

# Bridged Polysilsesquioxanes. Highly Porous Hybrid Organic–Inorganic Materials

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## I. Introduction

This contribution reviews a new family of inorganic–organic hybrid materials that are assembled by sol–gel polymerization of polyfunctional molecular building blocks. These bridged polysilsesquioxanes are three-dimensional network materials that are distinguished by incorporation of an organic fragment as an integral component of the network (Figure 1). The intimate association of the organic and inorganic phase, a true *molecular composite*, coupled with the variability of the organic component, permits engineering of both chemical and physical properties of the material.

## II. Background

Sol–gel polymerization of tetraalkoxysilanes, Si(OEt)<sub>4</sub> (TEOS) and Si(OMe)<sub>4</sub> (TMOS), is a mild and convenient method for the synthesis of amorphous silica gels. The chemical steps involved in sol–gel polymerization, hydrolysis and condensation, result in the creation of Si–O–Si chemical linkages from alkoxy silanes (Figure 2).<sup>1</sup>

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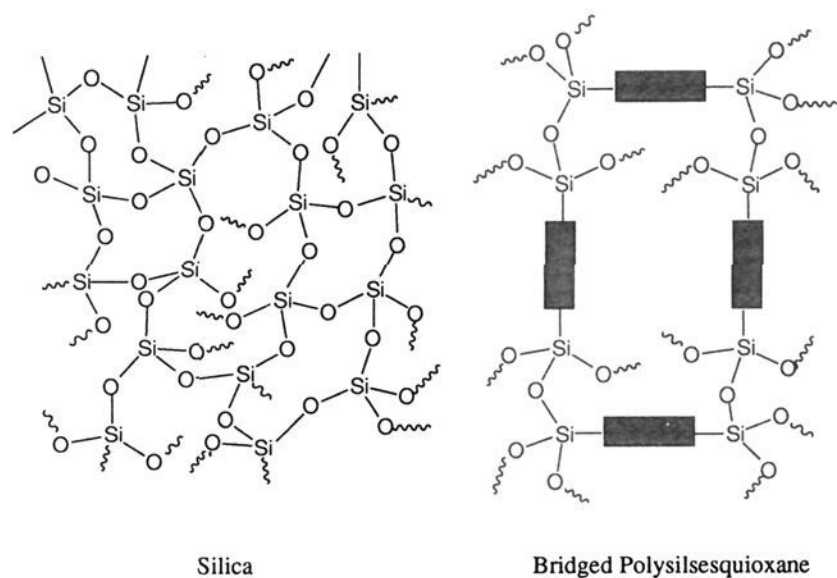


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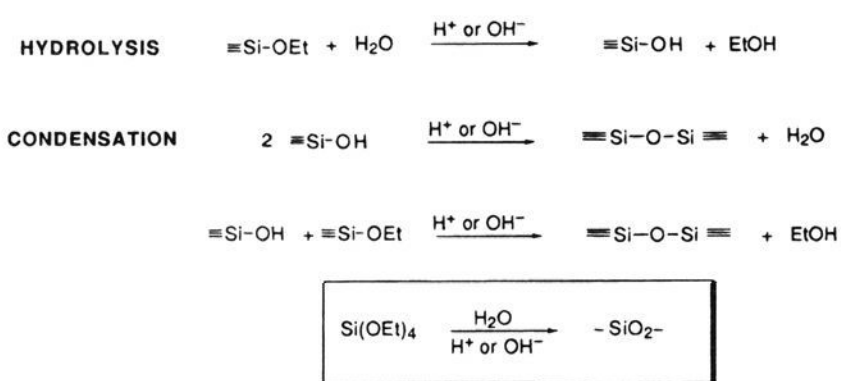
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The sol–gel reactions are catalyzed by both acids and bases and produce solutions of silica polymers. The silica polymers grow until they reach a size where a gel transition occurs and a solidlike gel is formed. The structure of sol–gel silica evolves as a result of these successive hydrolysis and condensation reactions and the subsequent drying and pro-

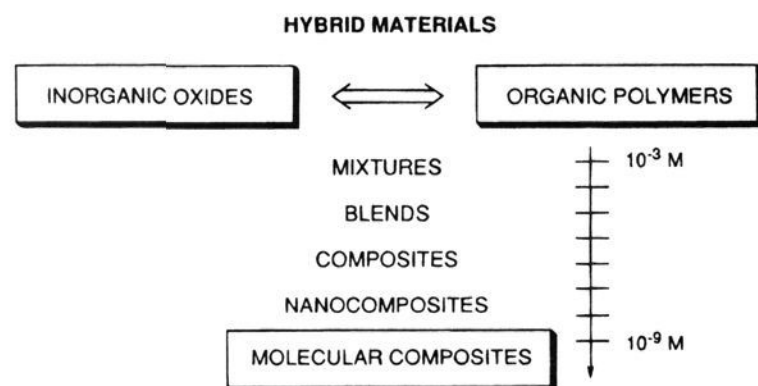


**Figure 1.** Representation of the chemical connectivities of silica and a bridged polysilsesquioxane. The shaded rectangles correspond to the variable organic fragment.

#### SOL GEL CHEMISTRY



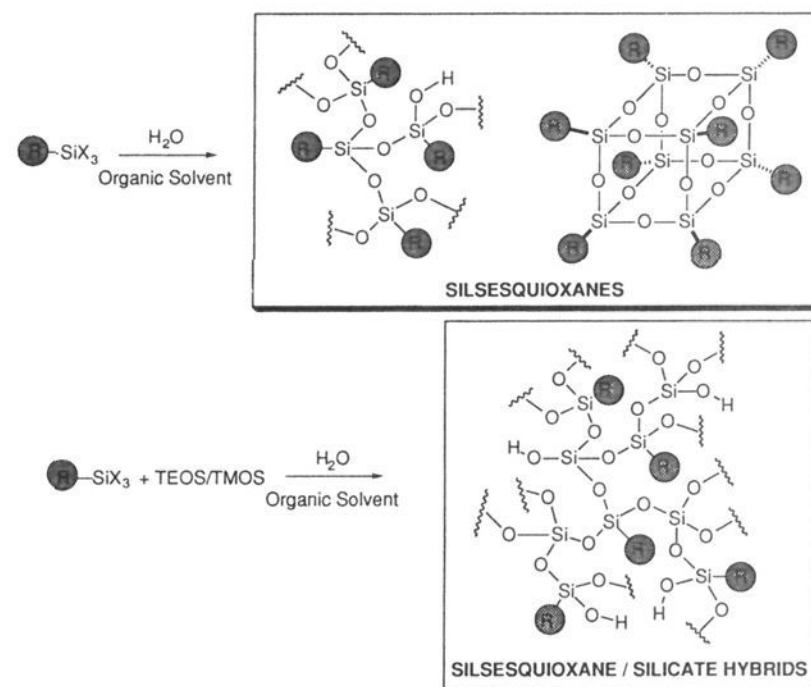
**Figure 2.** Summary of the key steps in sol-gel polymerization of ethoxysilanes.



**Figure 3.** Illustration of the range of domain sizes in hybrid materials.

cessing (i.e., sintering). The final morphology of silica therefore, may be influenced by changing any one of these steps during its formation. Many important physical properties of silica, such as porosity and transparency, can be controlled by the choice of polymerization method and subsequent processing conditions.<sup>1,2</sup>

The breadth of physical and chemical properties of inorganic polymers such as silica can be greatly extended by the introduction of organic groups into the inorganic framework. The resulting hybrid organic-inorganic materials can range from physical mixtures of inorganic oxide and organic molecules or macromolecules to hybrid materials that utilize covalent attachment of the organic fragment to silicon (Figure 3).<sup>3</sup> The properties of physical mixtures of inorganic oxides and organics are influenced by each of the components and their domain size. Often, improved physical properties can be achieved by reduction of the domain size, which increases the

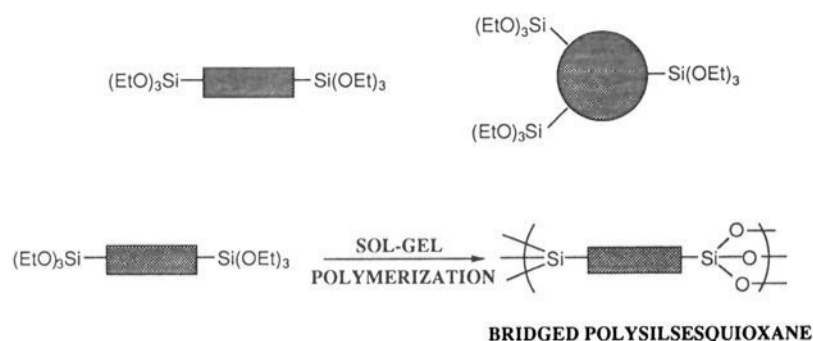


**Figure 4.** Hydrolytic condensation products of trifunctional organosilanes and copolymers with TEOS.

interfacial surface area. The demand for improved standards of performance has stimulated research in the area of *nanocomposites*, hybrid materials with domains on the nanometer scale.<sup>4</sup> Further reduction in domain size accesses the molecular level. This may be accomplished by incorporating the polymerizable inorganic group and an organic constituent in the same molecule. Examples include the products from sol-gel polymerization of trifunctional organosilanes (e.g.,  $\text{CH}_3\text{SiCl}_3$  or  $\text{CH}_3\text{Si(OEt)}_3$ ). These materials, which are referred to as silsesquioxanes, may be viewed as true molecular composites with the empirical formula of  $\text{RSiO}_{1.5}$ . Interestingly, despite the high level of functionality in trifunctional organosilanes, their sol-gel polymerization products, for all but the smallest of R groups, are incompletely condensed T-resins or the topologically interesting polyhedral silsesquioxanes (Figure 4). Their synthesis, structure, and properties are reviewed by Baney et al. in an accompanying review in this issue.<sup>5</sup> Network materials can be formed from  $\text{RSiX}_3$  by cocondensation with monomers that contain a higher level of functionality, such as TEOS or TMOS (Figure 4). The resulting morphology of the hybrid material is modulated by the  $\text{RSiX}_3/\text{TEOS}$  ratio as well as the processing conditions.<sup>6,7</sup> Indeed, a range of morphologies are available by this approach. In this review, we focus on a family of cross-linked networks of silsesquioxanes with the chemical connectivity illustrated in Figure 1. They are prepared from molecular building blocks that contain two or more trifunctional silyl groups (Figure 5). They are homogenous materials with a completely uniform distribution of organic and inorganic oxide at the molecular level.

