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Polyhedral Oligomeric Silsesquioxanes: A New Class of Amphiphiles at the Air/Water Interface

Jianjun Deng, Joseph T. Polidan, John R. Hottle, Catherine E. Farmer-Creely,[‡] Brent D. Viers,[†] and Alan R. Esker*

Department of Chemistry, Virginia Polytechnic Institute and State University, Blacksburg, Virginia 24061, and ERC/PRSM, Air Force Research Laboratories, Edwards Air Force Base, California 93524

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Over the past decade, polyhedral oligomeric silsesquioxane (POSS) molecules such as those shown in Figure 1, have attracted considerable interest as "self-healing" high-temperature nanocomposites and space-survivable coatings,[1,2] low-k dielectric materials,[3] and as templates for the preparation of nanostructured materials such as liquid crystalline polymers,[4] catalysts,[5,6] dendrimers,[7] and multiarm star polymers.[8] POSS molecules represent hybrid organic−inorganic materials with a core−shell structure derived from the controlled hydrolysis of trichloro- or trialkoxysilanes (T units).[9] Synthetic control over the hydrolysis process[10] leads to an enhancement of cage structures vs ladderlike or branched structures seen for classical silsesquioxanes.[11] The rigid inorganic core provides the strength and oxidative stability of a ceramic, while synthetic control over the organic coronae (R) provide processability and compatibility with other materials. The "self-healing" aspect of POSS-based coatings upon oxidation of the organic coronae occurs when a SiO_2 layer forms, thereby preventing further oxidation of the underlying material. While surface and interfacial properties lie at the heart of many potential POSS applications, relatively little is actually known about the surface properties of POSS.[11−13] Utilizing Brewster angle microscopy (BAM)[14] on Langmuir monolayers, this study demonstrates that the partial cage trisilanolisobutyl-POSS, $T_7R_7(OH)_3$, forms uniform monolayers such as classical surfactants,[15] while the fully condensed octaisobutyl-POSS cages, T_8R_8, are not amphiphilic.

Trisilanolisobutyl-POSS or octaisobutyl-POSS obtained from Hybrid Plastics, Inc. and used without further purification was dissolved in chloroform (~0.5 mg/mL, HPLC grade) and spread onto the surface of a standard Langmuir trough (500 cm^2, 601BAM, Nima Technology) filled with ultrapure 18.2 MΩ water (Millipore, Milli Q Gradient A-10) maintained at 22.5 °C in a Plexiglas box. The surface pressure was measured using a paper Wilhelmy plate to ±0.1 mN·m^{-1}. Compression rates of 10 to 20 cm^2·min^{-1} were used to vary the surface concentration and BAM studies (MiniBAM, NanoFilm Technologie) were carried out simultaneously with film compression.

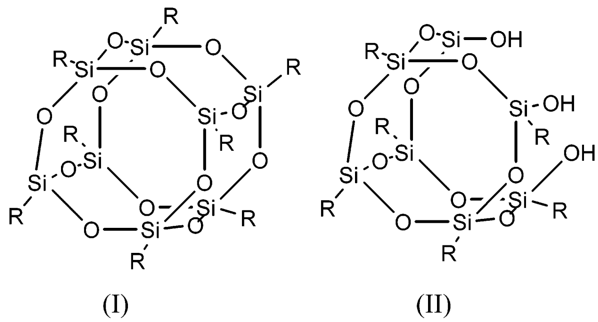

Figure 1. (I) T_8R_8, (II) $T_7R_7(OH)_3$, R = isobutyl.

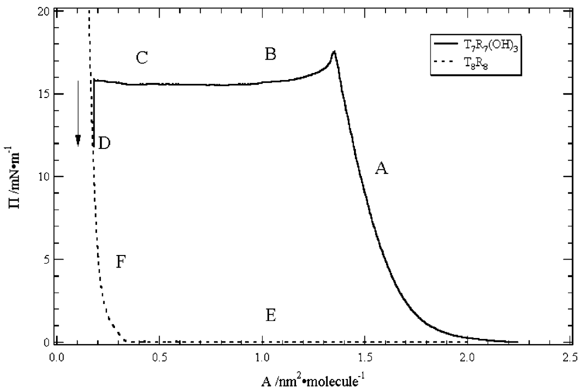

Figure 2. ($\Pi - A$) isotherms of T_8R_8 and $T_7R_7(OH)_3$, R = isobutyl. The arrow shows equilibrium relaxation of the surface pressure in the biphasic regime of the $T_7R_7(OH)_3$ film. The letters on the figure correspond to the BAM images in Figure 3.

