# Bridged Polysilsesquioxanes. Molecular-Engineered Hybrid Organic−Inorganic Materials

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The class of hybrid organic−inorganic materials called bridged polysilsesquioxanes are used for everything from surface modifiers and coatings to catalysts and membrane materials. This paper examines how bridged polysilsesquioxanes are prepared, processed, characterized, and used. In particular, it describes how attaching several “inorganic” cross-linking trialkoxysilanes on organic bridging groups permits facile formation of network polymers and gels with high levels of chemical functionality. There are a number of synthetic entries into bridged polysilsesquioxane monomers that have allowed a multitude of different bridging groups to be integrated into *xerogels* (dry gels) or *aerogels* (supercritically dried “air gels”). Much of the research to date has been successfully focused on engineering of the size of pores through the choice of the bridging groups. For example, materials with some of the highest known surface areas in porous materials have been prepared, and parameters allowing control of the pore size distributions are well understood. More recently, however, the focus has shifted to building functionality into the bridging groups to make materials with controlled porosity that are capable of selective adsorption or catalysis or electronic and optic effects. This is the area where the full potential of bridged polysilsesquioxanes as molecular-engineered materials is being explored.

## Introduction

Hybrid materials lie at the interface of the organic and inorganic realms. These materials offer exceptional opportunities not only to combine the important properties from both worlds but to create entirely new compositions with truly unique properties. *Bridged polysilsesquioxanes* are a family of hybrid organic−inorganic materials prepared by sol−gel processing of monomers (Scheme 1, A) that contain a variable organic bridging group and two or more trifunctional silyl groups.[1−5]

The polysilsesquioxanes can be prepared as gels, films, or fibers. The organic group, covalently attached to the trifunctional silicon groups through Si−C bonds (Scheme 1, A), can be varied in length, rigidity, geometry of substitution, and functionality. Because the organic group remains an integral component of the material, this variability provides an opportunity to modulate bulk properties such as porosity, thermal stability, refractive index, optical clarity, chemical resistance, hydrophobicity, and dielectric constant. Many porous silica supports are modified through introduction of an organic functionality with surface modification in a subsequent step. In contrast, bridged polysilsesquioxanes are prepared in a *single step* from molecular precursors. The fine degree of control over bulk chemical and physical properties has made these materials excellent candidates for applications ranging from optical device fabrication[5] to catalyst supports[6] and ceramics precursors.[7]

Representative monomers are shown in Figure 1. The organic fragments in the building blocks range from rigid arylenic (**1**−**10**),[2,8−12] acetylenic (**11**−**13**),[2,12,16] and olefinic (**14**−**16**)[14,15] bridging groups to flexible alkylenes ranging from 1 to 14 methylene groups (**17**−**28**) in length.[11,17−19] They also include a variety of functionalized groups such as amines (**29**),[20] ethers (**30**),[21] sulfides (**31**−**33**),[22] phosphines,[23] amides,[24] ureas (**34**),[25] carbamates,[26] and carbonates (**35**).[21c,27] In addition, bridging groups have included organometallics in which the metal is part of the bridge (**36**)[28] or pendant to the bridge (**37**).[29]

Sol−gel polymerization of these molecular building blocks permits the rapid formation of polymers that irreversibly form gels. The organic group, which comprises approximately 40−60 wt % of the material, is an integral part of the network architecture. Upon drying, these gels afford amorphous xerogels or aerogels whose surface areas can be tailored, through selection of the organic spacer, to be as high as 1800 $m^2/g$ (supercritical processed aerogels)[30] or nonporous glassy xerogels.[17,18] Bulk properties such as *pore size* may be controlled with a fidelity that is more reminiscent of surfactant-templated mesoporous molecular sieves.[31] Optical properties can be manipulated by incorporating chromophores in the bridging organic component.[1e] Most recently, functional bridged polysilsesquioxanes have been prepared for use as high-capacity adsorbents.[32]

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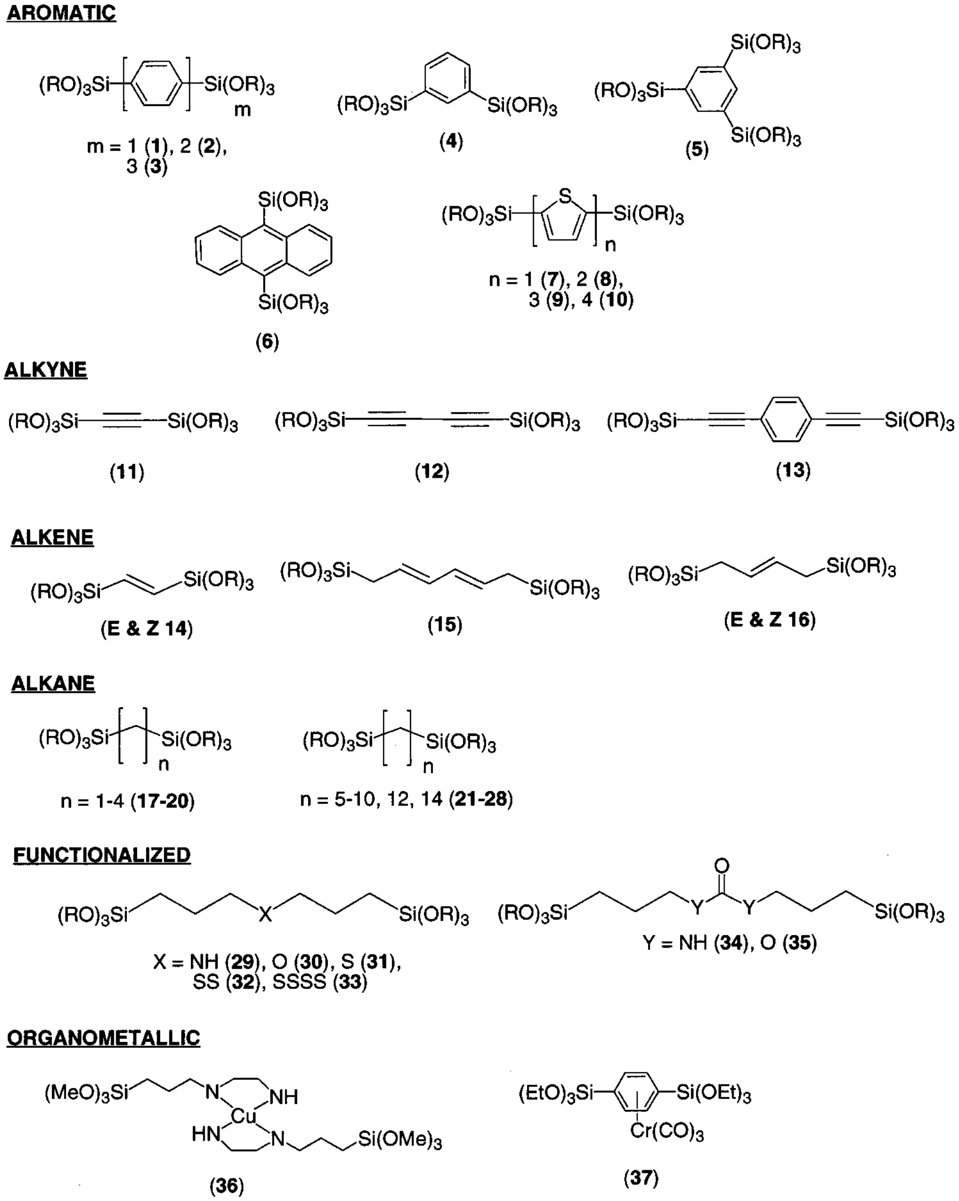