### III. Bridged Polysilsesquioxanes

Highly cross-linked hybrid organic-inorganic materials can be prepared from molecular building blocks that contain a variable organic fragment attached to two or more trifunctional silyl groups by nonhydrolyzable carbon-silicon bonds. Sol-gel polymerization of such poly(trialkoxysilyl) monomers inherently leads to network materials, bridged poly-



**Figure 5.** Schematic of monomeric building blocks containing two or more triethoxysilyl groups as precursors to bridged polysilsesquioxanes. The organic component (shaded area) may include alkylene, arylene, akenylene, and alky-nylene groups.

silsesquioxanes (Figure 5). The bridging motif allows for development of the full potential of both organic and inorganic components in amorphous polymers with engineered properties at the molecular level of design. Bridged polysilsesquioxanes can be prepared with a broad range of organic bridging groups incorporated as an integral part of the network. Furthermore, these molecular composites may contain a wide range of organic and inorganic ratios without phase separation.

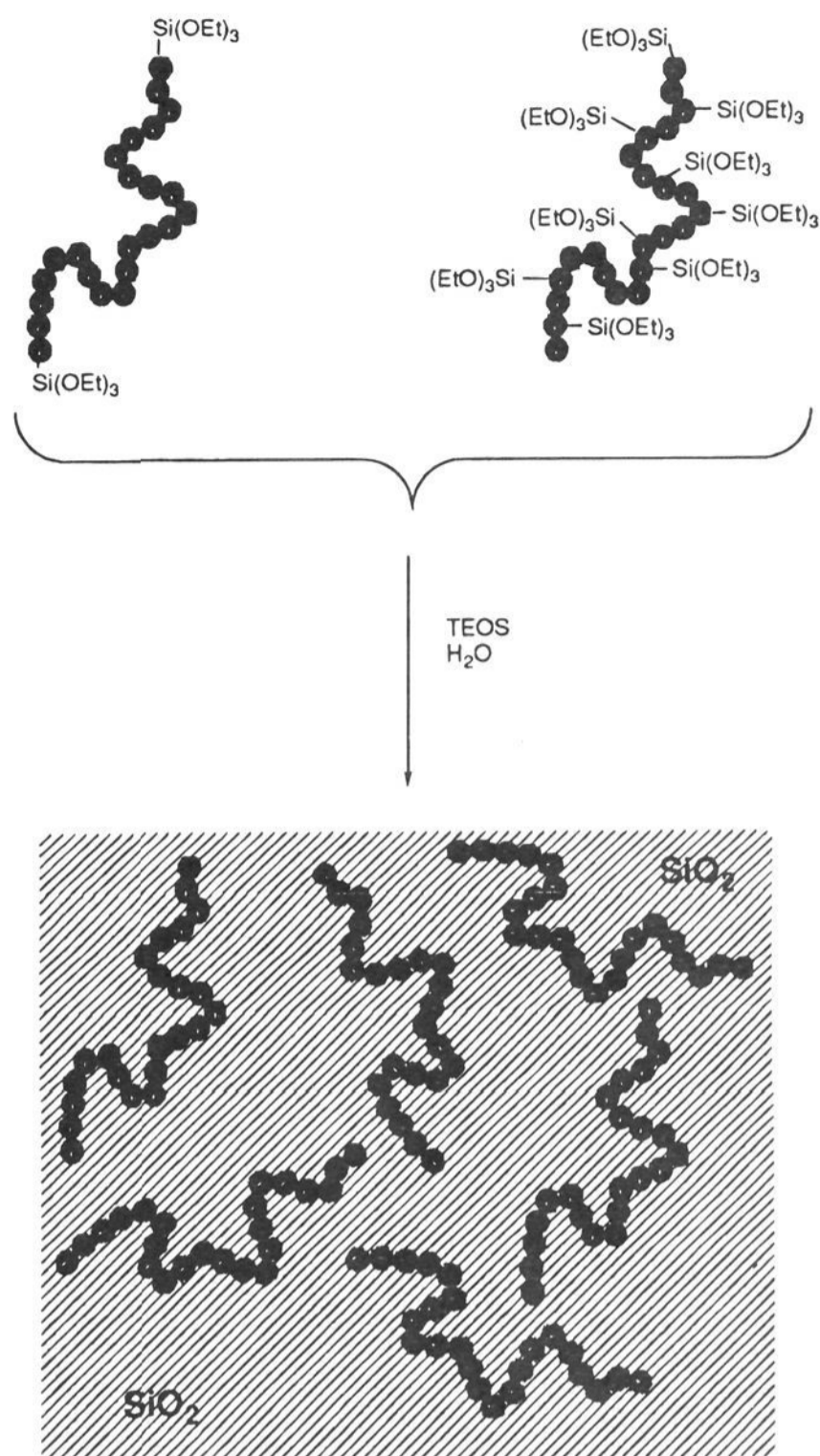
Some of the first examples of these materials can be found in sol-gel copolymerization reactions of TEOS or TMOS with hydroxy-terminated or trialkoxysilyl-functionalized polymers (Figure 6).<sup>7</sup> The condensation reaction produces polymers that are covalently attached to the inorganic phase.

In one example, telichelic polyisoxazolines, terminated with triethoxysilyl groups, were cocondensed with TEOS.<sup>8</sup> The organic component of the resulting hybrid silicate-polyisoxazoline material was oxidatively removed, leaving a porous silica matrix. In this case, the polymer functioned as a pore-forming agent in the silica gel. The high ratios of organic polymer to inorganic oxide result in physical properties (i.e., rubber-like elasticity) that are dominated by the polymer. These "polymer-bridged" polysilsesquioxanes represent one extreme for which the inorganic component is small compared to the organic one. Attempts to increase the percentage of inorganic material often result in phase separation during copolymerization. Reviews of the synthesis, characterization, and physical properties of these materials are available.<sup>7</sup>

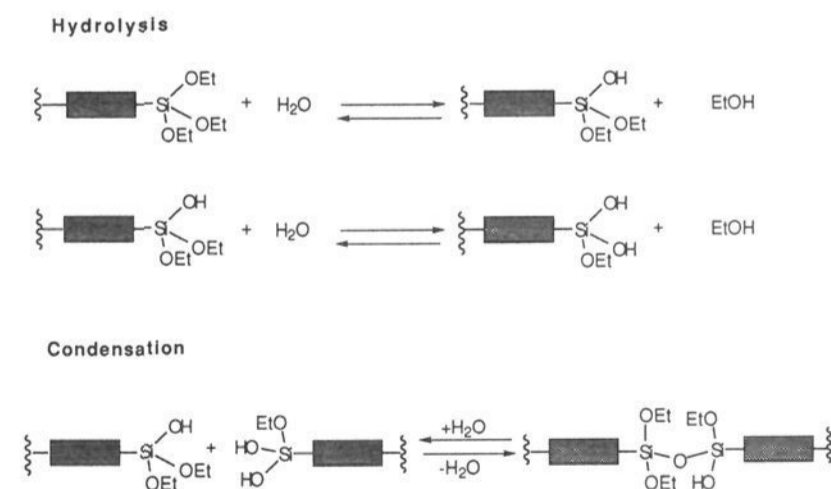
With low molecular weight bridging groups, the ratio of silica to organic material is approximately equal. A greater degree of control over morphology can be achieved under these conditions utilizing bis- or tris(trialkoxysilanes) as the molecular building blocks for the hybrid materials (Figure 5).<sup>9-17</sup> The synthesis and characterization of hybrid materials of this constitution are described in the following sections.

### A. Sol-Gel Polymerization

Bis(trialkoxysilyl) monomers (Figure 5) are hydrolyzed and condensed under relatively mild conditions that are typical for sol-gel polymerizations. Monomers are dissolved in ethanol or tetrahydrofuran (0.4 M), and the polymerizations are initiated with the addition of aqueous acid, base, or fluoride catalyst. An excess of water is employed ( $>3\text{H}_2\text{O}$ ). Alkoxide

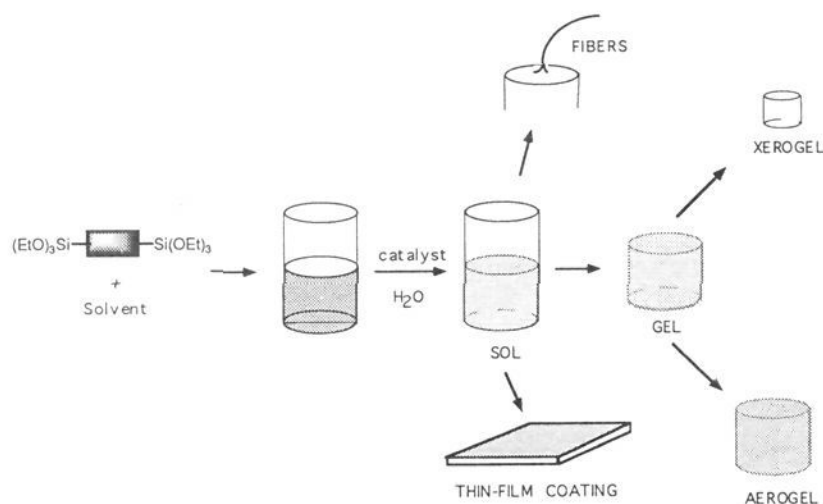


**Figure 6.** Schematic of the copolymerization of triethoxysilyl-functionalized polymers with TEOS to produce a covalently bound organic polymer in a silicate matrix.



