

Polyhedral Oligomeric Silsesquioxane (POSS)-Based Polymers

Joseph J. Schwab^{1*} and Joseph D. Lichtenhan²

¹Hughes STX Corporation, Phillips Laboratory, Propulsion Directorate Edwards AFB, CA 93524, USA

²Phillips Laboratory, Propulsion Directorate, Edwards AFB, CA 93524, USA

A diverse and entirely new class of monomer and polymer technology based on polyhedral oligomeric silsesquioxane (POSS) reagents has been developed. POSS reagents are unique in that they are physically large (approx. 15 Å diameter and 1000 amu) and are composed of a robust silicon–oxygen framework that can be easily functionalized with a variety of organic substituents. Appropriate functionalization of POSS cages allows for their incorporation into traditional thermoplastic resins without modification of existing manufacturing processes. The incorporation of POSS segments into linear copolymer systems results in increased glass transition and decomposition temperatures, increased oxygen permeability and reduced flammability and heat evolution, as well as modified mechanical properties relative to conventional organic systems. © 1998 John Wiley & Sons, Ltd.

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INTRODUCTION

Since their discovery almost 70 years ago, synthetic polymers have played an increasingly important role in daily life. This is especially true today, when polymers and plastics are finding their way into an evermore diverse array of products and applications. However, along with this increased use have come more demanding requirements, such as higher temperatures of use and greater resistance to oxidation. Although the polymer industry has

been able to keep abreast of these demands, through the use of additive, filler and blend technologies, as well as increased empirical understanding of polymer microstructures, new developments tend to be incremental and the existing technology and knowledge are rapidly being pushed to their limits by the more demanding requirements of end-users. Although the range and types of plastic and polymer systems are quite impressive, much of this work has been accomplished using a relatively limited number of basic chemical building blocks, i.e. the monomers which make up the primary structure of the polymer system. Without exception, these monomers are based on organic systems and the pool of available building blocks has remained almost static over the past 25 years.

A recent approach to meeting these demands has been the development of new plastics that have properties intermediate between those of traditional organic systems (i.e. polymers) and those of traditional inorganic systems (i.e. ceramics). This interest, along with the concomitant research effort, has given rise to the field of hybrid materials research, which endeavors to combine the properties of traditional organic polymer systems (i.e. processability, toughness, cost) with the properties of inorganic compounds (i.e. thermal and oxidative stability) (Fig. 1). For reviews and leading references on recent progress in hybrid materials, the reader should consult Refs 1–3.

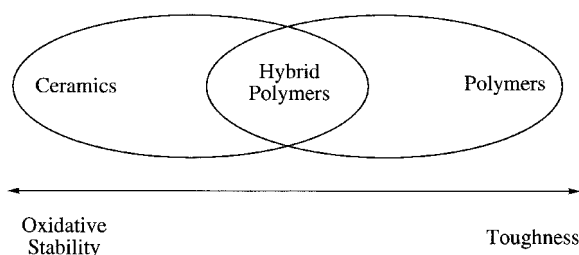


Figure 1 Schematic representation of the area of hybrid materials.

* Correspondence to: Joseph J. Schwab, Hughes STX Corporation, Phillips Laboratory, Propulsion Directorate Edwards AFB, CA 93524, USA.