**Figure 1.** Representative monomers used to prepare bridged polysilsesquioxanes.

## Historical Background

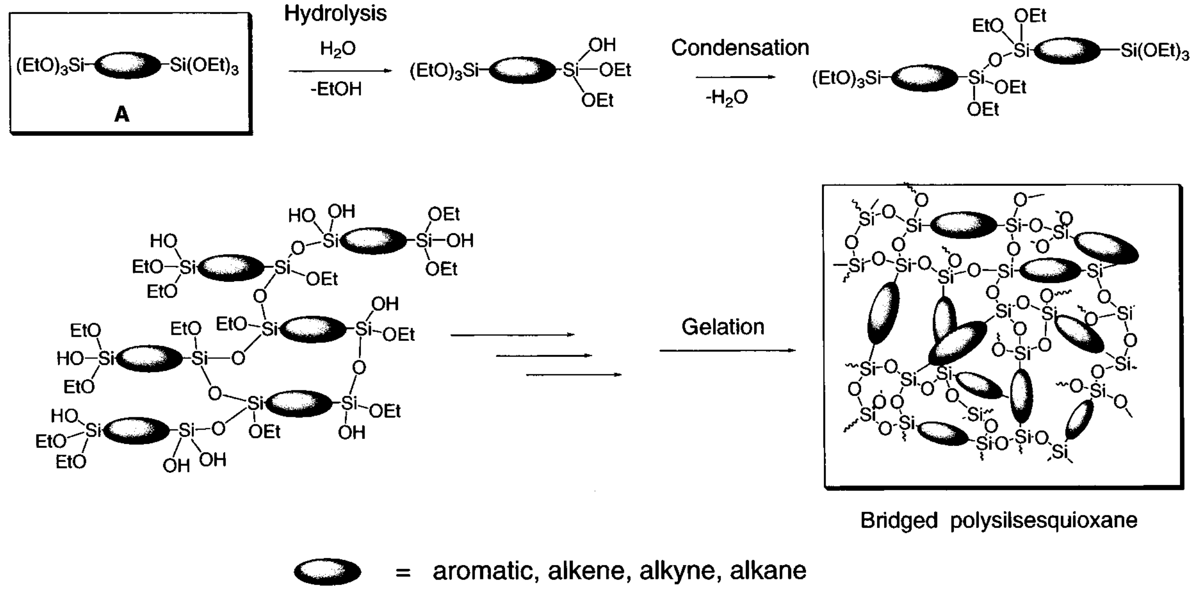
Sol–gel processable monomers containing two or more trichlorosilyl or trialkoxysilyl groups (Scheme 1) have been known for over 55 years.[33] Prior to the late 1980s, virtually all of these compounds were used as coupling agents, surface modifiers, or coatings and as components of adhesive formulations. For example, the phenylene (**1**) and acetylene (**11**)[34] bridged monomers were first prepared in the 1950s for use as coatings on glass. The dipropyltetrasulfide-bridged monomer or "Si-69" (**33**) was developed as a coupling agent for elastomers in the 1970s.[22] More than 30 × $10^6$ kg of the monomer is produced each year; much of this is used in silica–rubber composites. The investigation of the sol–gel polymerization of molecular precursors to bridged polysilsesquioxanes was undertaken to determine if the porosity of amorphous hybrid materials could be controlled at the molecular level. Rigid arylene (**1**–**6**) and acetylene (**11**) bridging groups were used in these initial studies.[2,8–10] Both trichlorosilyl- and triethoxysilyl-substituted systems were examined before the triethoxysilyl group was selected because of its lower reactivity and opportunity for greater degree of control over the sol–gel process. The investigation into the origins and molecular level control of porosity in bridged polysilsesquioxane xerogels and aerogels has continued for the last 14 years.

These efforts have broadened in scope to include control of the optical,[1e] thermomechanical,[35–37] and chemical properties.[20,23,27,38–42] Other research programs independently developed related sol–gel processing conditions for bridged polysilsesquioxanes using trimethoxysilyl groups instead of triethoxysilyl groups along with a number of new bridging groups.[5,12,16,23,40–43] The bridging organic group has also been reported as an expedient means for securely attaching organic functionalities, such as dyes[44–53] or metals,[25,32,54–65] to existing porous materials.

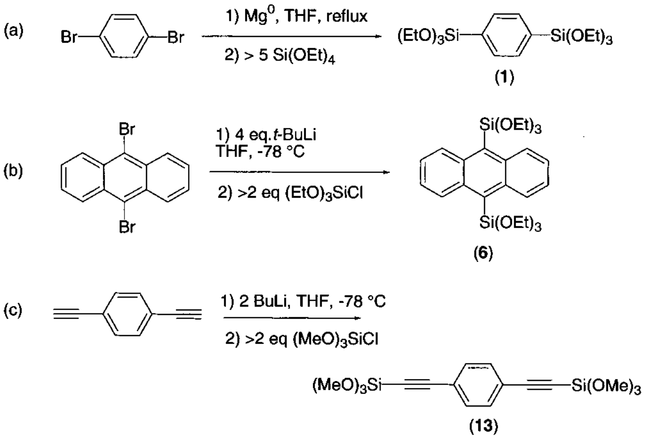
## Monomer Synthesis

There are a number of synthetic approaches to prepare the monomers for bridged polysilsesquioxanes. Nearly all of the approaches were designed to permit

**Scheme 1. Formation of Bridged Polysilsesquioxanes by the Hydrolysis and Condensation of Monomers with Two or More Trihalosilyl (Not Shown) or Trialkoxysilyl Groups Attached to Organic Bridging Groups**



**Scheme 2. Preparation of Monomers by Metal–Halogen Exchange or Metallation Chemistry**

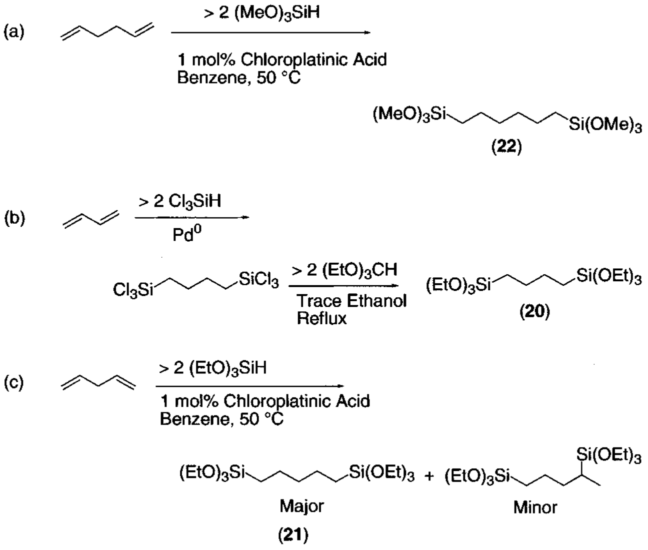


the sol–gel monomer to be prepared in 1–2 steps from readily available starting materials. The three most commonly used approaches are by (1) metalation of aryl, alkyl, and alkynyl precursors followed by reaction with a tetrafunctional silane, (2) hydrosilylation of dienes (or polyenes) or, less commonly, diynes, and (3) reaction of a bifunctional organic group with an organotrialkoxysilane bearing a reactive functional group.

**Metalation.** Metalation (Scheme 2) includes Grignard reactions (Scheme 2a),[2] lithium–halogen exchange (Scheme 2b),[2,11–13] and deprotonation of acetylenes (Scheme 2c)[2,12] or treatment of bis(trialkoxysilyl)methane with a Grignard, organolithium, or metal hydride.[62] In each case, the resulting organometallic reagent is reacted with a tetraalkoxysilane or chlorotrialkoxysilane to give the final product in moderate to good yields.

**Hydrosilylation.** Hydrosilylation (Scheme 3) is an efficient reaction for preparing bridged monomers in high yields from chemicals bearing two or more terminal olefins.[17,18] It has been used for alkylene and heteroatom-functionalized bridging groups. The addition of the

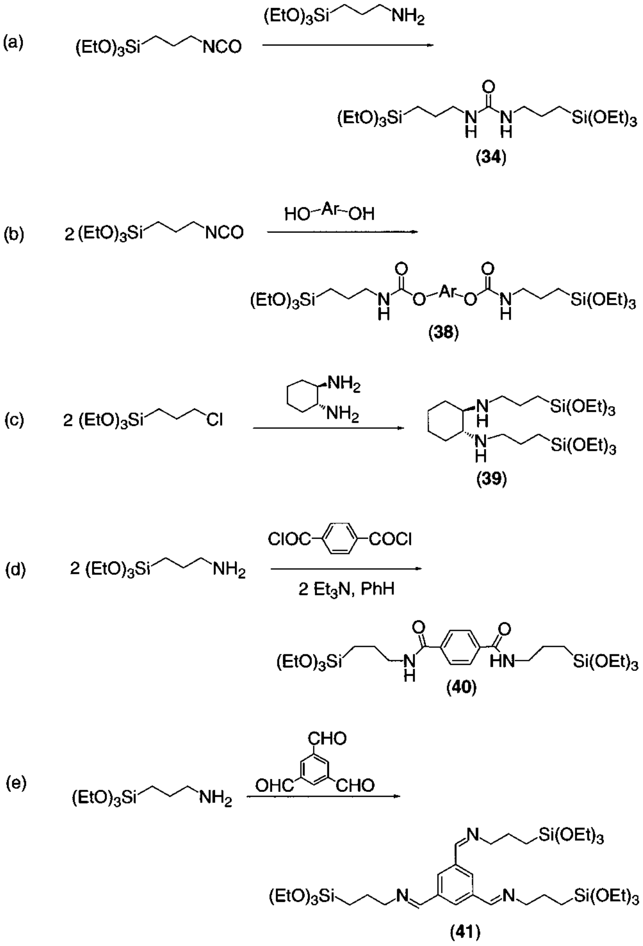
**Scheme 3. Preparation of Monomers by Hydrosilylation of Dienes**



Si–H group in trichlorosilanes or trialkoxysilanes is generally catalyzed with a noble metal catalyst such as chloroplatinic acid or Karsted's or Spier's catalyst.[63] The hydrosilylation reaction shows fair regioselectivity generally favoring silicon at the terminal position of the double bond. The butylene-bridged monomer (**20**) can be prepared from butadiene by the palladium-catalyzed hydrosilylation, in situ isomerization to afford the 3-butenyltrichlorosilane, followed by a second hydrosilylation (Scheme 3b).[17a] Trichlorosilanes are readily converted to trialkoxysilanes with trialkylorthoformates (Scheme 3b)[15] or with alcohols and an amine (Scheme 5b).[2]

**Functionalization of an Organotrialkoxysilane.** This synthetic route has become increasingly common because it permits a great number of bridging groups to be prepared from readily available starting materials (Scheme 4). For example, an electrophilic substituent on the organotrialkoxysilane can be reacted with any organic molecule with two or more nucleophilic groups.