**Figure 7.** Sol-gel chemistry of triethoxysilyl monomers: hydrolysis and condensation reactions. Under both acidic and basic conditions in the presence of  $>3$ -fold excess of  $\text{H}_2\text{O}$ , the degree of hydrolysis is almost complete and the degree of condensation is  $>85\%$ .

groups on the silicon atoms are hydrolyzed to silanols that subsequently condense with each other or with ethoxysilanes to give rise to siloxane bonds (Figure 7). As hydrolysis and condensation progress, highly branched polysilsesquioxanes grow in size, causing the solutions to become more viscous. Prior to



**Figure 8.** Processing of bridged polysilsesquioxanes.

gelation, the sol containing the growing polymers can be cast as thin films or drawn into fibers (Figure 8). If undisturbed, the polymerization of most bridged monomers affords gels within a few hours. After gelation the solvent can be removed, to leave a three-dimensional network that resembles, to some degree, the original polymeric structure that formed in the pregel solution. Sol-gel polymerization and processing of bis(trialkoxysilyl) monomers parallel, in almost all respects, those of the purely inorganic precursors such as TEOS.

One of the more striking differences between bridged polysilsesquioxanes and sol-gel polymers derived from triethoxysilanes and tetraethoxysilane is the low concentrations at which the former produces gels. For example, 1,4-bis(triethoxysilyl)benzene forms gels at concentrations as low as 0.04 M. In comparison, sol-gel preparations of silica gels require concentrations of TEOS near 1.9 M for gelation.<sup>18</sup> At the concentration used to make silica gels, bridged monomers gel instantaneously. At 0.4 M concentration, TEOS will not form gels, whereas bridged monomers gel within a few hours.

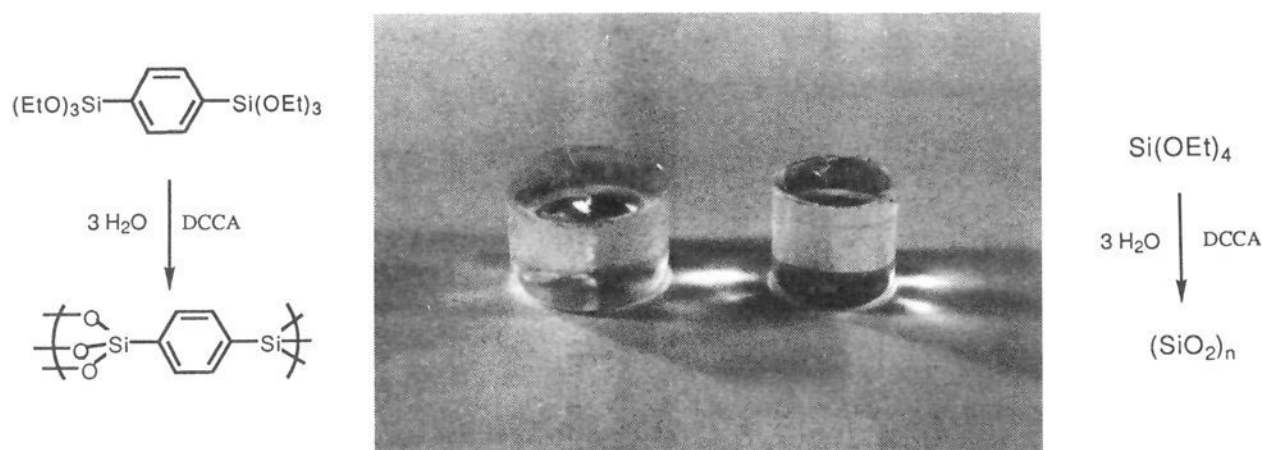
Upon gelation, the entire volume of the polymer solution becomes a rigid gel. Some minor shrinkage (syneresis) occurs upon gelation or with aging. The gels are firm yet tough enough to be handled without damage. Gels prepared with acidic catalysts are generally transparent with a blue tint due to light scattering from micron-sized defects.<sup>19</sup> The same bridged monomers are often found to form opaque white gels when alkaline catalysts are used. The bridged polysilsesquioxane gels are aged for a period of time before drying to form xerogels (dry gels) or aerogels (air gels).<sup>20</sup>

## B. Gel Processing

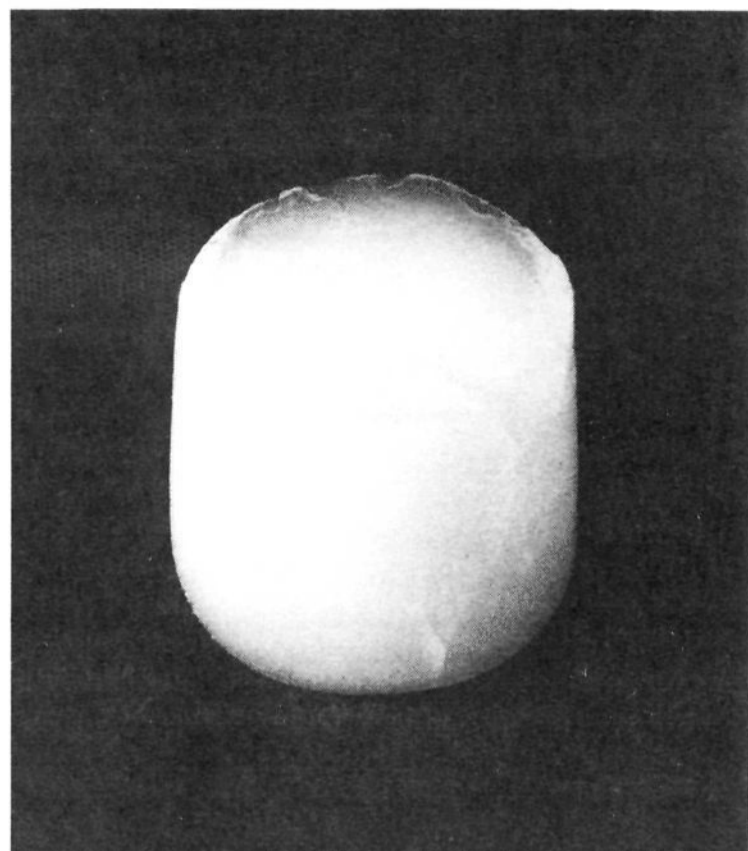
Xerogels are gels that have been air-dried. The most important defining characteristic of a xerogel is that it undergoes considerable shrinkage during the drying process. Silica gels prepared by sol-gel polymerization of TEOS or TMOS undergo shrinkage on the order of 50–70%.<sup>21</sup> Bridged polysilsesquioxane gels undergo 90–95% shrinkage during drying. Much of the shrinkage in bridged polysilsesquioxanes is due to the loss of 6 equiv of ethanol for each equivalent of monomer and the low monomer concentrations (0.2–0.4 M) used in the preparation of these materials. As a result of the large volume loss and stresses incurred during solvent evaporation,<sup>22</sup> cracking of monolithic polysilsesquioxane xerogels is difficult to avoid. However, monoliths can be prepared by slow air drying of gels prepared with chemical additives such as dimethylformamide. These have been referred to as drying control chemical agents (DCCA) which reduce the rate of solvent evaporation (Figure 9).<sup>23</sup> For many applications that do not require optical clarity, such as chromatographic or catalytic supports, monoliths are not necessary. Xerogels of bridged polysilsesquioxanes can be prepared quickly as powders by crushing and rinsing the wet gel with water before drying under vacuum at 100 °C.<sup>14</sup> Xerogels prepared in this fashion have similar porosities to those prepared by the more time-consuming air-drying process. For example, for two identical xerogels, **X-1**, the one that was solvent-processed with final air-drying had a surface area of 691 m<sup>2</sup>/g, while the other, which was water-processed with final air-drying, had a surface area of 553 m<sup>2</sup>/g.

## C. Aerogels

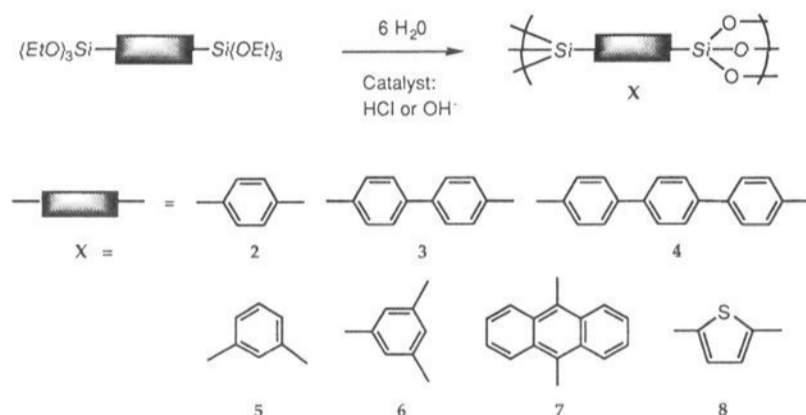
Aerogels are gels that have been dried in such a fashion as to avoid much of the shrinkage caused by the loss of solvent and stress of drying.<sup>20</sup> As a result, aerogels are closer in volume and structure to the original wet gel. Historically, aerogels have been made by drying the wet gel (alcogel) at a temperature and pressure above the supercritical point of the alcohol in the gel. Supercritical carbon dioxide extraction has also proven to be an effective alternative method for preparing aerogels. Carbon dioxide extractions involve first replacing the original solvent in the gel with supercritical carbon dioxide and then slowly venting the carbon dioxide to afford a dry aerogel. Carbon dioxide extractions are increasingly



**Figure 9.** Photograph of sol-gel silica monolith (TEOS, 2.0 M) and a phenyl-bridged polysilsesquioxane (0.4 M) monolith prepared by acid-catalyzed polymerization in the presence of formamide, a (DCCA), and air-dried for 3 weeks.



**Figure 10.** Photograph of a bridged polysilsesquioxane aerogel prepared by sol-gel polymerization of 4,4'-bis-(triethoxysilyl)biphenyl (0.4 M, THF,  $\text{NH}_4\text{OH}$  cat.) and processed by supercritical  $\text{CO}_2$  extraction. The supercritical  $\text{CO}_2$  processing leaves macropores that are responsible for the opacity.

