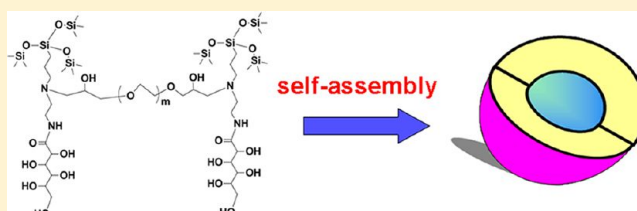


Adsorption and Aggregation Behaviors of Tetrasiloxane-Tailed Gemini Surfactants with (EO)_m SpacersWang Guoyong,[†] Qu Wenshan,[‡] Du Zhiping,^{*,†,§} Wang Wanxu,[†] and Li Qiuxiao[†][†]China Research Institute of Daily Chemical Industry, Taiyuan Shanxi, 030001, P. R. China[‡]Department of Chemistry, Shanxi Datong University, Datong Shanxi, 037009, P. R. China[§]Department of Chemistry, Shanxi University, Taiyuan Shanxi, 030006, P. R. China

S Supporting Information

ABSTRACT: Adsorption and aggregation behaviors of novel tetrasiloxane-tailed gemini surfactants *N,N'*-ditetrasiloxane-*N,N'*-digluconamide oligo ethylene glycol diglycidyl (Si-*m*-Si, where *m* is the number of ethylene glycol of 1, 2, and 3) were investigated using surface tension, bromophenol blue encapsulation, dynamic light scattering (DLS), and transmission electron microscope (TEM) methods. The static surface tension of the aqueous Si-*m*-Si solutions measured at the critical aggregate concentration (CAC) was observed to be lower than that of traditional hydrocarbon gemini surfactants. This suggests that these newly synthesized gemini surfactants are capable of forming a closely packed monolayer film at the air/aqueous solution interface. With a combination of DLS data, TEM measurements, and bromophenol blue entrapment studies, formations of vesicles in Si-*m*-Si solutions appear to occur at a concentration well above the CAC. Moreover, the size of vesicles depended on their *m* values.



1. INTRODUCTION

Gemini surfactants containing two hydrophobic and two hydrophilic groups in one molecule have attracted much attention over the past few years due to their superior properties compared with conventional single-chain surfactants.^{1–4} They exhibit lower critical micelle concentration and higher efficiency in lowering the surface tension. Furthermore, gemini surfactants exhibit unusual properties such as vesicle formation at low concentration and premicellar aggregate formation at concentrations below the CMC.^{5–8}

Thus, considerable efforts have gone into the design and synthesis of new forms of gemini surfactants; structures of gemini surfactants have been extensively varied by changing the spacer,^{9–11} head groups,^{12,13} and tail groups and even through synthesis of heterogemini surfactants containing two non-identical surfactants.^{14,15}

However, most of these efforts have focused on the hydrocarbon-tailed gemini surfactants. Only a few reported studies of heteroatom-tailed gemini surfactants are available. Some fluorinated gemini surfactants have been reported,¹⁶ and their adsorption and aggregate properties were considerably different from those of typical hydrogenated gemini surfactants because of the stiffer fluorocarbon chain.

Up until now, research on siloxane-tailed gemini surfactant has not been reported. With conventional single chain surfactant, changing the hydrocarbon-tailed group to a siloxane-tailed group leads to significant variations to the surface properties and aggregate behavior.^{14,17–20} As gemini surfactants have two tail groups, introduction of siloxane into tail groups may have greater influences on the molecular