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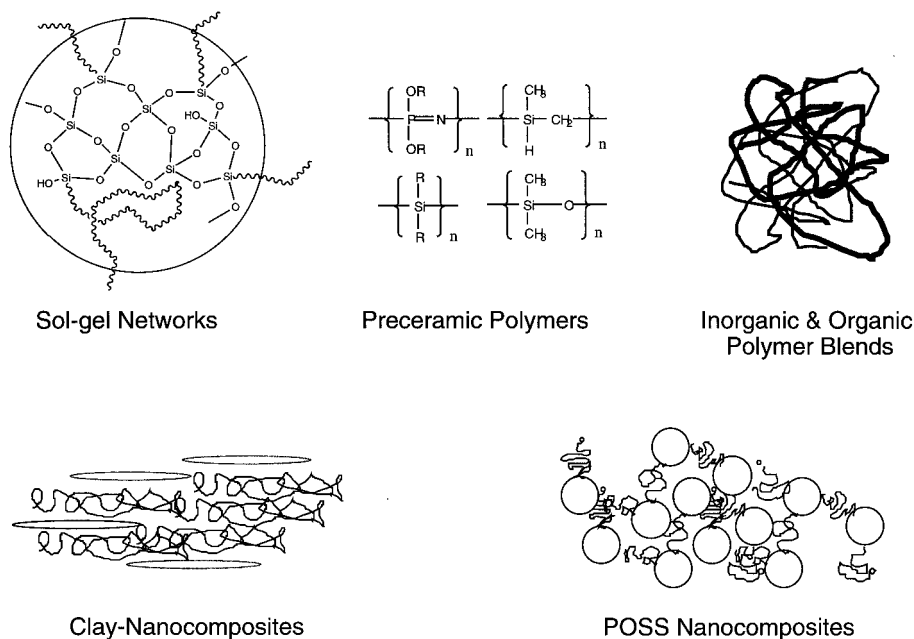


Figure 2 Schematic representations of different hybrid plastics.

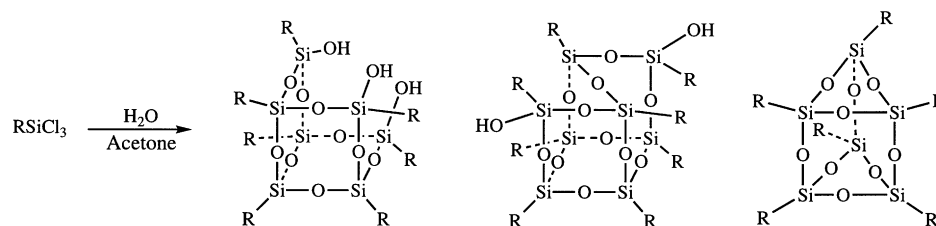
Using this basic idea, several broad classes of hybrid plastics have been developed and are shown schematically in Fig. 2. Examples of these include the sol-gel networks, which are three-dimensional crosslinked systems having a dispersed inorganic, silica-like phase in a polymer matrix; preceramic polymers, such as the polyphosphazenes, polycarbosilanes, polysilanes and polysiloxanes; and inorganic/organic polymer blends. Furthermore, a revitalization of clay-filler technology has occurred with the development of methods for exfoliating layered clays into sheets which then become dispersed on a finer level than previously possible. More recently a diverse and entirely new chemical technology of polyhedral oligomeric silsesquioxane (POSS) nanocomposites has been developed. This technology affords the possibility of preparing plastics that contain nanoscale reinforcements (POSS segments) directly bound to the polymer chains. Unlike previous hybrid systems, the POSS technology materials have the additional advantage of being employable in the same manner as organic monomers or in the form of blendable resins.

Here we describe some of our preliminary efforts to prepare well-defined, nanoreinforced, thermoplastic polymeric hybrids with enhanced properties that can be understood and tailored at the molecular level.

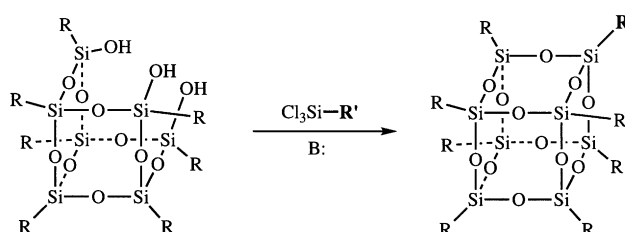
RESULTS

Whereas the majority of the work on the synthesis of hybrid materials has been directed towards use of the sol-gel process,⁴ our approach has been to prepare hybrid materials which can be incorporated into traditional linear, thermoplastic polymer systems. The hybrid materials developed in our laboratory are based on POSS precursors.^{5,6} POSS precursors are discrete, structurally well-defined compounds composed of a silicon-oxygen framework having the general formula $(\text{RSiO}_{3/2})_n$, and are prepared via the hydrolysis of organotrichlorosilanes as shown in Scheme 1.^{7,8,9}

