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A Giant Surfactant of Polystyrene−(Carboxylic Acid-Functionalized Polyhedral Oligomeric Silsesquioxane) Amphiphile with Highly Stretched Polystyrene Tails in Micellar Assemblies

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Abstract: A novel giant surfactant possessing a well-defined hydrophilic head and a hydrophobic polymeric tail, polystyrene−(carboxylic acid-functionalized polyhedral oligomeric silsesquioxane) conjugate (PS−APOSS), has been designed and synthesized via living anionic polymerization, hydrosilylation, and thiol−ene "click" chemistry. PS−APOSS forms micelles in selective solvents, and the micellar morphology can be tuned from vesicles to wormlike cylinders and further to spheres by increasing the degree of ionization of the carboxylic acid. The effect of APOSS−APOSS interactions was proven to be essential in the morphological transformation of the micelles. The PS tails in these micellar cores were found to be highly stretched in comparison with those in traditional amphiphilic block copolymers, and this can be explained in terms of minimization of free energy. This novel class of giant surfactants expands the scope of macromolecular amphiphiles and provides a platform for the study of the basic physical principles of their self-assembly behavior.

Small-molecule amphiphiles (surfactants and lipids) and amphiphilic block copolymers are well-known to form nanoscale morphologies in solution.[1] In small-molecule amphiphile assemblies, the ionic heads of the molecules strongly interact with each other and with the solvent, and their alkyl tails are mostly in the extended form with an all-trans conformation. The study of the thermodynamics and kinetics of their self-assembly plays an essential role in understanding biological systems (e.g., membranes) and developing advanced biotechnologies (e.g., targeted drug delivery).[2] On the other hand, the self-assembly mechanism of amphiphilic block copolymers usually involves random-coil-like flexible chains in both the coronas and cores. These flexible chains in the micellar assemblies possess a variety of chain conformations that are interchangeable and interdependent, which significantly affects their free energy and the overall aggregation behavior, making the study of the self-assembly mechanism difficult.[3] Therefore, amphiphilic block copolymers behave very differently from small-molecule amphiphiles. It is thus intriguing to study "giant surfactants" having molecular sizes comparable to those of amphiphilic diblock copolymers but an overall molecular shape similar to that of small-molecule surfactants having a polar head with a rigid conformation.

Polyhedral oligosilsesquioxane (POSS), the smallest precisely defined cubic silica nanoparticle, has received much attention as an important nanobuilding block.[4] It has been used to build amphiphilic molecules either by itself[5] or in conjugation with other materials, such as poly(ethylene oxide) (PEO) and poly(acrylic acid) (PAA).[6] In all of these cases, a hydrophobic POSS head was usually invoked because of its synthetic facility. Such an arrangement is the opposite of that in traditional surfactants and lipids. Their self-assembly thus exhibited less-defined morphologies and very different phase behaviors. To the best of our knowledge, there have been no reports on the use of hydrophilic POSS as a building block in the construction of POSS amphiphiles. In this communication, we report the design, synthesis, and self-assembly of a polystyrene−(carboxylic acid-functionalized polyhedral oligomeric silsesquioxane) conjugate (PS−APOSS) as a prototype "giant surfactant" with a hydrophilic POSS cage as the polar head. The rationale for their self-assembly mechanism in terms of minimization of the free energy of the micelles will also be discussed.

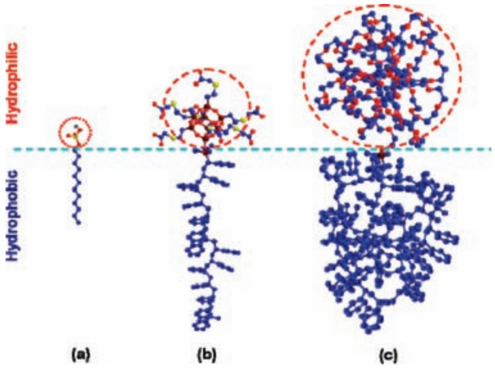

Figure 1. Structural comparison of (a) a typical small-molecule surfactant, sodium dodecyl sulfate; (b) a giant surfactant, PS−APOSS; and (c) a typical amphiphilic block copolymer, PS-*b*-PEO.