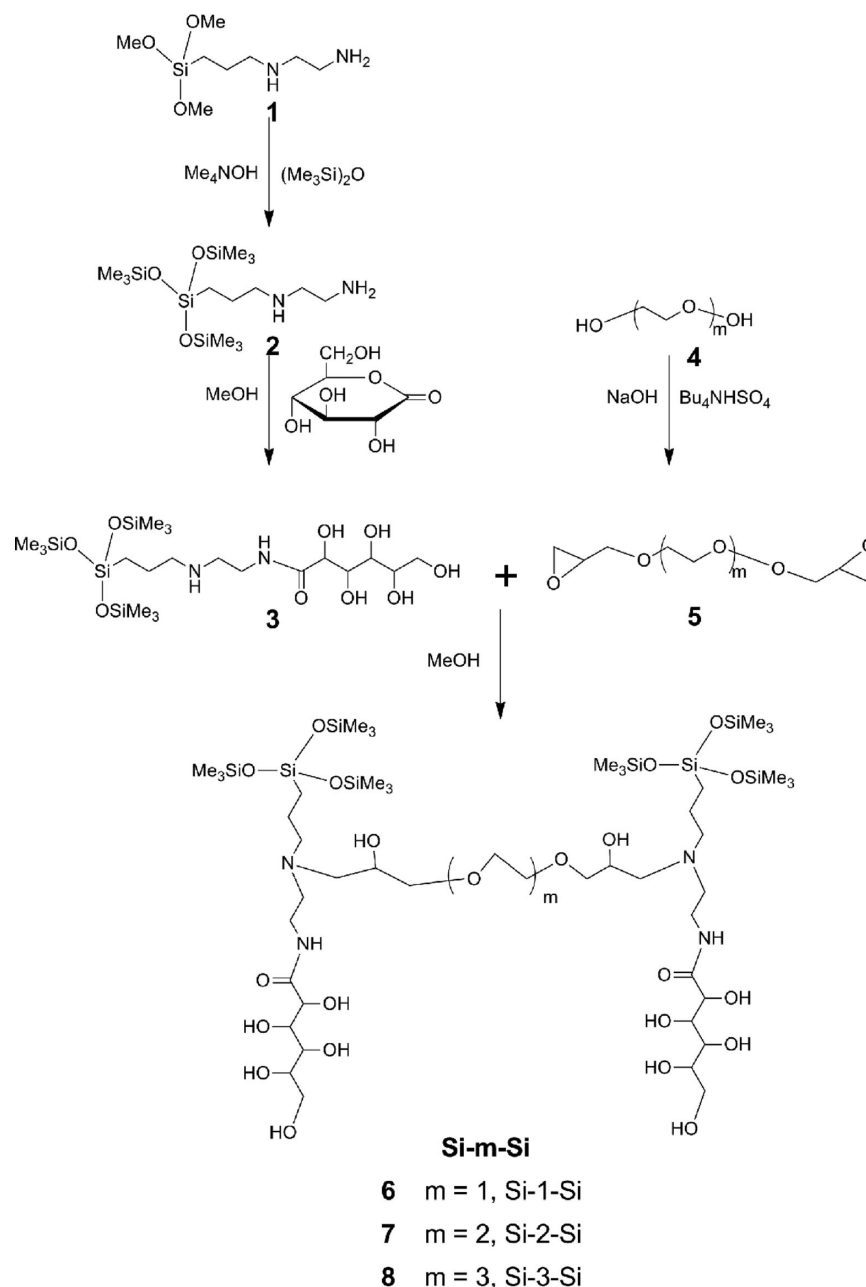
properties. With the corresponding increase of hydrophobic effect of the whole amphiphile, there would be more obvious structure effects on gemini surfactants. On the other hand the stronger hydrophobic interaction and the resultant strong aggregation tendencies allow molecules to form larger aggregates than micelles. On the other hand, the spacer length has been shown to have a profound effect on aggregation behaviors of gemini-type surfactants. Studying *m-s-m* type geminis [alkanediyl- α,ω -bis(alkyldimethylammonium bromide) gemini surfactants, *m* and *s* are the carbon numbers of the alkyl and alkanediyl groups], Zana et al.²¹ have reported that geminis with short spacers (a length containing 2 and 3 carbon atoms) form threadlike micelles and that those with medium length (a length containing 5–12 carbon atoms) form spherical micelles, with vesicles, often double-lamellar, observed in solutions of 12-16-12 and 12-20-12 surfactants. Engberts et al.²² synthesized some gemini bisphosphate surfactants of the type 12-*s*-12, with *s* = 6, 8, 12, 18, and 24 carbon atoms. These 12-6-12, 12-8-12, and 12-12-12 geminis form micellar structures. The 12-18-12 and 12-24-12 geminis formed vesicles in aqueous solution, as observed by electron microscopy. Santanu Bhattacharya et al.²³ synthesized dimeric pseudoglycerol lipids with (CH₂)_{*m*} spacers. The transmission electron micrograph (TEM) and dynamic light scattering (DLS) of their aqueous dispersions confirmed the formation of vesicular type aggregates. Vesicle sizes and morphologies depended strongly on the *m* value, the methods,

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Scheme 1. Synthetic Routes and Acronyms of Si-*m*-Si (*m* = 1, 2, and 3)

and thermal history of the vesicle preparations. On the basis of these data, we designed a series of tetrasiloxane-tailed gemini surfactants Si-*m*-Si (*m* = 1, 2, and 3) with 1–3 EO groups in the spacer and investigated the effect of EO spacer on the adsorption and aggregation behaviors of tetrasiloxane-tailed gemini surfactants.

