

Sol–Gel Synthesis of Hybrid Organic–Inorganic Materials. Hexylene- and Phenylene-Bridged Polysiloxanes

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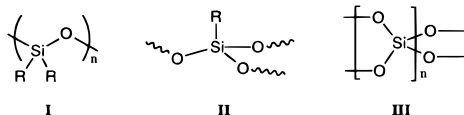
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New highly cross-linked polysiloxanes were prepared by sol–gel polymerization of 1,6-bis(diethoxymethylsilyl)hexane (**1**) and 1,4-bis(diethoxymethylsilyl)benzene (**2**). Hydrolysis and condensation of **1** and **2** under acidic and basic conditions with 4 equiv of water led to the rapid formation of hexylene- and phenylene-bridged polysiloxane gels. The dry gels (xerogels) were intractable, insoluble materials that were noticeably hydrophobic, exhibiting no swelling in organic solvents or water. Most of the xerogels were high surface area, mesoporous materials. Hexylene-bridged polysiloxanes prepared under acidic conditions were always *nonporous* regardless of whether they were processed to afford xerogels or supercritically dried as aerogels. Hexylene-bridged polysiloxanes prepared under basic conditions and all of the phenylene-bridged polysiloxanes were mesoporous with surface areas as high as 1025 m²/g.

Introduction

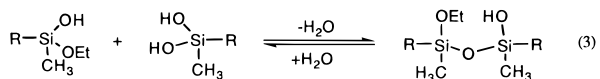
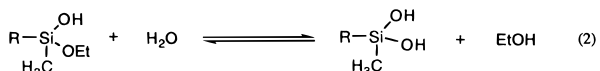
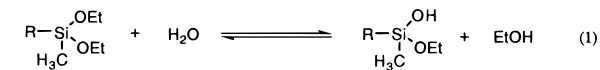
Polymers made by the formation of siloxane (Si–O–Si) bonds are an important and diverse body of materials, ranging from organically modified linear polysiloxanes **I** at one extreme to inorganic silicates and silica



gels **III** at the other.³ In between lies a spectrum of hybrid organic–inorganic network polymers with numerous applications for the preparation of optical devices,^{4–6} electronics,⁷ and catalytic^{8–10} and chromatographic^{11,12} supports.

Siloxane-based materials **I–III** are readily prepared by the polymerization of diethoxysilane, triethoxysilane, and tetraethoxysilane precursors, respectively. The

polymerizations involve the hydrolysis of ethoxide groups (eqs 1 and 2) and subsequent condensation of silanols to form siloxane bonds (eq 3).¹³



Polymerization of diethoxysilanes leads to the formation of linear polysiloxanes or cyclic oligosiloxanes, **I**. For polysiloxanes **I** to be prepared as network polymers, one or more additional polymerizable groups (for example, a vinyl substituent) must be attached to the silicon to permit cross-linking. A symmetrical approach to preparing network polysiloxanes is to polymerize “bridged” monomers with diethoxysilyl groups attached to either side of a hydrocarbon spacer through silicon–carbon bonds (Scheme 1). Polymerization of four ethoxide groups per monomer would ideally lead to a highly cross-linked structure in which the organic bridging group would be an integral part of the polymeric architecture rather than a pendent functionality. The homogeneity of the inorganic and organic phases allows for molecular engineering of the bulk properties of the hybrid organic–inorganic materials without the com-

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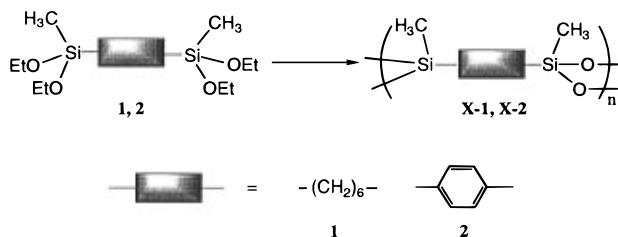
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Scheme 1. Synthesis of Hydrocarbon-Bridged Polysiloxanes



lications of nanoscale phase separation commonly seen with organic polymer-inorganic hybrids.^{14,15}

The objective of this study was to determine if hydrocarbon-bridged polysiloxanes would form gels under conditions similar to those used to prepare the analogous bridged polysilsesquioxanes (derived from monomers bearing two or more polymerizable triethoxysilyl groups).¹⁶⁻²⁶ Because tetraethoxysilane will not form gels at monomer concentrations below 1.3 M,²⁷⁻²⁹ it was not certain whether the bridged polysiloxane precursors **1** and **2**, also with four ethoxide groups per monomer, would polymerize to afford gels at the concentrations typically used to make bridged polysilsesquioxanes (0.2–0.4 M). Also of interest were the effects of the pendant methyl groups attached to the silicons on the polymerization process and final material properties such as porosity and hydrophobicity.

