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# The Synthesis of Hybrid Materials by the Blending of Polyhedral Oligosilsesquioxanes into Organic Polymers

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## Abstract

The study of organic/inorganic hybrid materials has become an increasingly widespread research focus. The advantage derived from such materials is the combining of two very different compounds which may result in something that bridges the performance gap between the two systems. We have previously reported such hybrid systems prepared by incorporating polyhedral oligosilsesquioxanes (POSS™) into traditional organic polymers by the copolymerization of POSS™ monomers and organic monomers. This presentation will discuss a more convenient method of incorporating POSS™ into a polymer: the blending of POSS™ into organic polymers. The research discussion will focus on the development of the POSS™ macromers used in our studies as well as the POSS™ polymer blends synthesized. One important property enhancement observed is the increase in surface hardness for a POSS™/polystyrene sample.

## Introduction

The synthesis of organic polymer/inorganic ceramic hybrid materials has become a very popular research topic in recent years. One of the benefits of these hybrid materials is the combining two disparate materials which can result in a new material that may bridge the performance gap between the two systems [1]. Previous research has shown that such hybrid systems can be prepared by incorporating polyhedral oligosilsesquioxanes (POSS™) into traditional organic polymers (polymethacrylate, polystyrene, polynorbornene)[2] by standard polymer preparation procedures. The development of each of these systems was not trivial.

A more convenient method of incorporating POSS™ into an organic polymer is to blend it into the polymer. With this method of POSS™ incorporation, there would be no covalent linkage between the POSS™ molecules and the polymer. The resulting hybrid material would not have the same properties as a POSS™ hybrid with a covalent linkage to the polymer and would more likely act like a filled polymer system. The main differences between our system blended with POSS™ and traditional filled systems are the size of the particles and the possibility for dispersion. The particle size in traditional filled polymer systems range from the micron to the nanoscale. The size distribution of these systems can also vary widely, especially at the lower sizes. These systems also have a tendency to aggregate to give even larger domains. Since an individual POSS™ molecule is a chemically distinct nanostructured™ species, there is only one possible size of 15Å which includes the organic side groups. In order to make a blend that maximizes property enhancements of the hybrid material, the silsesquioxane should be evenly dispersed in the polymer. Since each POSS™ molecule has a $Si_8O_{12}$ core covered with alterable organic side groups, it is believed that a finer dispersion into the polymer matrix may be possible by increased interaction of compatible side groups and the polymer.

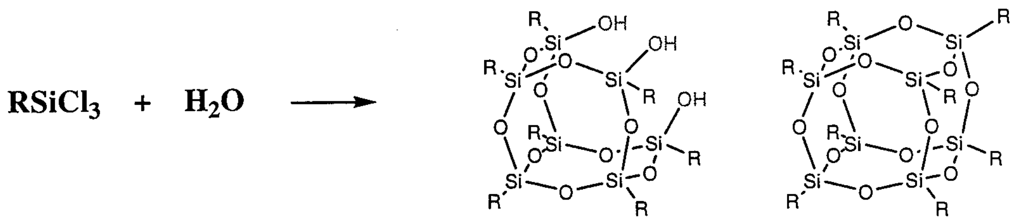
## Experimental

Monomer synthesis: cyclopentyl$_7$T$_7$(OH)$_3$, cyclopentyl$_8$T$_8$ (**1**), cyclopentyl$_7$T$_8$styryl (**3**) and vinyl$_8$T$_8$ (**2**) (Hybrid Plastics) were used as received. Styrenyl$_8$T$_8$ (**4**) and Phenethyl$_8$T$_8$[3] (**5**) were prepared according to literature methods. TEMs were performed on a Hitachi 2000 TEM with 200 keV. Hardness testing was performed on an MST nano-indentation tester. General Procedure for solvent casting TEM samples: Equal amounts of high molecular weight, low polydispersity polystyrene ($M_w$= 2,000,000 D = 1.1, Pressure Chemical) and cyclopentyl$_8$T$_8$ (**1**) are dissolved in tetrahydrofuran. This solution is syringed onto a glass plate and very thin films that can be directly observed by TEM are prepared by slow solvent evaporation. A portion of the film is then placed into a Hitachi 2000 transmission electron microscope and pictures were taken. This procedure was repeated with compound **2-5** above and polystyrene. General procedure for preparing DACA blends: 1 gram of phenethyl$_8$T$_8$ and 4 grams of polystyrene were added to the DACA mixer which was heated to 175 °C. After blending for 10 minutes at temperature, the material was extruded to give a string of optically clear material.