2. EXPERIMENTAL METHODS

2.1. Materials. 2-Aminoethyl-3-aminopropyltrimethoxysilane and glucose δ -lactone were purchased from Aldrich Chemical Co. Bromophenol blue and other chemicals were purchased from Sinopharm Chemical Reagent Co. All reagents were of analytical grade and were used as received. Double distilled water was used for all analysis and measurements of primary properties.

2.2. Characterization of Surfactant Structures. Nuclear magnetic resonance (NMR) (^1H and ^{13}C NMR) spectroscopy (Varian INOVA-400 MHz spectrometer) and Fourier transform infrared spectroscopy (FT-IR) (Hitachi 270-30) were used to characterize the structures of synthesized surfactants. Because of overlapping signals with some of the methyl groups in the surfactants, TMS was not suitable as an internal standard for NMR, therefore CDCl_3 , of which the residual proton is at 7.26 ppm, was selected. Elemental analysis was also carried out by a PerkinElmer 2400 CHN analyzer.

2.3. Studies of Aqueous Solution Behaviors of the Surfactants. *Surface Tension.* Surface tension was determined using a KRÜSS K12 Processor Tensiometer by the Wilhelmy plate method at 25 ± 0.1 °C. The length and thickness of the platinum plate were 19.9 and 0.2 mm, respectively. The dipping distance was 2 mm. The platinum plate and glassware were

cleaned with strong basic solutions and rinsed with doubly distilled water. The tensionmeter was calibrated with doubly distilled water before each use. Concentrated stock solutions of surfactants (pH \approx 7.5) were freshly prepared in doubly distilled water, and then diluted to appropriate concentrations. The different solutions were aged for at least 24 h before the determinations. For each concentration, the surface tension was measured three times with the interval of 120 s after stirring and with an average deviation of less than $0.2 \text{ mN}\cdot\text{m}^{-1}$.

Dynamic Light Scattering (DLS). Aggregation behaviors of surfactant solutions were monitored by dynamic light scattering (DLS) with a Zeta Plus Particle Size Analysis (Brookhaven, USA) with a He–Ne laser beam at 658 nm (scattering angle: 90°). All solutions were filtered with a $0.45 \mu\text{m}$ (mixed cellulose acetate) membrane filter and equilibrated at 25°C for 8 h prior to experiments. Resulting autocorrelation functions were fitted using a non-negatively constrained least-squares algorithm to estimate the diffusion coefficient (D), which is then related to the hydrodynamic diameter (d_h) of the surfactant aggregates (e.g., micelles or vesicles) through the Stokes–Einstein relation, $d_h = kT/(3\pi\eta D)$, where k is the Boltzmann constant, T is the absolute temperature, and η is the viscosity of the disperse medium.

Transmission Electron Microscopy (TEM). Structures of surfactant aggregates in solutions were studied using transmission electron microscopy, JEM-1011, at 100 kV using the negative-staining method and freeze fracture technique. A droplet of the surfactant solution was placed on a carbon-coated grid and allowed to equilibrate for 2 min. Excess liquid was removed by carefully touching one end of the grid with filter paper. When the grid was partially dried, a drop of staining solution (2% phosphotungstic acid) was added onto the grid. Again, excess liquid was removed by filter paper after 2 min, and the grid dried at room temperature. Fracturing and replication were carried out in a freeze fracture device (Balzer BAF 400, Germany) equipped with a JEE-4X vacuum evaporator. Micrographs were obtained using a JEM-100 CXII transmission electron microscope.

Entrapment of Bromophenol Blue and Gel Filtration. Dye encapsulation experiments for the surfactant solutions were also performed to identify the structure of the aggregation phase. Solutions were prepared with $5 \times 10^{-4} \text{ mol/L}$ bromophenol blue and aged at room temperature for 6 h. 0.5 mL of the surfactant solution was eluted at a velocity of 0.5 mL/min through a $1.0 \text{ cm} \times 25 \text{ cm}$ chromatography column packed with Sephadex G-25 gel (medium grade). When the water-soluble dye gets inside vesicles, it should be eluted early on, as there is less absorption on beads. The concentration of the dye in the effluent was determined by UV–vis spectrophotometer at a wavelength of 590 nm.

