

Flame Resistant Polymers from Natural Resources

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Abstract

We have developed routes to simple, low cost Al and Si containing monomers and polymers starting directly from $\text{Al}(\text{OH})_3$ and SiO_2 (e.g. rice hull ash) that offer potential as novel flame resistant materials. $\text{Al}(\text{OH})_3$ reacts with HO_2CH to form H_2O soluble $\text{Al}(\text{O}_2\text{CH})_3 \cdot \text{H}_2\text{O}$. Formate exchange with allyloxyacetic acid gives $\text{Al}(\text{OH})(\text{O}_2\text{CHCH}_2\text{OCH}=\text{CH}_2)_2$, which can be polymerized. Triethanolamine (TEAH_3) reacted with SiO_2 in ethylene glycol gives $\text{TEASiOCH}_2\text{CH}_2\text{OH}$ (silatrane glycol). Silatrane glycol reacts with acetic anhydride giving $\text{TEASiO}_2\text{CCH}_3$ which reacts with ROH = allyl alcohol, allyloxyethanol and methacrylic acid to give polymerizable TEASi-OR compounds. Reacting rice hull ash (97 wt. % SiO_2) with Me_4NOH in methanol followed by reaction with HMe_2SiCl gives octahedral silsesquioxane, $(\text{HMe}_2\text{SiOSiO}_{1.5})_8$ or spacer cube. This cube reacts with functionalized alkenes to give liquid methacrylates, epoxides and polyenes that polymerize to organic-inorganic nanocomposites. Epoxy resins offer mechanical properties equal to wholly organic resins but with > 30 wt. % SiO_2 . Highly porous, insulating materials ($\text{SSAs} = 400 \text{ m}^2/\text{g}$) form at 20°C that are 85 wt. % SiO_2 .

Introduction

The synthesis of easily-processed polymers with good strength and stability at high temperatures is a subject of continuing and intense interest because such polymers can potentially replace metal and ceramic components in a wide variety of applications, especially in aerospace structures. A number of rigid-rod/liquid crystalline engineering polymers currently in commercial production meet the high strength and high temperature stability criteria. These polymers are slowly finding application in critical aerospace components; however, high synthesis and/or high processing costs continues to limit their utility. Although considerable efforts are being directed towards reducing both synthesis and processing costs; rigid-rod polymers, by their very nature are likely to always be difficult to process. Thus, finished components will also be relatively expensive. There continues to be a need for low-cost, easily processed polymers that coincidentally offer good mechanical properties at high service temperatures and that offer flame resistance.

There are three general approaches to imbuing a polymer with flame resistance. One is to incorporate aromatic units that promote char formation rather than supporting combustion. The second and more cost effective approach is simply to mix common organic polymers with inorganic fillers, especially those that form glass melts at temperatures attained during combustion. The resulting glass melts can smother any combustion process. Still a third way is to incorporate inorganic species in the polymer chains. This latter process has led to the development of halogenated polymers which are much less flammable but release toxic substances on charring. The only wholly inorganic polymers that offer good properties are the polydimethylsiloxane (PDMS) based polymers, e.g. those that consist primarily of Me_2SiO groups. PDMS polymers offer excellent flexibility, good flame resistance, and good stability

because of a very low T_g (-127°C), the absence of saturated moieties, e.g. alkyl groups, and an Si-O bond dissociation energy >120 kcal/mol. PDMS polymers are also very stain resistant because they are second only to Teflon® in their resistance to wetting.

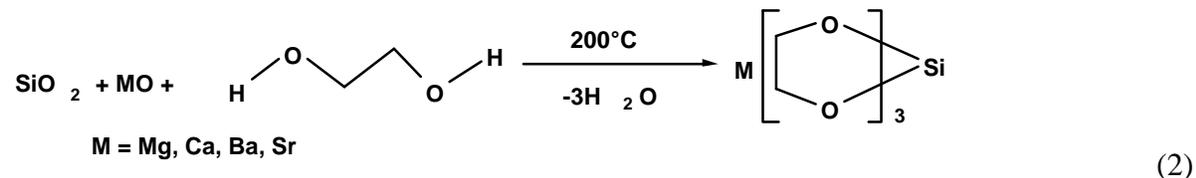
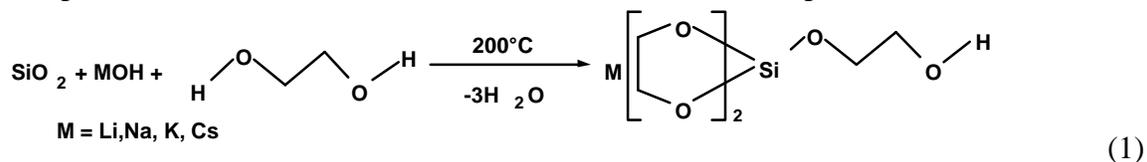
Unfortunately, PDMS polymers offer very poor mechanical properties because their resistance to wetting also limits their ability to chain entangle. As a result, they have very poor tear resistance which typically limits their utility. Furthermore, they tend to depolymerize on heating or in the presence of base or acid, especially at higher temperatures. In contrast, the related silsesquioxane ($\text{RSiO}_{1.5}$) polymers are stable to high temperatures. For example, methyl- and arylene silsesquioxanes, $-(\text{RSiO}_{1.5})_n-$ where $\text{R} = \text{Me}, \text{Ph}$; are stable to temperatures approaching 600°C .¹⁻³ However, silsesquioxane polymers are often quite brittle and must be carefully modified to impart acceptable mechanical properties. An additional problem is that PDMS and silsesquioxanes are produced from chlorosilanes that derive from Si metal produced by carbothermal reduction of silica at temperatures of 1200°C . Thus, they are relatively expensive compared with organic polymers.

Despite this, the very high Si-O bond dissociation energy (BDE) is attractive for the development of new polymers with good high temperature properties. Al-O bond dissociation energies are equivalent to Si-O BDEs and should, under appropriate circumstances, also be useful in producing new polymers with high temperature properties. Thus our recent discovery of methods of using silica, SiO_2 , and aluminum hydroxide, $\text{Al}(\text{OH})_3$, as a direct source of silicon and aluminum metalloorganics⁴⁻⁶ suggests novel and inexpensive routes to silicon and aluminum containing polymers with novel properties not otherwise obtainable. The following section provides an overview of the basic science behind the current studies.