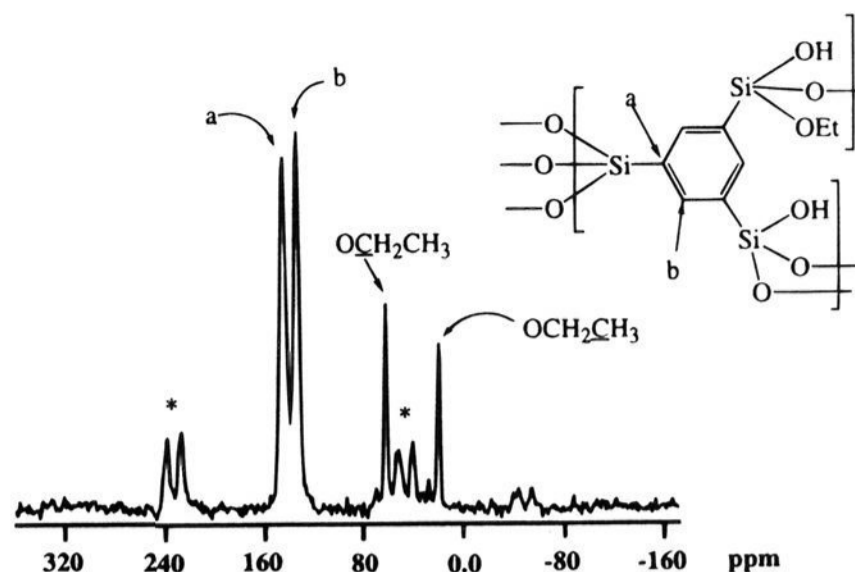


**Figure 11.** Representative arylene-bridged polysilsesquioxanes.

popular because of the safety concerns of working at high pressure with supercritical alcohols. A photograph of a biphenylene-bridged polysilsesquioxane aerogel is shown in Figure 10.

#### IV. Arylene-Bridged Polysilsesquioxanes

A family of arylene-bridged polysilsesquioxane xerogels were the first representatives of the bridged polysilsesquioxanes to be prepared.<sup>9-14</sup> The objective was to determine if a rigid molecular spacer would introduce porosity in the resulting xerogel and if the length of the spacer would have any effect on the pore size and pore distribution in sol-gel processed materials. The arylene monomers were prepared by metalation of dibromoarylene compounds followed by quenching with tetraethoxysilane or chlorotriethoxysilane. A variety of arylene-bridged monomers were prepared and polymerized (Figure 11) to afford gels that were subsequently processed to produce both xerogels and aerogels. Most importantly, a series of arylene-bridged xerogels with 1,4-phenylene (**2**), 4,4'-biphenylene (**3**) and 4,4''-terphenylene (**4**) bridging groups were prepared in order to examine the effect of rigid molecular spacers on the amorphous network



**Figure 12.**  $^{13}\text{C}$  CP MAS NMR spectrum of 1,3,5-phenylene-bridged polysilsesquioxane (**X-6**). \*Spinning side bands.

polymer structure. The resulting bridged polysilsesquioxane xerogels and aerogels have a number of distinguishing properties. These are presented in the sections that follow together with a structural analysis that contributes to an understanding of the origins of these properties.

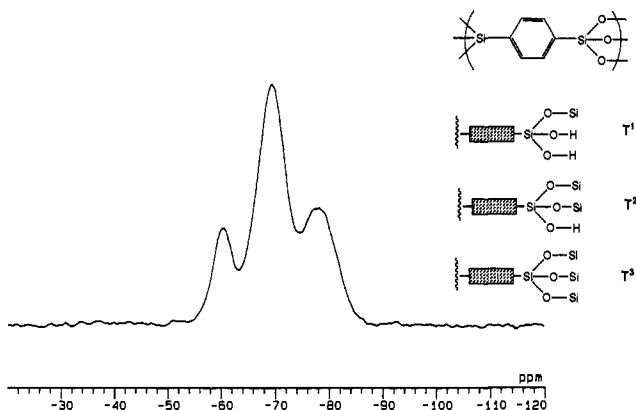
#### A. Molecular Structure

Bridged polysilsesquioxane xerogels are brittle, glassy materials that do not swell or dissolve in either water or organic solvents. Their method of synthesis and absence of long range order as determined by X-ray diffraction imply that the materials are amorphous. Their chemical composition has been determined by a number of spectroscopic techniques including solid state nuclear magnetic resonance (NMR) spectroscopy.

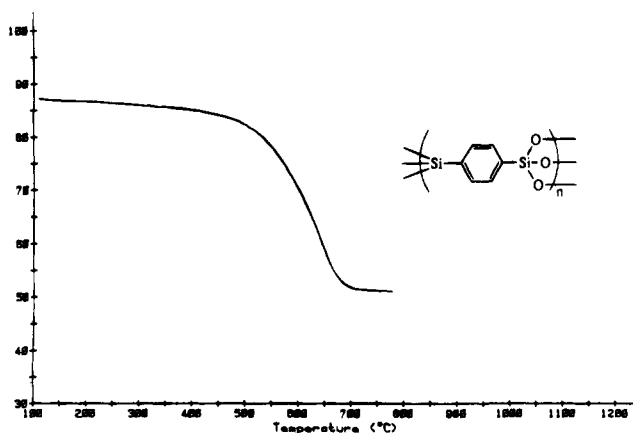
##### 1. Solid State NMR Spectroscopy

The molecular structure of bridged polysilsesquioxanes can be determined by  $^{13}\text{C}$  and  $^{29}\text{Si}$  cross polarization magic angle spinning (CP MAS) NMR spectroscopies. These techniques reveal if the molecular building block survives the sol-gel polymerizations intact or if silicon-carbon bond cleavage occurs. For example, Figure 12 shows the  $^{13}\text{C}$  CP MAS NMR spectrum of the 1,3,5-phenylene-bridged polysilsesquioxane xerogel (**X-6**) prepared from 1,3,5-tris(triethoxysilyl)benzene (**6**).<sup>11</sup> The two peaks at approximately 145 ppm are due to the carbon nuclei in the aromatic ring. The similarity of the  $^{13}\text{C}$  CP MAS NMR spectra of the xerogels to  $^{13}\text{C}$  NMR spectra of the monomer (**6**) suggests that none of the arylene-bridged polysilsesquioxanes experienced measurable loss of the bridging groups. The two peaks at 58 and 18 ppm are due to residual  $\text{SiOCH}_2\text{CH}_3$  (ethoxysilyl) groups. The amount of these groups could be determined semiquantitatively by comparing the intensities of the peaks to those of the bridging group carbons. In all cases, more than 95% of the ethoxide groups had been hydrolyzed during sol-gel polymerization even when it was carried out in ethanol.

$^{29}\text{Si}$  CP MAS NMR spectroscopy could be used to quantitatively measure the degree of condensation (extent of reaction) in the gels by the relative



**Figure 13.**  $^{29}\text{Si}$  CP MAS NMR spectrum of a 1,4-phenylene-bridged polysilsesquioxane prepared under acidic conditions. From the integrated intensities of the  $T^1$ ,  $T^2$ , and  $T^3$  resonances, the xerogel is calculated to be 68% condensed.



**Figure 14.** TGA trace of 1,4-phenylene-bridged polysilsesquioxane.

abundance of the  $T^1$ ,  $T^2$ , and  $T^3$  silicon nuclei (Figure 13). By these studies, it was determined that bridged polysilsesquioxanes are highly condensed materials. Like silica gels,<sup>1</sup> bridged polysilsesquioxanes exhibit higher degrees of condensation when prepared with basic catalyst (80–90%) than with an acidic catalyst (65–75%).<sup>24</sup> A consequence of this is that bridged polysilsesquioxanes prepared under basic conditions have fewer residual silanols and would be expected to be more hydrophobic than those gels prepared under acidic conditions. The absence of Q resonances in the  $^{29}\text{Si}$  NMR spectra (a silicon atom attached to four oxygen atoms) confirms that carbon–silicon bond cleavage has *not* occurred during sol–gel polymerization.

## 2. Thermal Stability

As with phenyl silsesquioxanes, arylene-bridged polysilsesquioxanes exhibit good thermal stability. The onset of decomposition of these materials occurs at temperatures intermediate between that of organic network polymers and the melting range of silicas. A thermogravimetric analysis (TGA) trace ( $\text{N}_2$ ,  $10^\circ\text{C}/\text{min}$ ) of 1,4-phenylene-bridged silsesquioxane is shown in Figure 14. Aside from loss of residual solvent ( $<100^\circ\text{C}$ , not shown in the figure) there is no weight loss until the temperature approaches  $500^\circ\text{C}$ . Continued heating to temperatures in excess of  $1000^\circ\text{C}$  leaves a black carbon-rich residue that has not yet

been fully characterized. The formation of oxidatively resistant silicon oxycarbide materials at elevated temperatures often makes combustion analysis results unreliable. The potential advantage of this is that the molecular-level mixing of inorganic silica and the organic bridge as a carbon source make bridged polysilsesquioxanes candidates for ceramic precursors.<sup>25</sup>

## 3. Porosity

Bridged polysilsesquioxane xerogels and aerogels are porous materials. Before discussing their properties, it is useful to define several terms commonly used to describe porous materials. Porosity in materials is evaluated by surface area ( $\text{m}^2/\text{g}$ ), pore volume ( $\text{mL}/\text{g}$ ), and average pore size. High surface areas are often desirable in materials used as adsorbents, chromatographic media, and catalyst supports. The pore size and breadth of distribution of pore sizes are also important properties. Nitrogen sorption porosimetry is a convenient method for determining surface areas using the multi-point BET (Brunauer–Emmett–Teller) method.<sup>26</sup> Nonporous materials have simple geometric surfaces with surface areas below  $10 \text{ m}^2/\text{g}$ . In porous materials, pores are divided into three groups based on the mathematical models used to calculate pore sizes from gas sorption data. Micropores are very small with pore diameters less than  $20 \text{ \AA}$  and are most conveniently measured by argon adsorption. Mesopores ( $20\text{--}500 \text{ \AA}$  in diameter) are those pores that are described by the Kelvin equation and are most accurately characterized by nitrogen sorption porosimetry. Pores larger than  $500 \text{ \AA}$  are designated as macropores. These pores are best evaluated by mercury porosimetry and electron microscopy. Silica xerogels exhibit surface areas that range from very low for nonporous materials to extremely high (i.e.,  $900 \text{ m}^2/\text{g}$ ), depending on the sol–gel conditions used for their preparation. Silica aerogels have been prepared with surface areas as high as  $1000 \text{ m}^2/\text{g}$ .<sup>27</sup>

One of the most distinguishing features of arylene-bridged polysilsesquioxanes was the discovery that these materials are porous and have extremely high surface areas. For example, surface areas of the mostly microporous 1,4-phenylene-bridged polysilsesquioxane xerogels (**X-2**) range between 600 and  $1200 \text{ m}^2/\text{g}$ .<sup>11</sup> The internal pore volumes range from 0.3 to  $0.6 \text{ mL}/\text{g}$ . All arylene-bridged polysilsesquioxane xerogels have high surface areas arising from pores that range in size from 10 to  $50 \text{ \AA}$ . However, there is no simple relationship between the average pore size and the length of the arylene spacer (Table 1). A representative argon adsorption isotherm and differential pore size plot for **X-1**, a xerogel prepared from monomer **1**, is given in Figure 15.