In this paper, the synthesis and characterization of 1,6-bis(diethoxymethylsilyl)hexane (**1**) and 1,4-bis(diethoxymethylsilyl)benzene (**2**) and their sol-gel polymerizations are described. Both rigid (phenylene) and flexible (hexylene) bridging groups were chosen to examine the effect of bridging group flexibility on porosity. Flexibility of the hydrocarbon spacer has been shown to have a pronounced impact on the porosity of bridged polysilsesquioxanes. While arylene-bridged polysilsesquioxanes are invariably porous,¹⁹ porosity in alkylene-bridged polysilsesquioxane gels has been shown to collapse during drying when the bridging group is long and flexible and the degree of condensation is low (i.e., under acidic conditions).²²

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Polymerizations of **1** and **2** were carried out under typical sol-gel conditions used to prepare bridged polysilsesquioxanes.^{19,22,23} The resulting gels were dried by standard procedures used to prepare xerogels¹⁹ and aerogels.^{20,31} The hexylene- and phenylene-bridged xerogels were characterized by ¹³C and ²⁹Si CP MAS NMR spectroscopy to provide details of the molecular structures, scanning electron microscopy to observe larger scale structure, nitrogen sorption porosimetry to determine surface areas and pore sizes, and thermal analysis to determine thermal stabilities.

Experimental Section

Materials. All reactions were run under dry argon using standard Schlenk techniques unless otherwise noted. Solvents were dried and distilled under argon by standard methods; alternatively, anhydrous solvents were used as received from Aldrich Chemicals, Inc., as were 1,5-hexadiene and 1,4-dibromobenzene. Diethoxymethylsilane was used as received from Hüls, Inc. Methyltriethoxysilane was distilled from CaH₂.

Instrumentation. Infrared spectra were obtained on a Perkin-Elmer 1750 Fourier transform infrared spectrophotometer. ¹H, ¹³C, and ²⁹Si solution NMR spectra were recorded on Bruker 300 and 400 MHz spectrometers. ¹³C CP MAS NMR spectra were obtained with a Bruker AMX-400 MHz spectrometer at 100.63 MHz. ²⁹Si solid-state CP MAS NMR spectra were obtained on a Bruker AMX-400 MHz spectrometer at 79.5 MHz. The ¹³C and ²⁹Si NMR spectra were acquired with magic angle spinning (MAS) speeds of ~5 and ~3–5 kHz, respectively.

The ¹³C NMR spectra were acquired using cross polarization (CP) with a relaxation delay of 1 s and a cross polarization time of 2 ms. Since the gels in this study are similar, these parameters were optimized on only one of the gels to obtain spectra with a satisfactory signal-to-noise ratio. ²⁹Si NMR spectra were acquired using single pulse excitation with a relaxation delay of 480 s. With ²⁹Si T₁ values ranging from 19 to 135 s, the relaxation delay is ≥3T₁, which is sufficient for quantitative spectra. The ²⁹Si CP MAS NMR spectra were deconvoluted using a Lorentz-Gaussian (50:50) fit.

Thermal analyses of the network materials were performed on a Perkin-Elmer differential scanning calorimeter and thermal gravimetric analyzer. Scanning electron micrographs were obtained with a JEOL 6400 scanning electron microscope. Samples for SEM were coated with either Au/Pd or carbon. No differences in images obtained with Au/Pd and carbon coatings could be detected at the magnifications used. Energy dispersive spectroscopy (EDS) was performed using a Noran Novar detector (Z > 4) and a Noran 5500 analyzer at an accelerating voltage of 15 kV. Elemental analyses were performed by Desert Analytics, Tucson, AZ. X-ray powder diffraction measurements were performed using a Siemens D-500 θ-θ diffractometer from 1–30° 2θ, 0.05 steps and 2 s/step. Porosimetry measurements were determined using a Quantachrome Autosorb-6 multipoint nitrogen porosimeter.

Monomer Synthesis. (EtO)₂MeSi(CH₂)₆SiMe(OEt)₂ (**1**). An oven-dried 250-mL three-necked round-bottom flask was fitted with a 60 mL addition funnel and a reflux condenser. The flask was charged with 7.82 g (95.2 mmol) of 1,5-hexadiene, 100 mL of freshly distilled benzene, and 0.05 g of H₂PtCl₆·6H₂O (0.1 mol % based on hexadiene). Upon addition of the catalyst, a small amount of gas evolution was observed. The addition funnel was charged with 33.16 g (247 mmol) of diethoxymethylsilane. Dropwise addition of the silane with stirring under argon resulted, after warming, in the formation of a yellow solution. Following complete addition, the mixture was stirred overnight at 40 °C. When the progress of the reaction had stopped (as determined by GC analysis), the volatiles were removed by rotary evaporation under vacuum,