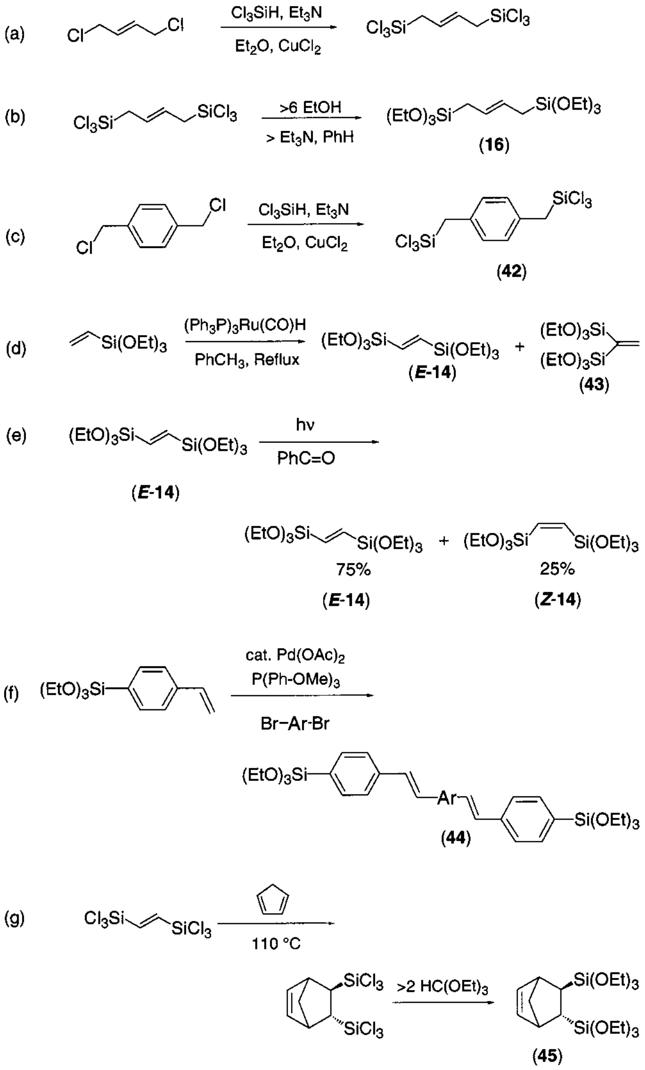
**Scheme 4. Preparation of Bridged Monomers from Organotrialkoxysilanes**



Electrophilic groups attached to organotrialkoxysilanes include isocyanates, alkyl or benzyl halides, epoxides, acrylates, and maleimides; isocyanates are the most frequently used. Isocyanates react readily with amines (Scheme 4a) to give urea linkages (**34**),[23] with alcohols (Scheme 4b) in the presence of tin or acidic catalysts to give urethane linkages (**38**),[26] or with carboxylic acids to give, after decarboxylation, an amide linkage. Alkyl halide substituted organotrialkoxysilanes (Scheme 4c) have been used with diamines to give bridging groups with amino functionalities (**39**).[56]

Alternatively, organotrialkoxysilanes with nucleophilic groups can be induced to react with organic groups with two or more electrophilic groups. Nucleophilic functionalities commonly available on organotrialkoxysilanes include amines and thiols. Hydroxyl groups exchange with alkoxide groups attached to the silicon and are not commonly found on organic groups attached to organotrialkoxysilanes. Amines have proven to be one of the most useful starting materials for preparing bridged monomers. A number of amide-containing bridges (Scheme 4d) have been prepared from precursors bearing two or more sulfonyl chlorides[51,52] or acid chlorides (**40** and **66**).[24b] Bridging groups based on Schiff bases (**41**) have been prepared by reacting (aminopropyl)trialkoxysilanes with di- or trialdehydes (Scheme 4e).[54]

**Scheme 5. Miscellaneous Methods of Synthesizing Monomers**



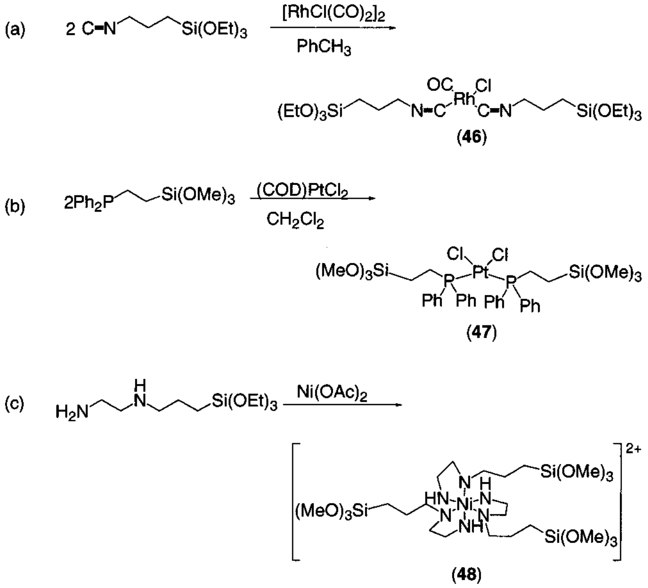
**Miscellaneous Approaches.** The reaction of the silyl anion of trichlorosilane with allyl or benzyl halides has been used with great success to prepare 2,4-hexadienylene (**15**),[15] 2-butenylene (**16**),[15,19e] and xylene (**42**)[43] bridged monomers (Scheme 5a,c). Other approaches to preparing bridged monomers include ruthenium-catalyzed silylation/desilylation (Scheme 5d; **14** and **43**),[14] photochemical isomerization of olefins (Scheme 5e; (*Z*)-**14**),[14] the Heck reaction (Scheme 5f) to afford crown-[41] or oligoarylenevinylene-bridged monomers (**44**),[53] and the Diels–Alder reaction (Scheme 5g) of 1,2-bis(trichlorosilyl)ethene with cyclopentadiene (**45**).[39]

Another method for forming bridging groups is through the formation of a metal complex[6b] (Scheme 6) using functional groups such as isocyanides (**46**),[64] phosphines (**47**),[59–62] amines,[65] thiols,[66] or diamines (**48**)[6b] as metal ligands in an organometallic bridging group.

## Sol–Gel Processing of Bridged Polysilsesquioxanes

Sol–gel polymerization of bridged trialkoxysilanes proceeds by a series of hydrolysis and condensation reactions.[1,5] The reactions are typically performed in the same alcohol generated by the monomer hydrolysis or in tetrahydrofuran. At least 3 equiv of water as the

**Scheme 6. Formation of Organometallic Bridged Polysilsesquioxanes**[6b]



coreactant are added to the polymerization reaction. Gels have also been prepared in nonpolar solvents such as toluene through a transesterification reaction between the triethoxysilyl groups and anhydrous formic acid.[37] The first reported sol–gel polymerization in supercritical carbon dioxide was used to prepare phenylene-bridged polysilsesquioxane aerogels in a single step from the anhydrous sol–gel polymerization of the phenylene monomer with 6 equiv of formic acid.[67]

The ease with which bridged polysilsesquioxanes form gels may be their single most distinguishing trait. The six reactive alkoxide groups result in rapid gelation times for both traditional aqueous and anhydrous formic acid sol–gel procedures. Gelation occurs in minutes to hours for many bridged polysilsesquioxanes at 0.4 M monomer concentration.[1] This concentration is approximately one-fifth of the concentration of tetraethoxysilane used in typical sol–gel formulations that require days for gels to form.[68] In contrast, the majority of organotrialkoxysilanes, $RSi(OR)_3$, will not form gels under any sol–gel conditions.[68] To date, only one type of bridged monomer, 5,6-bis(triethoxysilyl)norbornene (**45**),[39] has resisted forming gels under all sol–gel conditions tested. Steric hindrance from the bridging norbornenylene group in (*E*)- and (*Z*)-5,6-bis(triethoxysilyl)norbornene monomers (**45**) is apparently sufficient to impede condensation so that stable solutions of hydrolyzed monomers and oligomers are obtained even after standing for months.

