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Tim Haddad....Shawn Phillips "Nanostructured Hybrid Organic/Inorganic Materials, Silsesquioxane Modified Plastics"

ACS National Meeting **(Statement A)**

NANOSTRUCTURED HYBRID ORGANIC/INORGANIC MATERIALS. SILSESQUIOXANE MODIFIED PLASTICS.

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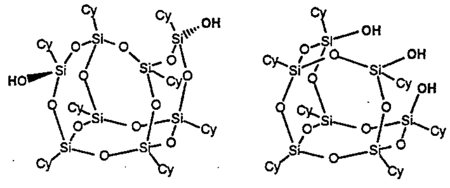
INTRODUCTION

The design of new materials with enhanced properties continues to be a driver for the investigation of hybrid inorganic/organic polymers. As hybrid materials are copolymers based on inorganic and organic comonomers, they display enhanced properties by bridging the property space between two dissimilar types of compounds.[1] A typical hybrid material will contain a crosslinked inorganic phase bound (often covalently) with an organic phase. Depending on the relative amounts of the two components, the properties of the resulting hybrid are intermediate between those of an inorganic and an organic polymer. Such methodology can be used to create either plastic inorganics or toughened plastics, and is superior to traditional blending methods.[1b] However, because such materials are crosslinked networks, they are difficult to study and control at the molecular level and are also difficult to process.

We have taken a unique approach to the synthesis of hybrid materials by designing polymerizable inorganic oligomers[2] with an exactly defined degree of polymerization of eight, $(RSiO_{1.5})_8$. These polyhedral oligomeric silsesquioxane (POSS) macromers have an inorganic silica-like core and are surrounded by inert organic groups to solubilize the inorganic framework. Each macromer is also designed to produce linear polymers with no crosslinking. Polymerization of the POSS macromer results in a linear polymer containing monodisperse, nano-size inorganic clusters[3] either pendent to an organic polymer backbone or else directly bound into the main polymer chain.

This paper describes a few of the polymers which can be obtained from using the two types of POSS macromers shown in Figure 1.

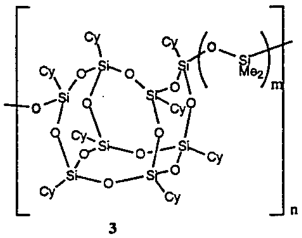


1 2

Figure 1. Two useful incompletely condensed polyhedral oligomeric silsesquioxanes obtained from the hydrolysis of cyclohexyltrichlorosilane.

RESULTS AND DISCUSSION

The hydrolysis of cyclohexyltrichlorosilane yields two useful POSS molecules (see Figure 1).[4] POSS macromer **1** is used directly in condensation polymerizations to produce linear "bead" type copolymers for which the POSS unit is a part of the polymer backbone. Condensation of disilanol **1** with chloride-terminated or dimethylamino-terminated siloxanes yields linear copolymers, **3**, such as that shown in Figure 2.

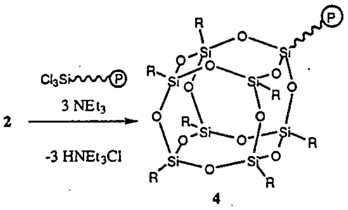


3

Figure 2. A POSS siloxane copolymer with a bead architecture derived from disilanol **1**.

Copolymers such as **3** are brittle materials whose T_g's are controlled by the nature of the bridging group between POSS cages. The POSS oligomer acts essentially as a hard segment with high thermal characteristics. For example, a copolymer with a dimethylsiloxane bridge is difficult to process as it has a T_g near the decomposition point of the polymer > 400 °C. However, a copolymer with a tetra(dimethylsiloxane) bridge has a T_g near 90 °C and is easily molded and shaped.

Polymerizable POSS macromers are obtained from the reaction of trisilanol, **2**, and various trichlorosilanes (see Figure 3). Polymerization of derivatives such as **4** results in polymers with the nanoscale inorganic particles pendent to the polymer main chain.

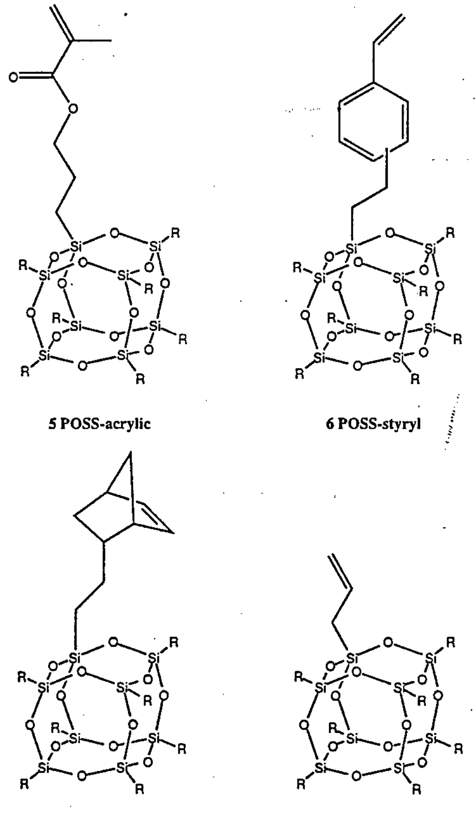


4

Ⓟ = a polymerizable functionality

Figure 3. High yield conversion of **2** into a polymerizable macromer. The seven R groups can be either cyclohexyl or cyclopentyl.