A structural comparison among small-molecule surfactants (e.g., sodium dodecyl sulfate), the giant surfactant PS−APOSS, and amphiphilic block copolymers (e.g., PS-*b*-PEO) is illustrated in Figure 1. Small-molecule surfactants are composed of a compact polar head and a hydrophobic alkyl tail typically containing 12−16 carbon atoms (Figure 1a). Amphiphilic block copolymers have polymeric, random-coil-like, covalently connected hydrophilic and hydrophobic blocks (Figure 1c). In contrast, the giant surfactant PS−APOSS reported herein possesses a hydrophilic POSS head with definite shape and size and a linear, hydrophobic polymeric tail with a length suitable to resemble the typical structure of a small-molecule surfactant (Figure 1b). To balance the ratio between hydrophilicity and hydrophobicity while maintaining a macromo-

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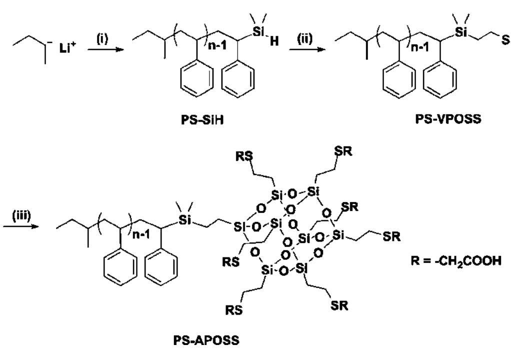
lecular size, multiple carboxylic acid groups were attached to the POSS head. The hydrophilicity could be tuned by attaching different polar groups to the periphery of the POSS cage, while the hydrophobicity could be controlled by the PS tail length. Thus, there is actually a class of “giant surfactants”. These giant surfactants are expected to exhibit rich self-assembly behavior that depends on the balance of the hydrophobic and hydrophilic interactions. Indeed, the PS−APOSS giant surfactants were found to self-assemble into different micellar morphologies, such as vesicles, wormlike cylinders, and spheres, in selective solvents. Moreover, the PS tails in the micelle cores were found to be highly stretched in comparison with those in traditional amphiphilic block copolymers, which is very unusual and has not been reported to date. This feature well resembles what is observed in small-molecule surfactants.

Scheme 1. Synthesis of PS−APOSS by Anionic Polymerization, Hydrosilylation, and Thiol−Ene “Click” Chemistry[a]



[a] (i) (a) Styrene, C_6H_6, r.t.; (b) $(CH_3)_2SiHCl$, 95%; (ii) OctaVinyl POSS, Karstedt’s catalyst, 60 °C, 36 h, toluene, 34%; (iii) $HSCH_2COOH$, DMPA, UV 365 nm, 0.5 h, THF, 52%.

The synthetic route is outlined in Scheme 1. The anionic polymerization of styrenic and diene monomers has been known to offer the best control over the major parameters affecting polymer properties, such as molecular weight, polydispersity, architecture, and functionality.[7] Following the general functionalization methodology (GFM) for anionic polymers,[8] chain-end silyl hydride-functionalized polystyrene (PS−SiH) was synthesized via anionic polymerization with a number-average molecular weight (M_n) of 2800 and a polydispersity (M_w/M_n) of 1.02 (95% yield) as studied here (we synthesized PS with M_n ranging between 2000 and 5000). PS−SiH was further reacted with excess octavinyl POSS in the presence of Karstedt’s catalyst (1,3-divinyltetramethyldisiloxane-platinum in xylene) to afford PS−VPOSS. Monofunctionalized PS−VPOSS ($M_n = 3400$, $M_w/M_n = 1.03$, 34% yield; see Figure S1 in the Supporting Information) was obtained after fractional precipitation from toluene with methanol five times. PS−VPOSS possesses seven reactive vinyl side groups on the POSS cage onto which a large variety of functionalities can be installed to tune the hydrophilicity. Thiol−ene “click” chemistry was utilized to functionalize the POSS cage because of its high efficiency and simple protocol.[9] In this case, seven carboxylic acid functionalities were readily introduced onto the POSS cage, giving rise to PS−APOSS with a PS weight fraction of 65% ($M_n = 4300$, $M_w/M_n = 1.03$, 52% yield). It should be noted that the “click” feature would allow modular construction of a family of giant surfactants for which PS−VPOSS would serve as a common precursor. The successful occurrence of the hydrosilylation and thiol−ene “click” reactions was confirmed by size-exclusion chromatography; FT-IR, ^{1}H NMR, and ^{13}C NMR spectroscopy; and MALDI-TOF mass spectrometry (Figures S2−S5).[10] The most convincing evidence was provided by the MALDI-TOF mass spectrum of the final product PS−APOSS, which is shown in Figure 2. The inset is the overview of the spectrum, which exhibits only one narrow distribution with molecular weights in accordance to the proposed structure. For example, a representative monoisotopic mass peak at *m/z* 4308.4 agreed well with the calculated monoisotopic molecular weight of 4308.5 Da for the 27-mer of PS−APOSS−Ag^+ $[C_4H_9-(C_8H_8)_{27}-Si(CH_3)_2(C_2H_4)-Si_8O_{12}(C_4H_7O_2S)_7-Ag^+]$. These results unambiguously established the structure and uniformity of the final product.