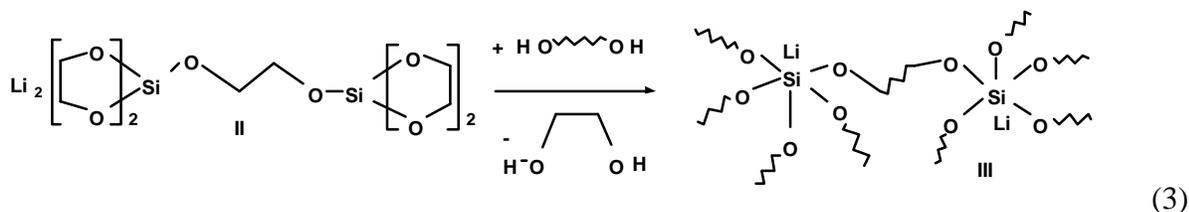
Background

Silicon based materials

High surface area silica will dissolve in ethylene glycol in the presence of a base to give either anionic pentacoordinated or dianionic hexacoordinated silicon complexes:

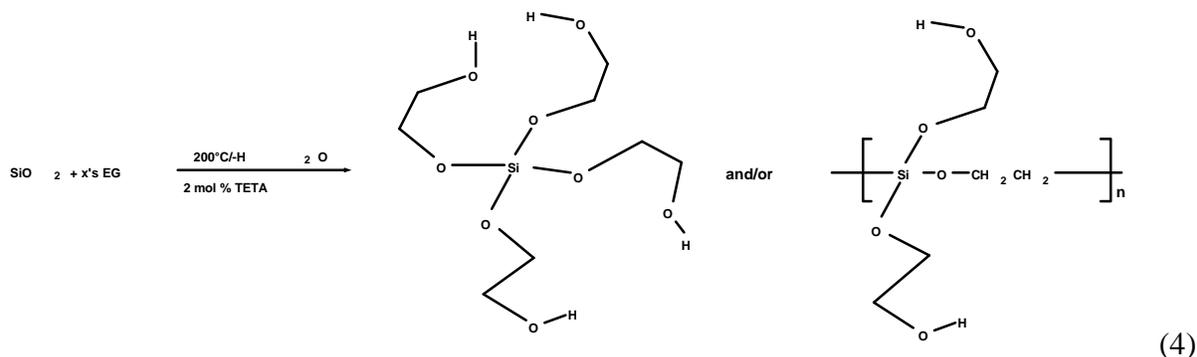


These compounds are all crystalline and ionic materials; however, they are easily converted to ionic polymers by exchange of the bidentate ethylene glycol ligands with longer chain diols that cannot act as bidentate ligands. Thus, heating the crystalline Li salt with tetraethylene glycol (PEG_4) such that the displace ethylene glycol (EG) distills off leads to a polymeric compounds that is ion conducting:⁷

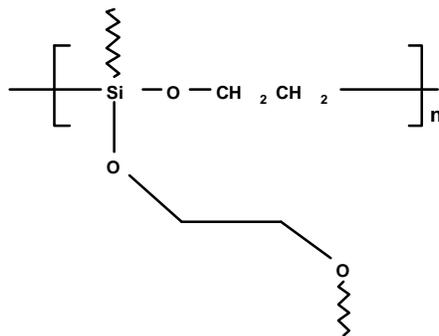


Surprisingly, all of these compounds and polymers are stable in air to temperatures of 330°-390°C, but are moisture sensitive.⁸

Based on the results in reaction (2) and work by Frye et al,⁹ we rationalized that the same reaction might occur using strong amine bases.¹⁰ We now find that it is possible to react SiO₂ with ethylene glycol using catalytic quantities of triethylenetetramine (TETA) to prepare ethylene glycol compounds:

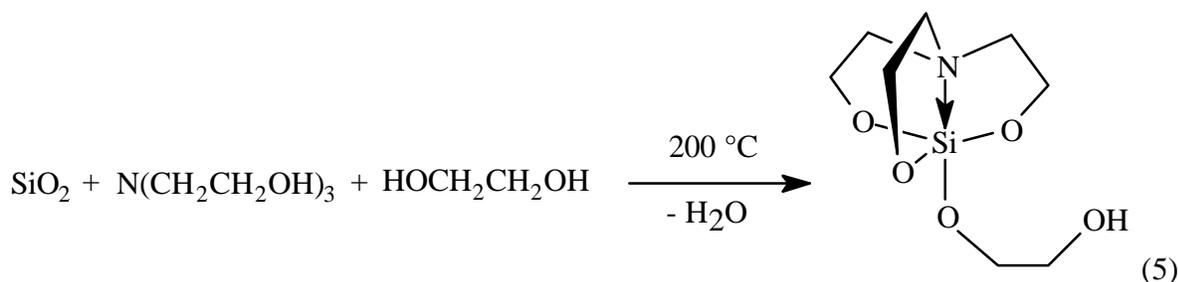


At 200°C, byproduct water distills off, leading in 10-30 h to complete dissolution to form a single silicon containing species, possibly Si(egH)₄, which can be isolated only as polymer, e.g. as shown in reaction (4). On further heating, this polymer fully crosslinks to a brittle material, Si(eg)₂, which by chemical analysis, TGA and solid state NMR appears to be:¹⁰



This polymer is stable in air to 390°C as shown in Figure 1 below and despite its being totally crosslinked, it will redissolve in EG (via pentacoordinated silicon species) and can be further processed.

Alternately, heating with other diols leads to exchange to form less brittle materials [e.g. Si(PEG₄)₂]. The Si(PEG₄)₂ polymer with longer intracrosslink chains appears to be more flexible than the Si(eg)₂ polymer. We have not as yet determined the moisture sensitivity of the Si(eg)₂ polymer but assume that it is only moderately stable. We have discovered however that by adding triethanolamine into the reaction mixture as a reactant and catalytic base, that we can quantitatively produce the silatrane glycol:¹¹



Silatrane glycol represents a very rare type of silicon alkoxide complex. It is soluble and stable in neutral water for weeks at a time and is even stable in boiling water for hours at a time. Thus,

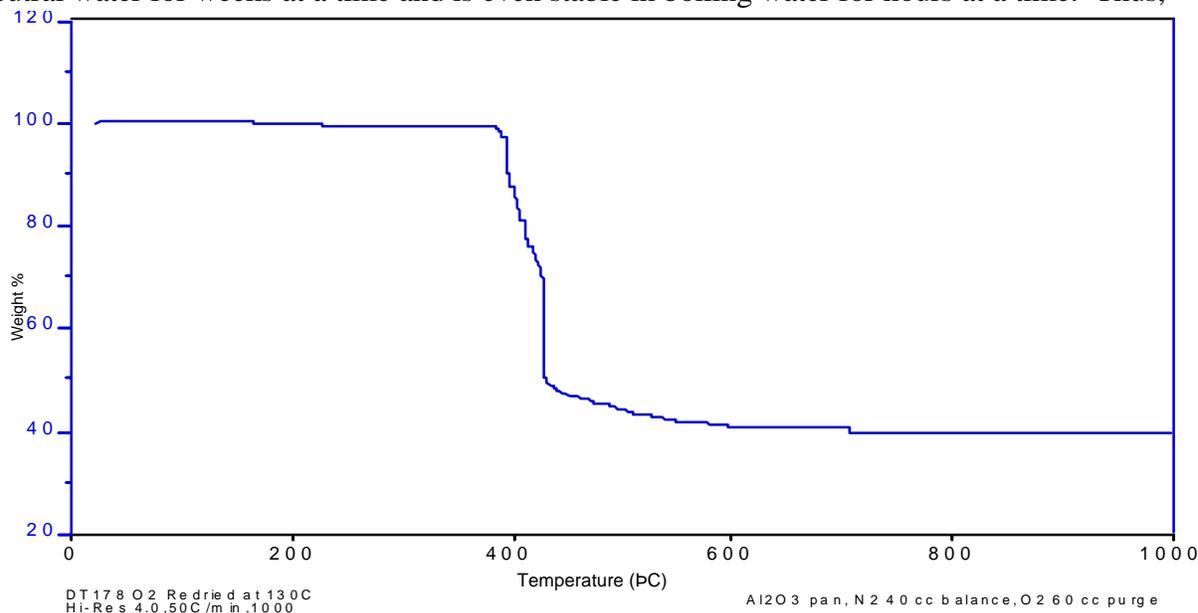
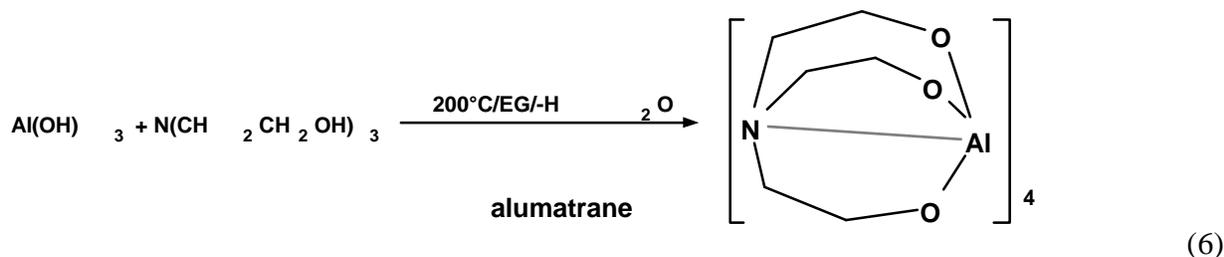