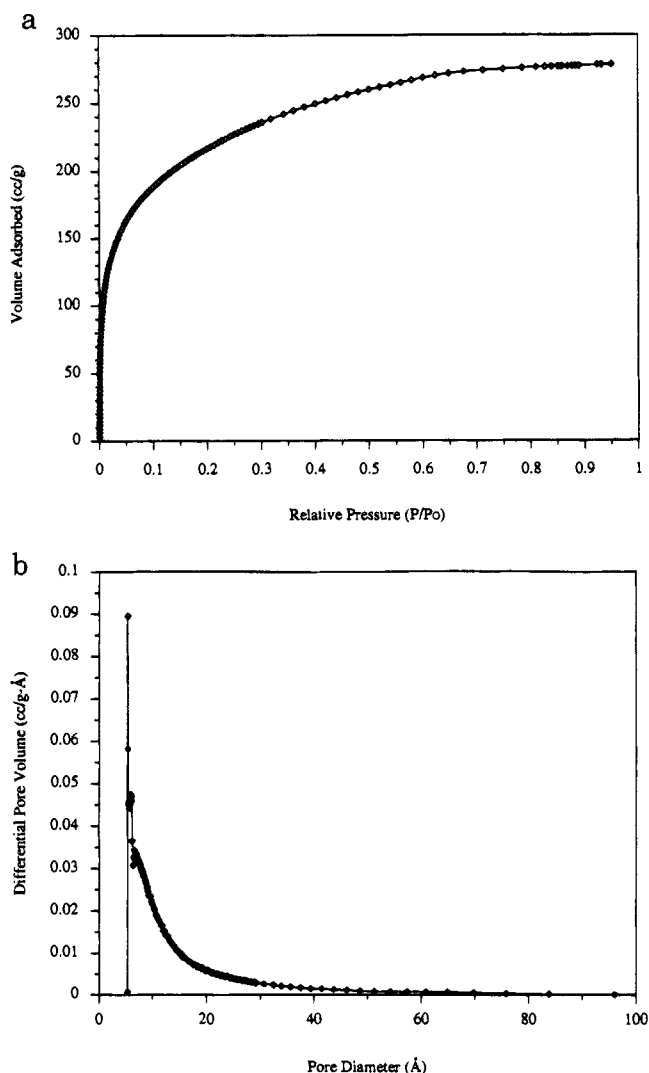
Phenylene-bridged aerogels have been prepared with surface areas as high as  $1880 \text{ m}^2/\text{g}$ .<sup>28</sup> Analysis of the pore distributions of the arylene-bridged aerogels revealed that much of the microporosity found in the xerogels was retained along with a new complement of mesopores ( $20\text{--}500 \text{ \AA}$  diameter pores).

## 4. Microscopy

Examination of the arylene-bridged aerogels with scanning electron and atomic force microscopes re-

**Table 1. Representative Surface Areas and Average Pore Sizes for Arylene-Bridged Polysilsesquioxane Xerogels**

monomer	sol-gel conditions	surface area (BET; m <sup>2</sup> /g)	mean pore diameter (Å)	pore volume (mL/g)
	0.2 M THF 10 mol % HCl	960	24.0	0.46
	0.2 M THF 570 mol % NH <sub>4</sub> OH	1180	8.0	0.71
	0.2 M THF 570 mol % NH <sub>4</sub> OH	1150	6.0	0.55
	0.2 M THF 570 mol % NH <sub>4</sub> OH	756	33.8	0.62
	0.2 M THF 570 mol % NH <sub>4</sub> OH	956	24.0	0.90



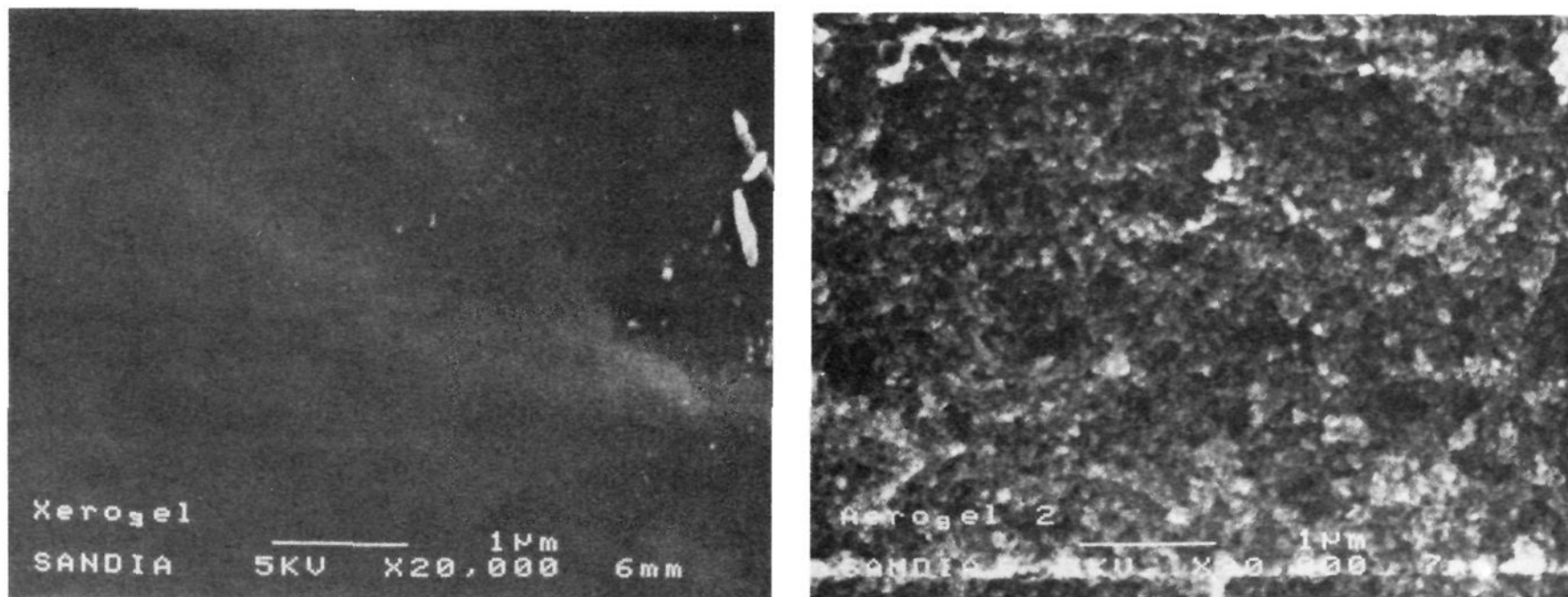
**Figure 15.** (a) Argon adsorption isotherm and (b) differential pore diameter plot of 1,4-phenylene-bridged xerogel X-1. The xerogel was prepared using basic conditions (0.4 M, NH<sub>4</sub>OH). The material has a surface area of 1180 m<sup>2</sup>/g, an average pore diameter of 11 Å, and an internal pore volume of 0.5 cm<sup>3</sup>.

vealed that the material is formed from aggregates of particles with little or no visible interstitial voids. In addition, the size of the particles does not appear to change with the pH of the polymerization reaction. The size of the particles making up the bridging

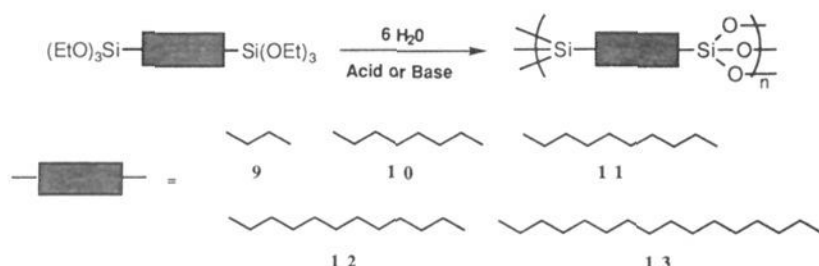
*aerogels* ranged from 50 to 200 nm. The *xerogels*, on the other hand, have a much finer gel-like texture, even at high magnification. Some evidence from SEM and AFM suggests a much smaller, finer particle size (5–30 nm), although the lack of contrast makes this difficult to determine. There is no evidence for formation of dense colloidal particles in these xerogels under either acidic or basic conditions (Figure 16). Small angle scattering (SAS) from arylene-bridged polysilsesquioxane xerogels and aerogels also revealed that gels prepared under acidic and basic conditions have identical surface roughness.<sup>29</sup> This study found that all of the arylene-bridged materials possessed fractal-like surfaces. The origin of porosity in bridged polysilsesquioxanes appears to arise from highly branched macromolecular clusters analogous in structure to tumbleweeds, rather than from ordered cylindrical pores.<sup>30</sup>