The sol–gel polymerization is generally acid or base catalyzed, although fluoride catalysts have also been used by several research groups.[5] Hydrochloric acid is typically used as the acidic catalyst. Ammonium hydroxide, sodium hydroxide, and potassium hydroxide have been used as basic catalysts. With aqueous sol–gels, acid catalysis results in gels with less condensed networks (65–75%) and more residual alkoxide and silanol groups than those prepared under basic conditions (75–90%).[1] The degree of condensation is directly related to the number of residual silanol and ethoxy groups at silicon. This, in turn, contributes to the overall polarity of the material and its surface properties. Less highly condensed materials, formed under acidic conditions, have a greater "presentation" of these polar groups.

Substituent effects on the sol–gel formation of bridged polysilsesquioxanes include the steric sensitivity of hydrolysis and condensation of alkoxysilane groups to the size of the alkoxide or bridging group, the electronic effects from the organic substituent, and the influence of flexible bridging groups on intramolecular condensations.[19] As would be expected from the sol–gel chemistry of tetraalkoxysilanes, the gelation rate decreases with increasing size of the alkoxide substituent (OMe > OEt > OPr).[18] Gels obtained from monomers with the more labile methoxy substituents often possess more mesopores (20 Å < pore diameter < 500 Å) and macropores (>500 Å) and fewer micropores when compared with those with ethoxy substituents. Hydrolysis and condensation rates of alkyl- and aryltrialkoxysilanes are significantly faster than tetraalkoxysilanes.[69] For example, simple alkyltriethoxysilanes hydrolyze 6–10 times faster than tetraethoxysilane (TEOS).

It is important to note that cyclization reactions are pervasive in siloxane-based polymerization chemistry and that cyclization reactions during the polymerization of tetraalkoxysilanes[70] and organotrialkoxysilanes[68] can delay or even prevent the formation of gels. What is interesting about bridged polysilsesquioxanes is that the formation of siloxane rings does not appear to be as important a factor in determining whether a gel will form, as is the case with silica or other siloxanes. This is probably due to the greater functionality of the bridged monomers, (hexafunctional) as opposed to tetrafunctional (TEOS) and trifunctional (trialkoxysilanes) that allows gels to form despite cyclic siloxane formation. It is only when *intramolecular* condensations leading to carbosiloxane rings (Figure 2) become significant contributors to the sol–gel chemistry of the bridged monomers that polymer growth dramatically slows. These intramolecular condensation reactions become important with monomers containing bridging groups between one and four methylene repeating units long (**17**–**20**)[19] or with cis substitution geometries [(*Z*)-**14** or -**16**].[14] These cyclization reactions take place during the early stages of polymerization and alter the composition of the basic structural units that are subsequently incorporated into the silsesquioxane network.

This phenomenon was discovered when an investigation of the sol–gel chemistry of a homologous series of alkylene-bridged silsesquioxane monomers uncovered striking discontinuities in gelation behavior. An investigation of the chemistry during the early stages of the polymerization has provided a molecular basis for these observations.[1a] Monomers containing from one to four methylene groups exhibit a pronounced tendency to undergo intramolecular cyclization to form carbosiloxanes. The cyclic intermediates have been characterized by in situ $^{29}$Si NMR, chemical ionization mass spectrometry,[14,19,71] and actual isolation of the intermediates from the reaction solutions.[14,19] One example is the sol–gel polymerization of 1,4-bis(triethoxysilyl)butane (**20**).[17,19] The gel time for this monomer is in excess of 6 months. Under the same "standard" conditions, the correspond-

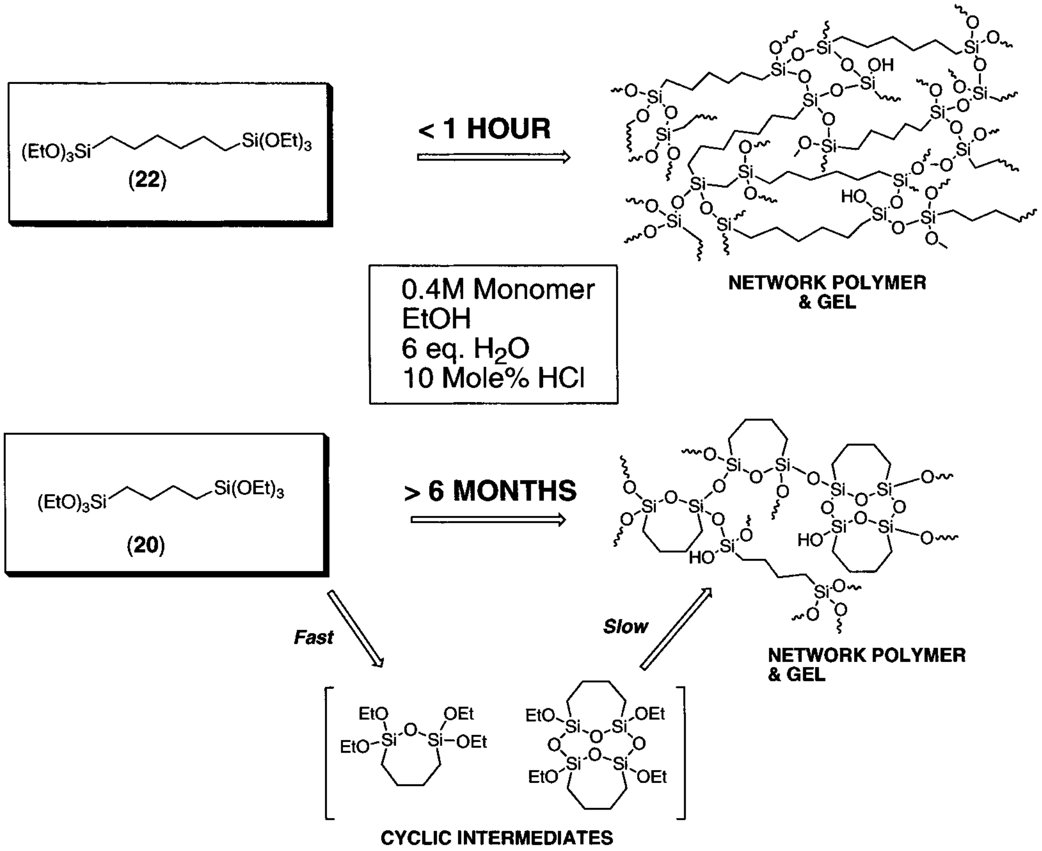


**Figure 2.** Effect of monomer structure on gelation times. Reducing the length of the alkylene bridging group by *two methylenes* increases cyclization reactions to the extent that gelation is delayed by months.

ing six-carbon, hexylene-bridged (**22**) homologue gels in less than 1 h.

These cyclic carbosiloxanes are local thermodynamic sinks that produce kinetic bottlenecks in the production of bridged polysilsesquioxanes with sufficiently high connectivity to become gels. The formation of cyclics results in retarding or, in some cases, preventing gelation. An additional finding is that the cyclic structures are incorporated intact into the final xerogel. Because cyclization alters the structure of the building block that eventually makes up the xerogel network, it is expected that this will contribute importantly to the bulk properties of the xerogel as well.

Once formed, the gels are aged and then dried. It is critical to control the aging time because it has been demonstrated to have profound effects on the porosity and texture of the resulting xerogels.[7,72] Xerogels (Figure 3) have been prepared by air-drying,[2] washing with water and then drying,[11,17a] or exchanging the polymerization solvent with one with a lower dielectric than that from slow air-drying.[2] Because of the low concentration of monomers used in the sol–gel processing, bridged polysilsesquioxane xerogels can lose as much as 80–95% of their volume upon air-drying. This shrinkage can result in the collapse of pores, resulting in nonporous materials.[11,19,21] However, most bridged polysilsesquioxane xerogels remain porous with surface areas between 200 and 1200 m$^2$/g. Thin film coatings can be readily prepared by spin casting, dip coating, or spraying. Gels can be processed as monolithic aerogels by replacing the original solvent with supercritical carbon dioxide extraction and then slowly venting (Figure 3).[17b,30] Alternatively, aerogels can be prepared by directly polymerizing the monomers with formic acid in supercritical carbon dioxide.[67]

**Figure 3.** Monolithic, bridged polysilsesquioxane aerogels (blue-tinted or white) and xerogels (transparent).

More recently, bridged polysilsesquioxanes have been prepared using surfactant templating techniques to give mesoporous materials (Figure 4).[31,36] In these materials, the polysilsesquioxane makes up the skeleton of a geometric array of pores in hexagonal close-packed cylinders or tetrahedral networks. The size and geometry of the mesopores depend on the surfactant and processing conditions. The bridged polysilsesquioxane adds improved toughness and organophilicity that may make these materials valuable for adsorbents of organic chemicals. However, it is not clear that there are advantages to the more time-intensive surfactant templating compared with the single-step sol–gel process-

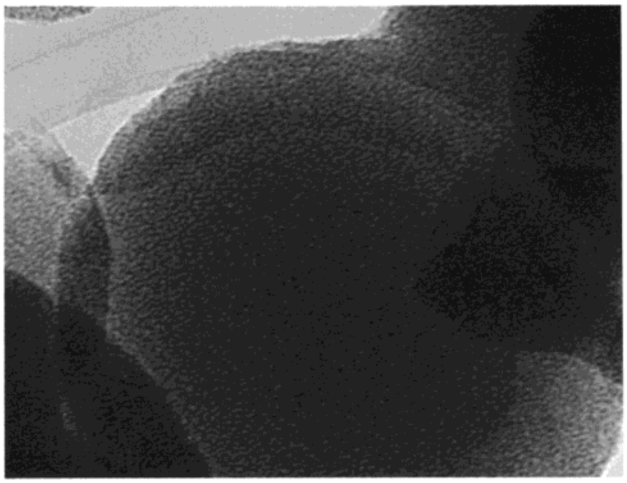


**Figure 4.** Electron micrograph of surfactant-templated ethylene (**18**) bridged polysilsesquioxanes.[31c]

ing of bridged polysilsesquioxane xerogels with higher surface areas and a comparable degree of control over the pore size distributions.