X-ray Diffraction (XRD). Self-supported cast films were prepared by dispersing surfactant solutions over precleaned glass plates, and then air-drying at room temperature. Finally, the plates were placed under a low vacuum for 15 min. X-ray diffraction (XRD) studies were carried out using an X-ray diffractometer (Shimadzu/XRD-6000). The X-ray beam was generated with a Cu anode at 40 kV and 200 mA, and the wavelength of the $K_{\alpha 1}$ beam was 1.5406 \AA . The beam was directed to the edge of film, and the scanning 2θ was recorded from 1 to 15° , using a step width of 0.01° .

3. RESULTS AND DISCUSSION

Three tetrasiloxane-tailed gemini surfactants were synthesized via a multistep reaction, as shown in Scheme 1; products were characterized by ^1H NMR, ^{13}C NMR, IR, and element analysis (see the Supporting Information for details).

3.1. Surface Properties. Static surface tension was measured to evaluate the surface activity of gemini surfactants. In Figure 1, surface tension was plotted against the

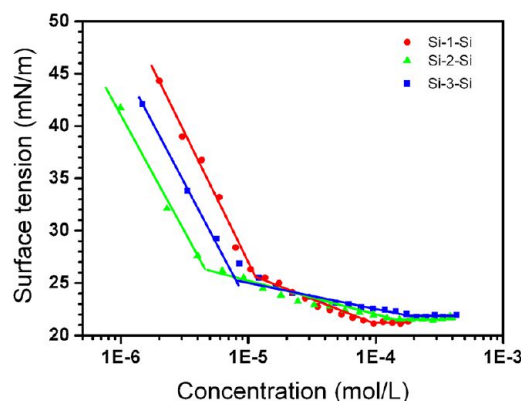


Figure 1. Surface tensions of aqueous Si- m -Si ($m = 1, 2$, and 3) solutions as a function of the concentration at 25°C : red circles = Si-1-Si, green triangles = Si-2-Si, and blue squares = Si-3-Si.

concentration of Si- m -Si ($m = 1, 2$, and 3) aqueous solutions. The surface tension of the monomer was not measured due to its poor solubility in water at room temperature. The critical aggregation concentrations (CACs) of surfactants were obtained by determining the intersection point of the plateau portion and the steeply downward sloping portion of the plots. The minimum surface tension (γ_{CAC}) was calculated by analyzing the plateau region of the plots. These gemini surfactants showed two transition points in their surface tension curves. This implied a different aggregation process for gemini surfactants compared to conventional surfactants. This unusual behavior (the first transition points) of the gemini molecules has also been observed by other investigators and was explained as due to the formation of premicellar aggregations (dimer, trimer, and oligomers).^{24,25} The values of CAC corresponding to the second transition points and γ_{CAC} are listed in Table 1, together with those reported for hydrocarbon gemini surfactants with sugar head groups N,N' -dialkyl- N,N' -diguconamide ethylenediamine [$\text{Glu}(n)$ -2- $\text{Glu}(n)$] (n = number of carbons in an alkyl chain, $n = 8, 10$, and 12)²⁵ and N,N' -dialkyl- N,N' -dilactobionylamide hexanediamide [$\text{Lac}(n)$ -6- $\text{Lac}(n)$] ($n = 12$ and 16).²⁶ As seen from Table 1, values for CAC were 9.17×10^{-5} , 1.44×10^{-4} , and $1.82 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$ for Si-1-Si, Si-2-Si, and Si-3-Si, respectively. Values of γ_{CAC} were 21.2, 21.5, and $21.9 \text{ mN}\cdot\text{m}^{-1}$ for Si-1-Si, Si-2-Si, and Si-3-Si, respectively. All three gemini surfactants significantly reduced the surface tension of water, as shown by the γ_{CAC} values of $21\text{--}22 \text{ mN}\cdot\text{m}^{-1}$. While the γ_{CAC} of $\text{Glu}(n)$ -2- $\text{Glu}(n)$ (n = number of carbons in an alkyl chain, $n = 8, 10$, and 12)²⁵ is around $30 \text{ mN}\cdot\text{m}^{-1}$, the γ_{CAC} of these siloxane gemini surfactants reduced the surface tension even further and were comparable to those reported for other siloxane surfactants.^{27–30} This result would be attributed to the branched tetrasiloxane portion lying flat on the water surface, exposing the highly surface active methyl groups to air.