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and the residue twice distilled to yield 16.31 g (49% yield) of 1,6-bis(diethoxymethylsilyl)hexane as a clear, viscous fluid, bp 113–116 °C at 200 mTorr. IR (neat) ν 2973, 2925, 2878, 2734, 1391, 1257, 1166, 1109, 1083, 952, 800 cm^{-1} . ^1H NMR (CDCl_3) δ 3.74 (q, 8H, $(\text{CH}_3\text{CH}_2\text{O})_2\text{MeSi}(\text{CH}_2)_6\text{SiMe}(\text{OCH}_2\text{CH}_3)_2$, $^3J_{\text{H-H}} = 7.0$ Hz), 1.30, 0.59 (m, 12H, m, 4H, $(\text{CH}_3\text{CH}_2\text{O})_2\text{MeSi}(\text{CH}_2)_6\text{SiMe}(\text{OCH}_2\text{CH}_3)_2$), 1.19 (t, 12H, $(\text{CH}_3\text{CH}_2\text{O})_2\text{MeSi}(\text{CH}_2)_6\text{SiMe}(\text{OCH}_2\text{CH}_3)_2$), $^3J_{\text{H-H}} = 7.0$ Hz), 0.07 (s, 6H, $(\text{CH}_3\text{CH}_2\text{O})_2\text{MeSi}(\text{CH}_2)_6\text{SiMe}(\text{OCH}_2\text{CH}_3)_2$). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3) δ 58.0 ($(\text{CH}_3\text{CH}_2\text{O})_2\text{MeSi}(\text{CH}_2)_6\text{SiMe}(\text{OCH}_2\text{CH}_3)_2$), 32.9, 22.7, 13.8 ($(\text{CH}_3\text{CH}_2\text{O})_2\text{MeSi}(\text{CH}_2)_6\text{SiMe}(\text{OCH}_2\text{CH}_3)_2$), 18.34 ($(\text{CH}_3\text{CH}_2\text{O})_2\text{MeSi}(\text{CH}_2)_6\text{SiMe}(\text{OCH}_2\text{CH}_3)_2$), -4.9 ($(\text{CH}_3\text{CH}_2\text{O})_2\text{MeSi}(\text{CH}_2)_6\text{SiMe}(\text{OCH}_2\text{CH}_3)_2$). ^{29}Si NMR (CDCl_3) δ -4.25. LRMS 351 amu. HRMS (CI, isobutane) calcd 350.2308, found 350.2305.

1,4-(EtO)₂MeSiC₆H₄SiMe(OEt)₂ (2).³⁰ An oven-dried 2000 mL three-necked flask with magnetic stir bar was fitted with a 250 mL addition funnel and an efficient reflux condenser, cooled under vacuum, and backfilled with dry argon. The flask was charged with 15.4 g (634 mmol) of oven-dried magnesium turnings, 400 mL of anhydrous THF, and 189 g (1.06 mol) of methyltriethoxysilane. After charging the addition funnel with a 125 mL THF solution of 1,4-dibromobenzene (50 g, 210 mmol), approximately 5 mL of the dibromobenzene solution was added, and the flask mixture stirred with warming until reflux was achieved. Heat was removed, and the remainder of the dibromobenzene solution was added dropwise over 60 min (at a rate sufficient to maintain reflux). When the addition was complete, the reaction mixture was refluxed with stirring for 16 h. The resulting salt suspension was cooled, and volatiles removed under vacuum until the flask contents was reduced to approximately 40% of its original volume. Anhydrous hexanes were added, and the suspension was stirred for 2 h at room temperature to precipitate additional magnesium salts. The suspension was filtered through a medium fritted funnel, and the filtrate volume reduced by rotary evaporation. Distillation of the residue under vacuum yielded 28.8 g (40% yield) of 98% pure (by GC analysis) 1,4-bis(diethoxymethylsilyl)benzene; an additional 18.77 g (26% product) of 96% pure material can be obtained by redistillation of the impure fractions, bp 102–104 °C at 17 mTorr. IR (neat) ν 3054, 2974, 2926, 2880, 1391, 1259, 1166, 1142, 1105, 1078, 956, 826, 788, 765 cm^{-1} . ^1H NMR (CDCl_3) δ 7.65 (s, 4H, 1,4- $(\text{CH}_3\text{CH}_2\text{O})_2\text{MeSiC}_6\text{H}_4\text{SiMe}(\text{OCH}_2\text{CH}_3)_2$), 3.82 (q, 8H, 1,4- $(\text{CH}_3\text{CH}_2\text{O})_2\text{MeSiC}_6\text{H}_4\text{SiMe}(\text{OCH}_2\text{CH}_3)_2$), 1.24 (t, 12H, 1,4- $(\text{CH}_3\text{CH}_2\text{O})_2\text{MeSiC}_6\text{H}_4\text{SiMe}(\text{OCH}_2\text{CH}_3)_2$), 0.36 (s, 6H, 1,4- $(\text{CH}_3\text{CH}_2\text{O})_2\text{MeSiC}_6\text{H}_4\text{SiMe}(\text{OCH}_2\text{CH}_3)_2$). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3) δ 136.6, 133.2 (1,4- $(\text{CH}_3\text{CH}_2\text{O})_2\text{MeSiC}_6\text{H}_4\text{SiMe}(\text{OCH}_2\text{CH}_3)_2$), 58.5 (1,4- $(\text{CH}_3\text{CH}_2\text{O})_2\text{MeSiC}_6\text{H}_4\text{SiMe}(\text{OCH}_2\text{CH}_3)_2$), 18.2 (1,4- $(\text{CH}_3\text{CH}_2\text{O})_2\text{MeSiC}_6\text{H}_4\text{SiMe}(\text{OCH}_2\text{CH}_3)_2$), -4.3 (1,4- $(\text{CH}_3\text{CH}_2\text{O})_2\text{MeSiC}_6\text{H}_4\text{SiMe}(\text{OCH}_2\text{CH}_3)_2$). ^{29}Si NMR (CDCl_3) δ -18.0. LRMS 343 amu. HRMS (CI, isobutane) calcd 342.1682, found M 342.1690.