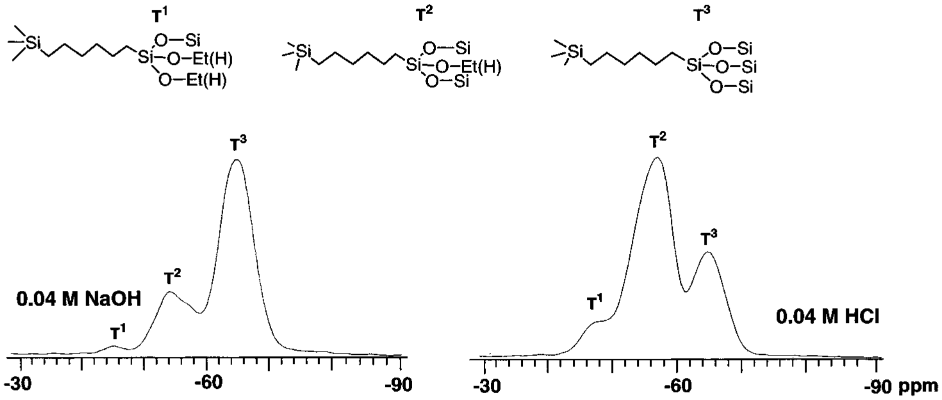
## Characterization of Bridged Polysilsesquioxanes

X-ray powder diffraction[2,12,71] as well as small-angle X-ray and neutron scattering[73] have been used to establish the composition of many bridged polysilsesquioxanes. Many of the materials are completely amorphous and exhibit fractal dimensions that are intermediate between a surface and mass fractal material. Solid-state $^{13}C$ and $^{29}Si$ NMR spectroscopies are widely used to determine the molecular structure of the bridged polysilsesquioxanes.[1−5,42] In particular, the integrity of the bridging group and the extent of reaction is elucidated by deconvoluting $^{29}Si$ NMR data (Figure 5). The extent of reaction can have an important influence on how porous the final gels may be (vide infra). Optical microscopy was recently used to reveal birefringence in thin films of polysilsesquioxanes with arylene bridging groups (**2**, **3**, **10**, and **13**), which suggests that there is significant ordering of the bridging groups present in the solution prior to gelation.[74]

## Porosity in Bridged Polysilsesquioxanes

**Control over the Porosity.** Porosity is a key property of materials used for the preparation of catalysts, chromatographic supports, membranes, and adsorbent materials.[3] High surface areas and control over the pore size are important goals for synthetic materials programs. The bridging organic group provides an opportunity to systematically vary the size, shape, geometry, and functionality of a molecular building block in order to probe how bulk structural properties, such as porosity, are affected. In amorphous bridged polysilsesquioxanes, the relationship between the bridging group and the porosity is subtle. Nevertheless, precise levels of control have been achieved. Important factors contributing to the porosity in these materials include the compliance of the network, which is a function of the degree of condensation at the silicon and the flexibility of the bridging group. For example, long flexible alkylene (**21**−**28**),[17−19] fluoroalkylene (**49** and **50**),[75] or even heteroatom-functionalized alkylene (**29**−**33**) bridging groups,[21] particularly when polymerized under acidic conditions, can lead to complete collapse of the porosity, resulting in nonporous xerogels or thin films (Figure 6). The ability to tailor nonporous bridged polysilsesquioxanes may be useful for fabricating chemical barriers, dense membranes, or optical coatings. It is also important to note that, because of the sensitivity of the sol−gel process to factors such as pH, catalyst, temperature, solvent, and aging time,[5c,7,72] these factors must be carefully controlled to permit the structure−property effects of the bridging group to be determined reproducibly.

**Pore Size Control.** Less compliant networks prepared with basic catalysts to give more condensed networks and/or more rigid bridging groups retain their porosity after drying. Arylene (**1**−**3**)[2,8−12,30] and ethenylene (**14**)[14] bridged polysilsesquioxanes give rise to



**Degree of Condensation**

| SOLVENT | NaOH | HCl |
|---|---|---|
| EtOH | 90.3% | 75.2% |
| THF | 89.1% | 76.4% |

**Figure 5.** $^{29}Si$ CP MAS NMR spectra of hexylene-bridged polysilsesquioxane aerogels prepared by base (left) and acid (right) catalyzed sol−gel polymerizations of 1,6-bis(triethoxysilyl)hexane (0.4 M solution of **22** in ethanol or tetrahydrofuran, 2.4 M $H_2O$, and 0.04 M catalyst).[18] From the deconvolution of the spectra, the degree of condensation (shown below the spectra) for the sol−gel polymerization can be calculated. The degree of condensation for the hexylene-bridged polysilsesquioxanes shows the general trend of more cross-linking in reactions prepared with base catalysts.

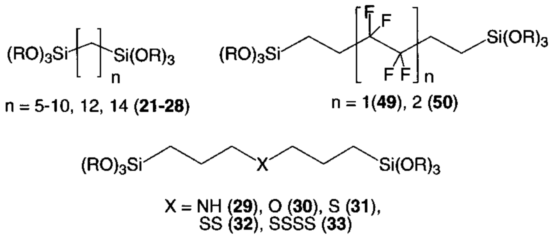


**Figure 6.** Bridged monomers with flexible bridging groups capable of forming more compliant networks that can be engineered to afford nonporous thin films by reducing the degree of condensation at silicon.

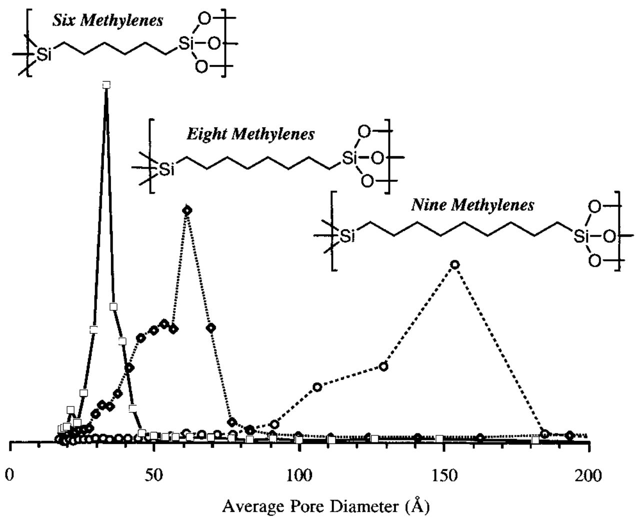


**Figure 7.** Change in the pore size distribution in alkylene-bridged polysilsesquioxane xerogels with increasing length of the alkylene bridging group from six (**22**) to eight (**23**) to ten (**25**) methylenes.[17]

materials with surface areas as high as 1800 $m^2/g$. The high surface area contains large contributions from micropores with mean pore diameters < 20 Å. Alkylene-bridged polysilsesquioxanes prepared with base catalysts and bridging groups up to 10 carbons in length are in the form of mesoporous xerogels (20 Å < mean pore diameter < 500 Å).[17] The mean pore diameter was shown to be roughly proportional to the length of the bridging groups (Figure 7). Introduction of unsaturated functionalities such as olefinic or aromatic groups into the organic bridges may decrease the flexibility and further prevent collapse of pores during drying. There is sufficient empirical data to predict with fair confidence if a given bridging group under a defined set of sol−gel polymerization conditions will be porous or not. This marks a fairly significant advance in our understanding of the molecular determinants of porosity.