Table 1. Parameters of Aggregation and Adsorption of Si-*m*-Si (*m* = 1, 2, and 3) at 25 °C

surfactant	γ_{CAC} (mN·m ⁻¹)	CAC (mol·L ⁻¹)	A_{min} (Å ² /molecule)	$-\Delta G_{\text{mic}}^0$ (kJ·mol ⁻¹)	Γ_{max} (mol·cm ⁻²)
TGA					
Si-1-Si	21.2	9.17×10^{-5}	37.8	33.0	4.39×10^{-10}
Si-2-Si	21.5	1.44×10^{-4}	40.2	31.9	4.13×10^{-10}
Si-3-Si	21.9	1.82×10^{-4}	42.7	31.3	3.89×10^{-10}
Glu(8)-2-Glu(8) ^a	30.7	2.68×10^{-5}	42.8	36.1	3.89×10^{-10}
Glu(10)-2-Glu(10) ^a	30.3	6.55×10^{-6}	41.2	39.6	3.99×10^{-10}
Glu(12)-2-Glu(12) ^a	29.6	1.46×10^{-6}	40.2	43.3	4.14×10^{-10}
Lac(12)-6-Lac(12) ^b	39.0	5.07×10^{-7}	119	45.8	1.40×10^{-10}
Lac(16)-6-Lac(16) ^b	50.2	1.27×10^{-5}	106	37.9	1.57×10^{-10}

^aFrom ref 25. ^bFrom ref 26.

The CAC values showed an increase with increasing numbers of oxyethylene groups in spacer from Si-1-Si to Si-3-Si, as would be expected from the increase in hydrophilic character of the molecules resulting from this change. A similar increase was reported about quaternary ammonium gemini surfactants containing polyoxyethylene spacer.³¹ The closely spaced values of γ_{CAC} are reasonable, as these surfactants differ only slightly in their EO chain length.

According to Gibbs' law, at equilibrium, adsorption of surfactants at a surface leads to a reduction of the surface tension. The saturation surface excess concentration, Γ_{max} , and the minimum area, A_{min} , per surfactant molecule can be calculated using the Gibbs adsorption isotherm equations (eqs 1 and 2). The standard free energy of aggregation can be calculated from eq 3.

$$\Gamma_{\text{max}} = -\frac{1}{2.303RT} \left(\frac{\partial \gamma}{\partial \log c} \right)_T \quad (1)$$

$$A_m^s = \frac{10^{16}}{N_A \Gamma_{\text{max}}} \quad (2)$$

$$\Delta G_{\text{mic}}^0 = RT \ln \left(\frac{\text{CAC}}{55.5} \right) \quad (3)$$

where *R* is the gas constant, *T* is the absolute temperature, and *N_A* is Avogadro's number. These parameters are shown in Table 1. Γ_{max} and γ_{CAC} both reflect the arrangement of amphiphile molecules at the air–water interface. Si-3-Si has a smaller Γ_{max} value than Si-1-Si and Si-2-Si, which is consistent with the larger γ_{CAC} , as discussed above due to the loose molecular arrangement at the air–water interface. Correspondingly, Si-3-Si has a bigger calculated A_{min} , which varies inversely with Γ_{max} .

From Si-1-Si to Si-3-Si, the Γ_{max} values decreased, while the A_{min} values increased with increasing spacer chain length. This is in agreement with the trends seen from the 12-*s*-12 and 12-EO*z*-12 (*z* is from 1 to 5) surfactants, which are bisquaternary ammonium bromide gemini surfactants possessing a spacer chain $-(\text{CH}_2)_s-$ or $-(\text{OCH}_2\text{CH}_2)_z-$.³²

The standard free energy of micellization is always negative, indicating tendencies to form micelles in solutions. Furthermore, the absolute values of ΔG_{mic}^0 of Si-1-Si are higher than those of Si-2-Si and Si-3-Si (Table 1), suggesting that micellization of Si-1-Si is easier than that of Si-2-Si and Si-3-Si.

