amount of H_2PtCl_6 was heated for 12 h at 60 °C. A fraction boiling at about 150 °C was collected to give **5** (2.41 g, 13.3 mmol) in 50% yield: ^1H NMR ($CDCl_3$) δ 0.37 (s, 6), 0.78–0.84 (m, 2), 1.16 (t, J = 7.0 Hz, 3), 1.60–1.70 (m, 2), 3.37 (t, J = 6.7 Hz, 2), 3.43 (q, J = 7.0 Hz, 2); ^{13}C NMR ($CDCl_3$) δ 1.5, 15.1, 15.3, 23.3, 66.0, 72.5; ^{29}Si NMR ($CDCl_3$) δ 32.2. Anal. Calcd for $C_7H_{17}SiOCl$: C, 46.51; H, 9.48. Found: C, 46.49; H, 9.14.

(3-Ethoxypropyl)dimethylsilane (2a). To a suspension of $LiAlH_4$ (0.23 g, 6.2 mmol) in ether (8 mL) was added **5** (2.24 g, 12.4 mmol) at 0 °C, and then the mixture was stirred at room temperature for 12 h and under reflux for 2 h. The usual workup gave **2a** (1.29 g, 8.8 mmol) in 71% yield: bp 122 °C (400 mmHg); ^1H NMR (CD_2Cl_2) δ 0.11 (d, J = 3.7 Hz, 6), 0.58–0.65 (m, 2), 1.18 (t, J = 7.1 Hz, 3), 1.56–1.66 (m, 2), 3.38 (t, J = 6.8 Hz, 2), 3.46 (q, J = 7.1 Hz, 2), 3.88 (sept, J = 3.7 Hz, 1); ^{13}C NMR (CD_2Cl_2) δ −4.3, 10.8, 15.6, 25.2, 66.4, 73.5; ^{29}Si NMR (CD_2Cl_2) δ −12.9. Anal. Calcd for $C_7H_{18}SiO$: C, 57.47; H, 12.40. Found: C, 57.29; H, 12.15.

(3-Ethoxypropyl)diphenylsilane (2b). To a mixture of allyl ethyl ether (1.46 g, 17.0 mmol) and a catalytic amount of H_2PtCl_6 was added diphenylsilane (2.80 g, 15.2 mmol) and the solution was allowed to react for 12 h at temperatures from 80 to 160 °C. Distillation at a reduced pressure gave **2b** (2.44 g, 9.0 mmol) in 59% yield, bp 101–110 °C (0.05 mmHg): ^1H NMR (CD_2Cl_2) δ 1.27–1.35 (m, 5), 1.82–1.92 (m, 2), 3.52 (t, J = 6.7 Hz, 2), 3.53 (q, J = 6.7 Hz, 2), 5.04 (t, J = 3.7 Hz, 1), 7.40–7.50 (m, 6), 7.60–7.80 (m, 4, $^1J_{Si-H}$ = 193 Hz); ^{13}C NMR (CD_2Cl_2) δ 8.4, 15.1, 24.6, 65.9, 72.7, 127.9, 129.4, 134.2, 135.0; ^{29}Si NMR (CD_2Cl_2) δ −13.3. Anal. Found: C, 75.41; H, 7.98%. Calcd for $C_{17}H_{22}OSi$: C, 75.50; H, 8.20.

Sample Preparation for NMR Measurements. (a) Reaction of Hydrosilanes with trityl-TFPB. An apparatus having two side arms was used for the preparation and sampling of the silyloxonium TFPBs for NMR spectroscopy. Typically, NaTFPB was treated with trityl chloride without solvent in a side arm at highly reduced pressure (<10^{-6} mmHg) yielding yellow solids; H_2O of hydrate NaTFPB was removed during this procedure. Then, CD_2Cl_2 was introduced to the mixture by trap-to-trap distillation; the resulting suspension was filtered through a sintered glass filter into a central tube giving a yellow solution of trityl-TFPB at ambient temperature. Trimethylsilane and diethyl ether were transferred to the frozen solution of trityl-TFPB and then the sample tube was sealed off at −196 °C. The mixture was warmed with a methanol bath to −70 °C to start the reaction; the characteristic yellow color of trityl ions disappeared immediately. For NMR spectroscopic measurements, the mixture was transferred into another side arm having an NMR tube, which was sealed off without raising the temperature higher than −50 °C.

(b) Reaction of Chlorosilanes with NaTFPB. A similar apparatus and procedure as described above was applied for the sample preparation. NaTFPB was dehydrated and pulverized by magnetic stirring under high vacuum for 2 h before use.

Preparation of Trimethylsilyl Perchlorate in the Presence of Diethyl Ether. By using a similar procedure as described above, the reaction of trimethylchlorosilane with silver perchlorate in the presence of 15 equiv of diethyl ether in CD_2Cl_2 at ambient temperature gave a solution of trimethylsilyl perchlorate together with the precipitate of AgCl. For NMR measurements, the solution was transferred into an NMR tube after removal of AgCl by decantation and sealed off.

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Supplementary Material Available: ^1H, ^{13}C, and ^{29}Si NMR spectra for the reaction mixture of trityl-TFPB with Me_3SiH and ^{29}Si NMR spectrum for **3a** (4 pages). Ordering information is given on any current masthead page.

Arylsilsesquioxane Gels and Related Materials. New Hybrids of Organic and Inorganic Networks

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Abstract: Molecular building blocks for the preparation of amorphous hybrid organic–inorganic network materials have been synthesized. Hydrolysis and condensation of bis(triethoxysilyl)aryl **1**–**4** and -ethynyl **5** monomers results in formation of aryl- and ethynyl-bridged polysilsequioxanes in the form of xerogels. The gels were glasslike materials composed of uniform aggregates of particles between 50 and 80 nm in diameter. Atomic force microscopy was used to examine the fine grained aggregate characteristics of phenyl-bridged polysilsesquioxanes. The aryl-bridged materials were microporous with surface areas as high as 1000 m^2/g and thermally stable to 400 °C in air. Solid state ^{13}C and ^{29}Si NMR spectroscopies were used evaluate the integrity of the aryl and ethynyl bridges and to determine the degrees of hydrolysis (semiquantitative) and condensation in the network materials.

Introduction

Silicates comprise the earth's most abundant mineral form.[1] A remarkable diversity of morphologies exist within the simple pattern of alternating silicon and oxygen atoms. Synthetic glasses, prepared by sol–gel processing of alkoxysilanes (eq 1), allows for the preparation of amorphous materials (xerogels) that can serve as precursors to high purity glasses, ceramics, coatings, and fibers.[2]

$$n\,Si(OEt)_4 \;+\; 2n\,H_2O \;\rightleftharpoons\; (SiO_2)_n \;+\; 4n\,EtOH \qquad (1)$$

The importance of synthetic silicates arises from the diversity of physical properties of the resulting materials. These properties can be influenced by changes in sol–gel reaction conditions or in the subsequent processing of the gel. Sol–gel chemistry allows for the fabrication of silicates with morphologies distinctly different from, and often more useful than, naturally occurring silicates. While the manipulation of polymerization and processing conditions allows for the preparation of a variety of silicates, an alternative strategy for designing new silicate-like materials is to

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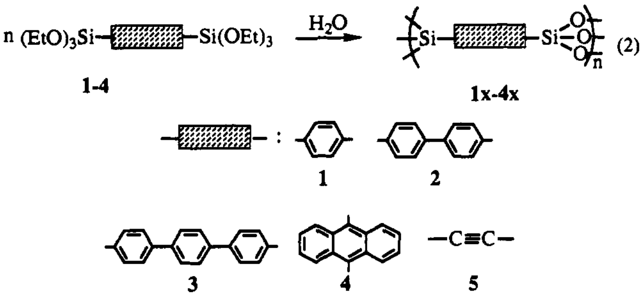
replace one or more of the siloxane linkages in the polymer with organic groups. For example, sol–gel processing provides for the preparation of organolithic macromolecular materials by cocondensing tetraethoxysilane (TEOS) with bishydroxy-terminated poly(dialkylsiloxanes)[3] or by replacing an alkoxy substituent on TEOS with an alkyl or aryl group to produce alkyl- or aryl-substituted polysilsesquioxanes (T-resins).[4] The organic component is capable of modifying the properties of the bulk material. Additional strategies for covalently incorporating organic functionality in a silicate-like matrix include the preparation of interpenetrating networks from the polymerization of TEOS and triethoxyvinylsilane and the subsequent copolymerization of vinyl monomers with pendent vinyl groups of the porous silicate network[5] and graft copolymerization of TEOS onto a linear polymethacrylate prepared by GTP.[6]

One objective of contemporary materials science is control of morphology of a material at the molecular level of design. We have a long-standing interest in porous network materials.[7] Despite the rather complex origins of porosity, we were intrigued by the possibility of "engineering" porosity in materials by assembling molecular sized building blocks into a three-dimensional scaffolding. It was reasoned that the gaps in such a scaffolding might be controlled by the size of the molecular building blocks. We were most interested in the meso to micropore domain, <500 Å, a scale that could provide materials capable of molecular sizing.

The approach to achieve this goal is to generate new silicate-like materials by inserting organic rigid-rod spacers at regular intervals into the silicate network (Figure 1). The organic spacers would be an integral part of the chemical connectivity of the material. By using different sized spacers, it may be possible to change certain fundamental properties of the material such as pore size.

Sol–gel chemistry (eq 1) appeared to be particularly suitable for the preparation of these materials. We envisioned hydrolytic condensation of bis(triethoxysilyl)aryl[8] or ethynyl monomers (eq 2) as a mild method of synthesis. The resulting network consists of an array of tetrahedral silicon atoms interconnected by three siloxane bonds. The fourth silicon linkage is joined to the aryl or ethynyl spacer that is also connected to the second silicon tetrahedron. The nature of these "building blocks" allows for their systematic variation with the potential for "controlled" alteration of the microstructure of the resulting material. The materials can be prepared under mild reaction conditions which could allow for reformulation or equilibration of the network.



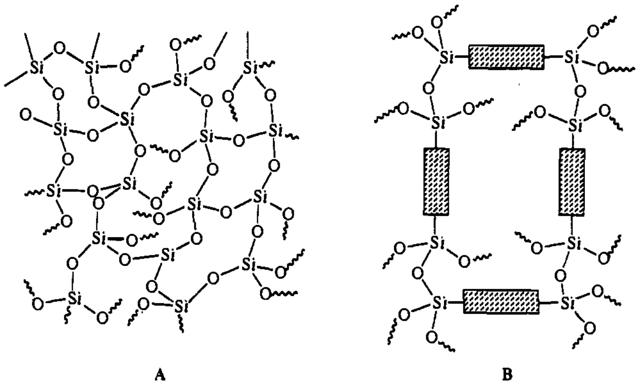
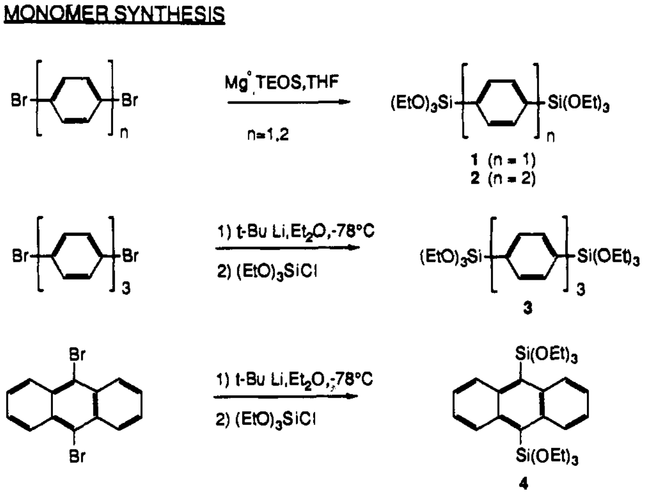


Figure 1. Amorphous silica A and bridged polysilsesquioxane B.

Scheme I



The following sections describe the synthesis and characterization of the first representatives of this family of new materials.