**Pore Templating.** Another strategy for creating porosity is to use the organic group as a template for porosity (Figure 8). While a common strategy in the preparation of zeolites, this has only recently been applied in hybrid sol−gel materials. Templating relies on an organic group to occupy space until calcination, chemical oxidation, chemical rearrangements, or hydrolysis eliminates the template (Scheme 7). This will leave a pore whose size and shape roughly correspond to that of the organic molecule. We first performed templating serendipitously with acetylene-bridged polysilsesquioxanes (**11**) that lost acetylene during thermolysis.[2] An alternative approach used a low-temperature, inductively coupled plasma to burn away organic bridging groups in bridged polysilsesquioxane xerogels.[38] The resulting silica gels were porous. If the xerogels were porous before oxidation, the mean pore diameter shifted to larger sizes. When nonporous alkylene-bridged polysilsesquioxane xerogels were treated, mesoporous silica gels were obtained. The size of the pores increased as the length of the bridging group increased. Bridged polysilsesquioxanes were subsequently used to template porosity in silica membranes.[76] A variety of chemical processes have also been explored for cleaving, chemically modifying, or removing portions of the organic bridging groups. These include the use of retro-Diels−Alder reactions (**45**) to modify[39] or cleave the bridging group,[26] decarboxylation of dialkyl carbonate bridging groups (**35**),[21c,27] and thermal decomposition of phenolic carbamate linkages in the bridging groups.[26]

Others have successfully used fluoride-catalyzed or thermally induced cleavage of Si−C bonds in acetylene- and arylalkyne-bridged polysilsesquioxanes, such as **12** and **13**, to template porosity in silica gels.[16] More recently, hydrolysis of carbamate linkages was used to prepare porous 3-aminopropyl-functionalized polysilsesquioxanes.[77]

## Thermal Stability and Mechanical Properties

Many bridged polysilsesquioxanes exhibit excellent thermal stability in inert atmospheres and in air. Phenylene-bridged polysilsesquioxanes (**1**−**3**) are stable to 500 °C.[2] Alkylene-bridged polysilsesquioxanes (**17**−**28**) are stable to over 400 °C.[17,18] The mechanical properties of bridged polysilsesquioxanes have been less well characterized than their thermal stability. Bisarylimide-bridged polysilsesquioxanes (**50**−**54**) can be pre-

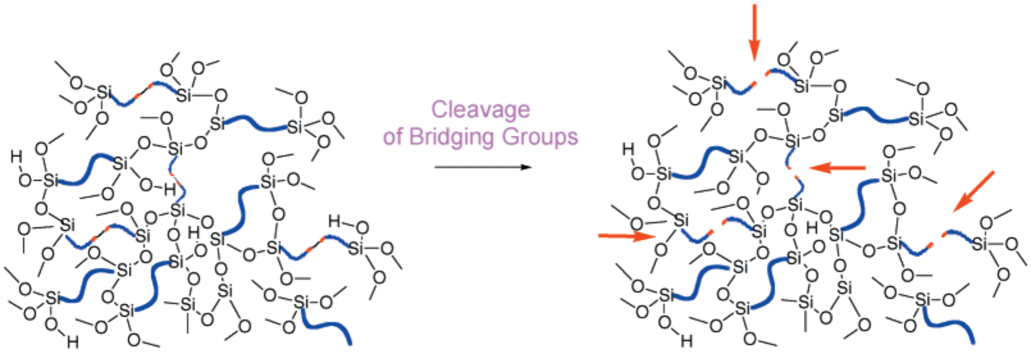
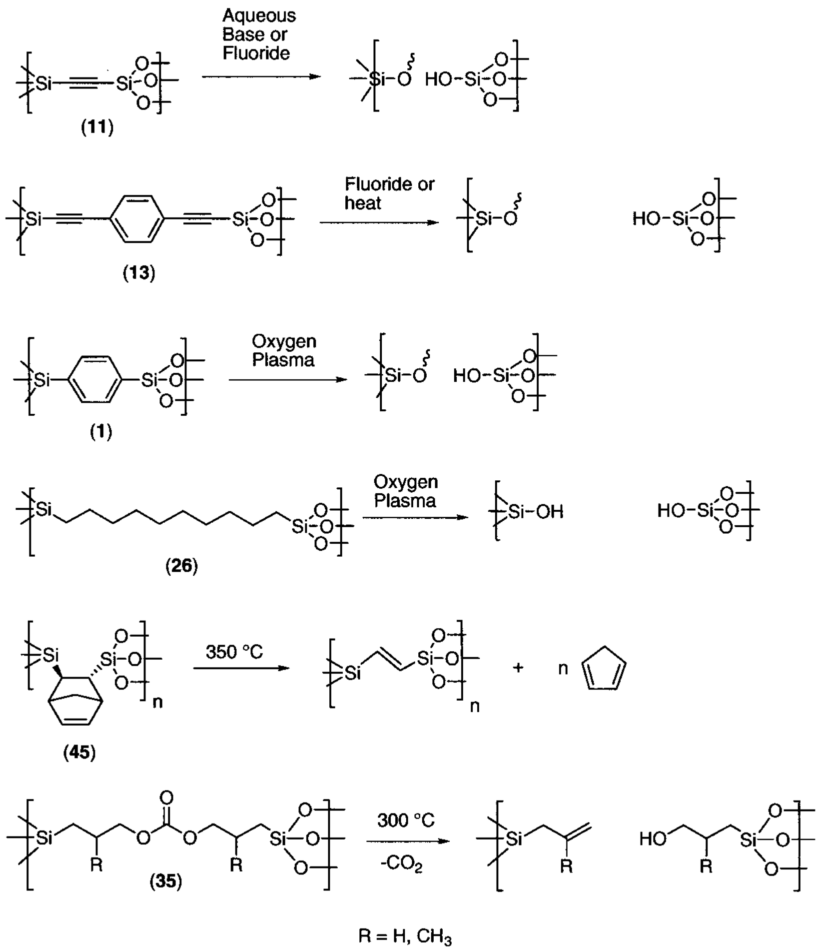


**Figure 8.** Templating porosity in bridged polysilsesquioxanes with the organic bridging group.

**Scheme 7. Templating Porosity in Bridged Polysilsesquioxanes**



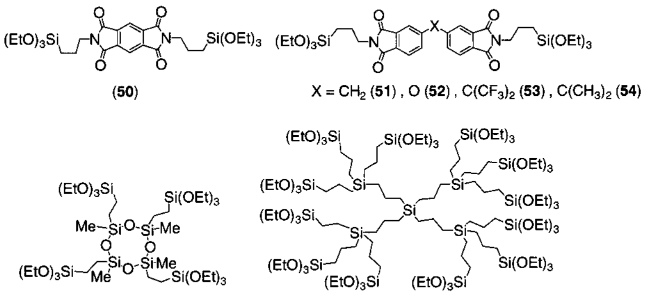


**Figure 9.** Aryl imide bridged monomers (**50**−**54**)[35] and monomers with dendritic bridging groups (**55** and **56**).[37]

pared in the form of hard thin films that are thermally stable at 400 °C for over 40 h (Figure 9).[35] The mechanical properties of some highly branched polysilsesquioxanes or "star-gels" (**55** and **56**) have resulted in their description as compliant gels or glasses.[37] Compressive strain studies revealed that the star-gels are considerably tougher than epoxy resins or silica gel. More recently, mechanical analysis of thin films of surfactant-templated ethylene-bridged polysilsesquioxanes (**18**) showed an increase in the modulus (4.3 GPa) and hardness (4.8 GPa) with increasing amounts of the ethylene bridging group.[36]

## Applications

The primary application of bridged polysilsesquioxanes has been for surface modification as coupling agents such as those with sulfides in the bridging group (**29**−**33**) that are used with silica-filled rubber.[22a] In addition, bridged polysilsesquioxanes have been widely applied as a part of coating formulations. Materials with alkylene (**17**−**28**),[19] ether (**28** and **57**),[20] and urea (**34** and **58**)[25] functionalized bridging groups can result in the formation of tough and relatively hard films (Figure 10) to protect easily scratched surfaces. Bridged polysilsesquioxane coatings can also be used as protective layers for metals[22b] or for microelectronic applications such as low *k* dielectrics[78] and photoresists.[79] A more recent application took advantage of the more hydrophobic, yet readily gelled, alkylene-bridged polysilsesquioxanes as encapsulating sol−gel networks for enzymes and cells.[80]

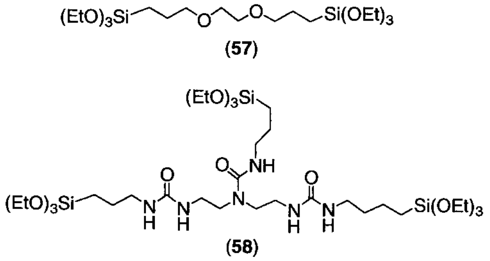


**Figure 10.** Ether (**57**)[21] and urea (**58**)[25] bridged polysilsesquioxanes for tough coatings.

**Optics and Electronics.** Incorporation of dyes into the sol−gel matrix is a useful strategy for preparing waveguides, lasers, sensors, light-emitting diodes, and