Polymerizations. Sol-gel polymerizations of **1** and **2** were carried out at 0.4 M concentrations in 10 mL of absolute ethanol. The monomers were dissolved in anhydrous ethanol (5 mL) in a volumetric flask. Then aqueous catalyst (7.5 mol % catalyst, 4 H₂O) in ethanol (4 mL) was added with stirring, and the volume of the solution adjusted to 10 mL. The resulting solutions were clear and colorless. The solutions were immediately transferred to scintillation vials and tightly sealed. After gelation, the monoliths were allowed to age for 2 weeks before further processing. Final workup of the gels consisted of crushing the gels in water (100 mL) and washing with water (1 × 100 mL) and then diethyl ether (100 mL). After air drying, the xerogels were placed under vacuum at 100 °C for 24 h.

Polymer Nomenclature. The dried gels are described by the following nomenclature: first, an **X** to denote xerogels (dried by an aqueous workup) or **A** to denote an aerogel (dried by supercritical carbon dioxide extraction), followed by the number designation of the monomer (**1** or **2**), and last, the type of catalyst (HCl or NaOH) used to prepare the gel. Thus a gel prepared by a NaOH-catalyzed polymerization of 1,6-bis(diethoxymethylsilyl)hexane **1** followed by supercritical extraction with carbon dioxide would be **A-1-NaOH**.

1,6-Hexylene-Bridged Polymethylsiloxane (X-1-NaOH). An oven-dried 25 mL volumetric flask was charged with 3.52 g (10 mmol, 0.4 M) of **1** and diluted with approximately 10 mL of dry absolute ethanol. In a separate vessel 1.08 mL of a 1 N aqueous NaOH solution and approximately 10 mL of absolute ethanol were mixed and then added to the ethanolic solution of **1** with thorough mixing. The total volume was adjusted to 25 mL with absolute ethanol and thoroughly mixed before being transferred to a dry scintillation vial. Gelation occurred within 4 h. After standing for 14 days, the wet gel was crushed in 100 mL of distilled water and filtered. The solids were washed with a second 100 mL volume of water, filtered, and washed with 100 mL of dry diethyl ether. After standing overnight, the white powder was heated under vacuum for 24 h at 100 °C. A total of 2.05 g (99% based on complete condensation of **1**) of **X-1** was recovered. IR (KBr) 3691, 2926, 1260, 1088, 796 cm^{-1} . ^{13}C CP MAS NMR δ 58.0, 33.0, 23.5, 18.7, 0.5. ^{29}Si CP MAS NMR δ -12.6 (D¹), -22.0 (D²). Anal. Calcd: C, 47.47; H, 8.96. Found: C, 44.15; H, 9.09. X-ray powder diffraction: one broad band, d spacing 8.0 Å. Nitrogen sorption surface area (BET) 297 m^2/g .

1,6-Hexylene-Bridged Polymethylsiloxane (X-1-HCl). A solution of **1** (3.52 g, 10 mmol) in dry ethanol was prepared as above. In a separate vessel 1.08 mL of a 1 N aqueous HCl solution and approximately 10 mL of absolute ethanol was mixed and then added to the ethanolic solution of **1** with thorough mixing. The total volume was adjusted to 25 mL with absolute ethanol and thoroughly mixed before being transferred to a dry scintillation vial. Gelation occurred within 4 h. Workup as described above gave 1.94 g (103% based on complete condensation) of **X-1**. IR (KBr) 3691, 2926, 1260, 1088, 796 cm^{-1} . ^{13}C CP MAS NMR δ 33.7, 23.8, 18.1, 0.3. ^{29}Si CP MAS NMR δ -12.6 (D¹), -22.0 (D²). Anal. Calcd: C, 47.47; H, 8.96. Found: C, 48.30; H, 9.24. X-ray powder diffraction: one broad band, d spacing 7.5–8.0 Å. Nitrogen sorption surface area (BET) 3 m^2/g .