Results and Discussion

Monomer Preparation. The aryl and ethynyl precursors of the bridged polysilsesquioxanes were synthesized as outlined in Scheme I. Monomers **1** and **2** were prepared by Barbier–Grignard reactions from the respective aryl dibromides and TEOS. The products were purified by distillation in yields up to 55% for **1**. Monomers **3** and **4** were prepared by lithium–bromine exchange between 4,4''-dibromoterphenyl or 9,10-dibromoanthracene with *tert*-butyllithium followed with chlorotriethoxysilane.[9,10] Monomer **1** was also prepared in moderate yield (32%) by lithium–bromine exchange with *t*-BuLi in the presence of LiCl to promote the solubility of the intermediate dilithio species,[11] followed by quenching with excess TEOS. Bis(triethoxysilyl)ethyne **5** was prepared from sodium acetylide and chlorotriethoxysilane in pyridine at 60 °C and was purified by fractional distillation.

Sol–Gel Processing. Polymerization of the monomers involves hydrolysis of the ethoxysilyl groups to silanols that condense with either other silanols or ethoxysilanes to generate siloxane bonds (Scheme II). Condensation reactions give rise to a solution of growing polysilsesquioxane. Branching and cross-linking in the solution continues until the network is sufficiently large for the

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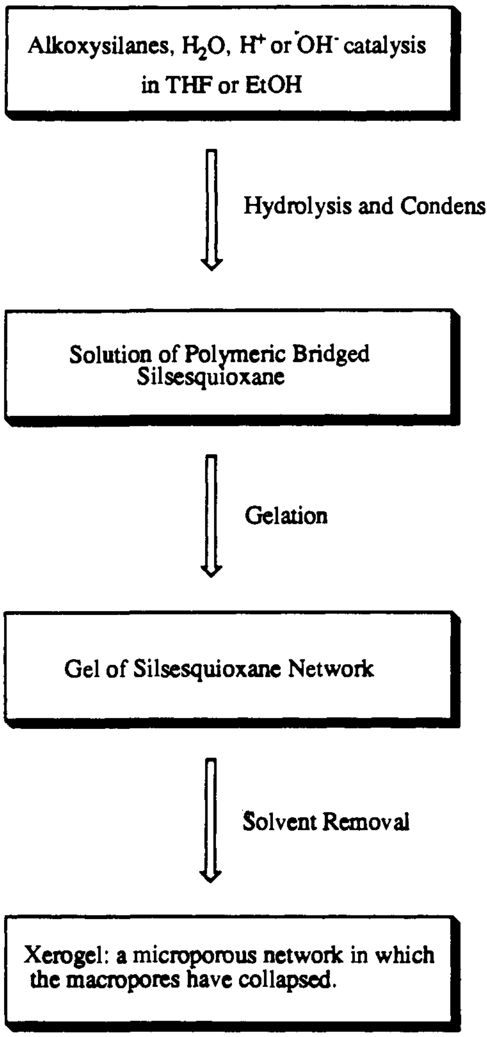
Scheme II. Sol–Gel Processing of Ethoxysilanes into Xerogels



gel transition to occur. The resulting gel consists of a solid polymer network phase interspered with solvent. In a subsequent step, the network collapses with loss of the supporting solvent to afford a polysilsesquioxane xerogel.[2]

Monomers **1–5** were polymerized in THF or ethanol solutions with a minimum of 3 equiv of water and either aqueous HCl (0.5–10.8 mol%) or aqueous NH_3 (5.0–570 mol%). The bridged monomers polymerized at concentrations as low as 0.20 M to form transparent gels. In contrast, TEOS failed to polymerize to gels below 1.3 M concentration, and (triethoxysilyl)benzene failed to form gels at concentrations as high as 2.0 M. The aryl- and ethynyl-bridged gels were rigid and somewhat brittle but could be cut with a spatula without cracking or shattering. The gels from both acid- and base-catalyzed polymerizations of **1–3** and **5** were slightly blue upon reflection and had a distinct yellow tint upon transmission, presumably from light scattering. A ruby red gel was obtained from the base-catalyzed polymerization of the anthracene monomer **4**. The red color may arise from a combination of excimer formation and light scattering. Acid-catalyzed (10.8 mol% HCl) polymerization of **1–3** typically afforded gels within 1 day. Polymerizations with identical quantities of NH_3 as catalyst required months for gelation to occur. Excess NH_3 and water, however, were found to afford gels as quickly as with acid catalysts. Less catalyst (0.7 mol%) was used with either the acid or base polymerizations of the ethynyl monomer **5** in order to minimize cleavage of the silicon–carbon bond.[12] In both cases gelation required 1 month to occur. After the gels were allowed to age for 48 h, the original solvent, typically THF, was exchanged with a series of solvents with decreasing dielectric until finally the gels were infused with 1,1,2-trichloro-1,2,2-trifluoroethane and then allowed to air dry. Xerogels prepared from 0.2–0.4 M solutions of aryl-bridged monomers lost 93–95% of their volume during the drying process. The glasslike xerogels were ground and dried under vaccum for characterization.

While most of the xerogels were ground into powders for analysis, the bridged polysilsesquioxanes could also be prepared as monoliths, thin films, and fibers. Monolithic xerogels were prepared to slow drying over months or using a drying control chemical agent (DCCA) such as formamide[13] as a component of the reaction medium. For example, polymerization of 1,4-bis(triethoxysilyl)benzene **1** in ethanol and formamide (40%) followed by slowly drying afforded a transparent monolith. For comparison, a monolith was prepared from tetraethoxysilane (TEOS). Thin films and fibers were prepared by casting or drawing from viscous solutions of the bridged polysilsesquioxanes before the onset of gelation.

Material Characterization. The bridged polysilsesquioxane xerogels were hard and brittle and could be ground into fine powders. Though the gels shrank substantially while drying, the resulting xerogels did not swell in water, benzene, or methanol indicating that condensation reactions continued during drying of the gel. To the eye, the monolithic xerogels appeared to be transparent glasses. Electron microscopy (SEM and TEM) of two phenyl-bridged polysilsesquioxanes prepared with either aqueous HCl (X-**1**-A) or NH_3 (X-**1**-C) catalysts reveal amorphous materials composed of an aggregate of fine granules between 50 and 100 nm in diameter. Similarly, atomic force micrographs (Figure 2) indicated that the phenyl-bridged polysilsesquioxanes were composed of aggregates of spherical particles between 50 and 80 nm in diameter. These micrographs represent the first application of AFM to sol–gel processed materials and suggest that the method has merit for evaluating silica morphologies. Using higher resolution transmission electron microscopy, the particles in both phenyl gels appear to be constructed of even smaller granules between 2.5 and 4.0 nm in diameter. Unlike silica gels prepared from TEOS, the morphology of the bridged gels appears to be independent of the catalyst used in their preparation. With the high potential for branching and crosslinking inherent in the bis(triethoxysilyl) monomers, fractal growth to spherical particles would seem to proceed regardless of pH.[14] No macropore structure was visible in the micrographs.

Gas sorption porosimetry was selected to evaluate pore structure of the aryl-bridged polysilsesquioxanes in greater detail.[15] Nitrogen and argon were used as the probe gases in these studies. The adsorption–desorption isotherms (Figure 3) for the bridged polysilsesquioxanes indicate substantial microporosity (<2.0 nm pore diameters). While several of the xerogels were solely microporous, most of the materials had an additional complement of mesopores with a mean pore diameter of 3.9 nm. The isotherms of these materials also exhibited hystereses suggestive of ink-bottle shaped mesopores. The mesopores may arise from voids between the particles (2.5–4.0 nm in diameter) observed in the transmission electron micrographs.

Of particular interest was the effect of different length aryl spacers on the meso- and microporosity. Nitrogen adsorption was unable to detect any differences in mean pore diameters down to 2.0 nm (Table I). Argon sorption experiments were used to evaluate mean pore diameters in the micropore region using the Horvath–Kawazoe model.[16] Micropore distributions of all the

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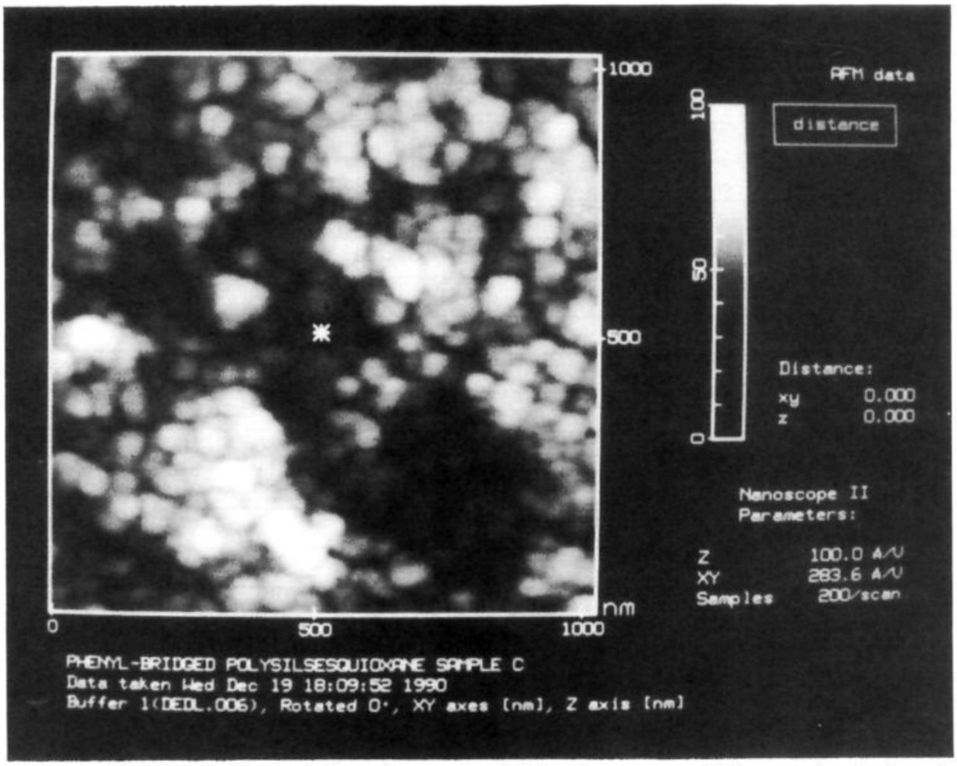

Figure 2. Atomic force micrograph of phenyl-bridged polysilsesquioxane xerogel. The gel was prepared by base catalyzed polymerization of **1** in THF followed by air drying to afford a monolithic xerogel. A small fragment was removed for the microscopy.

Table I. Summary of Surface Area, Mean Pore Diameter, and Pore Volume Data^d

xerogel	surface area (m^2/g)	mean pore diameter (nm, N_2 analysis)	mean pore diameter (nm, Ar analysis)
X-**1**-A	958^a	2.40^a	
X-**1**-B	797^a	2.30^a	
X-**1**-C	**691**^{b}	2.30^c	1.13^b
X-**1**-D	553^b	1.96^b	1.04^b
X-**2**-B	765^a	2.00^a	
X-**2**-C	**676**^{b}		0.84^b
X-**3**-B	**622**^{b}	1.90^b	0.84^b
X-**4**-B	222^a		

^{a} Analysis performed at DuPont, Wilmington, DE. ^{b} Performed on Micromeretics ASP 2000. ^{c} Performed on Quantachrome Autosorb 2. ^{d} BET surface areas determined with nitrogen in plain text; determined with argon in bold.

Table II. ^{13}C NMR Data for Bridged Polysilsesquioxanes

xerogels	$^{13}C_{bridge}$ (ppm)	$^{13}C_{methylene}$ (ppm)	$^{13}C_{methyl}$ (ppm)
X-**1**-A	133.6	56.4	17.6
X-**1**-B	134.3	59.6	17.5
X-**1**-C	134.1	N/A	N/A
X-**2**-A	142.7, 135.3, 131.4, 126.9	60.3	17.9
X-**2**-B	142.8, 135.1, 131.5, 126.3	59.5	17.1
X-**3**-A	140.6, 135.5, 127.5	59.4	18.4
X-**3**-B	140.6, 135.1, 126.6	59.0	17.3
X-**4**-B	137.2, 129.4, 125.3	59.0	18.1
X-**5**-A	105.9, 97.0, 82.4	60.3	18.1
X-**5**-B	106.6, 97.6, 83.2	59.8	18.0

xerogels rise to a maximum near 0.6 nm. However, the pore distributions were broad with most of the micropore volume arising from micropores above 1.0 nm. Thus, the *mean micropore diameters* range between 0.80 and 1.14 nm. No trend in the micropore diameters was observed between the phenyl-, biphenyl-, and terphenyl-bridged polysilsesquioxanes with Si–aryl–Si distances of 0.67, 0.87, and 1.08 nm. It would appear that in the processed xerogels examined thus far, the micropore structure, as determined by pore size analysis, was more dependent on the materials' macromolecular structure than upon spacer length. Surface areas (BET) ranged from 256–1000 m^2/g.