### V. Alkylene-Bridged Polysilsesquioxanes

When a flexible organic bridging group was used instead of a rigid arylene, a whole new dimension of control over porosity in amorphous materials was revealed.<sup>15</sup> Alkylene-bridged polysilsesquioxanes (**9–13**) were prepared by sol-gel polymerization of  $\alpha,\omega$ -bis(trialkoxysilyl)alkanes (Figure 17). The bridging groups in the monomers varied in length from 2 to 14 carbon atoms. The monomers, synthesized by hydrosilation of terminal dienes, were polymerized to give molecular composites with rigid inorganic domains and organic domains with *variable* flexibility. In the homologous series of alkylene-bridged polysilsesquioxanes prepared under *basic* conditions (0.2 M, EtOH, 6:1 mole ratio H<sub>2</sub>O:monomer, 10.8 mol % NaOH catalyst:monomer), the surface area *decreases* as the length and flexibility of the bridging group increases (Figure 18). Short, stiffer alkylene chains (C<sub>2</sub>, C<sub>4</sub>) have relatively high surface areas (>700 m<sup>2</sup>/g), but as the alkylene chain is lengthened, the surface area falls off until, at 14 carbons, a complete collapse of porosity is noted. These results suggest that a certain degree of stiffness in the organic component of the molecular building block is required to *sustain* porosity in these xerogels. These alkylene-bridged polysilsesquioxane xerogels are mesoporous (20 Å < mean pore diameters < 500 Å). The pore distribution varies as the size of the



**Figure 16.** Scanning electron micrograph of 1,4-phenylene-bridged polysilsesquioxane xerogel (left) and aerogel (right). The gels were prepared under identical conditions (0.4 M, THF,  $\text{NH}_4\text{OH}$ ). The xerogel was prepared by slow air-drying and the aerogel was prepared by supercritical  $\text{CO}_2$  extraction.

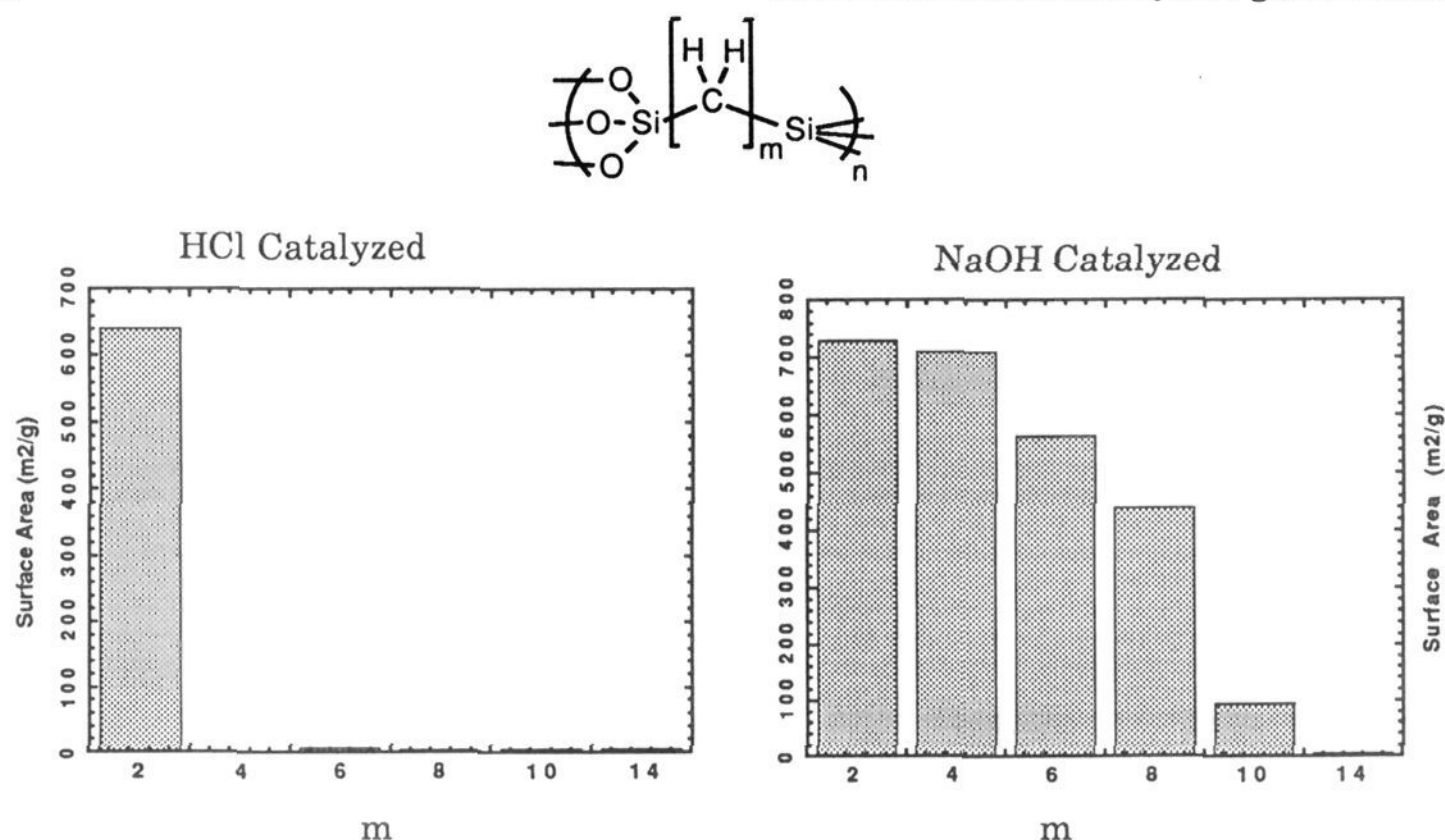


**Figure 17.** Alkyne-bridged polysilsesquioxanes **9–13**.

alkylene-bridging group increases. For example, the ethylene-bridged xerogel (**9**) has a mean pore diameter (MPD) of 44 Å while the MPD of the octylene-bridged polysilsesquioxane (**11**) is 67 Å. Polysilsesquioxanes with bridging groups longer than 10 methylenes are nonporous. Interestingly, in xerogels prepared under acidic conditions (0.4 M, THF, 6:1 mole ratio  $\text{H}_2\text{O}$ :monomer, 10.8 mol % HCl catalyst: monomer), collapse of porosity occurs when the alkyne bridging groups are longer than five methylene groups.

Many factors influence the collapse of porosity during the sol-gel process, including the pore structure and compliance of the wet gel, solvent, temperature, rate of evaporation, and geometry of the gel.<sup>31</sup> The presence of a substantial organic component in the gel network will very likely introduce other factors that distinguish the drying of these hybrid materials from silica gels.

Inspection of Figure 1 reveals that one difference between silica and bridged polysilsesquioxanes is that the spacing between cross-links is greater in the hybrid materials. The compliance or tendency to collapse the hybrid gel may therefore be compromised to varying degrees depending upon the stiffness of the organic component. This comparison with silica is appropriate only if the degree of condensation in the two materials is comparable. A comparison of solid state  $^{29}\text{Si}$  NMR of silicates and bridged polysilsesquioxanes supports this comparison. A second consideration is that the hybrid gels contain a substan-



**Figure 18.** Surface areas for alkyne-bridged polysilsesquioxanes **9–13** with varying length alkyne-groups ( $m$ ) prepared under acidic (left) or basic (right) conditions.



tial component of hydrophobic material as part of the network. It is known that surfactants can be added to the pore liquid to reduce the interfacial energy and reduce the capillary stress.<sup>32</sup> Hybrid gels therefore have an "internal lubricant" to reduce the surface tension that produces pore collapse. One final consideration is that the organic groups can associate to produce microstructural domains in the gel.

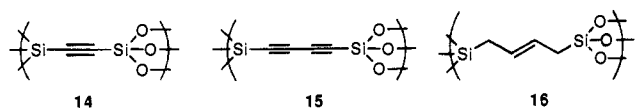
The surface area and porosity data in Figure 18, obtained from a family of closely related materials that were prepared and processed under identical conditions, is useful for understanding the influence of the organic fragment in determining the final xerogel morphology.

How can some of the trends in Figure 18 be understood in terms of the above considerations? Base-catalyzed gels are more condensed than acid-catalyzed gels and are expected to be less compliant (more rigid) than acid-catalyzed gels. The more highly condensed base-catalyzed gels are also more hydrophobic (fewer SiOH groups) than those prepared under acidic conditions. Both of these factors contribute to less pore collapse and a more porous xerogel. Within the same catalyst series, however, longer chain alkylenes are more *flexible*, allowing greater collapse of pores to occur. This is observed by a complete collapse of porosity at C<sub>14</sub>.

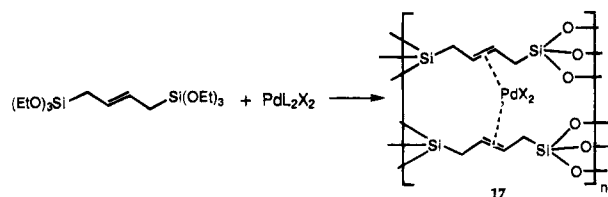
Bridging group flexibility must be very important since the relatively stiff arylene-bridged polysilsesquioxanes are always porous, regardless of spacer length, degree of condensation, and drying process. However, experiments in supercritical processing of alkyne-bridged gels reveal that alkyne-bridged aerogels are porous even with tetradecane bridges prepared under acidic conditions,<sup>33</sup> thus, drying certainly is important in determining the final morphology of xerogels prepared with more flexible organic bridging groups.