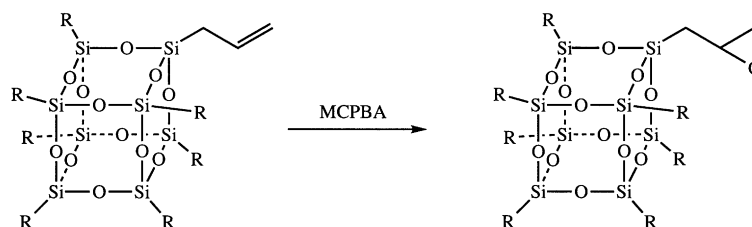
Although some of the POSS precursors isolated from the hydrolysis mixture can be used directly in polymerization reactions, additional functionalization is often required. In order to incorporate the POSS reagents into linear polymer systems and thus avoid the formation of intractable, crosslinked networks, it is necessary to limit the number of functional groups to no more than one or two. Functionalization of the POSS framework is most easily accomplished by corner capping of the POSS-trisilanols with silane coupling agents containing organic groups suitable for polymerizations and/or grafting reactions (Scheme 2). Isolated yields from the corner capping reactions exceed



Scheme 1 POSS products from the hydrolysis of cyclohexyltrichlorosilane, ($R = \text{c-C}_6\text{H}_{11}$).



Scheme 2 Synthesis of polymerizable POSS reagents ($R =$ non-reactive functionality; $R' =$ polymerizable or graftable functionality).



Scheme 3 POSS functional group interconversion.

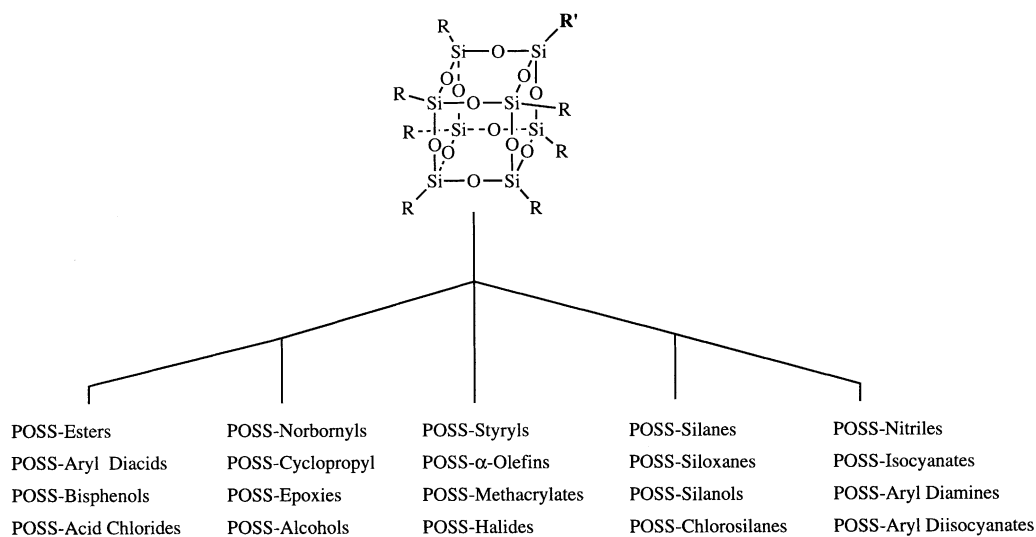


Figure 3 Some of the functionalities which can be prepared from POSS-trisilanol precursors.