Solid State NMR. Solid state ^{13}C and ^{29}Si NMR spectroscopies proved to be most useful for providing chemical information regarding bridged polysilsesquioxanes. ^{13}C CP MAS–NMR reveals the aromatic and ethynyl carbons of the bridging groups (Table II), the residual ethoxysilyl groups, and residual solvents in the bulk materials. The spectra of the aryl-bridged gels are dominated by the aromatic carbon resonances between 120 and 150 ppm. The spectra of ethynyl-bridged xerogels (X-**5**-A and X-**5**-B) have three ethynyl peaks between 82 and 107 ppm. Any methyl and methylene resonances from residual ethoxy groups lie at 17.1–18.4 and 56.4–60.3 ppm, respectively.

The two types of aromatic carbon signals of the phenyl-bridged polysilsesquioxanes (X-**1**) are observed as a single peak between 133.6 and 134.1 ppm. The analogous resonances from the phenyl monomer **1** at 133.45 and 134.36 ppm are separated by less than the half-width (6 ppm) of the aromatic resonance in the solid polymer. X-**1**-C, prepared by NH_3 catalyzed polymerization in the presence of excess water and subsequently dried under vacuum at 100 °C, still revealed barely perceptible peaks from residual solvent. No detectable ethoxy residues remained indicating 100% hydrolysis.

In the acid-catalyzed materials, the ethoxy resonances in the polysilsesquioxanes were thought to be due to unhydrolyzed ethoxysilyl groups in the gels rather than adsorbed or entrapped ethanol on the basis of interrupted decoupling experiments.[17] The interrupted decoupling experiments with bridged polysilsesquioxanes reveal that peaks arising from THF at 25 and 68 ppm were not reduced indicating mobility on the time scale of tens of kHz. The ethoxy methylene, however, was observed to be attenuated suggesting that the ethoxy group had restricted mobility as would be expected for ethoxysilyl groups. It is not inconceivable, however, that the ethoxy carbon resonances could arise from the combi-

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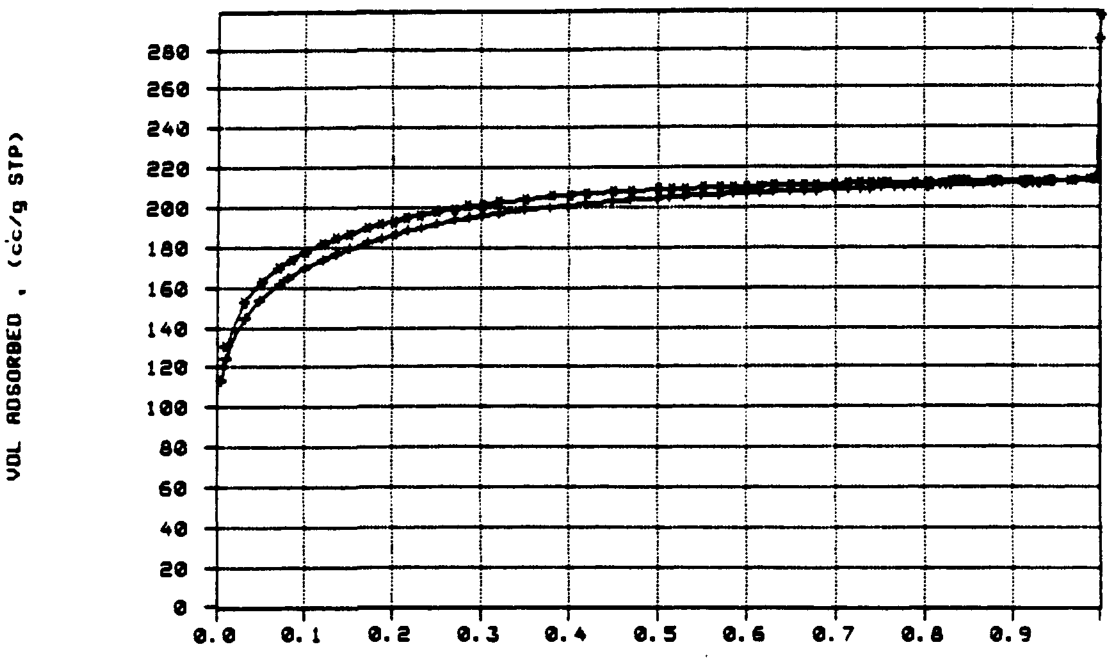

Figure 3. Type I sorption isotherm (N_2) for microporous terphenyl-bridged polysilsesquioxane (X-3-B). Adsorption (lower trace) and desorption (upper trace).

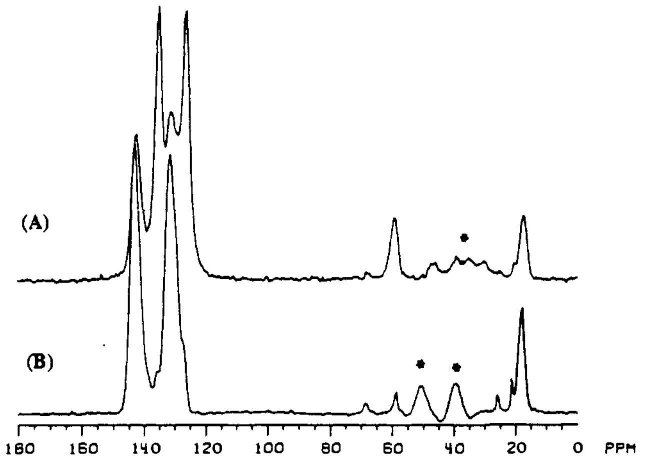

Figure 4. ^{13}C CP MAS-NMR spectrum (A) and interrupted decoupled spectrum (B) of biphenyl-bridged polysilsesquioxane (X-2-B). The peaks with asterisk(s) represent the spinning side bands. The four peaks around 135 ppm are due to the biphenyl bridge and those at 17 and 59 ppm arise from residual ethoxy groups.

Figure 5. Ethynyl-bridged polysilsesquioxane **A** and polyethynylsilsesquioxane **B**.

Table III. Degree of Hydrolysis for Aryl-Bridged Xerogels

xerogel	concn monomer (M)	catalyst (mol%)	H_2O (equiv)	deg of hydrolysis (%)
X-1-A^c	0.20^a	HCl (10.8)	6.0	98
X-1-B^c	0.40^b	HCl (10.8)	6.0	89
X-1-C^d	0.20^a	NH_3 (570)	>10	100
X-2-A^c	0.20^a	HCl (10.8)	6.0	98
X-2-B^c	0.40^b	HCl (10.8)	6.0	89
X-3-A^c	0.18^a	HCl (10.8)	6.0	81
X-3-B^d	0.20^a	NH_3 (570)	>10	96
X-4-B^c	0.20^a	NaOH (5.4)	3.0	86

[a] Prepared in THF. [b] Prepared in EtOH. [c] Dried under vacuum at room temperature. [d] Dried under vacuum at 100 °C.

nation of ethoxysilyl moieties and ethanol in the xerogel with the same results from interrupted decoupling experiments.

The ^{13}C CP MAS-NMR spectrum of biphenyl-bridged xerogel (X-**2**-B, Figure 4) has four aromatic resonances as expected. Interrupted decoupling experiments distinguished between the different aromatic carbon signals by suppressing signals of carbons with directly attached hydrogens. With interrupted decoupling, the four aromatic resonances collapse to two peaks at 142.9 and 131.5 ppm that can be assigned to the substituted positions on the biphenyl. The ^{13}C CP MAS-NMR spectrum of terphenyl-bridged polysilsesquioxane (X-**3**-A) displays only three broad peaks out of the expected six resonances observed in the spectrum of monomer **3**. As observed in the phenyl-bridged materials (X-**1**), the missing peaks were obscured through coincidental overlap. The broad bands in the spectrum of X-**3**-A blanket the aromatic region from 125 to 147 ppm. The interrupted decoupling experiment kept the peaks at 140.5 and 135.5 ppm, and replaced the peak at 127.5 ppm with two peaks at 130.5 and 128.8 ppm. The remaining carbon signal probably lies underneath the observed signals. The spectrum of anthracene-bridged polysilsesquioxane (X-**4**-B) has only three aromatic peaks instead of the expected four peaks observed in the monomer **4** (137.75, 131.46, 129.96, and 125.26 ppm). Interrupted decoupling of X-**4**-B sharply reduced the peak at 129.4 ppm and eliminated the peak at 125.3 ppm. The resonance at 137.0 ppm remained, and the hidden fourth resonance at 131.0 ppm was revealed.

Due to the hydrolytic instability of the silicon–carbon bond in (alkoxysilyl)acetylenes, no acetylenic polysilsesquioxanes have been previously prepared and characterized. The monomer **5** has an ethynyl carbon resonance at 104.3 ppm. Two ethynyl resonances at 108 and 104 ppm were observed by ^{13}C NMR in a pregelation solution during the HCl catalyzed polymerization. While the 104 ppm resonance is probably due to unreacted monomer, the single resonance at 108 ppm may have been due to partially hydrolyzed and condensed monomer in solution. The ^{1}H NMR spectrum revealed no evidence of ethynyl hydrogens from Si–C cleavage at this stage of the polymerization. The ^{13}C CP MAS-NMR spectrum of the dried ethynyl-bridged xerogel (X-**5**-A) displays three carbon resonances at 105.9, 97.0, and 82.4 ppm. Three resonances can be explained by a mixture of ethynyl-bridged polysilsesquioxane **A** and the "terminal" polyethynylsilsesquioxane **B** that would result from cleavage of one of the Si–C bonds (Figure 5). Silica and acetylene would be the side products of the bond

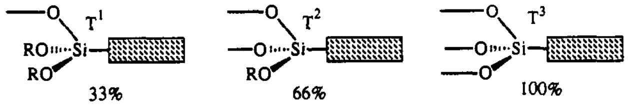

Figure 6. Modified Q^n notation for silsesquioxane silicons (each structure shown with degree of condensation).

Table IV. Summary of Corrected Areas for T^1, T^2, and T^3 and Calculated Degree of Condensation for Aryl-Bridged Polysilsesquioxanes

xerogel	area T^1	area T^2	area T^3	deg of condensation (%)
X-1-A	20.4	61.7	17.9	65.8
X-1-B	17.4	60.8	21.8	68.1
X-1-C	13.4	54.0	32.5	73.0
X-2-A	23.6	62.1	14.4	63.7
X-2-B	20.2	61.8	18.0	65.9
X-3-A	42.4	49.6	8.0	55.2
X-3-B	10.0	40.6	49.4	79.8
X-4-B	16.2	42.4	41.4	75.1

cleavage.[12] As the chemical shifts of aryl carbons directly attached to silsesquioxane groups were insensitive to changes in the degrees of hydrolysis and condensation (Tables II and III), it follows that the chemical shift of the ethynyl carbons in the ethynyl-bridged polysilsesquioxanes should be similar to that of the monomer **5**. Thus, the peak at 105.9 ppm can be assigned to the bridging ethynyl carbons. The remaining two ethynyl peaks are most likely due to terminal or nonbridging ethynylsilsesquioxane groups.[18] Interrupted decoupling showed a marked decrease in the intensity of the peak at 97.6 ppm suggesting that this was the ethynyl carbon with a hydrogen attached. The peak at 82.4 ppm was not reduced in intensity and may represent the ethynyl carbon directly attached to the silsesquioxane group shown as **B** in Figure 5. Clearly, the ethynyl-bridged monomers are more sensitive to both acid and basic hydrolysis and condensation conditions used to prepared the bridged polysilsesquioxanes. Ignoring any differences in cross polarization rates between the ethynyl carbons, the ethynyl polysilsesquioxane appears to be composed of approximately equal fractions of bridging and terminal ethynyl moieties.