Figure 1. TGA of $\text{Si}(\text{eg})_2$ in air.

it represents one of the more important discoveries in our work because its moisture stability suggests that it can be used to produce novel polymers that will offer flame resistance. Furthermore, because it can be made directly from silica, including rice hull ash, it represents a very low cost starting material. Our work with this compound is discussed below.

Alumina based materials

The success of reaction (5) and the stability of silatrane glycol suggested that the same reaction might produce an aluminum alkoxide of very high stability. We thus explored the reaction of aluminum hydroxide with triethanolamine:¹²

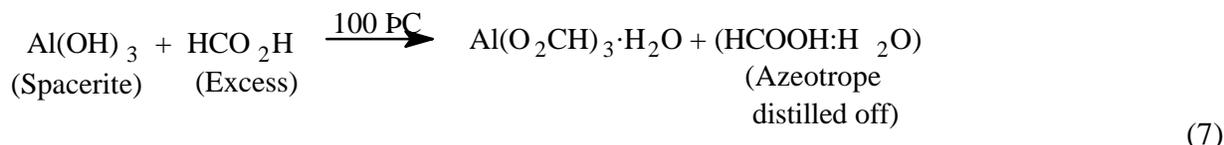


The alumatrane produced quantitatively in reaction (6) is much more stable than any other aluminum alkoxide currently available commercially. Unfortunately, it is not easily modified as is

the silatrane glycol for incorporation into polymers. Thus, we sought other chemistry that might provide ligands around Al that are more easily modified.

It is well known that aluminum oxides and hydroxides dissolve in strong mineral acids to form $\text{Al}(\text{H}_2\text{O})^{3+}$ ions in solution. Thus, it might be possible to dissolve aluminum hydroxides in strong organic acids to form aluminum carboxylates suitable for incorporation into polymeric materials. For example, 1M solutions of formic acid in water have a $\text{pK}_a \approx 5 \times 10^{-5}$ which suggests that concentrated formic acid solutions should be strongly acidic.

The literature describes the synthesis of aluminum formate, $\text{Al}(\text{O}_2\text{C})_3 \cdot 3\text{H}_2\text{O}$, by reaction of formic acid with amorphous $\text{Al}(\text{OH})_3$; however, amorphous $\text{Al}(\text{OH})_3$ can only be prepared by hydrolysis of AlCl_3 or $\text{Al}(\text{OR})_3$ which are made from aluminum metal which defeats the purpose. We now find that aluminum formate can also be made directly from gibbsite (commercial name from Alcoa is spacerite) $[\alpha\text{-Al}(\text{OH})_3 \cdot 3\text{H}_2\text{O}]$ and boehmite, $[\text{Al}(\text{O})(\text{OH})]_n$ which are produced directly from bauxite.¹³ Gibbsite is produced in 10^6 tons/yr.

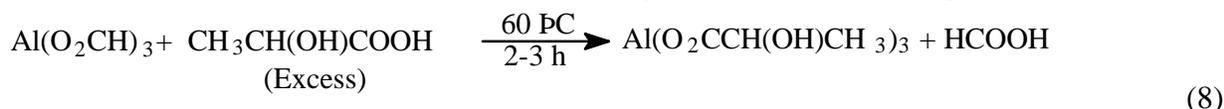


Aluminum formate is soluble in hot water and can be used as a starting point for the synthesis of several materials that offer potential for forming air and moisture stable aluminum compounds that can be used to form polymers, as described in the following section.

Current work

Polymerizable aluminum monomers.

Our efforts to produce aluminum containing polymerizable carboxylate monomers were driven by two goals: (1) develop moisture stable monomers, and (2) learn to functionalize these monomers to introduce polymerizable groups without jeopardizing the stability of the carboxylate linkage. The first goal was easy to accomplish. Aluminum lactate, $\text{Al}(\text{O}_2\text{CCH}(\text{OH})\text{CH}_3)_3$, is known to be highly water soluble and quite resistant to hydrolysis except in strongly acidic media. The reaction of lactic acid with aluminum formate gives aluminum lactate quantitatively:



Thus, a water stable, water soluble aluminum compound can be made quantitatively in two steps from $\alpha\text{-Al}(\text{OH})_3 \cdot 3\text{H}_2\text{O}$.¹³ The stability of the lactate compound derives from the additional hydroxyl group which coordinates to the aluminum making the approach of water (to promote carboxylate hydrolysis) difficult. Furthermore, these hydroxyl groups improve hydrogen bonding to greatly enhance water solubility compared with the formate.

The next step was to learn to introduce functionality to form compounds that offer the stability of aluminum lactate. By recognizing that an additional oxygen is most likely necessary to stabilize the complex, we also examined the formation of the methoxyacetate derivative. Surprisingly, methoxyacetic acid reacts directly with $\alpha\text{-Al}(\text{OH})_3 \cdot 3\text{H}_2\text{O}$ to form a water soluble, water stable compound:¹³

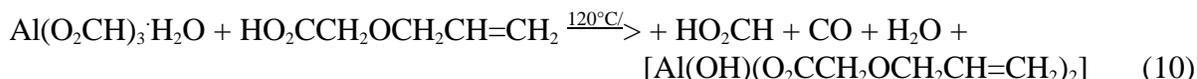


(9)

Efforts to use lactic acid in place of methoxyacetic acid were unsuccessful.

The methoxyacetic acid complex is completely water soluble. It is easily isolated in pure form and gives a TGA ceramic yield of 21.2 wt. % which is theoretical for this material. Thus, this compound proves that it is possible to place a carbon on the additional oxygen and still achieve the stability needed to proceed to more functionalized compounds.