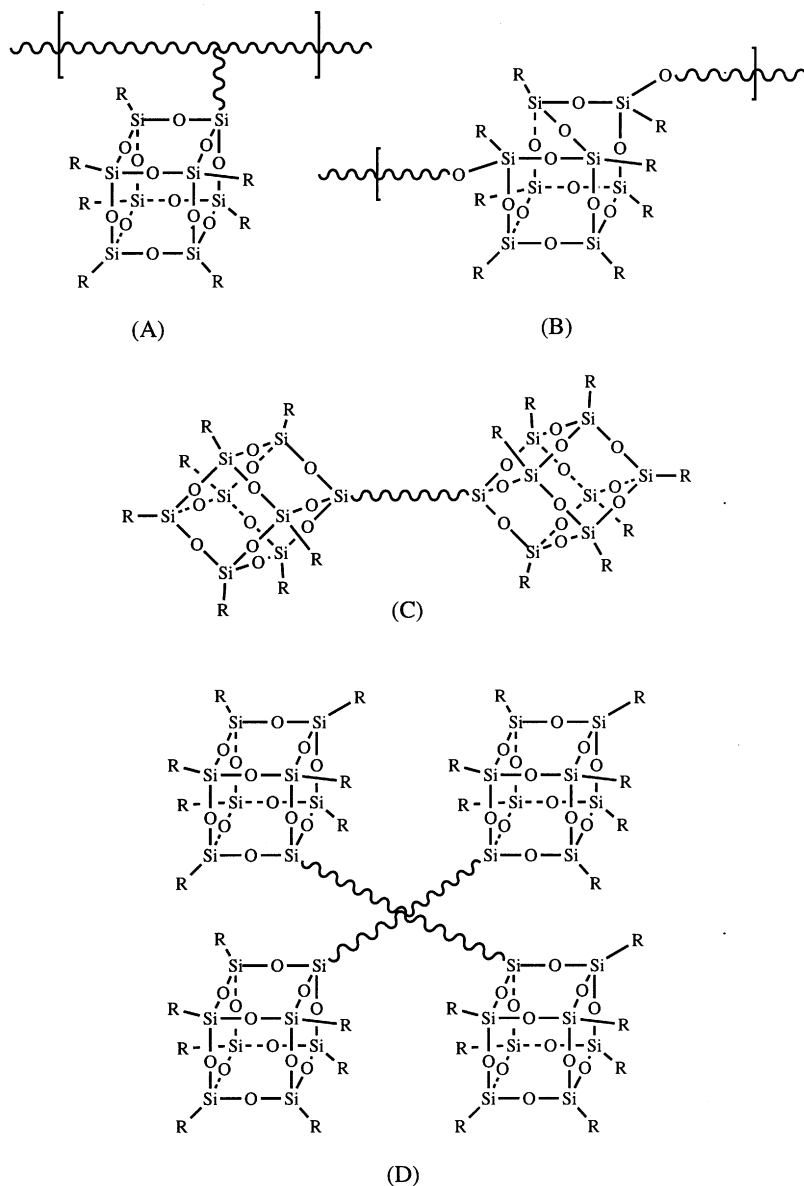


Figure 4 Polymer architectures available from POSS monomers: (A) pendant; (B) AB multiblock 'bead', (C) ABA triblock; (D) star.

90% and are typically greater than 95% if care is taken to exclude moisture from the system.

In cases where the appropriate functionality is not directly available by the corner capping sequence, subsequent functional group transformations of the reactive group on the unique silicon are

possible. For example, the conversion of POSS- α -olefins to POSS-epoxides using *m*-chloroperbenzoic acid (MCPBA) is shown in Scheme 3.

Using these methods, we have built up a large catalogue of POSS reagents containing polymerizable and/or graftable functionalities. This makes

