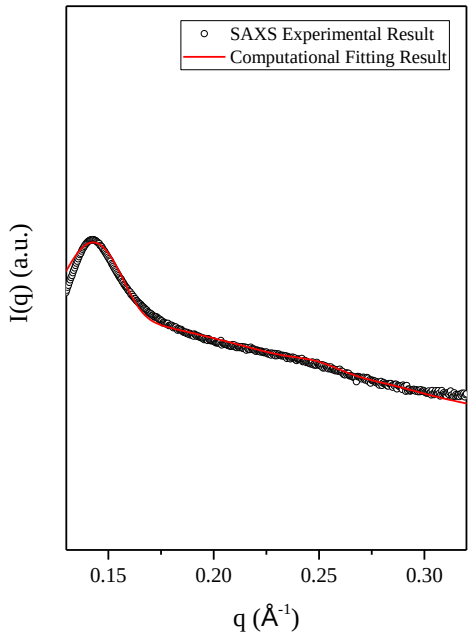

Figure S2. The scattering profile of distorted hexagonal columnar (Col_{dh}) phase obtained from SAXS experiment (the line with symbol O) and from paracrystalline model calculation.

3. Measurement of Actual Surfactant Binding Ratio (X_a) by ^{1}H NMR Spectroscopy

^{1}H NMR spectroscopy was employed to investigate the actual composition of complexes. The experimental procedures and the calculation of actual binding ratio, X_a, from ^{1}H NMR results followed the methods adopted in our previous study.[1] Figure S3 manifests the actual binding ratio, X_a, of PAMAM G4 dendrimer-SDS complexes calculated from ^{1}H NMR results with various dendrimer d_p with respect to X_n. Although X_a may in general deviate from X_n prescribed by the feed molar ratio of SDS to the amine groups of dendrimer, the experimentally determined value of X_a correlated positively with X_n, where it increased with increasing X_n.

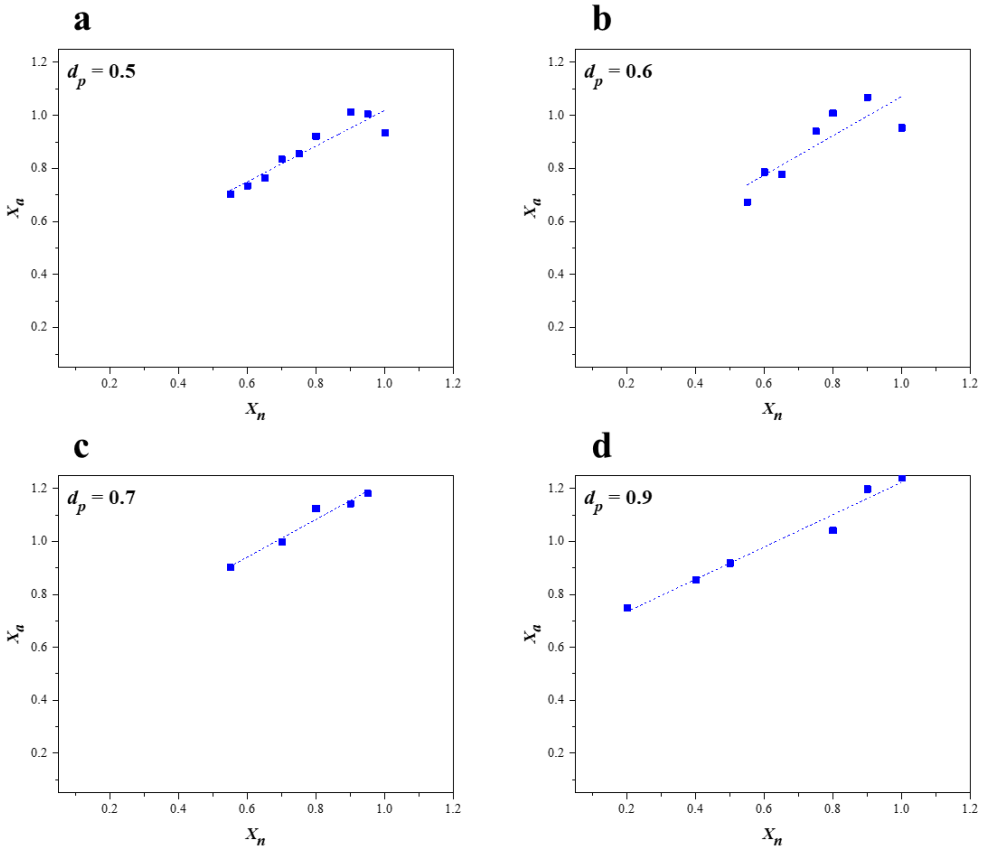

Figure S3. Actual binding ratio, X_a, of PAMAM G4 dendrimer-SDS complexes calculated from ^{1}H NMR results with d_p = (a) 0.5, (b) 0.6, (c) 0.7 and (d) 0.9, with respect to X_n.

4. Calculation of Dendrimer Geometry Parameters for Col_{ob} Phase

In the Col_{ob} lattice illustrated in Figure S4, $\overline{A'D'}$ equals to lattice parameter, l, $\overline{D'B'}$ equals to lattice parameter, a, and ∠A'D'B' equals to lattice parameter, γ. The semi-radii of the deformed dendrimer, a_d and b_d, is calculated by subtracting the semi-radii of SDS cylinders, a_s and b_s, from $\overline{D'B'}$ and the diagonal, $\overline{A'C'}$. The length of $\overline{A'C'}$ is calculated by means of trigonometric functions. Since from trigonometric functions, the value of $\angle A'OD'$ can also be approximately estimated, we can tell that the SDS micelle cylinders and the dendrimers slightly tilted (within 5°) to enhance the contact so as to retain the contact area.

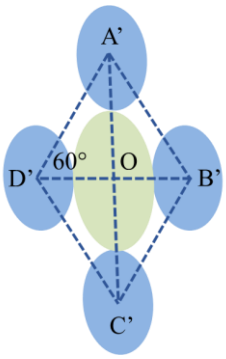

Figure S4. Schematic illustrations of the placement of the deformed dendrimers and the SDS micelle cylinders in Col_{ob} lattice from the enlarged top view within a unit lattice.

Reference

1. Young, C.-M.; Chang, Y.-F.; Chen, Y.-H.; Chen, C.-Y.; Chen, H.-L., Ribbon Phase of Dendrimer–Surfactant Complexes. *Macromolecules* **2019,** *52* (23), 9177-9185.