The degree of hydrolysis in the aryl-bridged polysilsesquioxanes ranges from 81% to 100% (Table III). High degrees of hydrolysis were generally obtained with acid catalysts in THF and with excess NH_3 and water in THF after drying at 100 °C. Both **X-1-B** and **X-2-B**, which were prepared in ethanol, retained somewhat more ethoxysilyl substituents (Table III).

The ^{29}Si CP MAS-NMR of polyarylsilsesquioxanes may be used for evaluating the degree of condensation in the insoluble networks by examining the contribution of various silicon species present in the condensed materials.[19] Siloxanes, including silsesquioxanes, are succinctly described by a modified form of the Q^n notation.[20] In this representation (Figure 6), silsesquioxanes with one siloxane bond are denoted as T^1, those with two siloxane bonds, T^2, and those with three siloxane bonds, T^3.

In the bridged polysilsesquioxanes with silicon groups on either end of the hydrocarbon bridge, the T^1 silicons may serve as terminal groups but are more likely significant contributors to the network (Figure 7). The completely unreacted silanetriol and its respective ethyl esters (T^0) represent the terminal functionality in these bridged materials. The corrected areas of the T^1, T^2, and T^3 species for the various bridged polysilsesquioxanes are shown in Table IV. The aryl T^1 resonances, expect for the anthracene-bridged xerogel, lie between −58.7 and −62.8 ppm, T^2 resonances between −66.0 and −72.0 ppm, and the T^3 resonances between −76.3 and −80.5 ppm (Figure 8). The chemical shifts of triethoxysilylaryl monomers lie between −55.0 and −58.3 ppm. The T^1 resonance in the xerogels was often observed just upfield from the chemical shift value for the aryl-bridged monomers. A similar effect is observed in silica prepared from tetraethoxysilane and can be attributed to the greater electronegativity of the hydroxy groups in T^1 and T^0 deshielding the silicon nuclei.[20]

The three resonances of the anthracene-bridged polysilsesquioxane, **X-4-B**, lie slightly downfield from those of the other aryl-bridged xerogels at −54.6, −66.0, and −75.8 ppm. In addition, the spectrum of **X-4-B** displays minor silica resonances at −91.0 (Q^2), −98.0 (Q^3), and −106.3 (Q^4) ppm from cleavage of Si–C bonds during the polymerization. Apparently, the anthracene-bridged polysilsesquioxane was susceptible to some nucleophilic cleavage during hydrolysis and condensation. None of the other aryl-bridged xerogels prepared under acidic or alkaline conditions showed any measurable sign of silicon–carbon bond cleavage.

The ethynyl-bridged polysilsesquioxanes prepared under both acidic and basic conditions display silicon peaks at −105 or −102, −93, and, barely discernible above the baseline, −85 ppm. Unlike the arylsilsesquioxanes, the ethynyl-bridged materials exhibit resonances in a chemical shift range overlapping that of silica.[21] Cleavage of the Si–C bond during polymerization of **5** affords a mixture of the nonbridging acetylene, ethynyl-bridged polysilsesquioxanes (observed in ^{13}C CP MAS–NMR) and silica making unambiguous peak assignments difficult. The coincidental overlap of silsesqui- and silica resonances and unpredictable differences in cross polarization rates in these systems make characterization difficult. The infrared peak at 2046 cm^{-1} and ^{13}C CP MAS–NMR ethynyl resonances strongly support the presence of ethynylsilsesquioxane moieties in the xerogels, but like the ^{29}Si NMR data, allow no quantitative assessment of the bridged polysilsesquioxane's or silica's relative contributions.[22] The ethynyl-bridged xerogels were prepared at concentrations (0.4 M) at which TEOS was shown not to form gels, particularly with only linear (Q^2) and trifunctional (Q^3) groups that are observed in the ^{29}Si NMR spectra. The residual hexafunctional ethynyl-bridged monomer would lower the gelation threshold when copolymerized with silicic acid formed from hydrolytic decomposition of **5**. We tentatively conclude, therefore, that the xerogels (**X-5-A** and **X-5-B**) are copolymers of silica and ethynylpolysilsesquioxanes.

In addition to determining the type of structures in the polysilsesquioxanes, solid state ^{29}Si NMR may allow estimation of the degree of condensation (percentage of siloxane bonds formed).[23] Quantification of the contribution of the silicon species involves deconvolution of the peaks, measurement of the individual peak areas, and correction of the areas for differences in magnetization rates between the silicon species (T^1, T^2, and T^3).

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(18) In support of the assignments of the solid state ^{13}C NMR peaks at 82.4 and 97.6 ppm as being due to terminal or nonbridging ethynylpolysilsesquioxanes, the ^{13}C resonances for ethynyltriethoxysilane were reported to be 81.76 ppm for C_1 and 92.87 ppm for C_2: Zicmane, L. I.; Lukevics, E. *J. Organomet. Chem.* **1986**, *306*, 167.

(19) If the contribution of the various silicon species (T^1, T^2, and T^3) can be quantified, then the degree of condensation can be calculated according to the equation

$$\text{degree of condensation} = \frac{(0.5)[\text{area } T^1] + (1.0)[\text{area } T^2] + (1.5)[\text{area } T^3]}{1.5}$$

(20) Brinker, C. J.; Scherer, G. W., *Sol–Gel Science*; Academic Press: London, 1990; pp 165–166.

(21) Experience with the aryl-bridged polysilsesquioxanes suggests that the T^1 resonance should have a chemical shift value not too different from that of the parent ethoxysilyl monomer. The slight shoulder observed at −75 ppm in (**X-5-A**) may be the T^1 resonance for the ethynylpolysilsesquioxanes. In which case the T^2 and T^3 resonances would lie at −85 and −93 ppm, respectively. Silica, Q^1 and Q^2, would also contribute to the resonances at −85 and −93 ppm. The peaks observed at −102 (**X-5-B**) and −105 ppm (**X-5-A**) would belong to Q^3 silica, whereas the shoulder at −110 would be the Q^4 form. These assignments are consistent with the chemical shift values for silica. The relatively low intensity of the peaks assigned to the ethynylpolysilsesquioxane in this model would indicate that the xerogel was primarily composed of silica with a smaller contribution from silsesquioxane species.

(22) Elemental analysis of **X-5-A** reveals 15.96% carbon, 32.88% silicon, and 1.82% hydrogen compared with the calculated values of 18.74% carbon and 43.82% silicon for the completely condensed ethynyl-bridged polysilsesquioxane. Unfortunately, it is also possible to propose partially hydrolyzed and condensed silica materials that have similar compositions.

(23) Glaser, R. H.; Wilkes, G. L.; Bronnimann, C. E. *J. Non-Crystalline Solids* **1989**, *113*, 73.

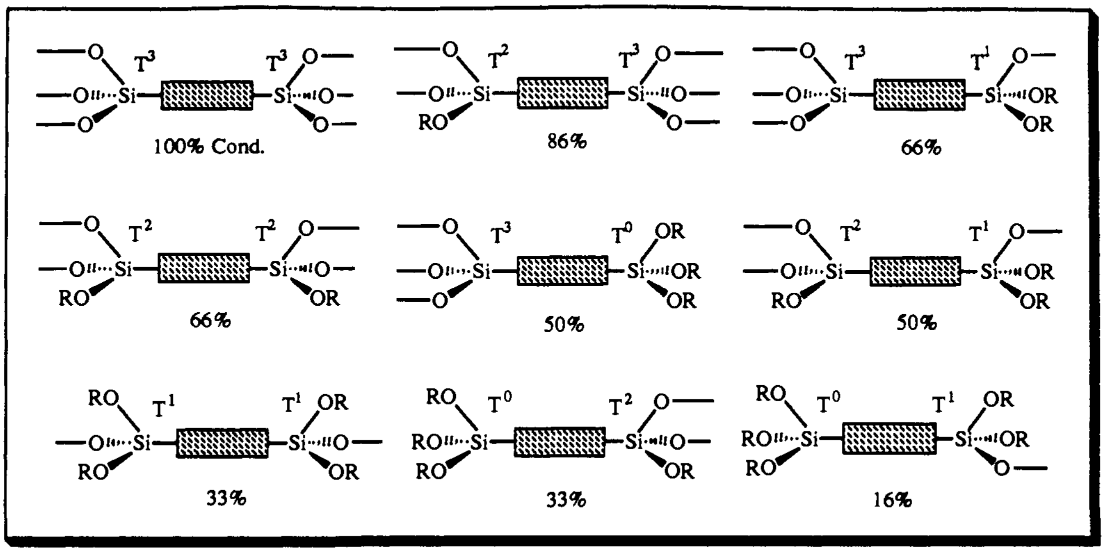

Figure 7. Possible monomer repeat units in bridged-polysilsesquioxanes with degrees of condensation.

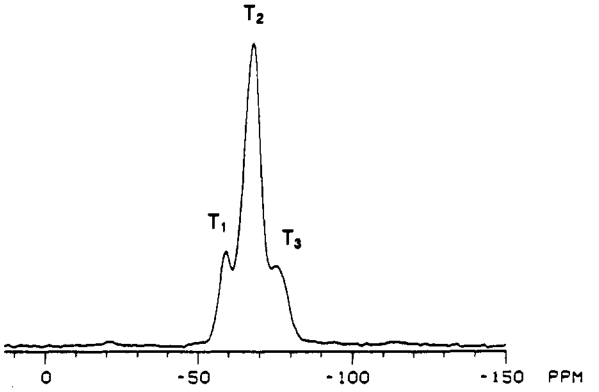

Figure 8. ^{29}Si CP MAS–NMR spectrum of phenyl-bridged polysilsesquioxane (X-1-A) showing T^1, T^2, and T^3 resonances.

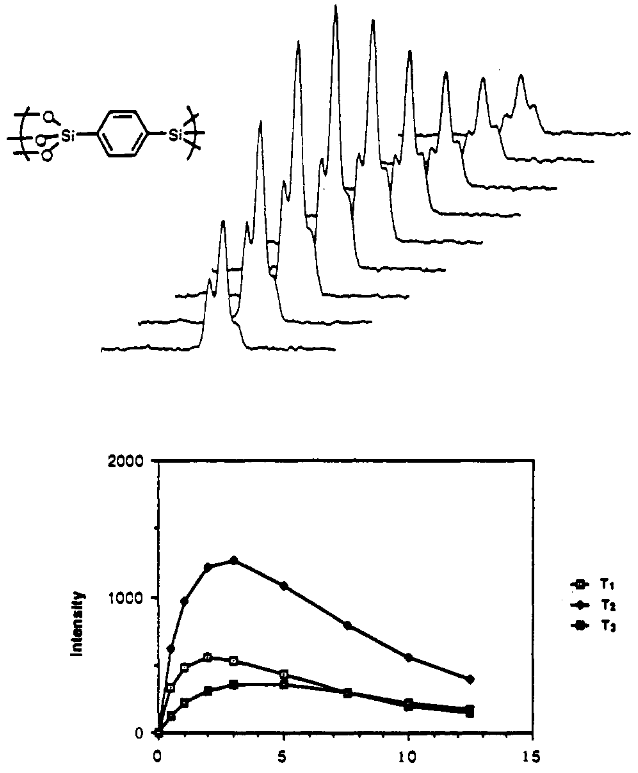

Figure 9. (a) Cascade plot of contact time study of phenyl-bridged polysilsesquioxane (X-1-B). Contact times were varied from 0.1 to 20 ms. (b) Plot of T^1, T^2, and T^3 peak intensities (heights) versus contact times for (X-1-B).