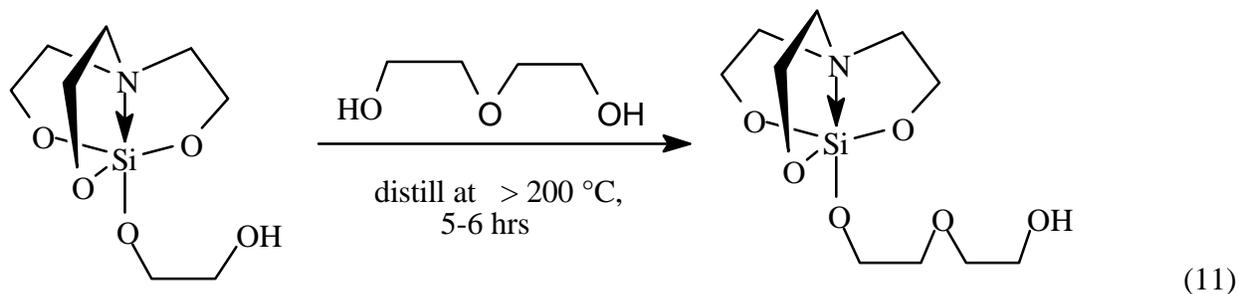
The next step was to explore the use of a polymerizable substituted acetate. We just recently discovered that allyloxyacetate can be used to produce a polymerizable material:¹³



The bisallyloxyacetate is stable in air and moisture but is not water soluble; however, it is soluble in a number of organic solvents including chloroform, dichloromethane, toluene and chlorobenzene. Heating the monomer in chlorobenzene in the presence of AIBN results in the formation of insoluble polymers. The bisallyloxyacetate will also dissolve in chloroform with methylmethacrylate and on solvent removal AIBN can be used to promote copolymerization to give crosslinked materials. We are currently exploring methods of processing these polymers and evaluating their properties.

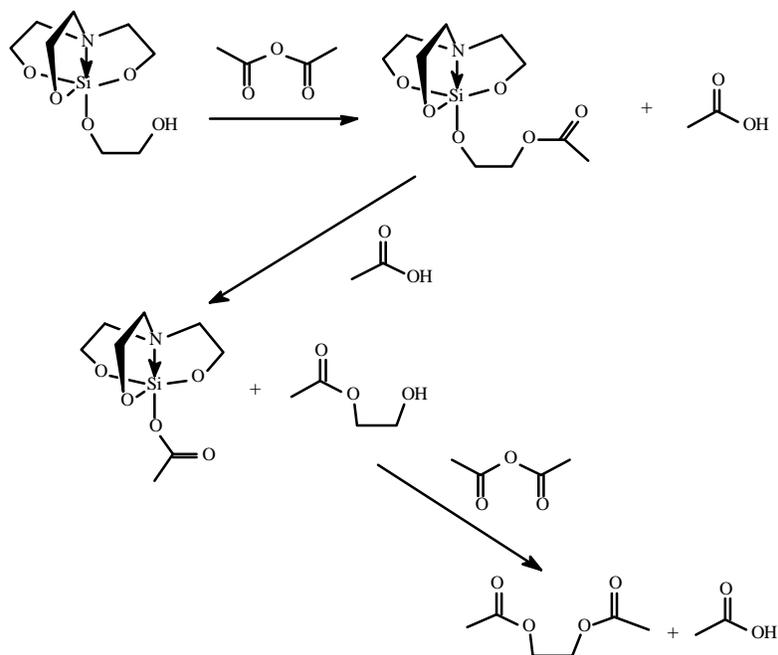
Polymerizable silicon containing monomers.

As with the aluminum derivatives, our first efforts focused on establishing the stability of the silatrane glycol.¹¹ Thus, we found that this compound is somewhat soluble (50 mg/ml) in water and stable for prolonged periods of time but is not stable in acidic or basic media. Efforts to improve the water solubility led to the synthesis of the diethylene glycol derivative:



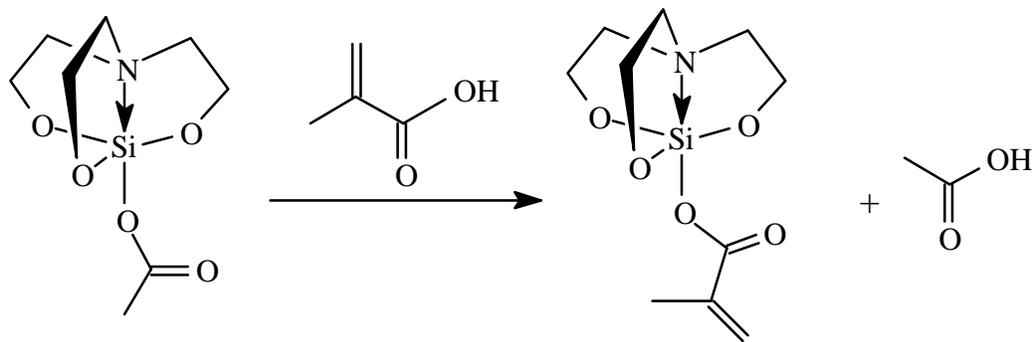
This compound shows improved water solubility (250 mg/ml) with similar stabilities. Efforts to prepare a glycerol derivative gave water soluble but polymeric materials from which little could be isolated.

The next step was to prepare polymerizable materials. Initial efforts focused on using alcohol exchange as a means of synthesizing allyloxy and allyloxyethylenoxyethanol derivatives. The goal was to reflux silatrane glycol in an excess of these alcohols to obtain complete exchange. Unfortunately, the exchange reactions never go to completion or even close and consequently we were forced to find another exchangeable, pendant ligand. Fortunately, acetic anhydride reacts with silatrane glycol, most probably by the mechanism shown below to give the monoacetate as suggested in Scheme I.