## Results and Discussion

### Synthesis of POSS™ Monomers

Critical to the success of this experiment is the availability of POSS™ monomers with tailorable side groups. Cyclopentyl$_7$T$_7$(OH)$_3$ and cyclopentyl$_8$T$_8$ (**1**) were prepared by the hydrolysis of cyclopentyltrichlorosilane in refluxing acetone.

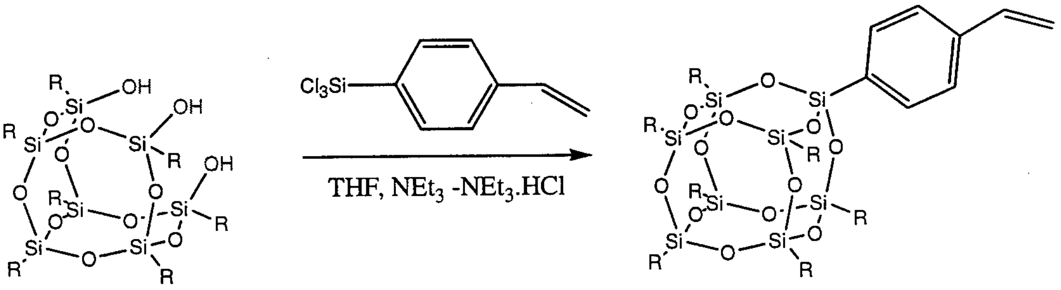


**R = cyclopentyl**
**vinyl**

**R = cyclopentyl**

**R = cyclopentyl (1)**
**vinyl (2)**

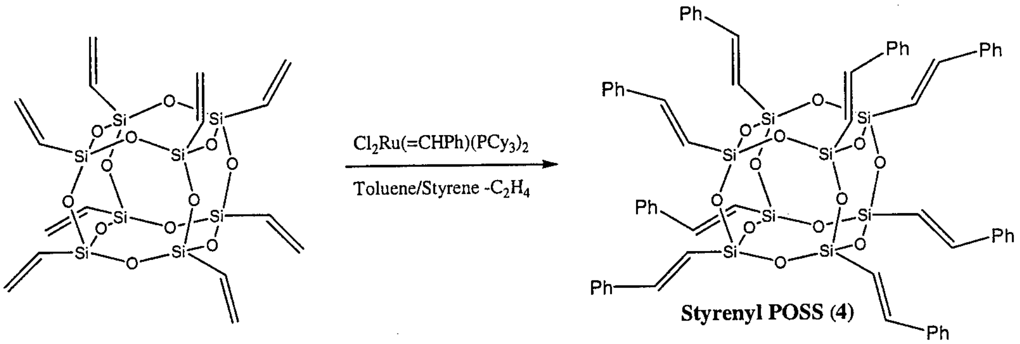
Cyclopentyl$_7$T$_8$styryl (**3**) is synthesized by the addition of styrylSiCl$_3$ to triol cyclopentyl$_7$T$_7$(OH)$_3$ in the presence of triethylamine to absorb the HCl generated.



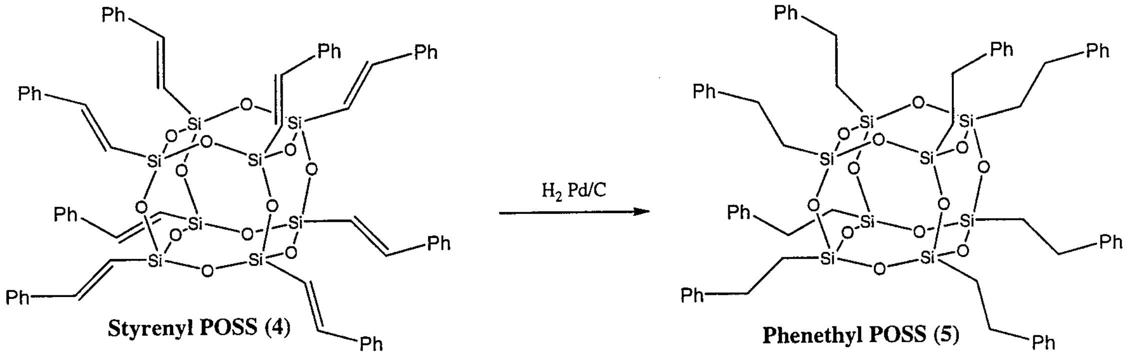
**R = cyclopentyl**

**R = cyclopentyl (3)**

Styrenyl$_8$T$_8$ (**4**) was synthesized by the cross metathesis of styrene and vinyl$_8$T$_8$ (**2**) using the Grubbs catalyst. The resulting solid was colorless, crystalline solid with a melting temperature above 200 °C.