1,4-Phenylene-Bridged Polymethylsiloxane (X-2-NaOH). An oven-dried 25 mL volumetric flask was charged with 3.43 g (10 mmol, 0.4 M) **3** and diluted with approximately 10 mL of dry absolute ethanol. In a separate vessel 1.08 mL of a 1 N aqueous NaOH solution and approximately 10 mL of absolute ethanol was mixed and then added to the ethanolic solution of **3** with thorough mixing. The total volume was adjusted to 25 mL with absolute ethanol and thoroughly mixed before being transferred to a dry scintillation vial. Gelation occurred within 30 min; the wet gel scatters light, as a pink tint was observed upon aging for 14 days. Aqueous workup as described above resulted in loss of fine-grained material through a coarse-fritted filter with a final yield of 1.24 g (63%) of **X-2-NaOH** as a white powder. IR (KBr) 3436, 3057, 2970, 1386, 1265, 1146, 1088, 777.0, 516.0, 490.0 cm^{-1} . ^{13}C CP MAS NMR δ 186.8 (spinning sideband), 180.4 (spinning sideband), 139.1, 132.7, 85.0 (spinning sideband), -1.6. ^{29}Si CP MAS NMR δ -23.5 (D¹), -32.7 (D²). Anal. Calcd: C, 49.44; H, 5.19. Found: C, 48.77; H, 5.46. X-ray powder diffraction: one broad band, d spacing 8.0 Å. Nitrogen sorption surface area (BET) 1024 m^2/g .

1,4-Phenylene-Bridged Polymethylsiloxane (X-2-HCl). A solution of **3** (3.43 g, 10 mmol) in dry absolute ethanol was prepared as above. In a separate vessel 1.08 mL of a 1 N aqueous HCl solution and approximately 10 mL of absolute ethanol was mixed and then added to the ethanolic solution of **2** with thorough mixing. The total volume was adjusted to 25 mL with absolute ethanol and thoroughly mixed before being transferred to a dry scintillation vial. Gelation occurred within 24 h; the wet gel scatters light, as a blue tint was observed upon aging for 14 days. Workup as described above yielded 1.33 g (69%) of white xerogel. IR (KBr) 3649, 3056, 2967, 1637, 1386, 1266, 1146, 1083, 1019, 775.0, 601.0, 515.0, 488.0 cm^{-1} . ^{13}C CP MAS NMR δ 187.0 (spinning sideband), 180.6 (spinning sideband), 139.2, 132.8, 85.0 (spinning sideband), -1.8. ^{29}Si CP MAS NMR δ -24.0 (D¹), -30.9 (D²). Anal. Calcd: C, 49.44; H, 5.19. Found: C, 48.48; H, 5.42. X-ray powder diffraction: one broad band, d spacing 8.0 Å. Nitrogen sorption surface area (BET) 676 m^2/g .

Supercritical Carbon Dioxide Extractions. Phenylene- and hexylene-bridged polysiloxanes were prepared by poly-

Table 1. Time Required for 1 and 2 To Gel under the Polymerization Conditions Used To Prepare the Xerogels and Aerogels^a

monomer	gelation time (min)	
	acid catalyst	base catalyst
1	200	104
2	435	30

^a The monomers were dissolved in ethanol along with 7.5 mol % catalyst (HCl or NaOH) and 4 equiv of water at room temperature. Gelation is defined as the point at which the polymerization solution stops flowing. The measurements were made in triplicate with no more than ± 2 min difference between samples.

merizing monomers **1** and **2** under conditions identical with those used to form wet gels in the previous section. Experiments were carried out in triplicate, and gel times (Table 1) were determined as the point at which the reaction mixture stopped flowing as a liquid. After 2 weeks aging, the gels were extracted with supercritical carbon dioxide (1400 psig) at 35 °C over 3 days, with intermittent purging of solvent-laden carbon dioxide and simultaneous recharging with fresh carbon dioxide. The carbon dioxide was vented gradually over 8 h to give the final aerogels.

1,6-Hexylene-Bridged Polymethylsiloxane (A-1-NaOH). The same procedure for preparing the wet gel precursor to **X-1-NaOH** was used prior to supercritical extraction. A white monolithic aerogel (2.16 g, 103%) was obtained. IR (KBr) 3468, 2927, 1655, 1364, 1261, 1098, 797 cm^{-1} . Anal. Calcd: C, 47.47; H, 8.96. Found: C, 46.02; H, 8.80. Nitrogen sorption surface area (BET) 14 m^2/g .