Because cross polarization rates are dependent on the distance to and number of hydrogens in the solid and because the system is typically not allowed to fully relax or reach thermodynamic equilibrium, the relative peak intensities may not accurately portray the populations in the sample.[24] However, the observed signal intensities can be corrected by performing variable contact time (cross polarization) studies. Figure 9 shows a cascade plot of a contact time study performed for X-1-C. The plots of intensity versus contact time for the phenyl-bridged polysilsesquioxane are shown in Figure 9. The T^1 peak magnetized the fastest owing to the greater number of neighboring hydrogens (including those in silanols and ethoxysilyl groups) that were available for cross polarization. The fully condensed T^3 species magnetized the slowest. However, differences between cross polarization rates for silsesquioxane species were typically less than those observed with silica (Q^1–Q^4).[24]

The contact time study yielded the cross polarization rate ($1/T_{SiH}$) and the proton spin locking relaxation constant $T_{1\rho H}$ for each resonance.[25] The cross polarization efficiency, $\beta_{Si}(t)/\beta_0$, was calculated from T_{SiH} and T_{1rH} using the eq 3

$$\frac{\beta_{Si}(t)}{\beta_0} = \left(\frac{1}{1-\lambda}\right)(1 - e^{-(1-\lambda)t/T_{SiH}})(e^{-t/T_{1\rho H}})$$

where t is the contact time at which all the resonances have become fully magnetized; λ is $T_{1\rho H}/T_{SiH}$.[26] Typically, contact times between 3 and 5 ms afforded the maximum magnetization of all three T^1, T^2, and T^3 silicons. The peak areas were corrected by normalizing the peak areas using the cross polarization efficiencies for each silicon species. The corrected areas were then used to calculate the degree of condensation in the xerogels (Table IV).

While the accuracy of quantitative ^{29}Si CP MAS–NMR is generally estimated to be around ±10%,[23,27] the peaks measured in this study are of the same silicon species (T^1, T^2, and T^3)

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(24) Klemperer, W. G.; Mainz, V. V.; Millar, D. M. *Better Ceramics through Chemistry II. Materials Research Society Symposium Proceedings* 73; Brinker, C. J., Clark, D. E., Ulrich, D. R., Eds.; Materials Research Society: Pittsburgh, PA, 1986; p 15.

(25) T_{SiH} and $T_{1\rho H}$ were determined from a double exponential fit of the intensity as a function of contact time from the contact time studies. Mehring, M. In *Principles of High Resolution NMR in Solids*, 2nd ed.; Springer: Berlin, 1983.

(26) Mehring, M. In *Principles of High Resolution NMR in Solids*, 2nd ed.; Springer: Berlin, 1983; p 153.

(27) Personal communication, Charles Bronnimann, NSF Regional NMR Center, Colorado State University, 1990.

measured in class of closely related materials. It is likely, therefore, that any errors in quantifying the areas of the silicon resonances will be consistent through the entire series allowing the *trends* in the degree of condensation to be portrayed with some accuracy. The degree of condensation in aryl-bridged polysilsesquioxanes (Table IV) ranges between 55.1% for **X-3-A** prepared by acid catalysis to 78.9% for **X-3-B** prepared by base-catalyzed polymerization. Xerogels prepared with acid appear to have a lower degree of condensation (63.7–68.1%) than those prepared with base (71.2 79.8%). The degrees of condensation reported for **X-1b-A** and **X-1b-B** were calculated using areas corrected with the cross polarization efficiencies from **X-1-C**. The two samples were identical save **X-1b-B** which had been dried at 100 °C under vacuum (0.01 mmHg) for 24 h. Surprisingly, only a negligible increase in the degree of condensation was observed. It may be that the silanols are too isolated to react in the matrix. Additional silanol groups probably lie on the extensive surface of the xerogel.[28]

Fluorescence Spectroscopy. The origin of the intense red color in the anthracene-bridged gel (X-4-B) was investigated using fluorescence spectroscopy. The excitation spectrum of the monomer **4** (10^{-4} M) in THF revealed an absorption maximum at 395 nm with vibrational fine structure and a mirror-image emission band with a maximum at 440 nm (Figure 10a). While the dilute solution of **4** fluoresced violet, the neat monomer or concentrated solutions appeared yellow-green ($l_{\max}$ = 550–600 nm) due to excimer formation.[29] It is not unreasonable to propose that excimer formation may also be occurring in the solid 9,10-anthracene-bridged polysilsesquioxanes. The fluorescence spectrum of the dry anthracene-bridged xerogel (**X-4-B**, Figure 10b) revealed significant red-shift of the emission maximum to 500 nm, enough to make the gel blue-green but not red. There may, however, be a contribution to the red color from the long bathochromic tail of the emission band. The copolymers of **4** with TEOS or **1** exhibit fluorescence spectra without the pronounced red shift of the emission band (Figure 10c). Instead the spectra of the amber xerogels appear similar to that of the monomer **4** in dilute solution.

Thermal Analysis. Differential scanning calorimetry (DSC) and thermal gravimetric analysis of the aryl-bridged polysilsesquioxanes demonstrated relatively high thermal stability with degradation of the material beginning above 400 °C in air.[30] However, a significant fraction of carbon remained in the materials when heated above 1000 °C indicating potential for these materials as silicon carbide precursors. The ethynyl-bridged xerogels (**X-5-A** and **-B**) began decomposition at 100 °C. Thermal analysis also revealed significant amounts of adsorbed moisture, and an exothermic loss of mass between 200 and 250 °C attributed to continuing condensation reactions in the network material. Thermal treatment of the bridged polysilsesquioxanes at 250 °C would be expected to cure the material by facilitating the reaction between free silanols without causing material degradation.

Conclusion

Molecular building blocks (**1–5**) for a new class of hybrid organic–inorganic network materials have been prepared. Aryl- and ethynyl-bridged polysilsesquioxanes were synthesized from the hydrolysis and condensation of these building blocks. The aryl bridges used in the study included those with different lengths such as the phenyl, biphenyl, and terphenyl groups. The insoluble and intractable materials were characterized using methods including gas sorption porosimetry, electron microscopy, fluorescence, and ^{13}C and ^{29}Si CP MAS-NMR spectroscopy. While MAS and CP MAS ^{29}Si NMR have been applied to quantify the degree of condensation in polysiloxane resins,[23,27] to our knowledge, no one has previously applied solid state ^{13}C NMR to gauge the degree of hydrolysis in polysiloxane resins.

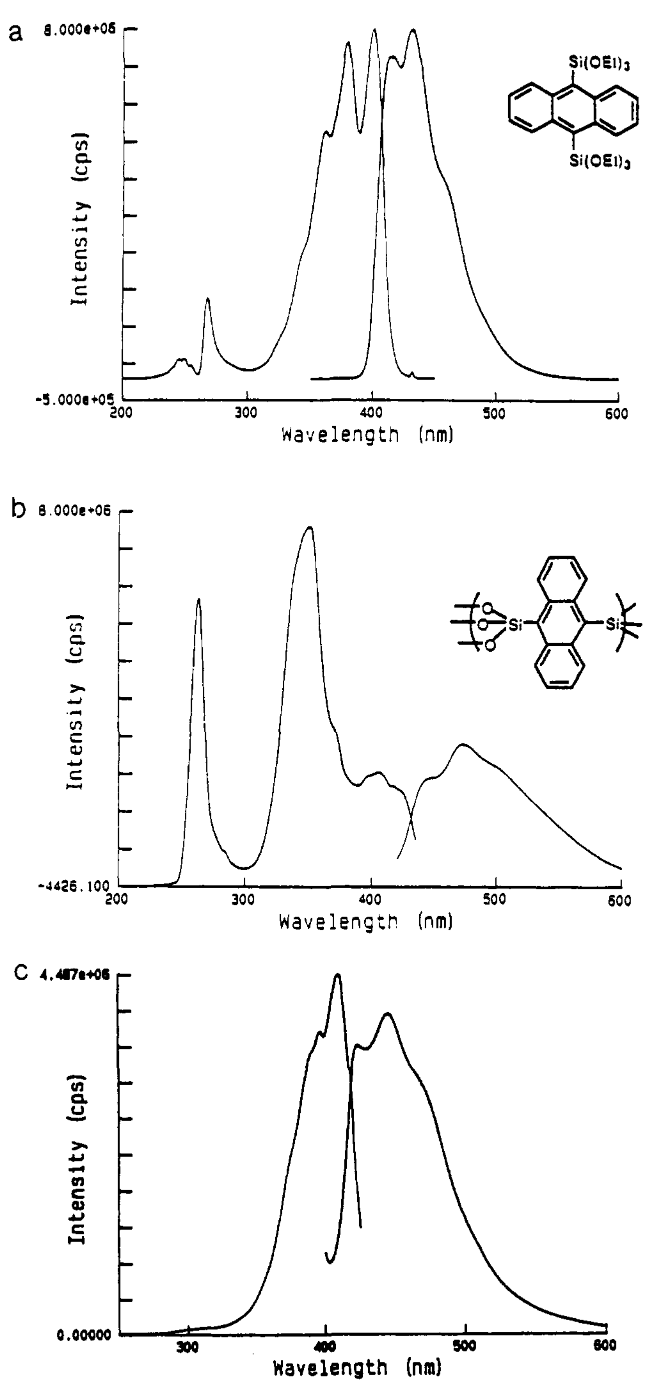

Figure 10. Fluorescence emission and excitation spectra of (a) 9,10-bis(triethoxysilyl)anthracene (**4**), (b) anthracene-bridged polysilsesquioxane (**X-4-B**), and (c) copolymer of bis(triethoxysilyl)benzene and **4** (500:1).

The aryl bridges were found, with only a few exceptions, to withstand the polymerization conditions to afford network polymers that gelled at concentrations as low as 0.20 M. The ethynyl bridge was found to be somewhat less stable toward Si–C cleavage under sol–gel conditions, thus, polysilsesquioxane materials with mixed ethynyl-bridged and terminal ethynylpolysilsesquioxanes were obtained from both base- and acid-catalyzed polymerizations of bis(triethoxysilyl)ethyne.

Polymerizations culminated in formation of transparent gels that were dried to afford glasslike xerogels. The aryl-bridged xerogels could be prepared in monolithic forms, coatings or fibers.

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(28) Silica gels have been shown to possess significant populations of surface silanols (Q^2 and Q^3) by ^{29}Si CP MAS-NMR: Maciel, G. E.; Sindorf, D. W. *J. Am. Chem. Soc.* **1983**, *106*, 1485.

(29) Coffey, S.; Van Alphen, J. In *Chemistry of Carbon Compounds*; Rodd, E. H., Ed.; Elsevier Publishing Co.: Amsterdam, 1956; Vol. IIIB, p 1361. Guillet, J. In *Polymer Photophysics and Photochemistry*; Cambridge University Press: Cambridge, 1985; pp 141–194.

(30) Fox, J. R.; White, D. A.; Oleff, S. M.; Boyer, R. D.; Budinger, P. A. *Better Ceramics through Chemistry II*. In *Materials Research Society Symposium Proceedings* 73; Brinker, C. J., Clark, D. E., Ulrich, D. R., Eds.; Materials Research Society: Pittsburgh, PA, 1986; p 395. *Adv. Ceramic Mater.* **1987**, *2*, 45.

The aryl-bridged polysilsesquioxanes were typically microporous materials with surface areas as high as 1000 m^2/g. Bridged xerogels prepared by both acidic and basic catalysts appear to be composed of aggregated spherical particles between 50 and 80 nm in diameter. These particles, in turn, appear to be composed of smaller very fine grained particles (2.5–5.0 nm in diameter). The mean pore diameters in the bridged xerogels were unaffected by the length of the aryl spacers, providing evidence for the hypothesis that porosity in amorphous silicates and silicate-like materials arises from macromolecular phenomena such as packing of particles and fractal topographies rather than silicon–silicon distances in a polymeric network.

Polysilsesquioxanes with rigid bridging groups form more readily than simple polysilsesquioxanes. The bridged polymers form highly condensed networks with the bridging group securely bound by two covalent bonds, minimizing loss of the bridging moieties if hydrolytic cleavage of the Si–C bond occurs. In this fashion, a variety of materials with unique properties and applications are possible simply by changing the identity of the bridging group. The synthesis of additional representatives of these new family of materials and a study of their properties and applications will be the subject of future reports.