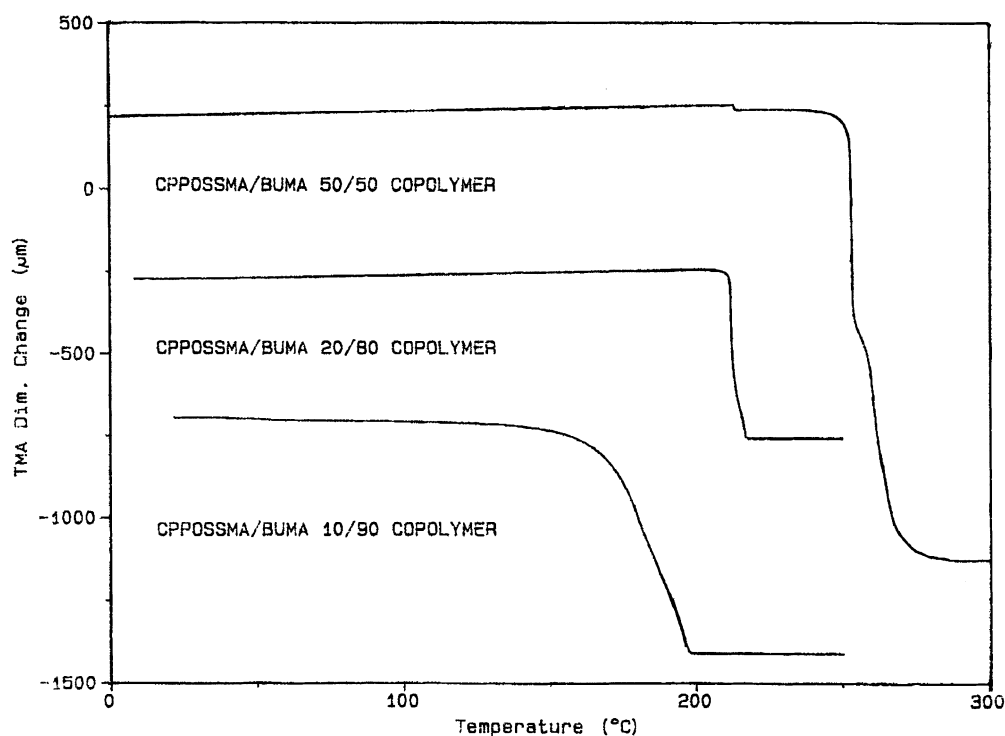


Figure 5 TMA data from cyclopentyl-POSS-methacrylate/butyl methacrylate copolymers: top, 50:50 copolymer; middle, 20:80 copolymer, bottom: 10:90 copolymer. (Au proportions in mol%.)

possible the incorporation of POSS units into traditional resin systems. Some typical functionalities are listed in Fig. 3.

These POSS reagents have a number of desirable physical properties. For example, they are highly soluble in common organic solvents such as tetrahydrofuran (THF), toluene, chloroform and hexane. They have high thermal stabilities,¹⁰ and can be polymerized using standard polymerization protocol (i.e. radical polymerizations, condensation polymerizations, ring opening polymerizations etc.) to provide polymers with a variety of architectures as illustrated in Fig. 4.

Whereas hybrid materials produced from either the sol-gel process or from multifunctional POSS precursors¹¹ (i.e. with functionality > 2) are highly crosslinked network polymers (akin to thermoset plastics) and as such tend to be difficult to process, our reagents can be used to produce thermoplastic polymers in which the inorganic portion of the hybrid is covalently linked to the organic polymer chain. It is this unique ability to start from well-defined hybrid monomers that makes it possible to

control the polymer architecture and ultimately to tailor the polymer properties at the molecular level.

Incorporation of POSS-silanol,¹² POSS-acrylate,¹³ POSS-styrene,^{14,15} POSS-norbornadiene,^{16,17} and POSS-bisphenol A monomers^{18,19} into the respective polysiloxanes, polyacrylates, polystyrenes, polynorbornadienes and polyurethanes has been demonstrated. All of the POSS-hybrid polymers prepared so far show thermoplastic behavior, and the POSS-urethanes exhibit full thermoplastic elasticity. To our knowledge these are the first hybrid organic/inorganic polymers to exhibit this behavior.