1,6-Hexylene-Bridged Polymethylsiloxane (A-1-HCl). The same procedure for preparing the wet gel precursor to **X-1-HCl** was used prior to supercritical extraction. A white monolithic aerogel (1.97 g, 97%) was obtained. IR (KBr) 3436, 2927, 1637, 1260, 1083, 797 cm^{-1} . Anal. Calcd: C, 47.47; H, 8.96. Found: C, 48.61; H, 9.10. Nitrogen sorption surface area (BET) 260 m^2/g .

1,4-Phenylene-Bridged Polymethylsiloxane (A-2-NaOH). The same procedure for preparing the wet gel precursor to **X-2-NaOH** was used prior to supercritical extraction. A white monolithic aerogel (2.13 g, 110%) was obtained. IR (KBr) 3467, 3056, 2967, 1626, 1365, 1265, 1146, 1087, 1019, 835, 777, 600, 516, 487 cm^{-1} . Anal. Calcd: C, 49.44; H, 5.19. Found: C, 48.77; H, 5.46. Nitrogen sorption surface area (BET) 762 m^2/g .

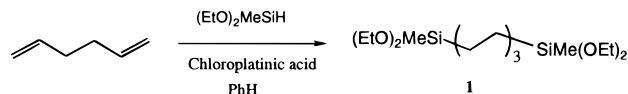
1,4-Phenylene-Bridged Polymethylsiloxane (A-2-HCl). The same procedure for preparing the wet gel precursor to **X-2-HCl** was used prior to supercritical extraction. A white monolithic aerogel (2.02 g, 104%) was obtained. IR (KBr) 3457, 3056, 2971, 1637, 1386, 1266, 1146, 1078, 1019, 774, 608, 516, 481 cm^{-1} . Anal. Calcd: C, 49.44; H, 5.19. Found: C, 49.79; H, 5.48. Nitrogen sorption surface area (BET) 1020 m^2/g .

Results and Discussion

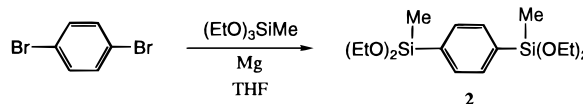
Hexylene- and phenylene-bridged polysiloxanes were prepared by sol-gel polymerization of **1** and **2** (Scheme 1), respectively. Hydrolysis and condensation of **1** and **2** led to the formation of gels within a few hours. After aging for 2 weeks, the gels were dried either by an aqueous workup (xerogels) or supercritical carbon dioxide extraction (aerogels). Each of these steps are described in more detail in the Experimental Section with accompanying characterization data.

Monomer Synthesis. 1,6-Bis(diethoxymethylsilyl)hexane (**1**) was prepared in a mild, one-step hydrosilylation from 1,5-hexadiene and diethoxymethylsilane in good yield (Scheme 2). The reaction was carried out neat or in benzene using chloroplatinic acid as catalyst at room temperature or with gentle heating (40 °C). Some rearrangement of the terminal olefinic bonds was observed, leading to mixtures of intermediate 6-silylhex-1-ene and 6-silylhex-2-ene isomers. The best yield and regioselectivity were obtained when the reaction was

Scheme 2. Synthesis of Monomer 1 by Hydrosilylation of 1,5-Hexadiene



Scheme 3. Barbier-Grignard Synthesis of Phenylene-Bridged Monomer 2



performed under air. The product mixture could be separated by simple distillation to afford the pure 1,6-regioisomer **1**.

1,4-Phenylene-bridged monomer **2** was prepared from 1,4-dibromobenzene by a Barbier-Grignard reaction with methyltriethoxysilane (Scheme 3).³⁰ As always with Grignard reactions, care had to be exercised with the addition of the 1,4-dibromobenzene due to the strongly exothermic nature of the reaction. A fair yield of pure 1,4-bis(diethoxymethylsilyl)benzene **2** was obtained after distillation. Losses were primarily due to multiple substitutions on the methyltriethoxysilane leading to "dimer" and polymer formation during distillation.

Sol-Gel Polymerizations. One of the greatest advantages of sol-gel polymerizations over other methods for preparing materials is the mild reaction conditions required for the hydrolysis and condensation reactions.¹³ Polymerizations of the monomers (0.4 M) were carried out at room temperature in ethanol. Hydrolysis and condensation reactions were catalyzed by aqueous acid (7.5 mol % HCl) or base (7.5 mol % NaOH). Ethanol is the preferred solvent for most sol-gel polymerizations due to its relatively low toxicity and ability to solvate nonpolar ethoxysilane monomers and aqueous catalysts. Though only 2 equiv of water is theoretically necessary to stoichiometrically convert the bis(diethoxymethyl) monomers **1** and **2** into fully condensed polymers, 4 equiv were used in order to ensure complete polymerization.