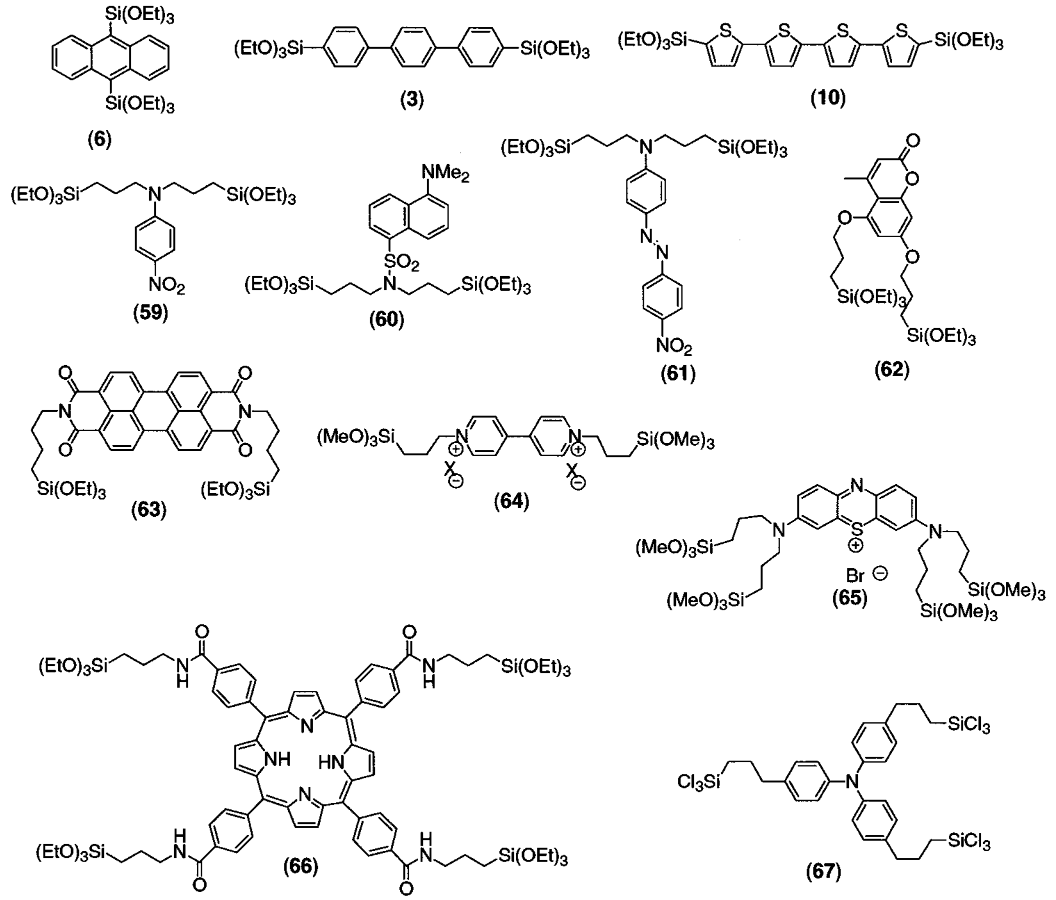


**Figure 11.** Bridged polysilsesquioxane monomers with chromophore bridging groups.

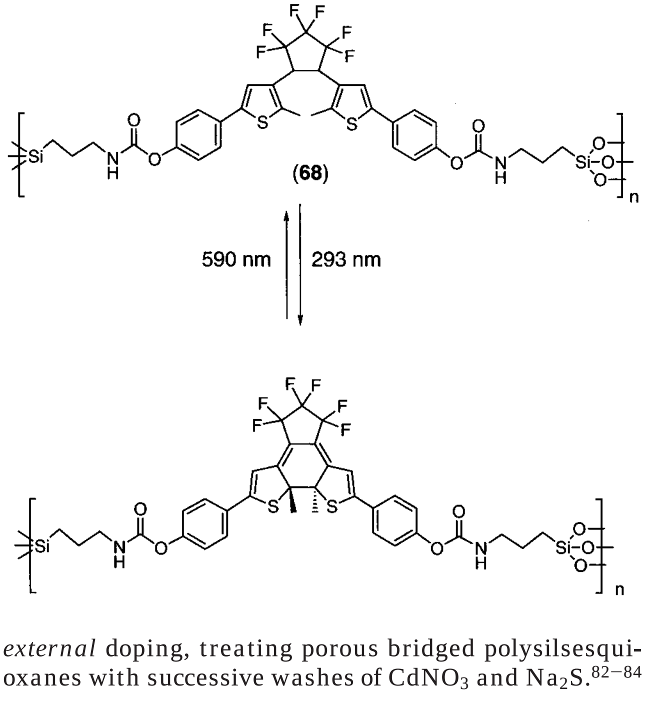
nonlinear optical (NLO) materials.[1e] The use of a dye molecule as a bridging group provides an exceptionally high loading of chromophores and ensures against leaching and/or phase separation of the dye molecule (Figure 11).

Dyes that have been incorporated into bridging groups include anthracene (**6**),[2] terphenylene (**3**),[2] coumarins (**62**),[44] fullerenes,[45,46] oligothiophenes (**10**),[13] viologens (**64**),[47] lanthanide complexes,[48] triarylamines (**67**),[49] nitroaromatics (**59** and **61**),[50] phthalocyanines,[51] porphyrins (**66**),[52] and phenylenevinylidene[53] functionalities. Dithienylethene-bridged polysilsesquioxanes (Scheme 8; **68**) are photochromic materials whose refractive index can be reversibly photoswitched.[81] These materials have significant potential for optical components for wave guiding.

This approach has also been used for the preparation of second-order NLO bridged polysilsesquioxanes containing 4-nitro-*N*,*N*-bis[(3-triethoxysilyl)propyl]aniline (**59**) in each monomer unit.[50d] Optical quality thin films were deposited by spin coating with concomitant electric field poling. The $\chi^{(2)}$ value corresponds to a $d_{33}$ coefficient of 18.9 pm/V and a $r_{33}$ value of 4.7 pm/V. The films displayed good temporal stability at temperatures above 100 °C.

Bridged polysilsesquioxanes offer a novel chemical approach to produce nanosized particles doped in transparent hybrid glass materials.[1e] These complex materials may have utility for electrooptical devices, as supported catalysts and as catalytic membrane materials. Nanosized CdS particles have been deposited by *external* doping, treating porous bridged polysilsesquioxanes with successive washes of $CdNO_3$ and $Na_2S$.[82-84]

**Scheme 8. Photoreversible Photochromic Dithienylethene-Bridged Polysilsesquioxane Copolymer with Polymethylsilsesquioxane[81]**



The CdS particles are distributed uniformly throughout the material. Although not perfectly monodisperse, the average CdS particle size correlates with the average pore size of the xerogel. Nanosized irregularly shaped Cr, Fe, Co, and Pt particles (10−90 nm) have

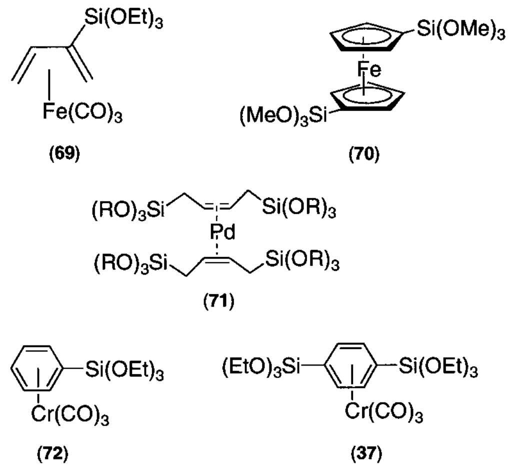


**Figure 12.** Monomers with metal-bearing bridging groups. Monomers **69**, **70**, **72**, and **37** are prepared and isolated before sol−gel processing; monomer **71** is thought to form in situ when the sol−gel is doped with palladium compounds.

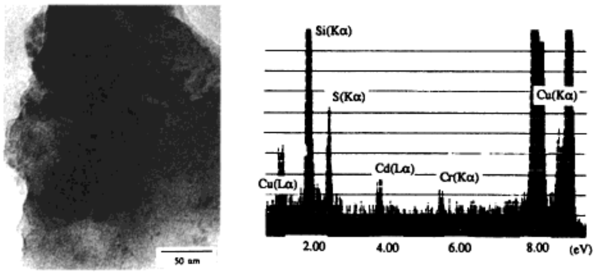


**Figure 13.** (Left) TEM image revealing an intimate mixture of nanosized CdS and Cr clusters. (Right) Elemental composition of the clusters established by high-resolution EDAX analysis.

been prepared in xerogels by an *internal* doping method. Zerovalent transition-metal complexes **69**, **71,** and **72**[85,86] (Figure 12) were incorporated in bridged polysilsesquioxanes by copolymerization with 1,4-bis(triethoxysilyl)benzene (**1**). In many cases, discrete metal particles can be formed by either heating or irradiating with light the dried xerogel under vacuum. In both internal and external methods, the deposition of nanoparticles slightly reduced the surface area but the overall porosity remained intact. In Scheme 9, both methods are employed to fabricate intimate nanosized composites of $Cr^0$/CdS.