Phenethyl$_8$T$_8$ (**5**) was synthesized by the hydrogenation of **4** using palladium on carbon. It is a colorless solid with melting temperature of 74 °C. Since there are no double bonds in this material, it should have superior oxidation resistance compared to **4**.



**Synthesis of POSS™-Polystyrene blends.**

The first blend looked into for this study is the mixture of cyclopentyl$_8$T$_8$ (**1**) and polystyrene in a 1:1 weight ratio. The film cast was opaque. The TEM (Figure 1) shows that there are large POSS™ crystallites that contain between 20K and 50K molecules with no apparent POSS™ in the polystyrene phase. The silsesquioxane would darken the polystyrene phase which is not observed in this sample. Apparently the cyclopentyl groups are not compatible with the polystyrene matrix.

The second blend looked into for this study is the mixture of vinyl$_8$T$_8$ (**2**) and polystyrene in a 1:1 weight ratio. The film that was cast was also opaque. The TEM (Figure 2)shows that there is no apparent POSS™ in the polystyrene phase although the crystallite size is considerably smaller than the above blend with polystyrene and **1**.

When one cyclopentyl group on cyclopentyl$_8$T$_8$ (**1**) is replaced by a styryl group and cast with polystyrene, a less opaque film is obtained compared to both of the previous blends.
A TEM of this blend of Styryl-POSS™ (**3**) and polystyrene is shown in Figure 3. The TEM shows that crystallite size drops off precipitously after the replacement of only *one* incompatible cyclopentyl group with a more compatible styryl group