Figure 2 shows surface pressure − area per molecule ($\Pi - A$) isotherms of trisilanolisobutyl-POSS and octaisobutyl-POSS. With the 20-μm lateral resolution of our BAM instrument, we are unable to observe coexistence between a liquid and gaseous film (L/G) at $\Pi = 0$ mN·m^{-1} for trisilanolisobutyl-POSS. At a surface concentration of $A = 1.95$ nm^2·molecule^{-1}, the trisilanolisobutyl-POSS shows a rise in surface pressure corresponding to the formation of a homogeneous (Figure 3A) liquidlike monolayer (L). Further compression of the monolayer results in the nonequilibrium formation of a more condensed phase (Figure 3B) starting at a surface concentration of 1.35 nm^2·molecule^{-1}. On the basis of the crystal structure for trisilanolcyclohexyl-POSS,[5] this area per molecule is consistent with size of a POSS molecule when the three silanol groups anchor the cage to the surface and the isobutyl substituents form a halo parallel to the interface around the inorganic core. Further compression leads to aggregation of the condensed domains (Figure 3C). If compression is stopped and the monolayer is allowed to relax (C → D), the pressure falls to an equilibrium value of 12.3 mN·m^{-1} after 80 min, and stable ring-like structures form (Figure 3D).

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* To whom correspondence should be addressed. E-mail: aesker@vt.edu.
[†] Edwards Air Force Base.
[‡] Present Address: Department of Chemistry, The Catholic University of America, Washington DC 20064.

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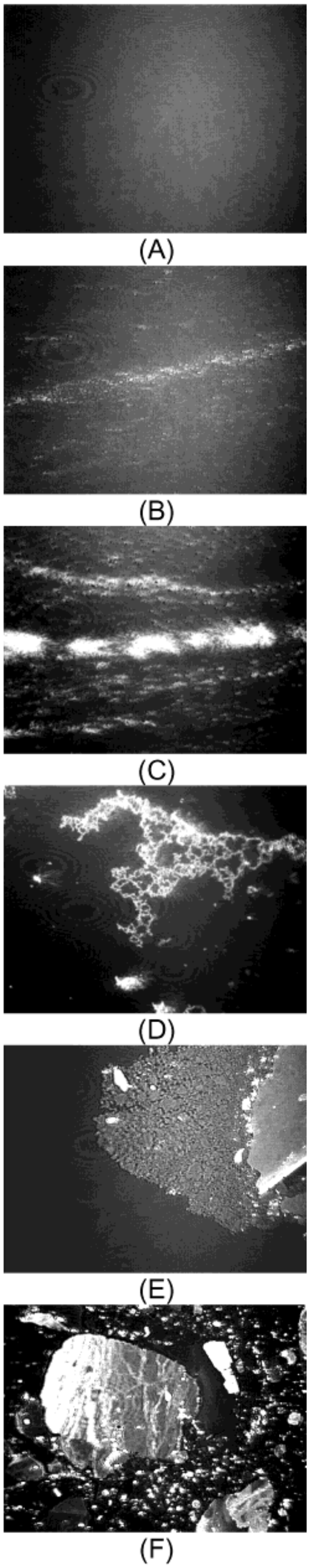

Figure 3. BAM images of $T_7R_7(OH)_3$. (A) Uniform liquid monolayer, (B) early stages of condensed phase growth, (C) aggregation of the condensed phase domains, and (D) relaxed structure. BAM images for T_8R_8 (E) at $\Pi = 0$ and (F) $\Pi > 0$ $\text{mN}\cdot\text{m}^{-1}$. All images are 4.8×6.4 mm^2, and the letters match the points on the isotherms in Figure 2.

The formation of stable ringlike structures is similar to the formation of equilibrium solidlike domains in lipid systems where the interplay of dipole density and line tension lead to the ring morphology.[16] For the trisilanolisobutyl-POSS systems, both the weak temperature ($\downarrow T$, $\uparrow\Pi_{\text{plateau}}$, $T = 5-35$ °C, $\Delta\Pi \lesssim 2$ $\text{mN}\cdot\text{m}^{-1}$) and compression rate ($\uparrow$Rate, $\uparrow\Pi_{\text{plateau}}$, Rate $= 10-300$ $\text{cm}^2\cdot\text{min}^{-1}$, $\Delta\Pi \lesssim 2$ $\text{mN}\cdot\text{m}^{-1}$) dependencies for the plateau pressure are consistent with the formation of a solid phase that is quite possibly a collapsed three-dimensional structure as compression of the monolayer does not lead to a further increase in Π.[17] In contrast to trisilanolisobutyl-POSS, octaisobutyl-POSS exhibits an isotherm with areas per molecule that are too small for a physically realistic monolayer state. Figure 3E,F shows that the octaisobutyl-POSS film is comparably heterogeneous both at $\Pi = 0$ and $\Pi > 0$ $\text{mN}\cdot\text{m}^{-1}$ which is consistent with three-dimensional aggregates observable at all surface concentrations.

In conclusion, breaking open the POSS-cage converts non-amphiphilic octaisobutyl-POSS into a surface-active molecule that self-assembles into a uniform monolayer at the air/water interface upon compression. Experimental data for trisilanolisobutyl-POSS packing are consistent with expectations from the known crystal structure of another trisilanol-POSS derivative.[5] Future work will focus on how substituent effects alter the phase behavior of these new amphiphilic materials relative to well-understood lipid systems, the surface viscoelastic properties of these materials, and their compatibility with polymeric materials as nanofillers for high-temperature coating applications.

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