3.2. Aggregate Properties. Our gemini surfactants showed two transition points in their surface tension curves, implying a different aggregation process. At the same time, solutions of Si-*m*-Si are bluish and turbid above CAC,

indicating the presence of large aggregates too. The hydrodynamic size distribution of these large aggregates was analyzed by dynamic light scattering (DLS). The intensity-weighted distribution graphs of Si-*m*-Si at 8 mmol·L⁻¹ are shown in Figure 2. These aggregates had bimodal distribution functions.

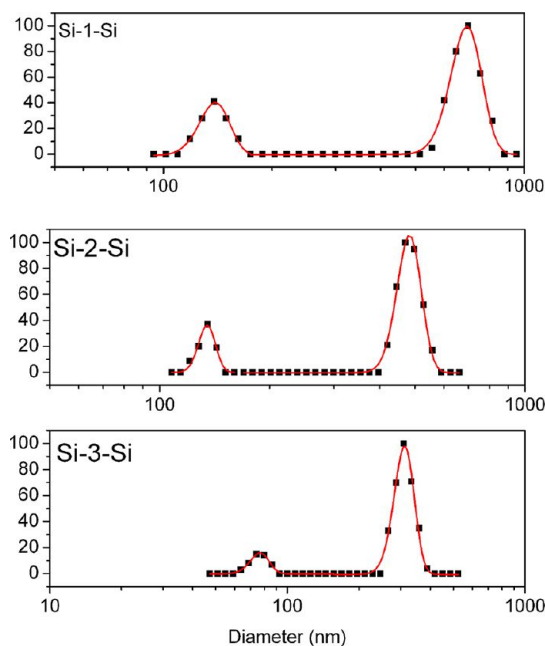


Figure 2. Intensity-weighted size distributions of aggregates formed in Si-*m*-Si solutions at a concentration of 8 mol·L⁻¹ as measured through DLS at 25 °C.

The intensity size distribution calculated from DLS often overestimates larger aggregates. In fact, in surfactant solutions we have studied, there were only few large aggregates; therefore, we did not pursue them further and are only using DLS measurement as an assistant method to confirm the presence of nanoscale aggregates. These aggregates have an average diameter of around 138.5 nm for Si-1-Si, 134.6 nm for Si-2-Si, and 76.9 nm for Si-3-Si, much larger than spherical micelles which typically have diameters in the range 3–5 nm;³³ therefore, large aggregates such as vesicles might exist in the solution. The size of aggregate was ~130–140 nm for Si-*m*-Si with *m* = 1 and 2 and then decreased to 76.9 nm for Si-*m*-Si with *m* = 3, illustrating the remarkable influence of spacer length in Si-*m*-Si on aggregate sizes when changing from *m* = 2 to *m* = 3. The size of vesicles depended on the spacer length; the surfactant with the longest spacer chain had the smallest aggregate size. This can be interpreted as a decrease in micellar

dimensions with increasing spacer length. The gemini surfactant with a short spacer has a lower curvature of the interfacial film due to a smaller headgroup distance, and thus, they favor forming a larger aggregate. Similar results have been reported for dimeric pseudoglycerol lipids with $(\text{CH}_2)_m$ spacers by other groups.²³

The morphology of aggregates was visualized through transmission electron microscopy (TEM).^{34,35} Figure 3 shows

