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Brent Viers (ERC); Alan Esker; Katie Farmer, "Polyhedral Oligomeric Silsesquioxanes Surfactants" (Paper)

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POLYHEDRAL OLIGOMERIC SILSESQUIOXANE (POSS) SURFACTANTS

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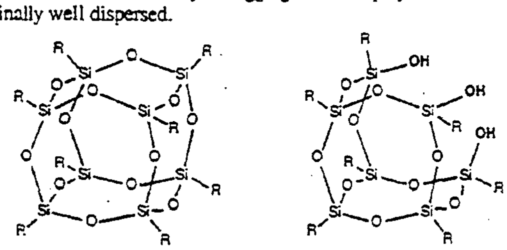
Introduction:

There has been recent interest in using polyhedral oligomeric silsesquioxanes (POSS) as the smallest particles of silica for reinforcement of polymers.[1] These materials are monodisperse, have tailored functionality (including a hydrophobic coating), and should thus act as model nanoparticulate filler. Feher et. al.[2] have shown that sol-gel condensation into cage compounds can yield two thermodynamically stable main isolates: a fully condensed R_8T_8 cube (Figure 1a) and an incompletely condensed $R_7T_4D_3(OH)_3$ trisilanol (Figure 1b). (T refers to a $SiO_{3/2}$ and D is a $SiO_{2/2}$ moiety in a silicate framework) There are large differences in the solubility of POSS in common organic solvents based on the substitution of the cages. For example, a fully condensed iBu_8T_8 cube (Figure 1a) is more soluble than a similar cyclohexyl Cy_8T_8 cube which in turn is more soluble than a cyclopentyl Cp_8T_8 substituted cube. Furthermore, the breaking of symmetry in the incompletely condensed cubes (Figure 1b) could also be expected to enhance solubility/compatibility. The dispersion of POSS will likely determine how well the material can act as a "nanofiller." Farmer et. al.[3] have recently performed molecular dynamics simulations which suggest that POSS molecules have no tendency for aggregation in a polymeric matrix if they are originally well dispersed.



1a **1b**

Figure 1 Representative POSS molecules. R can be cyclohexyl (Cy), cyclopentyl (Cp) or isobutyl.(IBu)

Silsesquioxanes (as a subclass of silicone materials) should be in general amphiphillic., and thus we might expect POSS to spread at the air/water interface. We have chosen to use Langmuir-Blodgett techniques and observe the compression behavior of the common POSS fully condensed cubes and incompletely condensed trisilanols.

Experimental

POSS fully condensed "molecular silica" (Cy_8T_8, IBu_8T_8) and silanols ($Cy_7T_4D_3(OH)_3$, $iBu_7T_4D_3(OH)_3$) were used as received from Hybrid Plastics (www.hybridplastics.com) The nominal purity (HPLC) was 95% or greater. Langmuir Blodgett compression was conducted on a NIMA 611 trough with paper Wilhielmy plates at 30 cm^2/min compression speed. Chloroform solutions (ca. 0.5 mg/ml) of POSS was spread on 18 mΩ Millipore water thermostatted to 22°C.

Results and Discussion

The surface pressure-area isotherms for the isobutyl (iBu_8T_8) fully condensed cube and the $Cy_7T_4D_3(OH)_3$ and $iBu_7T_4D_3(OH)_3$ trisilanols are shown in Figure 3. The iBu_8T_8 and Cy_8T_8 (not shown in Figure 3) showed only a single collapse at very small area; much smaller than any characteristic size of a POSS cube. This likely indicates that the molecule is too (uniformly) hydrophobic, and thus exists as stacked aggregates on the water surface. The collapse indicates packing of these aggregates into a bulk agglomerate-like phase. Conversely, the hydrophilic pocket in the trisilanol POSS allows for anchoring to the water surface, and thus these POSS can spread into a monolayer. The average "size" for $Cy_7T_4D_3(OH)_3$ based on single crystal X-ray diffraction (Figure 2) is approximately 16 Å. This corresponds to a (spherical) cross sectional area of 200 $Å^2$, which agrees well with the extrapolated collapse of 180 $Å^2$/molecule. As expected, the smaller isobutyl group gives a smaller collapse area. However, the collapse pressure is much higher-approximately 20 mN/m^2. This likely indicates that the lessened van der Waals interaction of the hydrophobic isobutyl groups allows for a stronger interaction with the subphase. Both trisilanols show a secondary collapse at small areas; likely to an aggregated phase very similar to the fully condensed cube collapse.

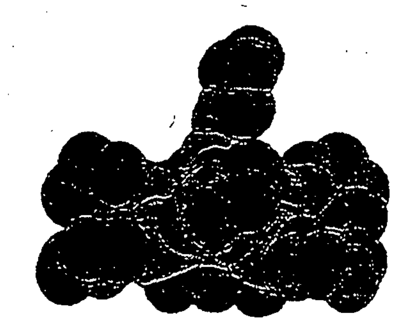


Figure 2 Molecular model of $Cy_7T_4D_3(OH)_3$ (Figure 1b) based on single crystal X-ray coordinates.(hydrogens not shown) Notice the localized hydrophilic trisilanol pocket at the base.

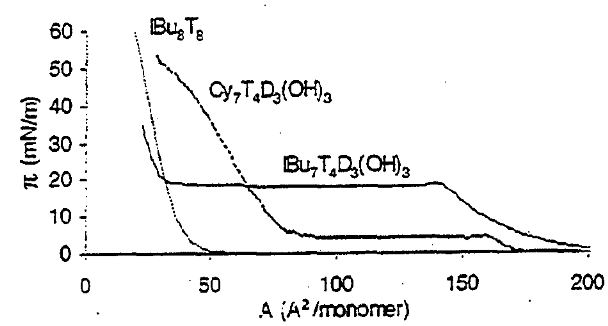


Figure 3 Surface Pressure-Area isotherms for various POSS.

Conclusions:

POSS can act as a surfactant and spread at the air water interface. The more hydrophilic POSS trisilanols appear to make monolayers, but all POSS show complicated collapse behavior. The behavior of POSS in thin films (blends, copolymers, etc.) will likely be affected by the state of aggregation.

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References:

(1) (a) Lichtenhan, J.D.; *Comm. Inorg. Chem.*, 1995, *15*, 115. (b) Lichtenhan J.D. et. al.; *Macromolecules*, 1993, *26*, 2141 (c) Haddad, T.S.; Lichtenhan J.D.; *Macromolecules*, 1996, *29*, 7302 (d) Lichtenhan, J.D.: "Silsesquioxane Based Polymers" in *Polymeric Materials Encyclopedia*; Joseph C. Salamone, Ed.; CRC Press:Boca Raton, 1996, pp 7768-7777, and references cited therein

(2) (a) Feher, F. J.; Newman, D.A.; Walzer, J.F.;*J. Am. Chem. Soc.*; 1989, *111*, 1741 (b) Brown, J.F.; Vogt, L.H.; *J. Amer Chem. Soc.*; 1965, 87, 4313 (c) Feher, F.J.; Budzichowski, T.A.; Blanski, R.L.; Weller, K.J.; Ziller, J.W.; *Organometallics*, 1991, *10*, 2526

(3) Bharadwaj, R.K.; Berry, R.J.; Farmer, B.L.; *Polymer Preprints (A.C.S. Div. Poly. Chem)*; 2000, *41(1)*, 530