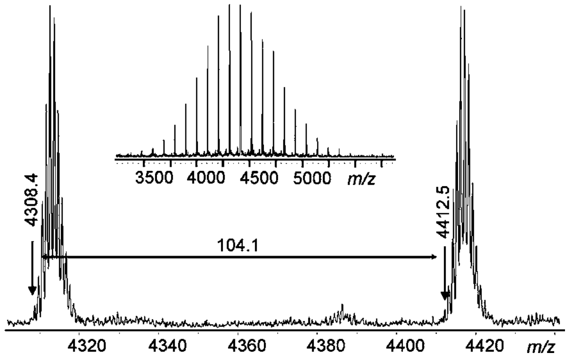


Figure 2. MALDI-TOF mass spectrum for PS−APOSS, showing only one narrow distribution with molecular weights that agree well with the proposed structure.

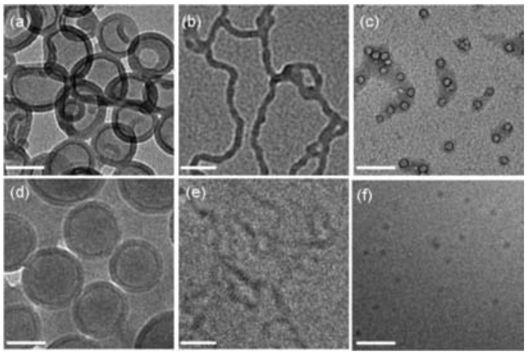


Figure 3. (a−c) TEM and (d−f) cryo-TEM images of PS−APOSS micelles in solution with an initial concentration of 0.8 wt % and a final water content of 50 wt % for the following common solvents: (a, d) 1,4-dioxane; (b, e) DMF; (c, f) DMF/NaOH. Scale bars represent 80 nm.

The self-assembly of PS−APOSS was conducted in selective solvents. To prepare micelle solutions, deionized water was added at a rate of 10 μL/min into a vial containing 5.00 g of a stock solution of PS−APOSS in a common solvent [1,4-dioxane or *N*,*N*-dimethylformamide (DMF)] with an initial concentration of 0.8 wt %. Self-assembly occurred at a water content of ∼25 wt % in 1,4-dioxane and ∼15 wt % in DMF. More water was added until the final water content reached ∼50 wt %. Although the micelle morphology could also be tuned by changing the water content, we chose to compare the stable micelle morphology at a relatively high, identical water content to reveal the effect of different types of common solvents on the ionization of the carboxylic acid groups and the resulting morphology. Stable aggregates were obtained by dialyzing the micelle solutions against deionized water for 3 days to remove the organic solvent. Figure 3 shows a set of transmission electron microscopy (TEM) and cryo-TEM images of PS−APOSS micelles formed in various common solvents. Contrary to small-molecule surfactants, the morphologies and dimensions observed using normal TEM and cryo-TEM in this case are surprisingly identical. This is probably due to the high glass transition temperature (T_g) of PS tails, which fixes the micelle morphology. Figure 3a shows a typical TEM image of the vesicles prepared in 1,4-dioxane/water. These vesicles are slightly collapsed as a result of the sample drying process. The cryo-TEM image in Figure 3d shows the intact vesicles that were frozen without any effects of drying. The average wall thicknesses measured from the two images were identical within the range of error (11.0 ± 0.5 nm) and were used to determine the radius of the hydrophobic PS core of the vesicles ($R_1 = 4.5 \pm 0.2$ nm) by subtracting the diameter of a POSS cage (1.0 nm).[4a] The formation of the vesicle morphology was further supported by dynamic light scattering (DLS). A slight angular dependence of the diffusion coefficient D_{eff} was observed in the plot of D_{eff} versus the square of the scattering vector q (Figure S6), which most likely suggests a spherical vesicle shape ($R_{\mathrm{h,app}} = 56 \pm 5$ nm; Figure S7). When the common solvent was changed to DMF, branched wormlike cylinders were observed (Figure 3b), which was also proven by cryo-TEM (Figure 3e). The average diameter of these wormlike micelles was determined to be 14 ± 0.6 nm. Thus, their hydrophobic PS core radius (R_2) was 6.0 ± 0.3 nm. When the common solvent was changed to a mixture of DMF and 0.01 M NaOH(aq) (molar ratio $r = N_{\mathrm{NaOH}}/N_{\mathrm{COOH}} = 0.04$), spherical micelles were formed, as shown in Figure 3c,f. The average diameter observed using TEM was 14.5 ± 0.6 nm, which determined the hydrophobic PS core radius of the spheres (R_3) to be 6.3 ± 0.3 nm. The morphology was also confirmed by DLS experiments (Figure S8).