Monomers **1** and **2** polymerized to form gels within a few hours (at approximately the same rate as the analogous hexylene- and phenylene-bridged *silsesquioxane* monomers). Table 1 shows the average times of gelation for **1** and **2** under acidic and basic conditions. As would be expected from previous studies of sol-gel polymerization kinetics of alkyl- and aryl-substituted ethoxysilanes,³² the arylene-bridged monomer **2** gelled at a slower rate than the alkylene-bridged monomer **1** under acidic conditions and faster than **1** under basic conditions. For both monomers, gelation occurred faster with NaOH than with HCl as catalyst. The gel transition from liquid (sol) to gel occurred within several minutes affording brittle transparent gels that "rang" when the container was lightly tapped. In all cases, the gels lost the capacity to ring within a day or two after gelation. The ability of the monomers **1** and **2** to form gels at relatively low monomer concentrations (0.4 M) may be related to the effects of the hydrophobic hydrocarbon-bridging group or perhaps greater mass and volume of the building block.

(32) Schmidt, H.; Scholze, H.; Kaiser, A. *J. Non-Cryst. Solids* **1984**, *63*, 1-11.

Wet gels prepared under acidic conditions were opaque white; those prepared under basic conditions were translucent. After gelation, all the gels shrank slightly from the walls of their containers and were aged for 2 weeks before further processing. Dry xerogels were prepared by crushing the gel in water before washing with water and diethyl ether. Hexylene- and phenylene-bridged polysiloxane gels did not wet with water, indicating that the materials were hydrophobic; hexylene- and phenylene-bridged polysilsesquioxanes wet easily with water. The resulting granular, white polymers were dried at 100 °C under vacuum. They were insoluble in organic solvents, brittle and easily ground with mortar and pestle into fine powders for analysis. Yields of the bridged polysiloxanes were typically at, or slightly above, 100% (vide infra) based on the completely condensed polymer, due to the presence of some residual silanols.

Supercritical carbon dioxide extraction of the gels over 48 h afforded monolithic (crack-free) aerogels. The gels experienced significant volume loss (85%) during supercritical extraction regardless of the type of bridging group (hexylene or phenylene) or the catalyst (HCl or NaOH) used in their preparation. This is in sharp contrast to studies of bridged polysilsesquioxane aerogels, which exhibit significant differences in shrinkage depending on whether acidic or basic catalyst was used.³¹

Characterization. Due to the intractable nature of these materials, it was necessary to use solid-state techniques for their characterization. X-ray powder diffraction studies revealed single broad peaks with *d* spacings near 8 Å in both hexylene- and phenylene-bridged materials. No long-range order was observed, indicating that the materials were amorphous.

Solid-State ¹³C NMR Spectroscopy. Solid-state nuclear magnetic resonance (NMR) spectroscopy was the most useful technique for characterizing these intractable polymers. ¹³C cross-polarization magic angle spinning (CP MAS) NMR spectroscopy was used to determine if the integrity of the bridging functionality had been maintained during the sol-gel process. In previous studies, for example, ¹³C and ²⁹Si CP MAS NMR spectroscopies revealed that acetylene bridging groups in polysilsesquioxanes were hydrolytically labile.¹⁹ As a rule, however, the alkylene and arylene bridging groups have been shown to be completely stable to the conditions used in these sol-gel polymerizations and subsequent processing.

The ¹³C CP MAS NMR spectrum of the hexylene-bridged polymethylsiloxane (**X-1-HCl**) is shown in Figure 1. There were four peaks in the spectrum as expected for the hexylene-bridged polysiloxane structure. Three types of bridging hexylene carbons were observed at 33.7, 23.8, and 18.1 ppm and were assigned to the carbons γ , β , and α to the silicon, respectively. The fourth peak at 0.3 ppm represents the methyl carbons attached to the silicons. Only a small amount (<<5%) of residual ethoxy substituents were left in the material as evidenced by a peak barely detectable above the baseline noise at 58 ppm; the ethoxy methyl would be expected to lie near 18 ppm, in the region obscured by the bridging carbons. The hexylene-bridged polymethylsiloxane prepared with NaOH catalyst (**X-1-NaOH**) showed slightly more residual ethoxide than the acid-catalyzed xerogel. The minor contribution by ethoxy groups in both spectra indicates that

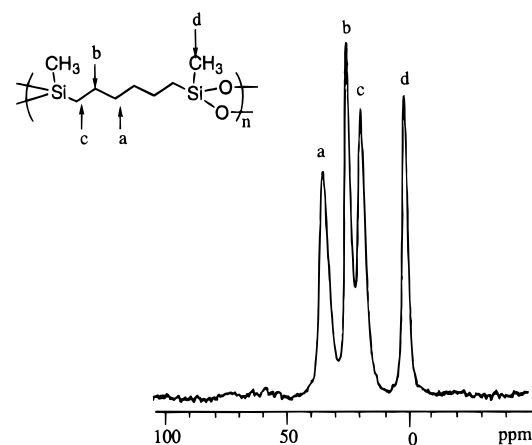


Figure 1. ¹³C CP MAS NMR spectrum of hexylene-bridged polysiloxane (**X-1-HCl**).