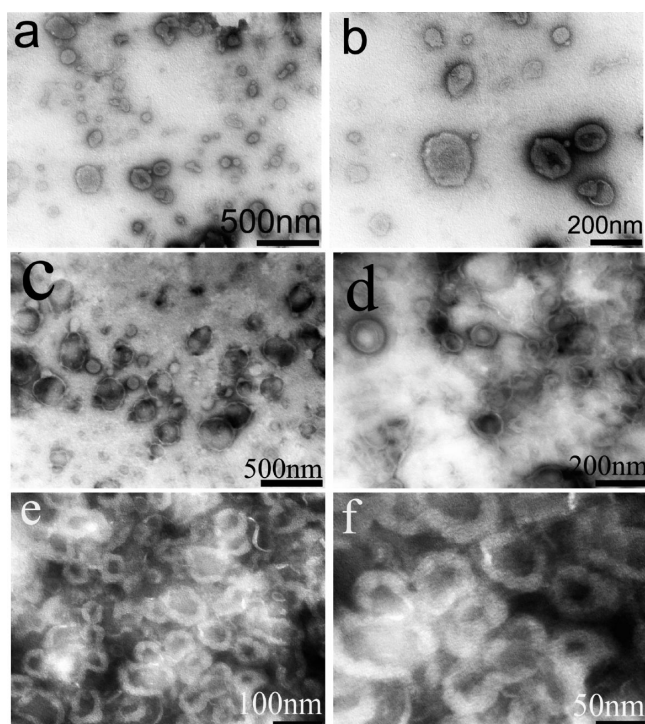


Figure 3. TEM images of Si-*m*-Si aqueous solutions at a concentration of $8 \text{ mol} \cdot \text{L}^{-1}$ by the negative-staining method: (a and b) Si-1-Si; (c and d) Si-2-Si; (e and f) Si-3-Si.

TEM images of Si-*m*-Si aqueous solutions at a concentration of $8 \text{ mmol} \cdot \text{L}^{-1}$ by the negative-staining method. TEM examination of individual, air-dried, bluish, and turbid aqueous solution on Formvar coated copper grids revealed the existence of closed spherical assemblies with dark outer rings,^{36,37} diameters ranging from 100 to 300 nm for Si-1-Si, 100 to 250 nm for Si-2-Si, and 50 to 90 nm for Si-3-Si. The size of vesicles calculated by electron microscopy was consistent with the result from DLS.

The vesicles were further characterized using FF-TEM, which allows us to observe vesicle morphology directly without the addition of staining agents. FF-TEM images (Figure 4)

demonstrated the presence of unilamellar vesicles. In these FF-TEM images, shadow (light) patterns showed vesicles both plucked from the fracture surface and protruding from the fracture surface.

Encapsulation of water-soluble compounds is an important characteristic of vesicles,³⁸ and such encapsulation makes vesicles potentially excellent drug delivery vehicles. The existence of vesicles can be confirmed by encapsulation of the bromophenol blue dye. Gel-filtration chromatography with a Sephadex G-25 column was performed to separate bromophenol blue-entrapped vesicles from free bromophenol blue. The encapsulation efficiency (EF) was calculated by the following equation:

$$\text{EF} = C_{\text{dye}} / C_{\text{t,dye}}$$

where C_{dye} and $C_{\text{t,dye}}$ are the caught and total dye concentrations, respectively.

The calculated EF is 2.43% for Si-1-Si, 2.64% for Si-2-Si, and 3.56% for Si-3-Si, respectively, which was close to EF for dimeric pseudoglycerol lipid vesicles previously reported in the literature.²³

The stability of vesicles with time was examined using TEM, with the TEM images of Si-2-Si solution on different days shown in Figure 5. Vesicles still existed in Si-2-Si solutions even after 30 days.

Bilayer widths of vesicular aggregates were experimentally determined from the cast films obtained using a procedure previously reported in the literature followed by XRD experiments. The XRD patterns obtained from the cast films are shown in Figure 6. 2θ values for each of the vesicular aggregates were obtained from the XRD experiments; the bilayer widths of the vesicular aggregates were calculated using Bragg's equation ($n\lambda = 2d \sin \theta$). XRD graphs of these vesicles showed one typical peak at about 2.78° of 2θ , and the corresponding bilayer width is 31.7 \AA .

From the energy minimized (MOPAC) structure using Chem 3D (version 8.0), we determined the theoretical length of the Si-*n*-Si surfactants. The theoretical bilayer width ($\sim 40.0 \text{ \AA}$) was calculated by multiplying the monolayer width obtained from the optimized structure by a factor of 2. It is clear that the bilayer width determined from XRD is smaller than that of the theoretical bilayer determined from its optimized structure but larger than the monomolecular length of the surfactant. This indicated the probable adoption of the tilted interdigitated packing model. Figure 6 shows a proposed scheme for the molecular arrangement in the vesicular membrane.