## VI. Alkynylene- and Alkenylene-Bridged Polysilsesquioxanes

Representatives of alkynylene- (**14**, **15**) and alkenylene- (**16**) bridged polysilsesquioxanes have also been prepared.<sup>11,34</sup> Like the arylene bridges, the 1,



2-ethynylene (**14**) and 1,3-butadiynylene (**15**) bridging groups are rigid hydrocarbon spacers that result in highly porous xerogels. However, the silicon-alkynyl bond can be hydrolyzed under alkaline conditions or with fluoride ion, leaving a porous silica structure. For example, the hydrolysis and condensation of 1,2-bis(triethoxysilyl)ethyne (**14**) under basic conditions are often accompanied by loss of acetylene, resulting in a complex mixture of silica, polyethynylsilsesquioxane, and ethynylene-bridged polysilsesquioxane.<sup>11,34</sup> Furthermore, treatment of ethynylene-bridged polysilsesquioxane xerogels with fluoride quantitatively transforms the hybrid organic-inorganic polymers into silica.



**Figure 19.** Palladium cross-linking of 2-butenylene-bridged polysilsesquioxanes (**17**).

Despite their chemical sensitivity, the 1,2-ethynylene and 1,3-butadiynylene bridging groups offer the opportunity for secondary modification of the polymeric architecture through polymerization of the carbon-carbon triple bond. An example is the thermal polymerization of the 1,3-butadiynylene bridge to form an interpenetrating network of silsesquioxane and butadiyne polymers.<sup>34</sup> The ease with which the butadiyne groups undergo 1,3-polymerization suggests favorable arrangements of the fragments in the amorphous xerogel.

The unsaturated bonds in the alkyne and alkenylene bridging groups are also convenient sites for  $\pi$ -complexation of metals (Figure 19). Addition of palladium complexes to the sol-gel polymerization of 1,4-bis(triethoxysilyl)but-2-ene yields bridged polysilsesquioxanes (**17**) with highly dispersed palladium. Formation of  $\pi$ -bonds between the metal and the carbon-carbon double bond increases the effective size of polymers growing in solution and increases the rate of gelation by 1 order of magnitude.<sup>35</sup> This coordination offers the potential for an additional method of controlling xerogel morphology.

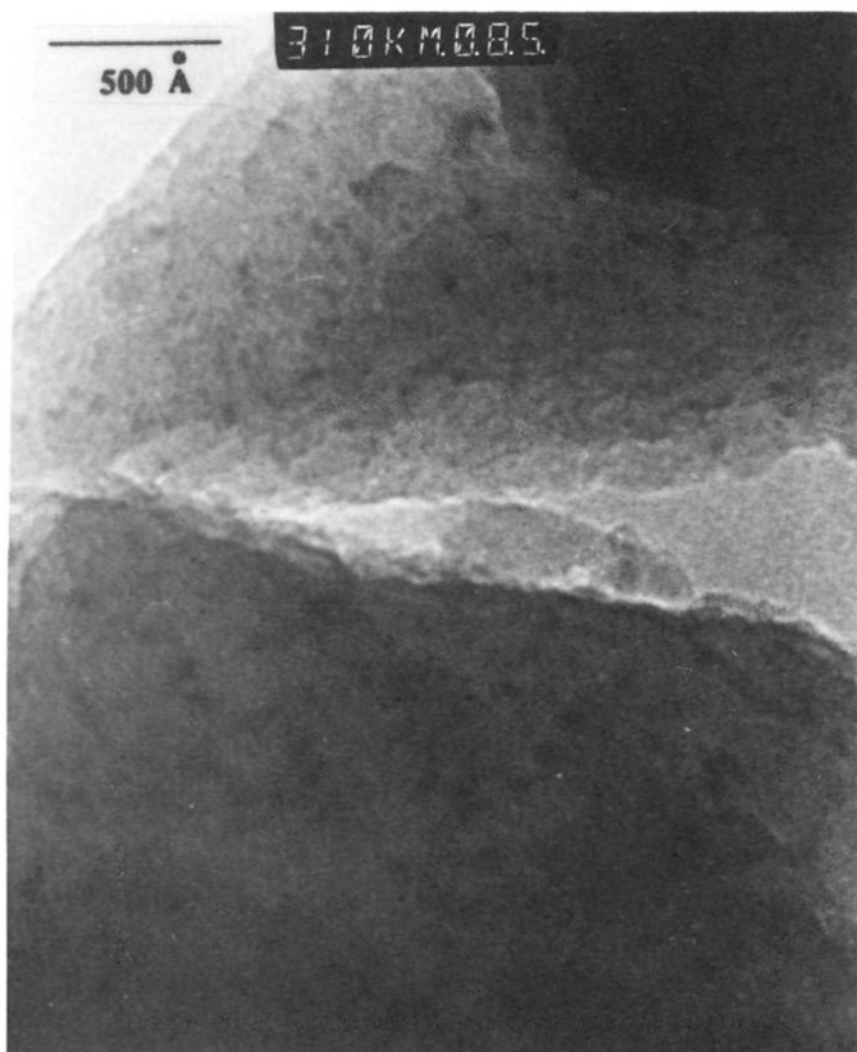
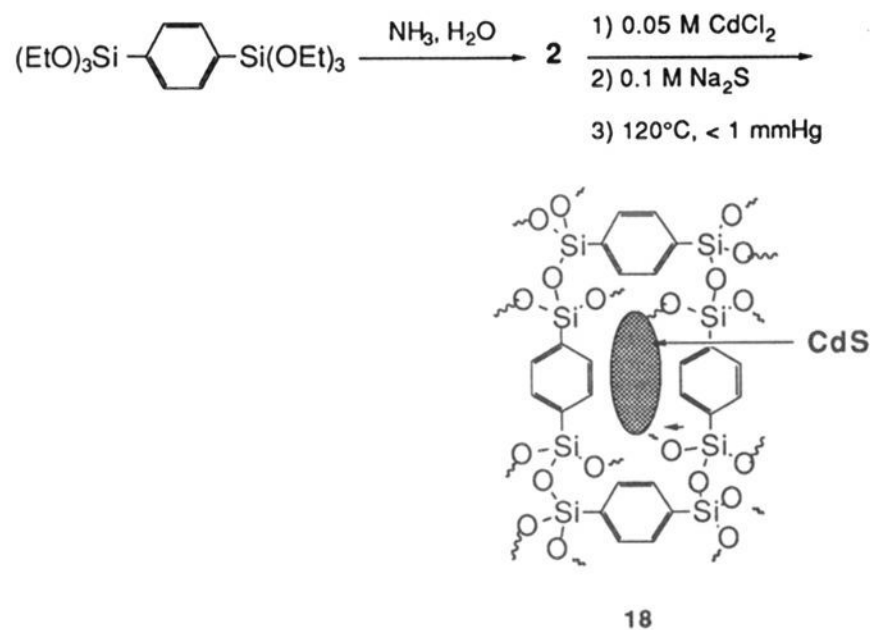
## VII. Applications

Applications of polysilsesquioxanes have only begun to be explored. In the few examples below, the pore structure of dried xerogels is exploited for growing nano-sized particles. The chemical compatibility of the sol-gel method also permits incorporation of transition metal complexes that serve as precursors to metal clusters. In other examples, the organic fragment is chosen because of its optical properties and potential for fabrication of NLO materials.