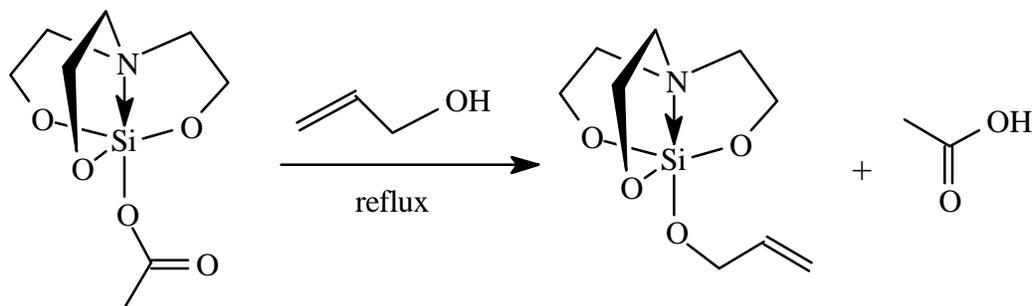


Scheme I

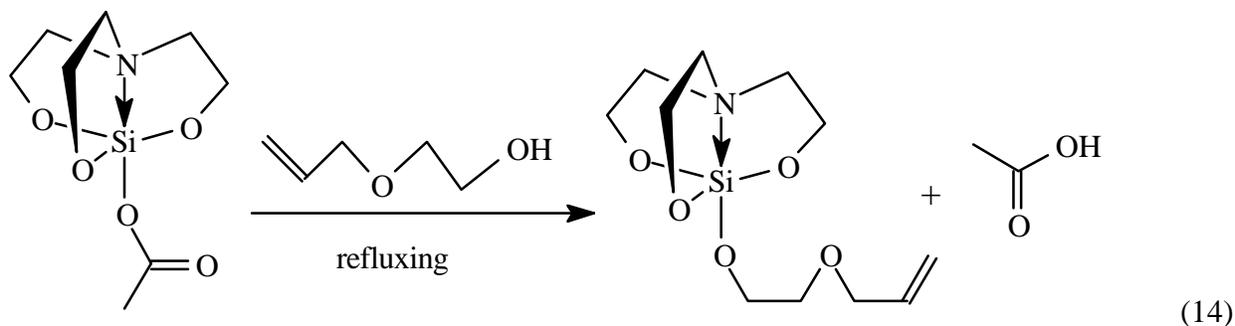
The monoacetate is water sensitive but is quite reactive and can be used to make a number of polymerizable materials as illustrated in the next set of reactions:



(12)



(13)



All of the above compounds offer potential for forming polymers or copolymers. Preliminary studies show that the methacrylate compound is soluble in chlorocarbon solvents. Solutions of the silatrane methacrylate in chlorobenzene can be polymerized by using AIBN and copolymerized with methacrylate. The resulting polymers and copolymers have not as yet been characterized. We are currently attempting to make epoxide materials from the products of reactions (13) and (14) and will report on this work and the resulting polymer products at a later date.

Silsesquioxane macromonomers and polymers.

As noted above, silsesquioxane polymers offer very good high temperature stability but often are quite brittle. One of our research goals is to learn to make silsesquioxane materials directly from natural resources and to learn to reduce the brittle nature of polymers that can be made from these materials. This objective drives one of our key research areas. Rather than making silsesquioxane polymers, we have focused on a special area of silsesquioxane chemistry involving polyhedral silsesquioxanes. Polyhedral silsesquioxanes are cage structures with properties engendered in and on nanometer sized grains of “sand” as shown below in Figure 2.

Two forms of octahedral or cubic silsesquioxanes are known, R_8T_8 and the ${}^R D_8Q_8$. The R_8T_8 materials are made by hydrolysis of organotrichlorosilanes which are produced directly from silicon metal.^{1,3} However, the ${}^R D_8Q_8$ or spacer “cube” compounds are commonly made

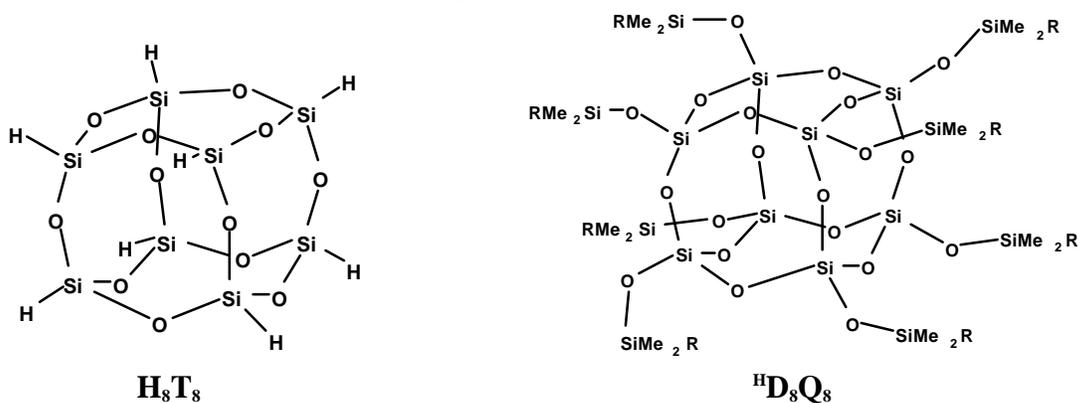
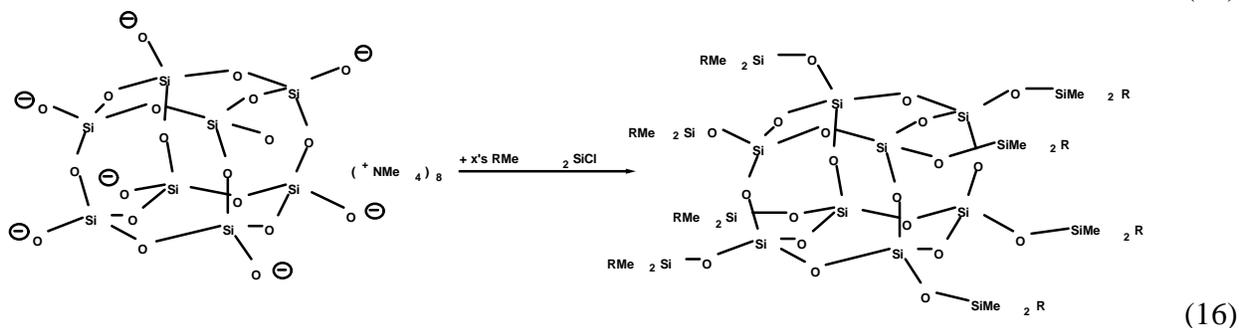
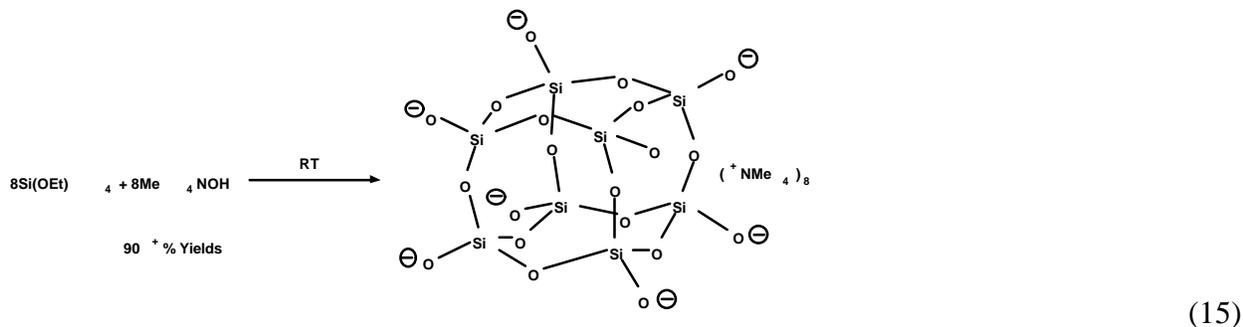
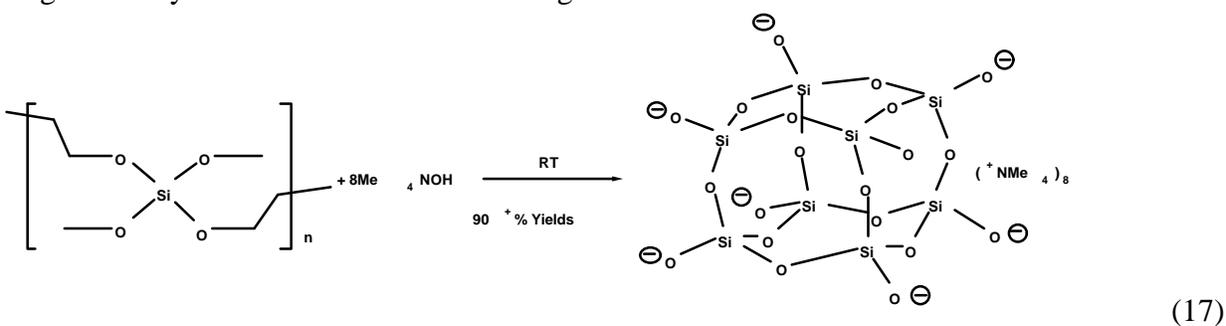