Experimental Section

Instrumentation. ^1H nuclear magnetic resonance (NMR) spectra were recorded on a Bruker WM-250 (250 MHz), General Electric QE-300 (300 MHz), QN-500 (500 MHz), or Omega-500 (500 MHz) spectrometers. The chemical shifts are reported on the scale in ppm with either tetramethylsilane (0.00 ppm), $CHCl_3$ (7.26 ppm), or DMSO (2.49 ppm) as internal standards. ^{13}C NMR were recorded with QE 300 (75.4 MHz), QN-500, and Omega-500 (125.5 MHz) spectrometers with $CDCl_3$ (77.0 ppm) and DMSO-d_6 (39.6 ppm) as internal standards. ^{29}Si NMR were obtained with the QN-500 and Omega-500 instruments (99.34 MHz) with tetramethylsilane (0.00 ppm) as internal standard. Infrared spectra were obtained with an Analect RFX-40 FTIR spectrometer.

Low resolution mass spectra were acquired on a Finnigan Model 4000 GC/MS/DS and are reported as mass/charge (m/z) using chemical ionization (CI, isobutane) or electron ionization (EI, 70 eV) with percent relative abundance. High resolution mass spectra were obtained with a VG 7070e high resolution mass spectrometer.

Monomers. ***General Procedures.*** Tetraethoxysilane was obtained from Petrarch and was distilled from CaH_2 before use. 1,4-Dibromobenzene, 4,4′-dibromodiphenyl, anthracene, and terphenyl were purchased from Aldrich Chemical Company and used as received. THF and diethyl ether were distilled from potassium–benzophenone ketyl, and hexane was distilled from CaH_2. Ethanol was dried with Na and distilled from NaOEt. 4,4″-Dibromoterphenyl was prepared from *p*-terphenyl (Aldrich) and bromine in glacial acetic acid.[11a] 9,10-Dibromoanthracene was prepared from anthracene and bromine in carbon tetrachloride.[11b]

1,4-Bis(triethoxysilyl)benzene (1). To a mixture of magnesium turnings (15.0 g) and TEOS (450 mL, 2 mols) in THF (300 mL) under nitrogen was added a small crystal of iodine, and the mixture was brought to reflux. A solution of 1,4-dibromobenzene (48 g, 20.4 mmol) in THF (100 mL) was added dropwise over 2 h. Within 30 min of initiating the addition, the reaction became mildly exothermic. The reaction mixture was kept at reflux 1 h after the completion of the addition of dibromide. The grey-green mixture was allowed to cool to room temperature before the THF was removed in vacuo. Hexane (200 mL, distilled off CaH_2) was added to precipitate any remaining magnesium salts in solution, and the mixture was quickly filtered under nitrogen to afford a clear, light brown solution. Hexane was removed in vacuo, and the remaining TEOS was distilled off in vacuo leaving a brown oil. The oil was distilled (0.2 mmHg, 130–5 °C) to give a clear colorless oil (**1**, 42 g, 55%); ^1H NMR (300 MHz, $CDCl_3$) δ 7.63 (s, 4 H, ArH), 3.82 (q, 12 H, J = 7.12 Hz, $\mathrm{OC}H_2\mathrm{CH}_3$), 1.19 (t, 18 H, J = 7.11 Hz, $\mathrm{OCH_2C}H_3$); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 134.36, 133.45, 59.09, 18.56; ^{29}Si NMR (MHz, $CDCl_3$) δ −57.72; IR (film on NaCl) 3058, 2976, 2886, 1391, 1168, 1147, 1102, 1079, 961, 778, 706 cm^{-1}; low resolution mass spectrum (EI, 70 eV) m/z 402 (M^+), 357, 329, 297, 285, 147, 119, 107, 100, 91, 79; high resolution mass spectrum (EI, 30 eV) calcd for $C_{18}H_{34}O_6Si_2$ 402.1890, found 402.1909.

4,4′-Bis(triethoxysilyl)biphenyl (2). A solution of 4,4′-dibromobiphenyl (100 g, 0.32 mol) in THF (750 mL) and TEOS (500 mL, 2.24 mol) was added to magnesium turnings (30 g, 1.25 mol), and the mixture was kept at reflux (75 °C) for 5 days. The resulting turbid, grey-green mixtures was worked up as with **1** to afford a viscous brown oil. Distillation (0.3 mmHg, 203–6 °C) gave a clear colorless oil **2** (52.68 g, 34%): ^1H NMR (250 MHz, $CDCl_3$) δ 7.70 (dd, 8 H, J = 8.14, 33.8 Hz, ArH), 3.90 (q, 12 H, J = 6.96 Hz, $\mathrm{OC}H_2\mathrm{CH}_3$), 1.26 (t, 18 H, J = 6.95 Hz, $\mathrm{OCH_2C}H_3$); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 143.07, 135.68, 130.28, 126.97, 59.14, 18.63; ^{29}Si NMR (99.34 MHz, $CDCl_3$) δ −58.02; IR (film on NaCl) 2975, 2927, 2886, 1600, 1390, 1167, 1131, 1102, 1079, 1004, 961, 811, 780, 736 cm^{-1}; low resolution mass spectrum (EI, 70 eV, relative percent) m/z 478, 433, 405, 361, 194, 181, 163, 147, 138, 119; high resolution mass spectrum (EI, 30 eV) calcd for $C_{24}H_{38}O_6Si_2$ 478.2207, found 478.2212.

4,4″-Bis(triethoxysilyl)terphenyl (3). A suspension of 4,4″-dibromoterphenyl (3.10 g, 8.0 mmol) in diethyl ether (130 mL) was cooled to −78 °C with an acetone–dry ice bath. With the addition of *tert*-butyllithium (19.0 mL, 1.68 M in hexanes, 4.0 equiv) the white suspension turned yellow. After 4 h, the mixture was warmed to room temperature for 1 h. The mixture was cooled to −78 °C again, before adding chlorotriethoxysilane (3.92 mL, 2.5 equiv) by syringe. After 30 min, the reaction was allowed to warm to room temperature. The mixture was filtered, and the diethyl ether and residual chlorotriethoxysilane were removed in vacuo. The resulting brown oil was distilled (bulb-to-bulb, 235 °C, 0.025 mmHg) to afford a clear colorless oil which solidified into a white solid **3** (1.04 g, 23.5%): ^1H NMR (500 MHz, $CDCl_3$) δ 7.70 (m, 12 H, ArH), 3.93 (q, J = 6.96 Hz, 12 H, $\mathrm{OC}H_2\mathrm{CH}_3$), 1.30 (t, J = 6.97 Hz, 18H, $\mathrm{OCH_2C}H_3$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.78, 140.49, 135.76, 130.16, 127.95, 126.85, 59.19, 18.66; ^{29}Si NMR (99.34 MHz, $CDCl_3$) δ −57.56; IR (film on NaCl) 3028.7, 2974.9, 2926.9, 2888.0, 1600.8, 1484.8, 1390.1, 1166.9, 1129.6, 1100.9, 1078.0, 960.57, 810.31, 782.54, 688.9 cm^{-1}; low resolution mass spectrum (EI, 70 eV, relative percent) 554 (M^+, 0.17), 509 (0.17), 347 (0.5), 291 (0.32), 232 (3.3), 176 (19.4), 168 (19.6), 147 (100), 119 (56), 103 (21), 91 (16), 79 (28), 73 (12), 63 (12); high resolution mass spectrum (EI, 30 eV) calcd for $C_{30}H_{42}O_6Si_2$ 554.2520, found 554.2530.

9,10-Bis(triethoxysilyl)anthracene (4). To a slurry of 9,10-dibromoanthracene (13.08 g, 38.9 mmol) in THF (250 mL) at −78 °C under nitrogen was added *tert*-butyllithium (156 mmol, 106 mL) by syringe. After 30 min at −78 °C, the slurry was warmed to room temperature for 2 h. Then the mixture was cooled to −78 °C, and chlorotriethoxysilane (15.5 g, 78 mmol) was added by syringe. The slurry quickly dissolved to a dark, clear solution. The THF was removed in vacuo, and hexane was added to precipitate out any residual lithium salts. The solution was removed by cannula from the salts, which were washed with hexane (2×, 50 mL). The hexane was removed in vacuo, and the residual yellow oil was distilled (2×, 166–174 °C, 0.80 mmHg) to afford a yellow-green solid (**4**, 6.29 g, mp 56–8 °C, 32%): ^1H NMR (250 MHz, $CDCl_3$) δ 8.98 (dd, J = 3.3, 7.01 Hz, 4 H, ArH), 7.48 (dd, J = 3.4, 7.00 Hz, 4 H, ArH), 3.92 (q, J = 6.9 Hz, 12 H, $\mathrm{OCH2CH_3}$), 1.28 (t, J = 7.03, 18H, $\mathrm{OCH_2CH3}$); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 137.75, 131.46, 129.96, 125.26, 59.16, 18.56; ^{29}Si NMR (99.34 MHz, $CDCl_3$) δ −55.0; IR (film on NaCl) 3077, 2976, 2926, 2918, 1636, 1517; 1442, 1390, 1174, 1164. 1075, 1033, 965.4, 843.9, 786.6, 718.3, 465.4 cm^{-1}; low resolution mass spectrum (EI, 70 eV, relative percent) m/z 502 (M^+, 77), 205 (59), 178 (78), 163 (100), 147 (19), 135 (16), 119 (51), 107 (19), 91 (21), 79 (56); high resolution mass spectrum (EI, 30 eV) calcd for $C_{26}H_{38}O_6Si_2$ 502.2207, found 502.2206.

Bis(triethoxysilyl)ethyne (5).[9] To a solution of chlorotriethoxysilane (18.7 g, 94.2 mmol) in pyridine (125 mL) was added a slurry of sodium acetylide (2.3 g, 0.52 equiv) in xylenes (13.0 g). The reaction mixture exothermed sufficiently to raise the temperature to 60 °C for 5 min. Heat was applied to maintain the reaction at 60 °C for 2 h. Upon cooling, the pyridine was removed in vacuo, and dry hexane was added to precipitate salts. The solution and two hexane washes (50 mL) were decanted from the salts, and the hexane and xylenes were removed in vacuo leaving a brown oil. Distillation (95 °C, 0.05 mmHg) afforded a clear colorless oil (3.10 g, 18.8%): ^1H NMR (500 MHz, $CDCl_3$) δ 3.84 (q, J = 7.01 Hz, 12 H, $\mathrm{OC}H_2\mathrm{CH}_3$), 1.22 (t, J = 7.00 Hz, 18 H, $\mathrm{OCH_2C}H_3$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 104.28, 59.52, 18.32; ^{29}Si NMR (99.34 MHz, $CDCl_3$) δ −75.69; IR (film on NaCl) 2978, 2929, 2891, 2046, 1444, 1392, 1296, 1169, 1103, 1082, 968.1, 800.3 cm^{-1}; low resolution mass spectrum (CI, isobutane, relative percent) m/z 352 (M + 2, 12.9), 351 (M + 1, 100), 331 (0.4), 189 (11), 181 (13), 125 (2), 109 (3), 107 (5), 101 (2); high resolution mass spectrum (CI, isobutane) calcd for $C_{14}H_{30}O_6Si_2$ 350.1581, found 350.1568.

Sol–Gel Processing. *A.* ***General Polymerization Procedure.*** Unless indicated otherwise, polymerization reactions were performed in THF. The solutions were prepared by introducing the ethoxysilyl monomer into a 25-mL volumetric flask. THF (10–12 mL) was added, and the solution was thoroughly mixed. The aqueous (acid or base) catalyst was premixed with THF (10 mL) and added in one portion to the volumetric. Aqueous acid (0.25–1.0 mL, 1 N) was miscible with the THF solution of monomers. Aqueous NH_3 (1–2 mL, 15 M) was immiscible with THF. Polymerizations using concentrated NH_3 as catalyst required up to 20 min of shaking before the aqueous phase dissolved. Additional THF was added to bring the solution to 25 mL. The solution was vigorously mixed before being poured into a 100-mL polyethylene bottle. The top of the bottle was closed, and the solution was allowed to stand at room temperature. Gelation was determined by the point at which the solution quit flowing as a liquid. In most cases the gel transitions were well defined with the solution becoming viscous and then "freezing" into gel over a span of a few minutes.