### A. Nanocluster Synthesis in Bridged Polysilsesquioxanes

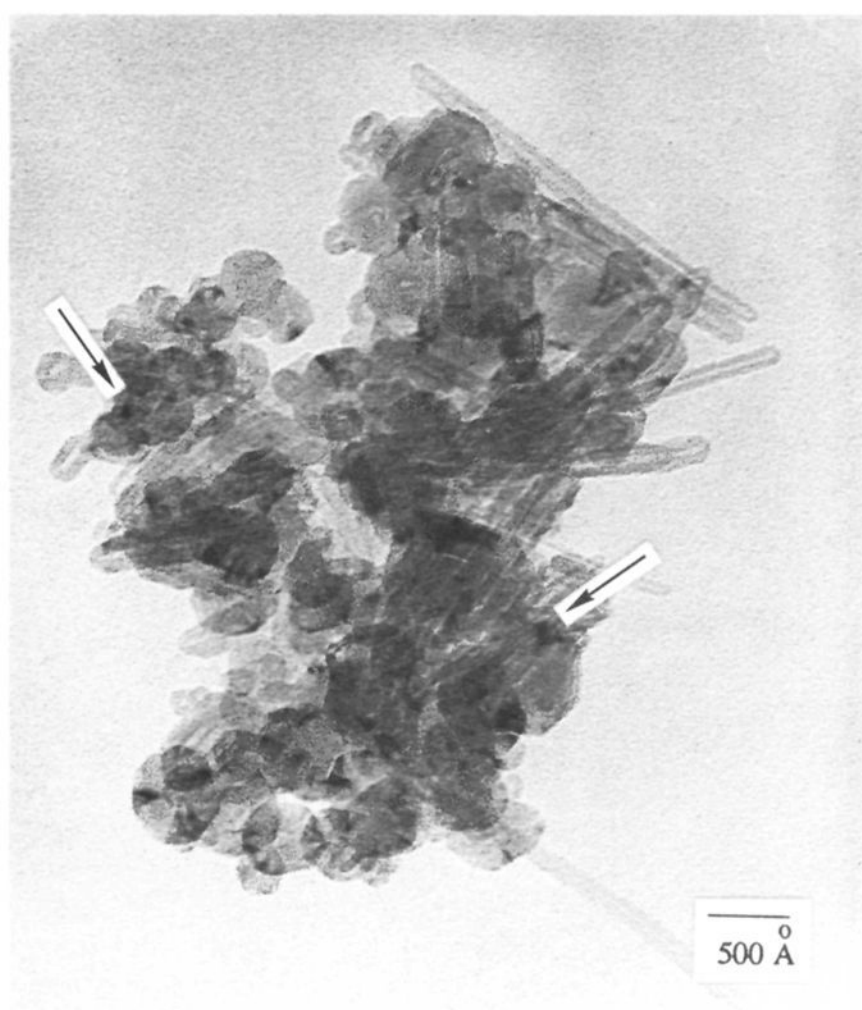
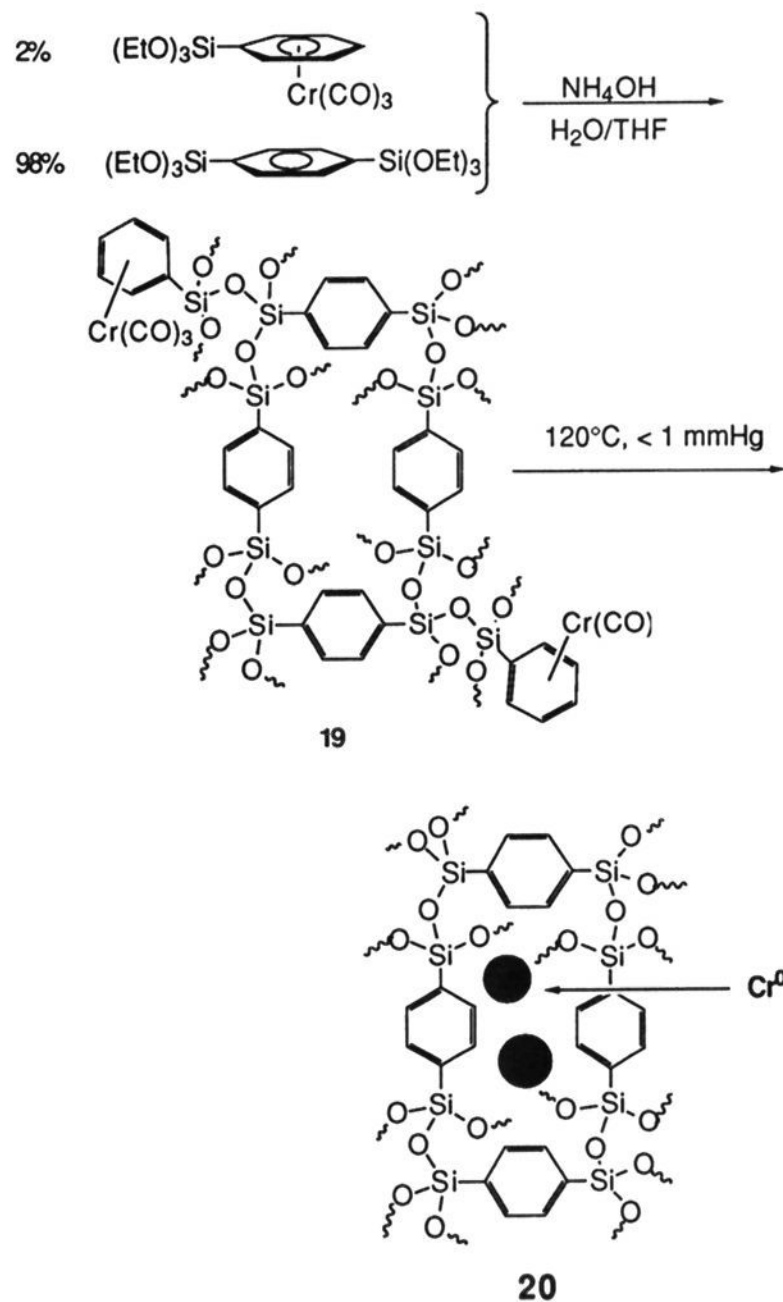
Porous bridged polysilsesquioxanes have been used as a confinement matrix for the growth of semiconductor particles and transition metal clusters. When dried xerogels prepared from 1,4-bis(triethoxysilyl)benzene were treated successively with aqueous solutions of CdSO<sub>4</sub> and Na<sub>2</sub>S, nanosized CdS particles (50 ± 20 Å) were deposited uniformly in the glassy matrix (Figure 20).<sup>36</sup> When polysilsesquioxanes with different bridging groups were employed, CdS with different average particle sizes was produced. A rough correlation between average pore size of the dried xerogel and semiconductor particle size was observed, suggesting some influence of the porous matrix on particle growth.<sup>37,38</sup>

The mild conditions employed for sol-gel polymerization and subsequent processing allow for the

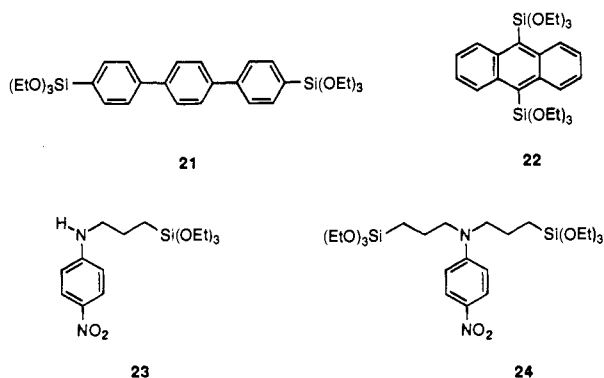


**Figure 20.** Preparation of CdS nanoclusters in pores within a phenylene-bridged polysilsesquioxane (**18**). Photo shows a TEM image of the CdS-doped xerogel. The dark images are microcrystalline CdS particles (hexagonal,  $50 \pm 20 \text{ \AA}$ ).

incorporation of many interesting and potentially useful organic functionalities into the hybrid organic and inorganic scaffolding. In one example, a zero-valent transition metal  $\pi$  complex was co-condensed with 1,4-phenylene-bridged monomers. This has resulted in the development of an internal doping procedure to prepare porous dried xerogels containing nano-sized transition metal clusters. The technique, illustrated in Figure 21, involves the copolymerization of (triethoxysilyl)benzenechromium(0) tricarbonyl with 1,4-bis(triethoxysilyl)benzene or other bridged monomers. Following sol-gel processing and air-drying to the xerogel (**19**), the metal tricarbonyl is decomposed with heat ( $120^\circ\text{C}$ ) under vacuum to afford crystalline nanoclusters ( $10\text{--}100 \text{ \AA}$ ) of chro-



**Figure 21.** Preparation of chromium(0) nanoclusters doped in 1,4-phenylene-bridged polysilsesquioxane xerogels (**20**) by decomposition of chromium carbonyl complexes (**19**).



**Figure 22.** Sol-gel processable fluorescent monomers.

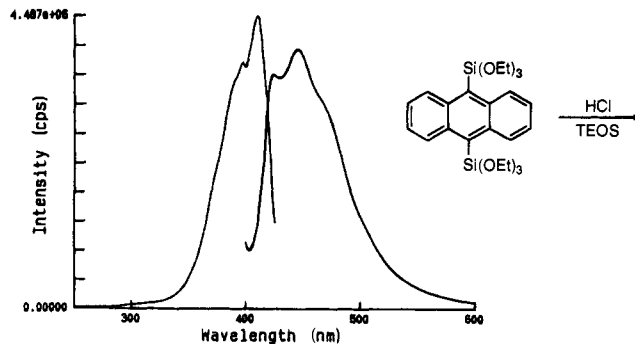
mium metal dispersed throughout the gel.<sup>39</sup> Interestingly, the porosity of the doped xerogel is not significantly reduced as a result of the doping. This allows for the exploration of these materials as catalysts.

## B. Optical Applications

Introduction of dyes into transparent glasses has been an important area of applied sol-gel research.<sup>40-44</sup> Monolithic gels containing organic dyes have been prepared for waveguide,<sup>45</sup> nonlinear optical (NLO),<sup>46</sup> and laser<sup>47</sup> applications. Organic dyes are commonly introduced into gels by physically dispersing the dye into the sol or precondensed oligomeric silica and trapping the dye with gelation. The dye is free to leach from the silica gel with time, unless it is larger than the pores and can be encapsulated. Leaching of the dye can be circumvented by attaching a triethoxysilyl group to the dye and copolymerizing it with TEOS or some other metal alkoxide.

Bridged polysilsesquioxanes allow the dye functionality to be built into the organic bridging group, assuring no phase separation, aggregation, or loss by leaching. A number of bridged polysilsesquioxanes have been prepared with arylene groups that have promising ultraviolet absorption and fluorescence characteristics. In fact, the terphenylene (**21**) and anthracene (**22**) bridging groups are very similar to commercially used laser dyes. The bis(triethoxysilyl)-arylene monomers were copolymerized with either TEOS or 1,4-bis(triethoxysilyl)benzene to make transparent xerogels that fluoresced when exposed to ultraviolet light (Figure 23).<sup>11</sup>

Similarly, NLO materials have been prepared from sol-gel processable dye molecules containing one or more of the triethoxysilyl groups **23** and **24** (Figure 22). Chromophores containing a single triethoxysilyl group (**23**) are cocondensed with other gel forming agents (i.e., TEOS)<sup>48</sup> while polyfunctional monomers (**24**) can be polymerized alone<sup>49</sup> or with TEOS<sup>50</sup> and cast directly as films. Optically transparent xerogel films are prepared by spin casting the bridged polysilsesquioxane solutions prior to gelation. Subsequent curing in the presence of a strong electric field to orient the molecular dipoles produces xerogel films with excellent optical properties and nonlinearities comparable to those of lithium niobate.<sup>49</sup> However, the long term stability of the NLO response at elevated temperatures, a requirement for device



**Figure 23.** Fluorescence excitation and emission spectra of xerogel copolymer of TEOS and 9,10-bis(triethoxysilyl)-anthracene (**7**) (400:1). The spectra is characteristic of dilute solutions (0.0001 M) of monomer **7**. No significant contribution from excimer is observed.

fabrication, has yet to be completely resolved. The area of sol-gel optics is a very active area of research.

## VIII. Conclusions

Bridged polysilsesquioxanes are a new family of hybrid organic-inorganic materials prepared by sol-gel chemistry. Trialkoxysilyl groups bridged by organic spacers permit the formation of network polymers capable of forming gels with a wide variety of organic functionalities, including arylene, alkylene, alkenylene, and alkynylene groups. The properties of these materials can be manipulated by changing the reaction or processing conditions to afford high surface area aerogels and xerogels or nonporous polymers. The capability for molecular engineering based on selection of the organic spacer distinguishes bridged polysilsesquioxanes from other sol-gel-processed materials.

## IX. Acknowledgments

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