Figure 2. Two Forms of Octahedral Silsesquioxanes

as shown in reactions (15) and (16):¹⁴

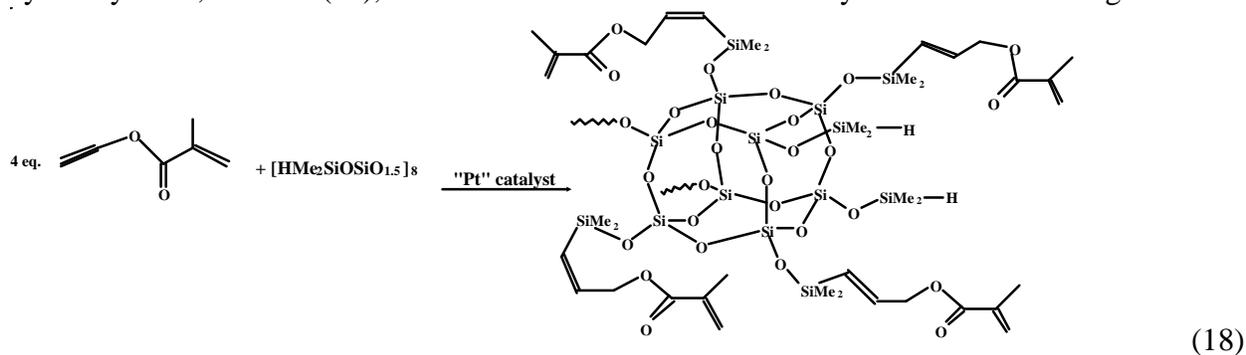


Given that Si(eg)_2 is a simple analog of Si(OEt)_4 , we explored the synthesis of the ${}^{\text{H}}\text{D}_8\text{Q}_8$ cube using it directly. With the result that we can generate the same octaanion via:



Still more recently, we have found that rice hull ash can be used directly to run reaction (17). Rice hull ash is produced by burning the rice hulls recovered during the “polishing” process that produces white rice. Rice hull ash is typically about 97% pure silica with 3 wt. % carbon and with surface areas of $> 10^2/\text{g}$. The reaction goes a little slower than in (17) but the yields of spacer cube are much the same.

Thus, we now have an octafunctional material (${}^{\text{H}}\text{D}_8\text{Q}_8$) produced directly from rice hull ash, that can be further functionalized. For example, we can produce liquid methacrylates by hydrosilylation, reaction (18), that have > 60 wt. % silica ceramic yields as shown in Figure 3.¹⁵



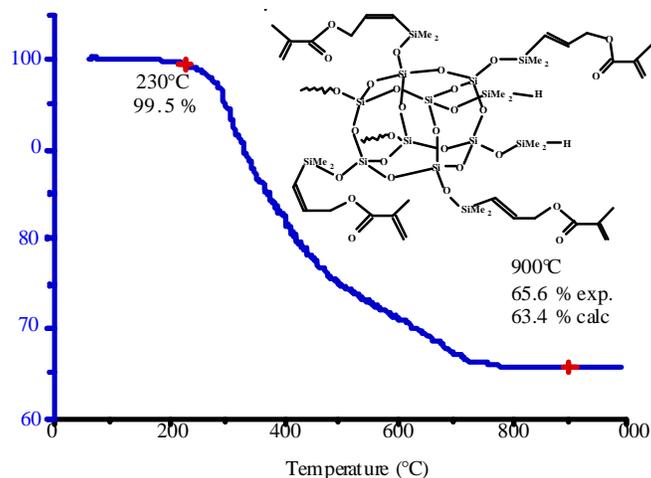
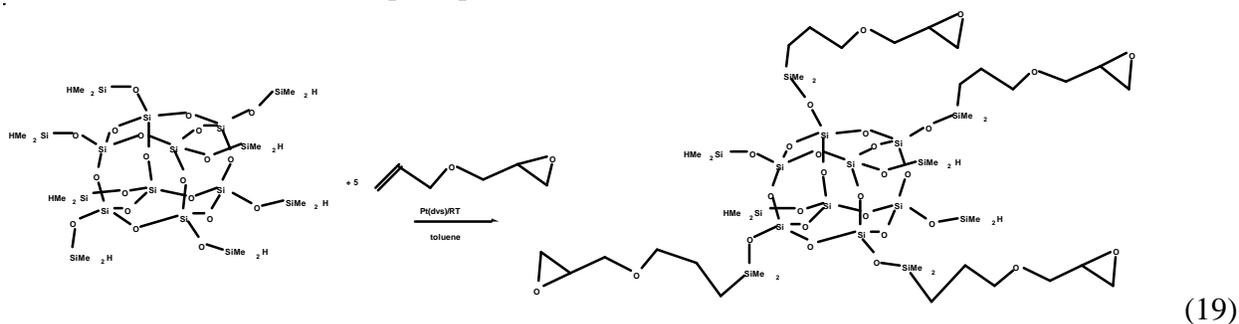
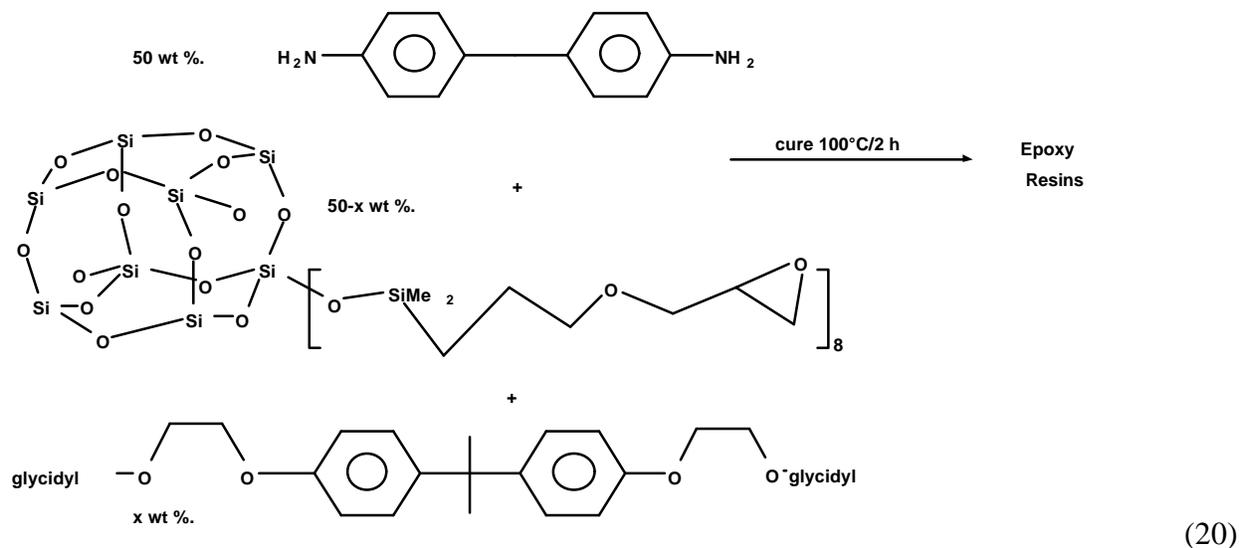


Figure 3. TGA of tetramethacrylate (ave substitution) functionalized octahedral octadimethylsiloxysilsesquioxane in air.