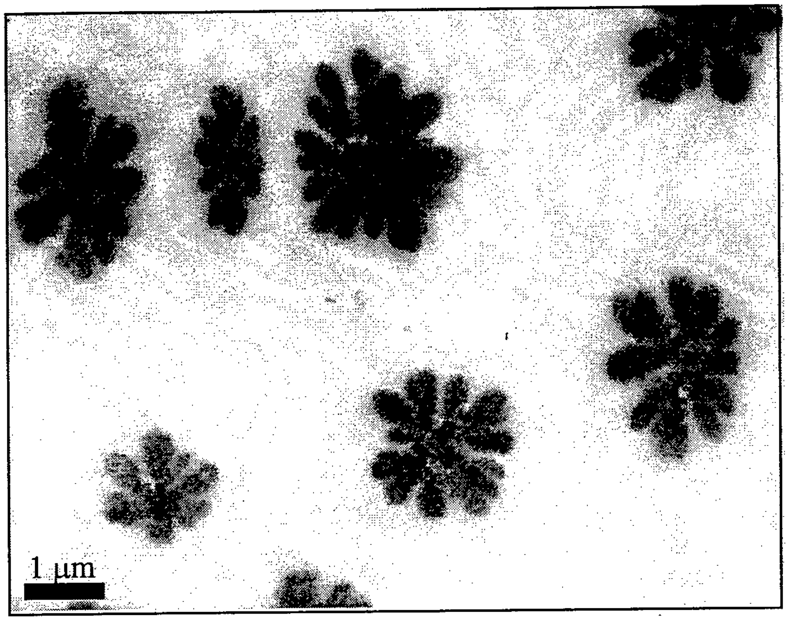


***Figure 1.*** *(cy-$C_5H_9)_8T_8$ (1) in 2 million MW Polystyrene (PS)*

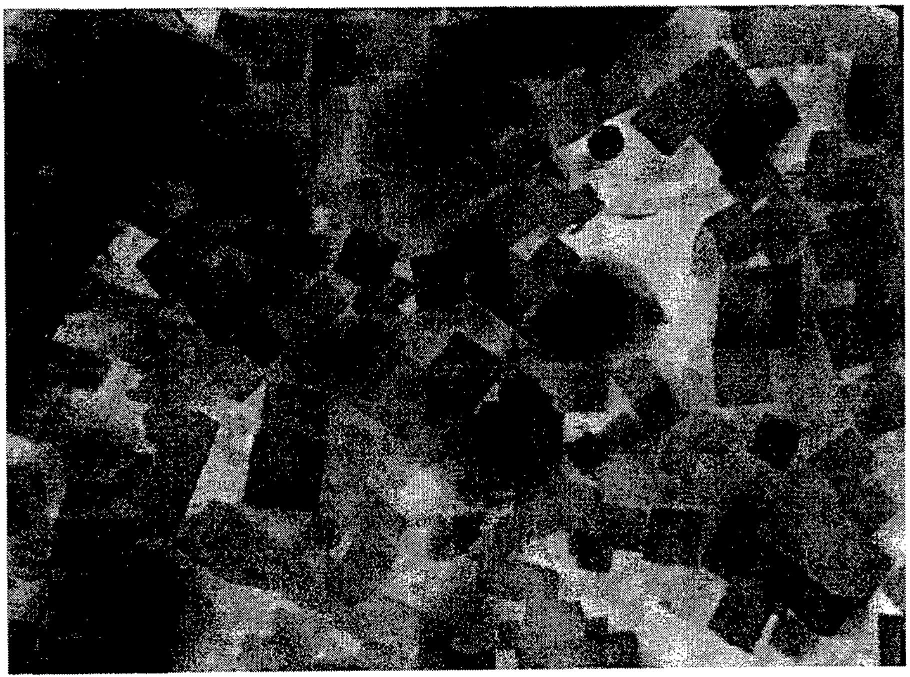


***Figure 2.*** *(vinyl)$_8T_8$ in 2 million MW Polystyrene (PS)*

When all eight cyclopentyl (or vinyl) groups are replaced by styrenyl groups and cast with polystyrene, an optically clear film is obtained. A TEM of this blend of Styrenyl$_8T_8$ (**4**) and polystyrene in a 1:1 weight ratio is shown in Figure 4. The TEM of this mixture contains isolated polystyrene domains as well as a gray area which represents the POSS™-PS domain. The black dots in the TEM are believed to be POSS™ crystallites in the POSS™-PS phase that contain <100 POSS™ molecules. It is also believed that the isolated polystyrene domains are a result of the solvent casting process. Processing issues aside, this shows that we now have a POSS™ molecule which is miscible with the polystyrene phase. In addition to the miscibility observed with the styrenyl-POSS™ monomer in the polystyrene matrix, a 30% increase in the surface hardness of film compared to undoped styrene is observed.