To explain these micellar morphological changes, it is critical to understand the APOSS−APOSS interactions. This is directly related to the degree of ionization of the carboxylic acid groups on the POSS cages, which could be estimated using FT-IR spectroscopy.[11] Figure 4 shows the spectra of PS−APOSS freeze-dried from micelle solutions of various common solvents. Two distinct vibrational absorption bands for the carbonyl groups of the carboxylic acid groups are highlighted: $\nu \approx 1710$ cm^{-1}, attributed to the C=O stretching of native −COOH groups, and $\nu = 1580-1620$ cm^{-1}, associated with the asymmetric stretching band of the ionized carboxylate (COO$^-$) group.[12] Assuming similar extinction coefficients for the two bands allowed the degree of ionization (α) to be estimated from the ratio of the intensity of the ν(COO$^-$) peak to the sum of the intensities of the ν(COO$^-$) and ν(COOH) peaks:[11a]

$$\alpha = \frac{I_{\nu(\mathrm{COO}^-)}}{I_{\nu(\mathrm{COOH})} + I_{\nu(\mathrm{COO}^-)}} \times 100\ \% \tag{1}$$

When the common solvent was changed from 1,4-dioxane to DMF and further to the DMF/NaOH mixture, the COOH band intensity decreased and the COO$^-$ band intensity increased as the acid groups became ionized. The degrees of ionization were calculated to be 45, 62, and 80%, respectively (Table 1). With an increase in the degree of ionization, the charge density on the POSS cage increased, resulting in stronger repulsive forces among the POSS cages. To minimize the electrostatic free energy of the APOSS heads, the surface area per chain, A, was forced to increase.[13] Experimentally, A can be calculated using the following equation:[3]

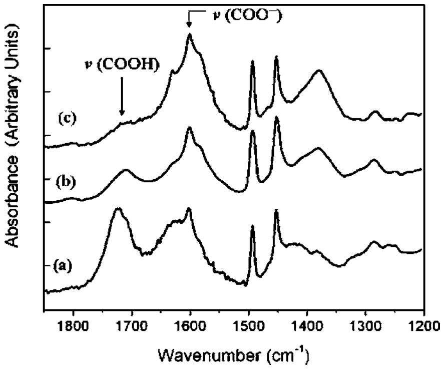


Figure 4. FT-IR spectra of PS−APOSS freeze-dried from micelle solutions in the common solvents (a) 1,4-dioxane, (b) DMF, and (c) DMF/NaOH.

$$A_i = \frac{iV_{\mathrm{S}}N_{\mathrm{PS}}}{fR_i} \tag{2}$$

where i is a micellar geometry dependent factor ($i = 1$ for vesicles, $i = 2$ for cylinders, and $i = 3$ for spheres), f is the volume fraction of PS tails in the core, V_{S} is the volume of the PS monomer, and N_{PS} is the degree of polymerization of the PS tails. If we assume sufficiently dense PS tails in the core, which is true when the selective solvent concentrations are high enough, f approaches unity. From the values of R_i, A_i values were calculated and found to increase in the order $A_1 < A_2 < A_3$ (Table 1), which corresponds well with the morphological changes from vesicles to wormlike cylinders and further to spheres. Therefore, in view of the fact that there is no corona interaction in the system, the morphological changes of these PS−APOSS micelles are mainly determined by the APOSS−APOSS interactions at the micelle surface.