B. Gel Processing. Once gelation had occurred, the gel was allowed to cure or stand at room temperature for an additional 48 h. During this time, the gels shrank slightly, pulling away intact from the walls of the polyethylene bottle. Polymerizations run in glass vials clung to the walls of the vial causing fractures to form. After curing, the polyethylene bottles were cut open, and the gel was removed intact for further processing.

The bridged polysilsesquioxane gels were solvent processed in order to minimize capillary stress and fracturing during drying. The gels were solvent processed by immersing the gel into a series of solvents with decreasing solvent dielectrics beginning with THF and ending with 1,1,2-trichloro-1,2,2-trifluoroethane. The gels were placed into a fine fritted glass funnel (60 mL) filled with THF. The solvent was allowed to slowly flow through frit at such a rate that 200 mL of the solvent passed over the gel in a period of 1 h. The gels were washed with the following series of solvents (ACS reagent grade, Fischer): THF, dichloromethane, chloroform, diethyl ether, toluene, carbon tetrachloride, and 1,1,2-trichloro-1,2,2-trifluoroethane. The gel was allowed to air dry for 24 h, before either drying intact under vacuum or crushing and drying under vacuum.

C. Materials Characterization. ^{13}C cross polarized magic angle spinning (CP MAS) NMR were performed by Colorado State University's NSF Regional NMR Facility on a Nicolet NT-150 spectrometer at 37.74 MHz. Interrupted decoupling (100 ms) experiments were performed on the Nicolet NT-150 at 37.74 MHz. ^{29}Si CP MAS–NMR were performed on the Nicolet NT-150 at 29.81 MHz and on a Nicolet NT-200 with a home-built CP MAS probe at 39.74 MHz. Spinning rates were between 3.5 and 4 kHz. The ^{29}Si CP MAS–NMR spectra were obtained with contact times between 3.0 and 5.0 ms. The ^{29}Si CP MAS–NMR of **X-1b-A** and **X-1b-B** were run on a Bruker instrument at 59.60 MHz.

Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN. Scanning electrons micrographs (SEM) and transmission electron micrographs (TEM) were obtained at the UCI Electron Microscope Facility. Nitrogen sorption analyses were performed by Micromeretics Instrument Co., Norcross, GA; Coulter Electronics, Hileah, FL; Du Pont Analytical Center, Wilmington, DE. Argon sorption analyses were performed by Micromeretics, Coulter Electronics, and DuPont. Surface areas were calaculated with the BET equation ($0.02 < p/p_0 < 0.30$). Thermal gravimetric and differential scanning calorimetry analyses were run on a Du Pont Instruments 2000 system at 10 °C/min ramps under N_2 (80 mL/min).

D. Material Syntheses. **1,4-Phenyl-Bridged Polysilsesquioxane (X-1-A).** A solution of **1** (3.01 g, 7.45 mmol) and aqueous HCl (0.80 mL) in THF (37 mL) was prepared in a polyethylene bottle. The gel set within 24 h. After curing for 48 h, the gel was solvent processed. The transparent gel with blue cast was air dried for 24 h, dried under vacuum for 24 h, ground, and dried under dynamic vacuum for 24 h (1.70 g, 127%): ^{13}C CP MAS–NMR (37.74 MHz) δ 230 (ssb), 133.6 (Ar), 68.3 (THF), 56.4 ($\mathrm{O}\mathit{C}\mathrm{H_2CH_3}$), 37.28 (ssb), 25.4 (THF), 17.61 ($\mathrm{OCH_2}\mathit{C}\mathrm{H_3}$); ^{13}C CP MAS–NMR (37.74 MHz, interrupted decoupling) δ 230.9 (ssb), 134.1 (Ar), 67.8 (THF), 37.8 (ssb), 25.4 (THF), 17.1 ($\mathrm{CH_2CH_3}$); ^{29}Si CP MAS–NMR (39.74 MHz) δ −58 (T^1), −68 (T^2), −76 (T^3); IR (KBr) 3430, 3061, 2981, 1635, 1385, 1154, 1092, 1019, 913.8, 808.5, 661.9, 522.3 cm^{-1}. Elemental anal. Calcd for $C_6H_4Si_2O_3$: C, 39.98; H, 2.24; Si, 31.16. Found: C, 36.02; H, 3.05; Si, 28.33.

1,4-Phenyl-Bridged Polysilsesquioxane (X-1-B). A solution of **1** (4.02 g, 10.0 mmol) and aqueous HCl (1.08 mL, 1 N) in ethanol (25.00 mL) was prepared in a 25-mL volumetric and transferred to a polyethylene bottle (100 mL). The solution became viscous within 24 h but took 96 h to gel. The gel was almost translucent blue from scattering. After solvent processing, air drying (48 h), and drying under vacuum (24 h), the gels were ground and dried under dynamic vacuum for 24 h (1.93 g, 107%): ^{1}H CRAMPS (187 MHz, BR-24) d 7.1 (ArH), 3.5 ($\mathrm{OC}\mathit{H}_2\mathrm{CH_3}$), 1.0 ($\mathrm{OCH_2C}\mathit{H}_3$); ^{1}H CRAMPS (187 MHz, interrupted decoupling) d 6.7 (ArH), 3.5 ($\mathrm{OC}\mathit{H}_2\mathrm{CH_3}$), 1.0 ($\mathrm{OCH_2C}\mathit{H}_3$); ^{13}C CP MAS–NMR (37.74 MHz) 237 (ssb), 134.27 (Ar), 59.56 ($\mathrm{O}\mathit{C}\mathrm{H_2CH_3}$), 31.82 (ssb), 17.52 ($\mathrm{OCH_2}\mathit{C}\mathrm{H_3}$); ^{29}Si CP MAS–NMR (39.74 MHz) d −59.6 (T^1), −68.3 (T^2), −75.1 (T^3); IR (KBr) 3420, 3062, 2979, 1635, 1385, 1259, 1155, 1092, 1020, 921.8, 526.5 cm^{-1}; Elemental Anal. Calcd for $C_6H_4Si_2O_3$: C, 39.98; H, 2.24; Si, 31.16. Found: C, 37.98; H, 4.52; Si, 26.37.

1,4-Phenyl-Bridged polysilsesquioxane (X-1-C). To a solution of **1** (2.01 g, 5.0 mmol) in THF (20 mL), NH_3 (1.9 mL, 15 M) was added, and the volume of the mixture was brought up to 25 mL. The mixture of aqueous NH_3 and THF were mixed for 30 min until a solution had formed. The solution formed a clear colorless gel after 5.5 h. The gel was cured for 48 h, solvent processed, and then air dried for 48 h. The gel was a transparent and colorless monolith. After drying overnight under vacuum, several cracks formed in the xerogel. Finally, the xerogel was ground into a powder and dried under vacuum (1–2 mmHg) at 100 °C for 4 h (0.86 g, 95%); ^{13}C CP MAS–NMR (37.74 MHz) δ 227.7 (ssb), 134.1 (Ar), 68.1 (THF), 42.2 (ssb), 25.5 (THF), −51.4 (ssb); ^{29}Si CP MAS–NMR (29.81 MHz) δ −61 (T^1), −71 (T^2), −79 (T^3); IR (KBr) 3429, 3072, 3024, 2977, 2925, 1728, 1602, 1385, 1138, 1003, 919.9, 808.0, 717.4, 516.8. Elemental Anal. Calcd for $C_6H_4Si_2O_3$: C, 39.98; H, 2.24; Si, 31.16. Found: C, 38.77; H, 3.19; Si, 23.37.

1,4-Phenyl-Bridged Polysilsesquioxane (X-1-D). In a similar manner, a 0.2 M solution **1** (16.18 g, 40.2 mmol) in THF was treated with aqueous NH_3 (15.2 mL, 15 M) leading to a gel in 3 h. After 2 days, the gel was crushed in H_2O (200 mL) and washed with H_2O (5 × 200 mL) and diethyl ether (3 × 150 mL). The gel was dried at 50 °C under vacuum (1 mmHg) for 2 days (7.93 g, 109%). Continued drying at 100 °C for 4 h under vacuum (1 mmHg) afforded 7.77 g (107%) of the xerogel: IR (KBr) 3430, 3062, 3026, 2979, 2929, 1635, 1385, 1259, 1155, 1091, 1020, 921.8, 526.5 cm^{-1}. Elemental Anal. Calcd for $C_6H_4Si_2O_3$: C, 39.98; H, 2.24; Si, 31.16. Found: C, 37.98, H, 4.52, Si, 26.37.

4,4′-Biphenyl-Bridged Polysilsesquioxane (X-2-A). A solution of **2** (2.00 g, 4.18 mmol) and aqueous HCl (0.45 mL, 1 N) in THF (20.0 mL) was prepared in a glass vial (25 mL). The clear yellow solution gelled within 1 h. After curing for 48 h, the gel was solvent processed and dried under vacuum for 24 h. The clear colorless xerogel had a volume of 3.45 mL. The hard gel was ground and dried under dynamic vacuum for 24 h (1.224 g, 114%, density = 0.354 g/mL): ^{1}H CRAMPS NMR (187 MHz, BR-24 pulse sequence) δ 6.9 (ArH), 3.55 ($\mathrm{OC}\mathit{H}_2\mathrm{CH_3}$), 1.40 ($\mathrm{OCH_2C}\mathit{H}_3$); ^{13}C CP MAS–NMR (37.74 MHz) δ 235 (ssb), 142.7 (Ar), 135.3 (Ar), 131.4 (Ar), 126.9 (Ar), 68.1 (THF), 60.3 ($\mathrm{O}\mathit{C}\mathrm{H_2CH_3}$), 42.6 (ssb), 38.9 (ssb), 34.8 (ssb), 31.3 (ssb), 25.8 (THF), 17.9 ($\mathrm{OCH_2}\mathit{C}\mathrm{H_3}$); ^{29}Si CP MAS–NMR (39.74 MHz) δ −59 (T^1), −65 (T^2), −77 (T^3); IR (KBr) 3400, 3021, 1602, 1139, 1168, 906.7, 807.1, 512.3 cm^{-1}. Elemental Anal. Calcd for $C_{12}H_8Si_2O_3$: C, 56.22; H, 3.14; Si, 21.91. Found: C, 50.10; H, 4.52; Si, 18.58.

4,4′-Biphenyl-Bridged Polysilsesquioxane (X-2-B). A solution of **2** (4.78 g, 10.0 mmol) and aqueous HCl (1.08 mL, 1 N) in ethanol (25.0 mL) gelled in 80 min. The gel was aged for 48 h before solvent processing. The xerogel was air dried for 48 h, ground, and dried under dynamic vacuum for 24 h (2.92 g, 114%): ^{13}C CP MAS–NMR (37.74 MHz) δ 230 (ssb), 142.8 (Ar), 135.1 (Ar), 131.5 (Ar), 126.3 (Ar), 59.5 ($\mathrm{O}\mathit{C}\mathrm{H_2CH_3}$), 39.0 (ssb), 17.1 ($\mathrm{OCH_2}\mathit{C}\mathrm{H_3}$); ^{13}C CP MAS–NMR (37.74 MHz, interrupted decoupling) δ 235.5 (ssb), 224.1 (ssb), 142.9 (Ar), 131.5 (Ar), 68.3 (THF), 58.5 ($\mathrm{O}\mathit{C}\mathrm{H_2CH_3}$), 50.2 (ssb), 39.9 (ssb), 25.9 (THF), 21.2, 17.6 ($\mathrm{OCH_2}\mathit{C}\mathrm{H_3}$); ^{29}Si CP MAS–NMR (39.74 MHz) d −58.7 (T^1), −67.1 (T^2), −74.8 (T^3); IR (KBr) 3415, 3024, 2974, 1602, 1385, 1138, 1051, 1003, 919.9, 808.0, 717.4, 514.9 cm^{-1}. Elemental Anal. Calcd for $C_{12}H_8Si_2O_3$: C, 56.22; H, 3.14; Si, 21.91. Found: C, 47.90; H, 4.54; Si, 16.20.