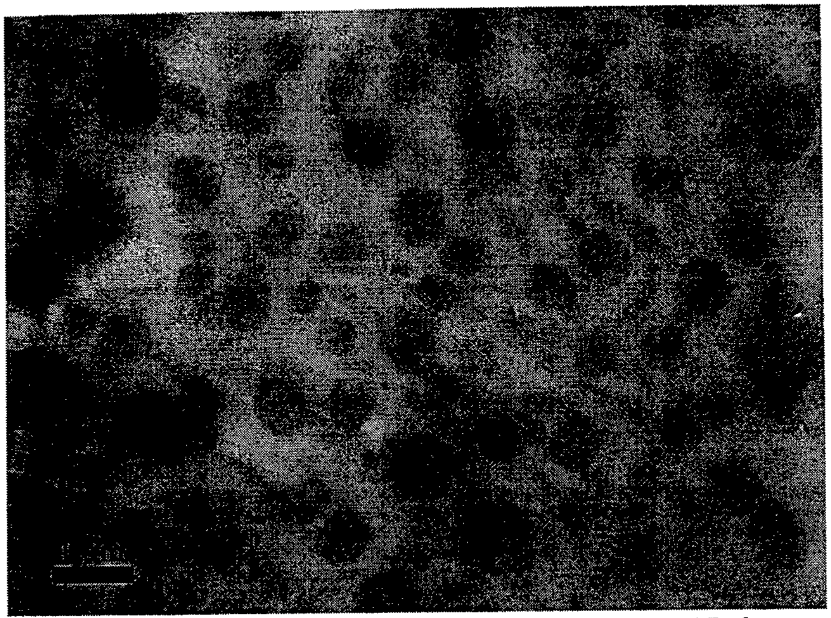


***Figure 3.*** *TEM of 50% Styryl-POSS™ in 2 million MW Polstyrene*

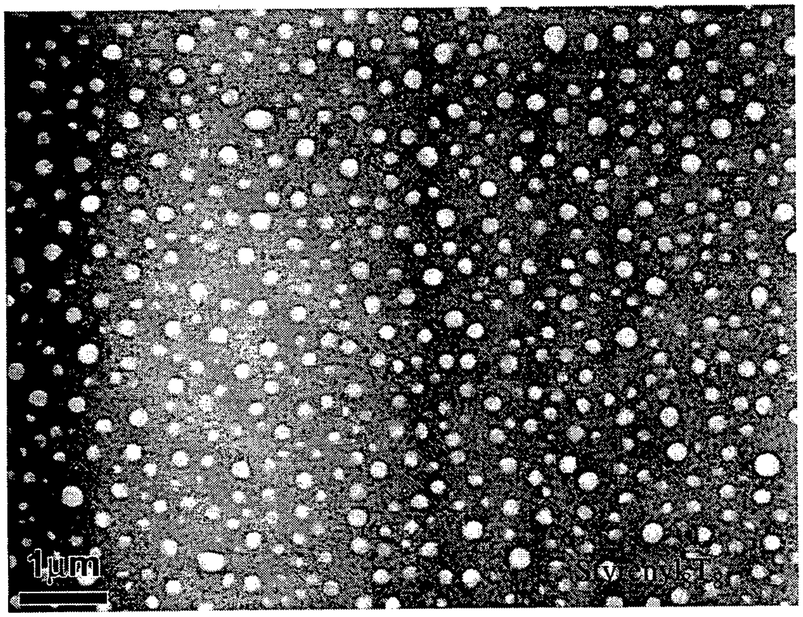


***Figure4.*** *(Styrenyl)$_8$T$_8$ in 2 million MW Polystyrene (PS)*

In order to overcome the processing issues with styrenyl-POSS™, the double bonds of **4** are removed by hydrogenation to give phenethyl-POSS™ **5**. The film cast with **5** and polystyrene is again optically clear. The TEM of this mixture (figure 5) shows sample homogeneity across the sample with POSS™ rich domains in the POSS™-PS phase which contain <100 POSS™ molecules. An X-ray powder diffraction spectrum for this polymer shows no observable crystallinity attributable to Phenethyl$_8$T$_8$. In addition, there is no observable transition for the melting of Phenethyl$_8$T$_8$ in the sample, which is consistent with the lack of large crystalline domains of Phenethyl$_8$T$_8$.

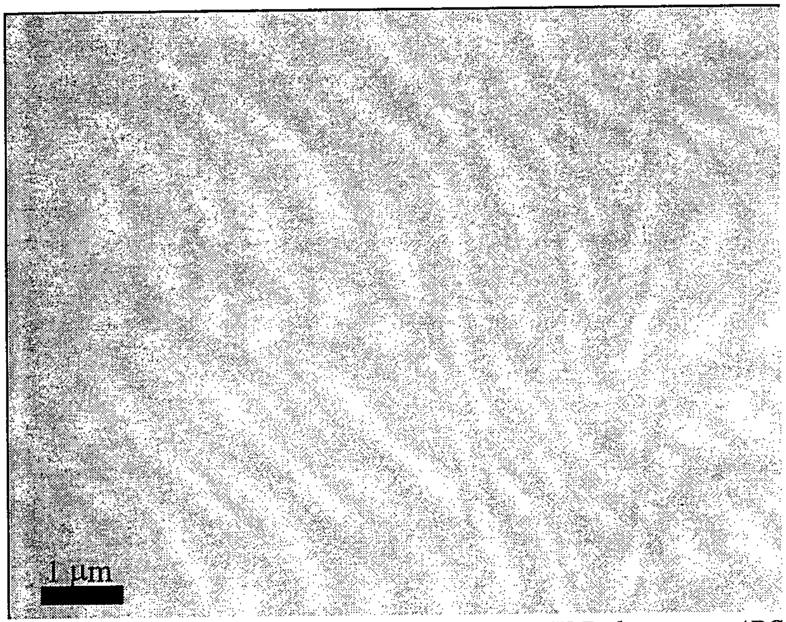


***Figure 5.*** *(Phenethyl)$_8$T$_8$ (5) in 2 million MW Polystyrene (PS)*

## Conclusions

We have demonstrated the ability to disperse polyhedral oligosilsesquioxanes into polystyrene. We have also shown that by altering the organic side groups POSS™ octamers to a more compatible group, we can fully disperse the POSS™ molecules into high molecular weight polystyrene. The surface hardness of the StyrenylPOSS™/polystyrene film increased 30%.

**Acknowledgement.** We gratefully acknowledge the Air Force Office of Scientific Research and the Air Force Research Laboratory, Rocket Propulsion Science Materials Branch for their financial support. RLB would also like to thank Mr. Justin Leland and Mr. Patrick Ruth for valuable synthetic and blending assistance.

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