Likewise, we can also make liquid epoxy cubes, reaction (19) that can be used to make flame



resistant epoxy resins:



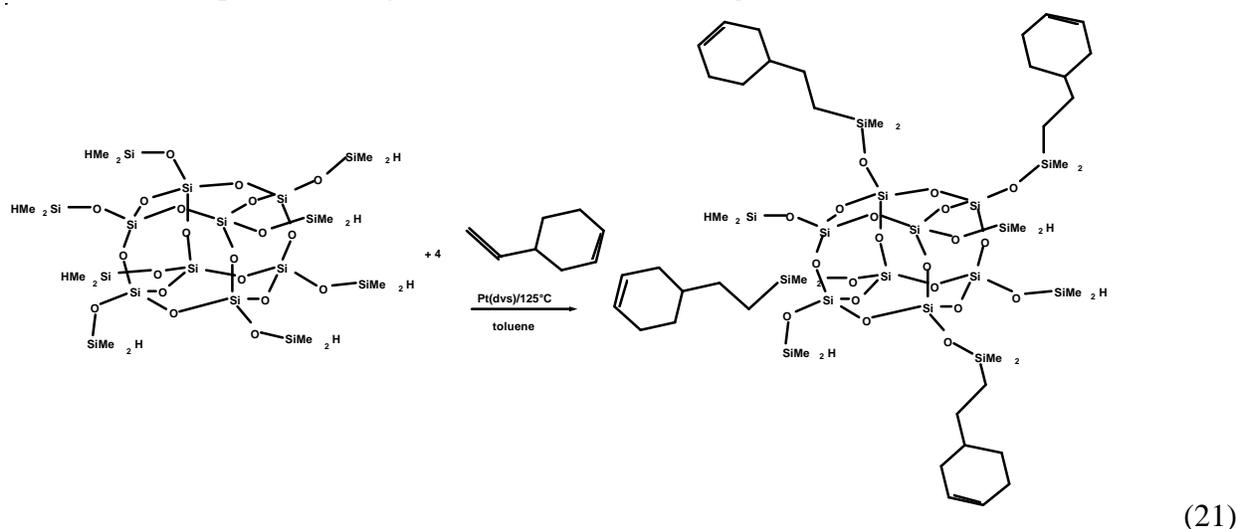
Preliminary studies on mechanical properties give the following results:

Table 1. Tensile and Fracture Strength in Glycidyl Cube Epoxy Resins

Wt. % Cube	Wt. % DEGBA	Modulus (GPa)	$K_{1C}/\text{MPa(m)}^{0.5}$
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40	40	1.2 ± 0.2	0.7 ± 0.1
40	42	2.4 ± 0.4	1.5 ± 0.4
58	24	1.5 ± 0.4	0.7 ± 0.4
83	0	1.2 ± 0.3	0.7 ± 0.2
45	0	1.6 ± 0.2	
0	50	1.6 ± 0.1	
Polyethylene		0.15	1.5
PMMA		2.5	1.1
Epoxy		2.8	0.5
Elastomer Toughened Epoxy		2.4	2.2

Most of the spacer cube materials decompose at temperatures of 225° to 300°C; however, one recent result points the way to materials with much higher stabilities:



The tetra(vinyl)cyclohexenyl derivative can be thermally self-cured at 200-250°C to give a transparent, flexible material that may offer utility as a high temperature gasket materials or for use in window applications. Once cured, this material is stable in air to 400°C as shown in Figure 4. We are currently looking into the thermal properties of these and related materials.¹⁷

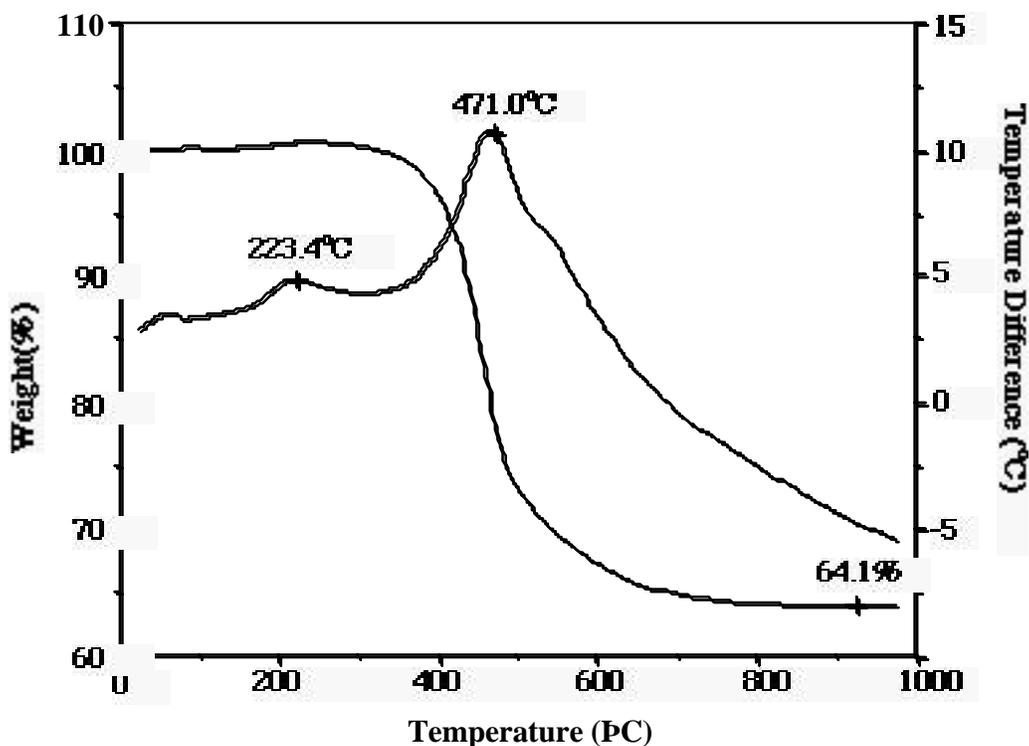
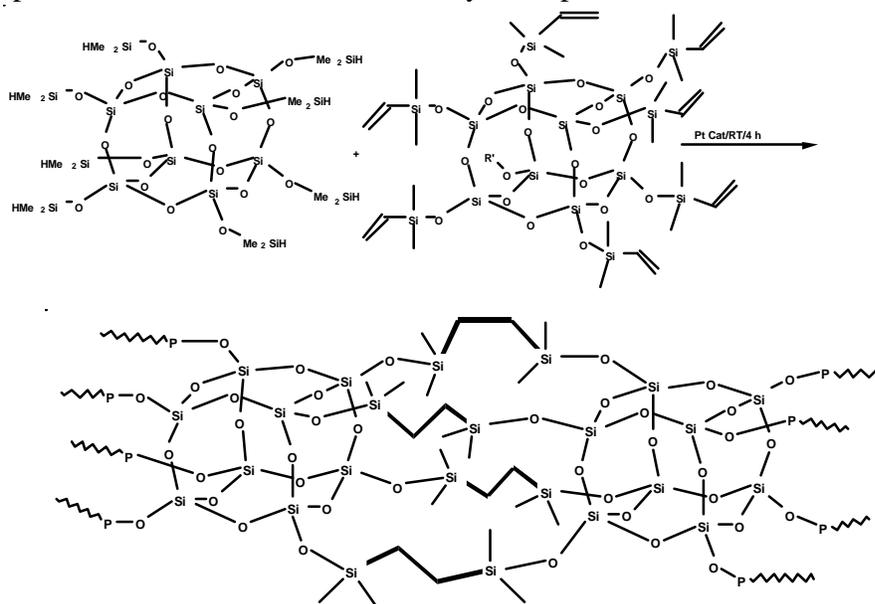