Incorporation of POSS monomers into ordinary polymers can have dramatic effects on the copolymer properties. For example, Fig. 5 shows the thermomechanical (TMA) data for a set of cyclopentyl-POSS-methacrylate/butyl methacrylate copolymers. Copolymers containing 10 mol% POSS have a softening point almost 130 °C higher than the 20 °C glass transition temperature (T_g) for atactic poly(butyl methacrylate). The value of T_g for atactic poly(butyl methacrylate) is taken from

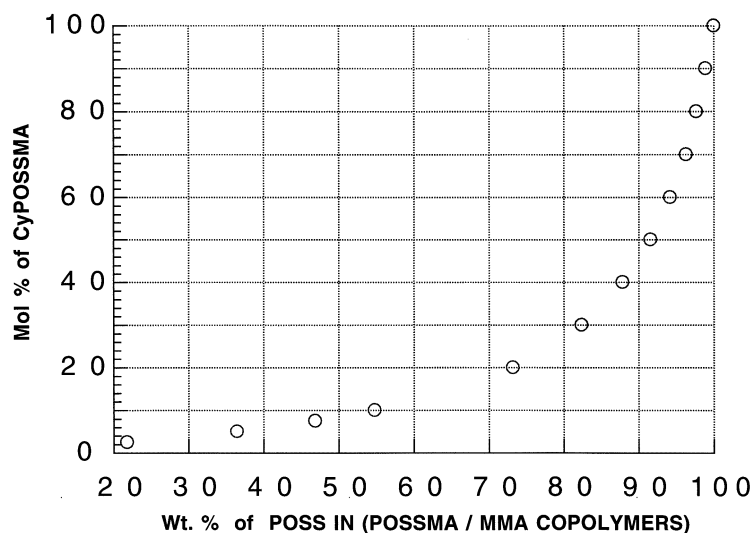


Figure 6 Relationship between mol as percentage and weight percentage of POSS in cyclopentyl-POSS-methacrylate/methyl methacrylate copolymers.

Ref 20 which also reports a range of 13–35°C. Incorporation of 20 mol% POSS results in a further increase in the softening point by approximately 70 °C, while a 50:50 (mol/mol) copolymer has a softening point over 220 °C higher than poly(butyl methacrylate). To date, similar results have been observed in every POSS copolymer system we have studied.

Furthermore, as a result of their high formula weights, incorporation of only a small mol percentage of POSS monomer is necessary to achieve incorporation of a high weight percentage of POSS (Fig. 6).

We also find that relatively small amounts of POSS monomer are necessary to achieve many of these property enhancements. For example, in cyclopentyl-POSS-methacrylate/methyl methacrylate copolymers we find that addition of only 5 mol% (35 wt%) POSS results in a 50 °C increase in T_g . Moreover, the relationship between the percentage POSS incorporation and the increase in T_g appears to be roughly linear up to the decomposition point, thus demonstrating the tailorability of POSS-containing hybrid polymers. In addition to increased T_g , we have also observed increased T_{dec} , increased resistance to oxidation, increased oxygen permeability, reduced flammability, reduced heat evolution, increased char yields and enhanced miscibility.

Although we are only now beginning to develop an understanding of the effects that POSS frame-

works have on polymer microstructure and the resulting effects on macroscopic properties, we believe that the observed property enhancements arise in part from the ability of the POSS segments to dominate polymer chain motions. Compared with traditional organic monomers, POSS monomers are physically very large. For example, the area swept out by an octomeric POSS monomer containing cyclohexyl substituents is approximately 15 Å, in diameter with an inner Si–Si diameter of 5.4 Å. Furthermore, POSS monomers have formula weights of greater than 1000 amu. By way of comparison, the dimensions or crystal lamellae in semicrystalline polymers are of the order of 10–25 Å × 0.1–1 μm with the amorphous layer thickness ranging from 5 to 10 nm.²¹ It therefore seems reasonable to consider POSS frameworks as macromeric with respect to polymer chain dimensions.

SUMMARY

The development of POSS-based reagents has provided polymer and materials scientists with a new class of hybrid building blocks. POSS reagents are discrete, well-defined monomers that can be incorporated into polymer systems using established polymerization protocol. The hybrid polymer systems into which POSS has been

incorporated have been shown to be thermoplastic in nature, and to have enhanced thermal, mechanical and oxidative properties relative to the non-POSS-containing polymers. In addition, the properties of a particular polymer system can be rationally tailored by controlling the percentage of POSS incorporated.

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