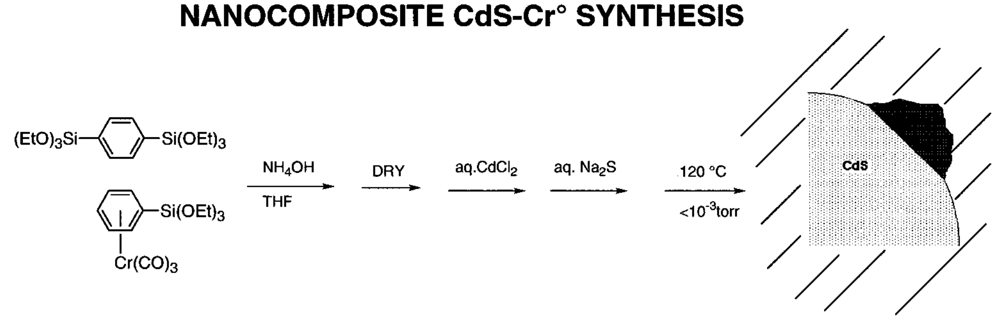
The size and identity of these clusters have been characterized by UV absorption, fluorescence, transmission electron microscopy (TEM), energy-dispersive analysis of X-rays (EDAX), electron spectroscopy for chemical analysis, and electron diffraction techniques. A TEM of nanosized Cr particles dispersed in phenylene-bridged polysilsesquioxane is shown in Figure 13.

**Separations Media.** The combination of high surface area with chemical functionality makes bridged polysilsesquioxanes ideal chromatographic supports for HPLC. The ability of phenylene (**1**) bridged polysilsesquioxanes as packing materials for HPLC columns to separate aromatic compounds compared favorably with similar silica gel filled columns.[88] Bridged polysilsesquioxanes have also been used as pore templates in inorganic membranes[76] and as a structural material.[36]

**Catalyst Supports.** Similarly, high surface area and chemical functionality make bridged polysilsesquioxanes excellent candidates for catalyst supports.[6,56c] The phenylene groups in phenylene (**1**) bridged polysilsesquioxanes have been sulfonated to generate acidic molecular sieve materials (**74**; Scheme 10).[89] An alternative approach is to use a bridging group that is a metal ligand. The metal can be pendent (**37**)[52,54−56,61] to the bridging group (Figure 13), or it can be part of the bridging group (**70** and **71**).[51,57−61,64−68]

The high surface area and high relative loadings of metals in organometallic bridged polysilsesquioxanes make them attractive for supported catalysts with tailored reactivities and selectivities.[6] A series of bridged polysilsesquioxanes with ruthenium, iridium,[90] and rhodium[64] complexes as part of the bridging group have been prepared and used for hydrogenation of aldehydes, olefins, or arenes with increased reactivity presumably because of prevention of less reactive dimers seen with the homogeneous catalysts. Bridged polysilsesquioxanes with rhodium and palladium have been used for hydroformylation of olefins with enhanced selectivities for the terminal carbonyl.[91] The degree of condensation and flexibility of the network were used to engineer the materials for their applications. Chiral rhodium catalysts based on an asymmetric diaminocyclohexyl-functionalized bridge (**39**) as the metal ligand have been prepared and used in asymmetric reductions.[56] A bridged polysilsesquioxane with a chiral binaphthyl bridging group coordinating rhodium was shown to provide moderate enantiomeric excesses in the asymmetric reduction of prochiral ketones.[58] More often, the bridged polysilsesquioxane is used as an agent for attaching a highly dispersed catalyst to a solid support of another

**Scheme 9. Process for the Sequential Doping of Porous Copoly-1,4-phenylenephenyl-$Cr(CO)_3$ Silsesquioxane**[a]



[a] The dried xerogel is treated successively with $CdNO_3$ and then $Na_2S$ to deposit nanosized CdS particles. Chromium metal is subsequently deposited by decomposing the aryl $Cr(CO)_3$ complex under vacuum (130 °C).

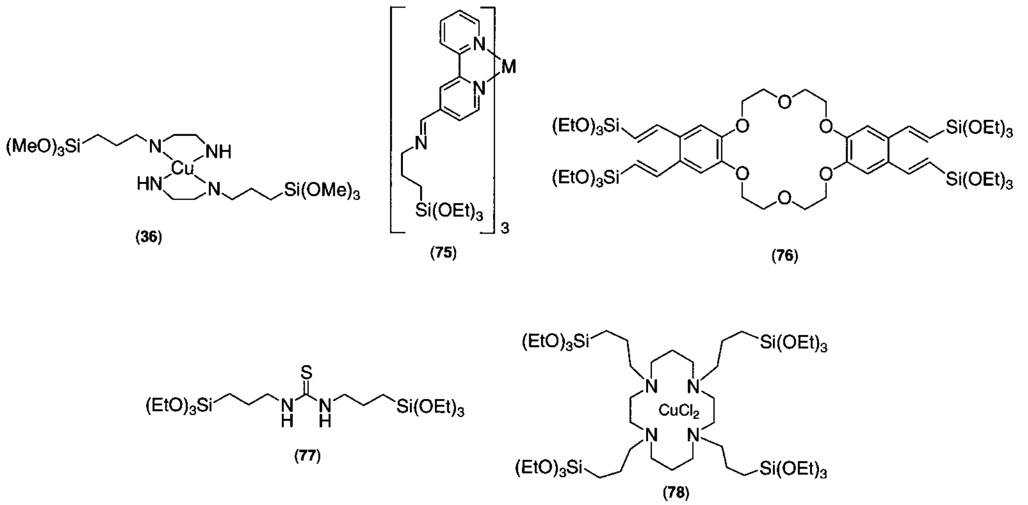
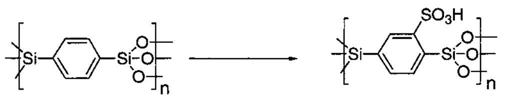


**Figure 14.** Bridged polysilsesquioxane monomers that have chemical functionalities that can perform as ligands for metal-selective adsorbents.

**Scheme 10. Formation of Porous, Sulfonic Acid Catalyst (74) from Phenylene-Bridged Polysilsesquioxane**[90]


(1) (74)

material. For example, a chromium(III)-bridged polysilsesquioxane, coordinated by two hydroxyaryl imines tethered to triethoxysilyl groups, was used to prepare a heterogeneous catalyst by surface silylation of silica gels.[92] The resulting heterogeneous catalyst was effective at gas-phase oxidation of alkylaromatics to carboxylic acid functionalized aromatics.

**Metal and Organic Adsorbents.** The same functionalities that make good ligands for catalysts can also be used to bind metals in adsorbent materials (Figure 14). Bridged polysilsesquioxanes with thiocarbamate groups (**77**) have been used extensively as porous, high surface area adsorbents for metals from solution.[32] The copper complex of 2 equiv of ethylenebis(aminopropyl)triethoxysilane (**36**) has been used to functionalize the interior of pores in a surfactant-templated "MCM-41" silica.[28] Copper was washed out of the bridging group, leaving the ethylenediamine groups positioned to preferentially sequester copper(II) from aqueous solutions. Assembly of bridged silsesquioxanes around a metal, such as that with the bipyridyl-based system (**75**), can be used to imprint surface metal selective coordination sites.[93] Crown ether bridged polysilsesquioxanes (**76**) have been prepared that can bind alkali-metal cations.[41] Thiourea-bridged polysilsesquioxanes (**77**) have been demonstrated to be effective sorbents for silver, gold, and platinum group metals.[94] Copper can also be incorporated into tetraazamacrocycle-bridged polysilsesquioxanes through both external and internal doping methods.[95] Internal doping occurred without a loss of copper because of the strong binding from the chelating ligand. Furthermore, the presence of copper in the macrocycle during the sol–gel polymerization appears to rigidify the bridging group, providing a new tool for modifying the structural features of these hybrids. Copolymeric xerogels of thiopropyltriethoxysilane and 1,4-bis(triethoxysilyl)benzene (**1**)[96] have been prepared that will remove more mercury (milliequivalents of Hg/grams of adsorbent) from aqueous solutions than any other known thiol-functionalized adsorbent.[97]

Because of the homogeneous distribution of organics throughout high surface area materials, bridged polysilsesquioxanes have great potential as adsorbents for volatile organic contaminants.

## Summary

In a relatively short period of time, bridged polysilsesquioxanes have emerged as a versatile class of materials. These hybrid organic–inorganic materials are built from precursors that integrate organic and inorganic groups at molecular length scales. A considerable body of experimental data have established that this configuration permits engineering of the physical properties of the resulting xerogels and aerogels. The materials can be fabricated into a variety of forms that range from nonporous films to high surface area microporous monolithic structures. More importantly, this process can be achieved in a single step. These features, coupled with the ability to prepare materials with organic functionality at every repeat unit without perturbing the formation of the gels or with adverse effects to the porosity, make these materials attractive for separations, catalysis, optics, sensors, and dielectric coatings.

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