Table 1. Morphology and Physical Parameters of PS−APOSS Micelles Formed Using Different Common Solvents

i	micelle	common solvent	α (%)[a]	R_i (nm)[b]	A_i (nm^2)[c]
1	vesicle	1,4-dioxane	45	4.5 ± 0.2	1.04 ± 0.04
2	cylinder	DMF	62	6.0 ± 0.3	1.56 ± 0.08
3	sphere	DMF/NaOH	80	6.3 ± 0.3	2.23 ± 0.11

[a] α is the degree of ionization of carboxylic acid calculated using eq 1. [b] R_i is the radius of the hydrophobic PS core. [c] A_i is the interfacial area per surfactant chain calculated using eq 2.

A surprising observation is that the size of R is close to the contour length of the PS tail (6.8 nm) in these assemblies, indicating that the PS tails in these micellar cores are highly stretched. This feature is similar to what is observed in assemblies of small-molecule surfactants.[14] Furthermore, the micellar core size was found to increase in the order $R_1 < R_2 < R_3$. This trend is the opposite of that for the PS-*b*-PAA micelle system reported by Eisenberg et al.[15] For example, the core size of the vesicle (R'_{vesicle}) was larger than that of the sphere (R'_{sphere}) in PS-*b*-PAA micelles when the common solvent was changed from 1,4-dioxane to DMF. The reason for these two unusual observations lies in the differences between the interactions (APOSS−APOSS interaction vs corona−corona interaction) and the surface tensions in these systems. It has been reported that the stretching of PS blocks in micellar cores is related to the PS−solvent interaction and the repulsive interaction between the PAA corona blocks. While these interactions have opposite effects on the stretching of the PS blocks, the average degree of stretching of the PS blocks must be dependent on the comparative balance of these two contributions.[15b] Because of the conformational rigidity of the APOSS cage, the electrostatic free energy could only be reduced through increasing the distance between the APOSS cages, which would increase the surface area per chain and thus the surface free energy. To reduce the interfacial area and minimize the overall free energy, the PS tails in the PS−APOSS micelles were forced to stretch much more than those in the PS-*b*-PAA micelles, though this is entropically unfavorable. We speculate that the surface tension in PS−APOSS is higher than that in the PS-*b*-PAA micelles since the interface in the PS−APOSS system would not be shielded as much because of the lack of a corona. Therefore, the strong APOSS−APOSS repulsive interactions dominate the stretching of PS tails in the PS−APOSS micellar core. In contrast, the stretching of PS tails in the PS-*b*-PAA micelles is dominated by the PS−solvent interaction. The relative importance of these two contributions qualitatively explains the opposite trend of the micellar core sizes. It is the conformational rigidity of the APOSS head groups that distinguishes it from amphiphilic diblock copolymers and makes it behave similarly to small-molecule surfactants.

In summary, a novel, precisely defined giant surfactant, PS−APOSS, possessing a rigid, polar hydrophilic POSS headgroup and a hydrophobic PS tail has been designed and synthesized via living anionic polymerization, hydrosilylation, and thiol−ene “click” chemistry. The micellar morphology of PS−APOSS in solution changed from vesicles to wormlike cylinders and further to spheres as the degree of ionization of the carboxylic acid groups increased. From the FT-IR spectra, the degree of ionization of the carboxylic acid in these micellar assemblies was found to follow the trend $\alpha_{\mathrm{vesicle}} < \alpha_{\mathrm{cylinder}} < \alpha_{\mathrm{sphere}}$. This is in accordance with the increase in repulsive forces among APOSS cages in these micellar assemblies and could explain the micellar morphological changes. Unexpectedly, the PS tails in the core of PS−APOSS micelles were found to be highly stretched. The trend of the core radii of the micelles was found to be $R_{\mathrm{vesicle}} < R_{\mathrm{cylinder}} < R_{\mathrm{sphere}}$, which is the opposite of that for the traditional PS-*b*-PAA block copolymer system. The conformational rigidity of the APOSS head groups and the strong APOSS−APOSS interactions in PS−APOSS micelles are believed to force the PS tails to stretch in order to minimize the overall free energy. This novel class of giant surfactants expands the scope of macromolecular amphiphiles and provides a platform for the study of the basic physical principles of their self-assembly behaviors.

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Supporting Information Available: Additional information on the synthesis and characterization of the compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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