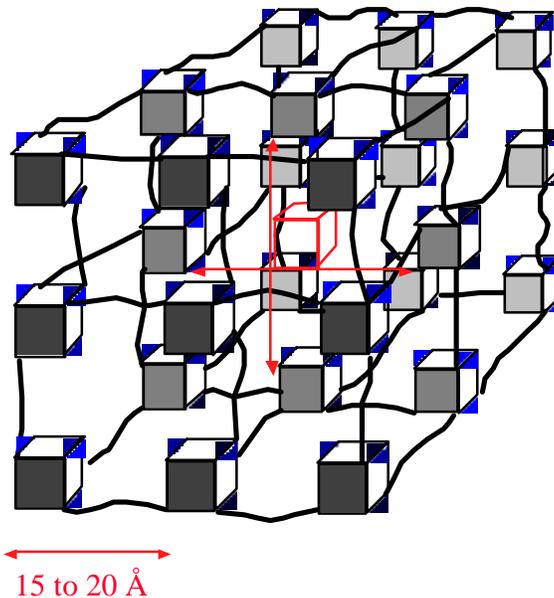
Figure 4. TGA/DTA of tetra vinylcyclohexenyl substituted cube heated at 10°C/min in air.

Finally, we have conducted a serious study of the polymerization process wherein the octavinyl spacer cube is reacted with the octahydridospacer cube.¹⁸ The basic reaction is:



(22)

Solid state NMR indicates that each cube forms an average of 6.5 links to other cubes, this corresponds to approximately cubic packing of the material, as suggested below:



The well defined polymerization which occurs at room temperature in toluene gives a very highly porous material with surface areas of $400 \text{ m}^2/\text{g}$ and very well defined pore sizes as shown in Figure 5. The very high surface areas and fine pore structure combined with the

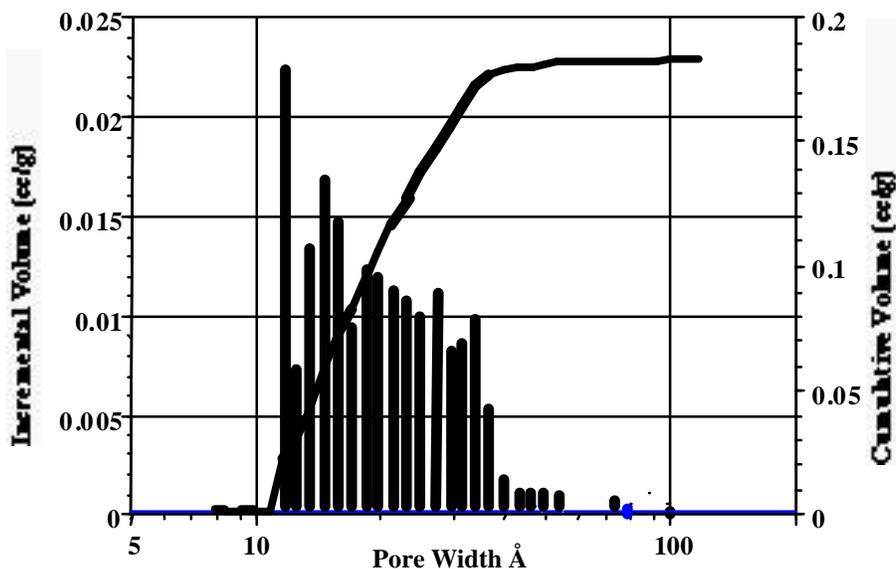


Figure 5. Pore volume distribution.

relatively good thermal stability and high silica content ($> 85 \text{ wt. } \%$) as shown in Figure 6 suggest that these materials offer good potential as insulating materials. They can also be made transparent, suggesting opportunities for use in window or control panel applications. The fine porosity may also be useful for filtration applications.

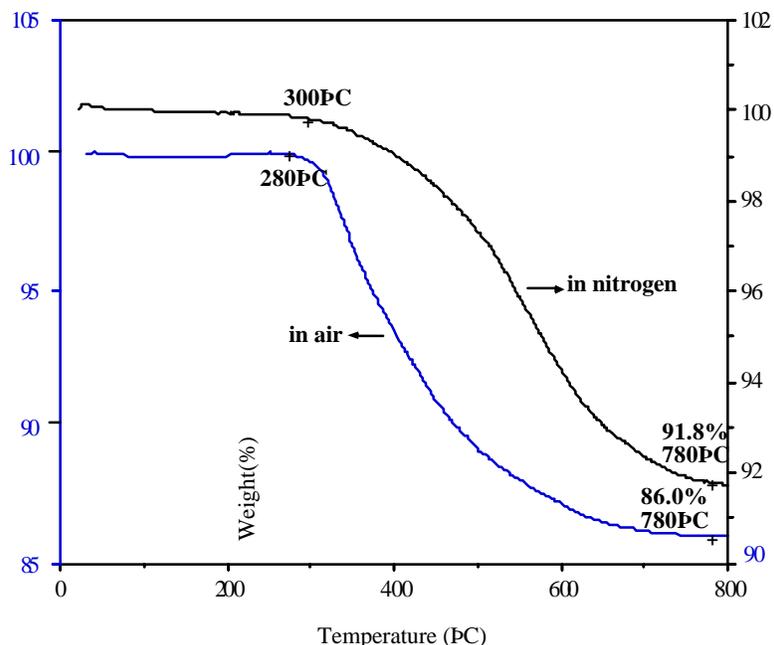


Figure 6. TGA of polymer from reaction (22) in air and nitrogen. Note that total ceramic (SiO_2) is > 85 wt. %.

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