The reaction to produce **4** offers a manifold of possibilities for different POSS macromers (see Figure 4). Almost any desired functionality can be placed on the POSS cage by variation of the trichlorosilane used to derivatize **2**. The acrylic and styryl macromers are easily copolymerized with various acrylates or styrenes using free radical techniques. Norbornenyl macromers are polymerized in a controlled living polymerization to produce random or blocked copolymers, and allyl derivatives are used in grafting reactions.



5 POSS-acrylic **6 POSS-styryl**

7 POSS-norbornyl **8 POSS-allyl**

Figure 4. Four polymerizable POSS macromers derived from trisilanol **2**. The seven R groups can be either cyclohexyl or cyclopentyl.

The most striking effect of randomly incorporating a pendent POSS group into a common resin, as with acrylate, styryl, or norbornenyl copolymers, is to increase the glass transition of the copolymer well above that of the POSS-free resin. The higher the POSS content the higher the glass transition, and in some cases the polymer decomposes before it reaches a softening point. In fact, the glass transitions of the homopolymers cannot be measured by DSC or TMA. The T_g enhancement is most pronounced for the methacrylate copolymers, while the styryl copolymers show the smallest increases. These differences may be related to the free volume available in the POSS-free resins, or perhaps to the polymer backbone stiffness.

Both random and diblock POSS norbornenyl copolymers were synthesized and their thermal transitions measured. The random copolymers show a steady increase in the T_g as the POSS content is increased (See Figure 5a). The diblock copolymers reveal only a single unperturbed glass transition for the POSS-free polymer blocks, regardless of the amount of POSS in the diblock (See Figure 5b).

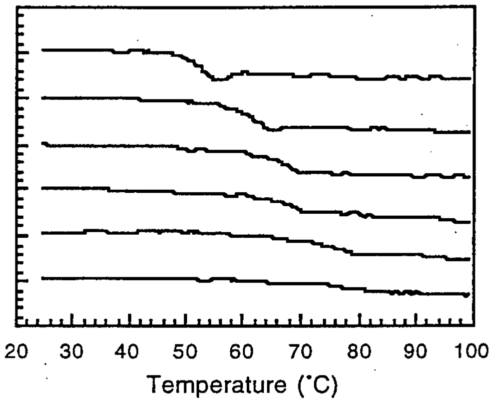


Figure 5a. DSC traces for a series of randomly polymerized POSS-norbornenyl copolymers. The graphs range from 0 % POSS (top) to 50 weight % POSS (bottom) in 10 weight % increments.

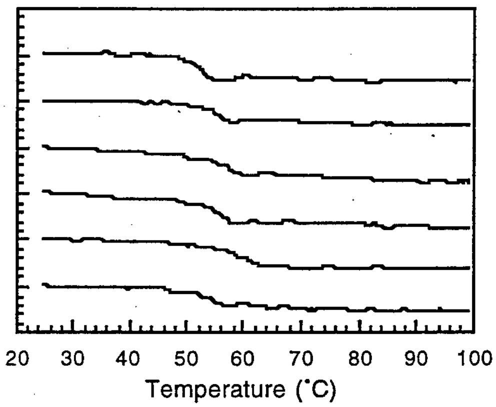


Figure 5b. DSC traces for a series of diblock polymerized POSS-norbornenyl copolymers. The graphs range from 0 % POSS (top) to 50 weight % POSS (bottom) in 10 weight % increments.

TEM pictures of the POSS-norbornenyl copolymers clearly image the POSS phases. As expected, the diblocks show a phase separation of POSS-blocks from the non-POSS containing blocks. However, the random copolymers also show that the POSS groups are associating to form a POSS network within the polymer matrix. Presumably, it is this network of physical crosslinking that causes the increases in glass transition.

The POSS allyl derivative, **8**, was grafted onto a poly(dimethyl-co-methylhydrido) siloxane to study the effect of a pendent POSS moiety on short chain linear siloxanes. Increases of over 200 °C in the glass transition temperature occur when just one POSS cage is added to each polymer chain (See Figure 6).

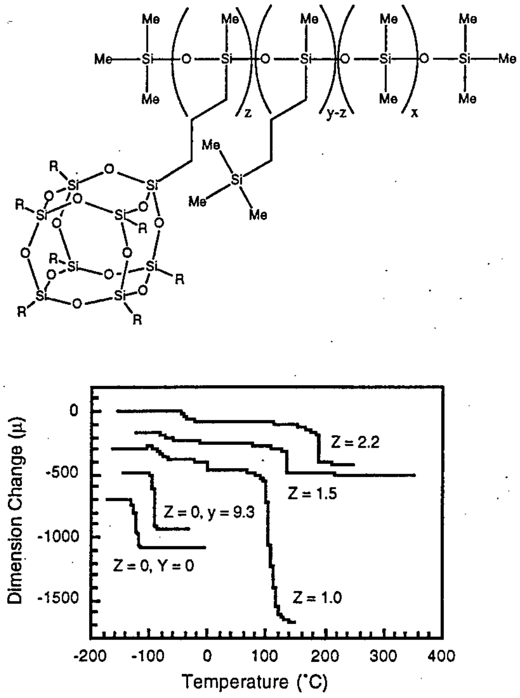


Figure 6. TMA traces for a series of POSS-derivatized siloxanes (x ~ 19 and z + y ~ 9)

CONCLUSIONS

We have demonstrated the ability to synthesize a variety of hybrid polymers containing nanoscale inorganic POSS macromers. Characterization of these materials shows that the POSS moieties act as hard segments and can retard chain motions. It would appear that POSS-POSS interactions are responsible for modifying polymer properties. Further work will focus on the synthesis and characterization of crosslinked POSS polymer systems such as epoxies and silicones.

ACKNOWLEDGMENTS

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