4. CONCLUSIONS

In summary, three tetrasiloxane-tailed gemini surfactants, Si-*m*-Si ($m = 1, 2, \text{ and } 3$) were successfully synthesized and

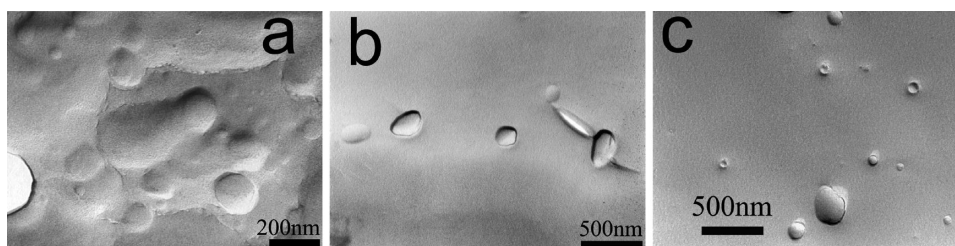


Figure 4. TEM images of Si-*m*-Si aqueous solutions at a concentration of $8 \text{ mol} \cdot \text{L}^{-1}$ by the freeze fracture method: (a) Si-1-Si; (b) Si-2-Si; (c) Si-3-Si.

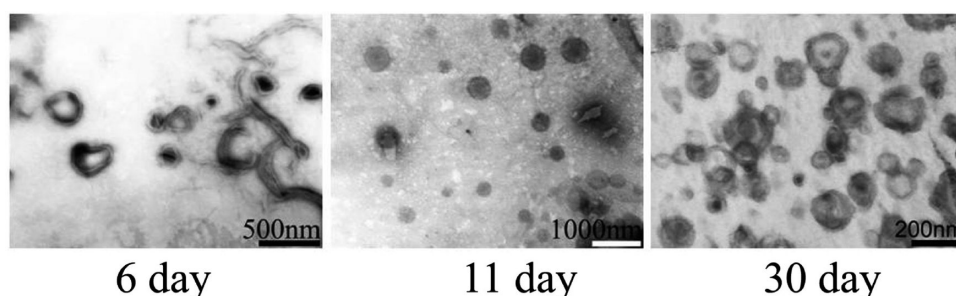


Figure 5. TEM images of Si-2-Si ($8 \text{ mol} \cdot \text{L}^{-1}$) at different time points: (a) 6 days; (b) 10 days; (c) 30 days.

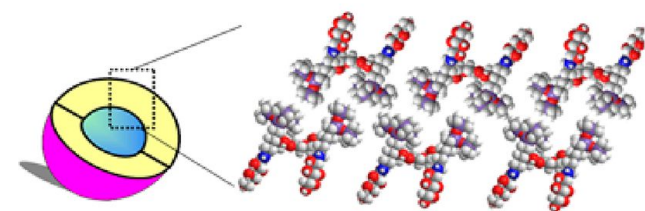
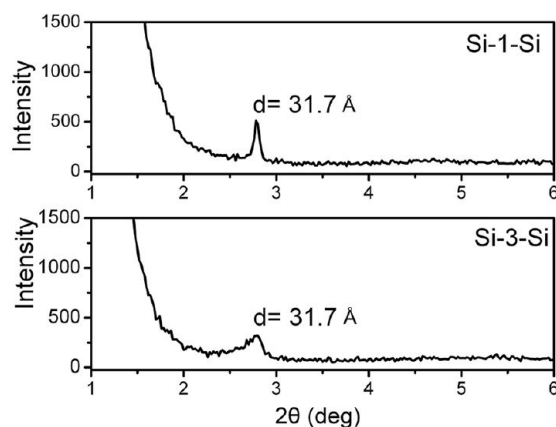


Figure 6. Small angle XRD measurements of the cast film of Si-*n*-Si vesicles ($8 \text{ mmol} \cdot \text{L}^{-1}$) on a glass plate (up) and the proposed arrangement of the molecules (Si-1-Si) in the vesicle wall (down).

characterized by elemental analysis, FT-IR, and ^1H and ^{13}C NMR spectrometry. The surface properties of these surfactants in water were evaluated by surface tension measurements and found to have excellent efficiency in surface tension reduction due to incorporation of a short chain bulky siloxane moiety. Aggregates of these three surfactants, formed in aqueous solutions, could be considered as spherical vesicles through DLS and TEM analysis, and the results were further confirmed by encapsulation of water-soluble compounds, bromophenol blue. Moreover, introduction of a $(\text{EO})_m$ spacer chain at the headgroup brings about a dramatic effect on the size of aggregates. These findings demonstrate the continuing need for new designs of synthetic surfactants to expand our understanding of their behaviors.

■ ASSOCIATED CONTENT

Supporting Information

IR, NMR, and elemental analyses data of each surfactant. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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