4,4′-Biphenyl-Bridged Polysilsesquioxane (X-2-C). As in the preparation of **X-1-C**, a mixture of **2** (2.38 g, 5.00 mmol) with NH_3 (1.9 mL, 15 M) in THF (25 mL) was mixed for 20 min until a homogeneous solution formed. Gelation occurred after 3 h. The clear colorless gel was cured for 48 h, processed by solvent series, and air dried for 48 h. The resulting monolith was dried overnight under vacuum and occupied only. The gel was ground and dried at 100 °C under vacuum (1 mmHg) for 4 h (1.25 g, 98%): IR (KBr) 3433, 3024, 1631, 1603, 1138, 1101, 1003, 919.9, 808.3, 719.3, 514.9 cm^{-1}. Elemental Anal. Calcd for $C_{12}H_8Si_2O_3$: C, 56.22; H, 3.14; Si, 21.91. Found: C, 53.93; H, 3.09; Si, 16.98.

4,4″-Terphenyl-Bridged Polysilsesquioxane (X-3-A). A solution of **3** (2.54 g, 9.2 mmol) and aqueous HCl (1.0 mL, 1 N) was placed in a polyethylene bottle. Gelation occurred after 24 h. The brittle yellow gel was cured for 48 h before solvent processing. The gel was dried for 18 h, before grinding and drying under dynamic vacuum for 24 h (1.61 g, 106%): ^{13}C CP MAS–NMR (37.74 MHz) δ 232 (ssb), 226 (ssb), 219 (ssb), 140.6 (Ar), 135.5 (Ar), 127.5 (Ar), 68.0 (THF), 59.4 ($\mathrm{O}\mathit{C}\mathrm{H_2CH_3}$), 51.9, 45.0 (ssb), 36.9 (ssb), 29.0 (ssb), 25.5 (THF), 18.4 ($\mathrm{OCH_2}\mathit{C}\mathrm{H_3}$); ^{13}C CP MAS–NMR (37.74 MHz, interrupted decoupling) δ 140.6, 135.5, 130.5, 128.7, 18.5; ^{29}Si CP MAS–NMR (39.74 MHz) δ −30.1, −59.7 (T^1), −67.8 (T^2), −76.3 (T^3), −92.1 (Q), −99.0 (Q); IR (KBr) 3420, 3062, 3026, 2923, 2852, 1601, 1485, 1385, 1261, 1132, 1095, 1003, 806.1, 757.9, 698.1, 540.0 cm^{-1}.

4,4″-Terphenyl-Bridged Polysilsesquioxane (X-3-B). As in the previous experiment, 4,4′-bis(triethoxysilyl)terphenyl **3** (0.89 g, 1.6 mmol) was mixed with THF (mL) and concentrated NH_3 (0.30 mL, 15 M). Gelation occurred after 6.25 h. the gel was blue on reflection and yellow on transmission. After 2 days of curing, the gel was solvent processed and air dried for 2 days, before grinding and drying under vacuum (<1 mmHg) for 4 h at 50 °C (0.57 g, 107%): ^{13}C CP MAS–NMR (37.74 MHz) δ 235 (ssb), 220 (ssb), 140.6 (Ar), 135.1 (Ar), 126.6 (Ar), 59.0 (OCH_2CH_3), 43–35 (ssb), 17.3 (OCH_2CH_3); ^{29}Si CP MAS–NMR (29.81 MHz) δ –61.9 (T^1), –70.6 (T^2), –79.0 (T^3); IR (KBr) 3442, 3072, 3028, 2976, 2927, 1604, 1489, 1392, 1136, 1076, 1003, 806.1, 757.9, 541.9 cm^{-1}. Elemental Anal. Calcd for $C_{18}H_{12}O_3Si_2$: C, 64.68; H, 3.62; Si, 17.35. Found: C, 61.23; H, 4.58; Si, 15.22.

9,10-Anthracene-Bridged Polysilsesquioxane (X-4-A). To **4** (2.50 g, 4.50 mmol) in THF (10 mL), a solution of aqueous HCl (0.25 mL, 1.0 N) in THF (8 mL) was added. The volume of the yellow-green solution was brought to 25 mL with additional THF. After thoroughly mixing, the solution was allowed to stand for 6 days without gelation. Then the solution was heated to 50 °C for 24 h and again without gelation. Aqueous KOH (1 N) was added dropwise to the solution resulting in the immediate formation of an orange-brown precipitate. The solid was collected by filtration, washed with diethyl ether (100 mL), and dried (1.02 g, 73%): IR (KBr) 3446, 1678, 1651, 1643, 1633, 1593, 1090, 960.4, 466.7 cm^{-1}. Elemental Anal. Calcd for $C_{14}H_8O_3Si_2$: C, 59.97; H, 2.88; Si, 20.03. Found: C, 16.97; H, 0.91; Si, 27.54.

9,10-Anthracene-Bridged Polysilsesquioxane (X-4-**B**). To **4** (2.50 g, 4.50 mmol) in THF (10 mL), a solution of aqueous NaOH (0.25 mL, 1 N) in THF (8 mL) was added with stirring. The solution was brought to 25 mL with additional THF and thoroughly stirred. After 6 days, no gel had formed, so the solution was heated to 50 °C. A red gel formed after 23 h. The gel was aged for 48 h, solvent processed, and air dried for 48 h. Next, the dark red gel was dried under vacuum for 24 h and ground into an orange powder. The powder was dried under dynamic vacuum for 18 h at room temperature (1.70 g, 122%): ^{13}C CP MAS–NMR (37.74 MHz) δ 231.9 (ssb), 225.2 (ssb), 220.0 (ssb), 137.2 (Ar), 129.4 (Ar), 125.3 (Ar), 66.3 (THF), 59.0 (OCH_2CH_3), 41.4 (ssb), 34.2 (ssb), 29.5 (ssb), 24.9 (THF), 20.7, 18.1 (OCH_2CH_3); ^{13}C CP MAS–NMR (37.74 MHz, interrupted decoupling) δ 231.9 (ssb), 136.6, 131.0, 129.4, 59.0, 41.9 (ssb), 18.1; ^{29}Si CP MAS–NMR (39.74 MHz) δ –54.6 (T^1), –66.0 (T^2), –75.8 (T^3), –91.0 (Q), –98.8 (Q), –105.7 (Q); IR (KBr) 3427, 3076, 2972, 2925, 2893, 1591, 1444, 1334, 1313, 1286, 1074, 964.3, 937.2, 750.2, 700.0 cm^{-1}. Elemental Anal. Calcd for $C_{14}H_8O_3Si_2$: C, 59.97; H, 2.88; Si, 20.03. Found: C, 56.68; H, 2.86; Si, 15.35.

Ethynyl-Bridged Polysilsesquioxane (X-5-A). A solution of **5** (1.40 g, 4.0 mmol) and aqueous HCl (0.288 mL, 0.1 N) in THF (10 mL) was placed in a closed vial. After 20 days no gel had formed so the ^{29}Si NMR spectrum was recorded: ^{1}H NMR (500 MHz, THF-d_8) δ 3.74 (m, THF), 3.63 (q, 2 H, $\mathrm{OC}\mathit{H}_2\mathrm{CH_3}$), 1.90 (m, THF), 1.22 (t, 3 H, $\mathrm{OCH_2C}\mathit{H}_3$); ^{13}C NMR (75.4 MHz, THF) δ 108, 104, 67.9 (THF), 57.4, 26.0 (THF), 18.4; ^{29}Si NMR (99.35 MHz, THF) δ –83, –92. Gelation occurred after a total of 30 days. The gel was cured for 48 h, solvent processed, and dried under vacuum (1 mmHg) at 50 °C for 4 h (0.65 g, 130%): ^{13}C CP MAS NMR (37.74 MHz) δ 205 (ssb), 181 (ssb), 105.9, 97.0, 82.4, 68.2 (THF), 60.0 ($\mathrm{O}\mathit{C}\mathrm{H_2CH_3}$), 32.4, 26.9 (THF), 18.2 ($\mathrm{OCH_2}\mathit{C}\mathrm{H_3}$), 15.9, 4.7 (ssb); ^{13}C CP MAS–NMR (37.74 MHz, interrupted decoupling) δ 202 (ssb), 180 (ssb), 105.0, 67.0 (THF), 59.4 ($\mathrm{O}\mathit{C}\mathrm{H_2CH_3}$), 31.8, 18.5 ($\mathrm{OCH_2}\mathit{C}\mathrm{H_3}$), 14.7, 5.9 (ssb); ^{29}Si CP MAS–NMR (29.81 MHz) δ –85, –93, –105; IR (KBr) 3449, 2985, 2056, 1078, 821.5 cm^{-1}. Elemental Anal. Calcd for $C_2Si_2O_3$: C, 18.74; Si, 43.82. Found: C, 15.96; H, 1.82; Si, 32.88.

Ethynyl-Bridged Polysilsesquioxane (X-5-B). A solution of **5** (1.40 g, 4.0 mmol) and aqueous NH_3 (0.224 mL, 0.1 N) in THF (10 mL) was kept closed in a vial. After 1 month, the solution gelled and was processed in an identical manner to **X-5**-A (0.64 g, 128%): ^{13}C CP MAS–NMR (37.74 MHz) δ 210 (ssb), 180 (ssb), 106.6, 97.6, 83.2, 68.0 (THF), 59.8 ($\mathrm{O}\mathit{C}\mathrm{H_2CH_3}$), 31.3, 26.8 (THF), 18.0 ($\mathrm{OCH_2}\mathit{C}\mathrm{H_3}$); ^{29}Si CP MAS–NMR (29.81 MHz) δ –93, –102; IR (KBr) 3436, 2060, 1631, 1074, 943.0, 833.1, 453.2 cm^{-1}. Elemental Anal. Calcd for $C_2Si_2O_3$: C, 18.74; Si, 43.82. Found: C, 14.75; H, 1.95; Si, 34.37.

Preparation of Monolithic Xerogels. *A. **Drying Control Chemical Agents***. **1,4-Phenyl-Bridged Polysilsesquioxane** (X-1-E). A solution of **1** (4.02 g, 10.0 mmol), formamide (10 mL), and aqueous HCl (0.3 mL, 1 N) in ethanol (25 mL) was prepared and found to gel in 5 h. The gel was allowed to air dry over 3 weeks to afford a monolithic xerogel.

B. Monolithic Silica Gel. A solution of tetraethoxysilane (10 mL, 77 mmol), formamide (10 mL), and aqueous HCl (1 mL, 1 N) in ethanol (25 mL) formed a gel after 4 days. The gel was allowed to slowly dry over 1 month to a monolithic xerogel.

*C. **Fluorescent Copolymers of 9,10-Bis**(**triethoxysilyl**)**anthracene** (4) **with Ethoxysilane Monomers***. **X-1-co-4 (500:1)**. Two identical solutions of **1** (4.03 g, 10.0 mmol), aqueous HCl (0.54 mL, 1.0 M), and **4** (10 mg, 0.02 mmol) in THF gelled in 25.5 h. The gels were slowly air dried to afford transparent, amber monolithic xerogels. One xerogel was ground and dried under vacuum (<1 mmHg) at 100 °C for 4 h: IR (KBr) 3440, 1734, 1635, 1384, 1086, 948.8, 468.6 cm^{-1}; fluorescence l_{emission} = 424, 445, 468 (shoulder) nm.

X-TEOS-co-4 (500:1). Aqueous HCl (1 N) was added dropwise to a solution of TEOS (50 mL, 257 mmol) and **4** (0.26 g, 0.51 mmol) in ethanol (60 mL) until pH 1 was reached. The solution was heated at reflux for 1 h, when the total volume was reduced to 50 mL. The solution was poured into three petri dishes and allowed to gel. The gels were crushed and washed with water and diethyl ether before drying at 100 °C under vacuum (1 mmHg). Fluorescence l_{emission} = 420, 432, 464 (shoulder) nm.

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Supplementary Material Available: A detailed report of the surface area analysis of **X-3-B** including micropore analysis and pore size and distribution plots (28 pages). Ordering information is given on any current masthead page.