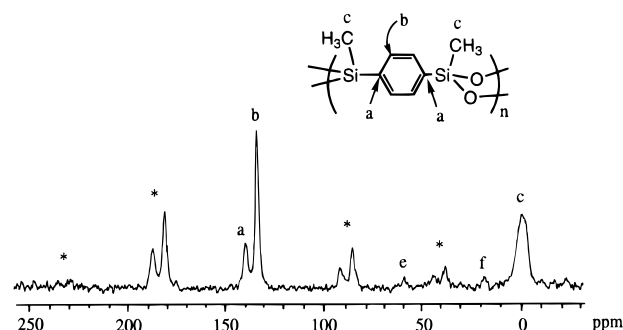


Figure 2. ¹³C CP MAS NMR spectrum of phenylene-bridged polysiloxane (**X-2-NaOH**). Peaks at e and f are due to residual ethoxide groups; peaks labeled with an asterisk are spinning sidebands.

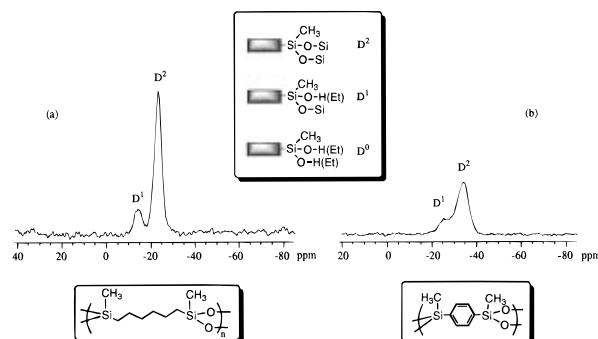


Figure 3. ²⁹Si CP MAS NMR spectra of (a) hexylene-bridged polysiloxane (**X-1-HCl**) and (b) phenylene-bridged polysiloxane (**X-2-HCl**).

hydrolysis of **1** was nearly quantitative with both formulations.

¹³C CP MAS NMR spectra of the phenylene-bridged siloxane gels (Figure 2) displayed two resonances in the aromatic region. The smaller peak at 139.2 ppm was assigned to the 1,4-substituted carbons in the bridging phenylene; a larger peak at 132.8 ppm was assigned to the remaining four aromatic (CH) carbons. The methyls attached to the silicon atoms appeared as a single peak at -2 ppm. As with the hexylene-bridged polysiloxanes, there was little evidence of residual ethoxy groups.

Solid-State ²⁹Si NMR Spectroscopy. ²⁹Si CP MAS NMR spectroscopy (Figure 3) was used to evaluate the degree of condensation (the relative number of siloxane bonds to each silicon atom) in the network polysiloxanes. Three distinct peaks for silicon atoms with different degrees of condensation are possible in these materials.

Table 2. Degrees of Condensation Calculated for Bridged Polysiloxane Xerogels from Deconvoluted ^{29}Si CP MAS NMR Spectra^a

polymer	bridging group	degree of condensation (%)
X-1-HCl	hexylene	92
X-1-NaOH	hexylene	96
X-2-HCl	phenylene	84
X-2-NaOH	phenylene	88

^a Experimental precision was determined to be $\pm 1\%$.

A D^0 peak represents silicon atoms with no siloxane linkages and would be expected to occur in either free monomer or monomer end groups attached to the surface of the network polymer. (Residual monomer is unlikely because of the excess water used in the polymerizations. In addition, any remaining monomer would be reacted or removed during the subsequent processing and drying.) D^1 peaks represent silicon atoms with one siloxane bond and one ethoxy (or hydroxy) substituent. D^2 resonances arise from silicons that are fully condensed with two siloxane bonds. In both siloxanes and silsesquioxanes, the ^{29}Si NMR resonances shift 7.5 to 10.0 ppm upfield with each increasing degree of condensation.^{19,33}

Two resonances were observed at -12.6 (D^1) and -22.0 (D^2) ppm in the spectrum of the hexylene-bridged polysiloxane (**X-1-HCl**, Figure 3a). From the relative intensities of the two peaks and the absence of a D^0 peak in all of the solid-state ^{29}Si NMR spectra of the hexylene-bridged polysiloxanes, it was clear that these materials were highly condensed. Similarly, two resonances at -24.0 (D^1) and -30.9 (D^2) ppm could be seen in the spectra of the phenylene-bridged methylsiloxanes with no sign of the D^0 silicon (**X-2-HCl**, Figure 3b).

The degree of condensation can be calculated semi-quantitatively from deconvoluted D^n peaks in the ^{29}Si CP MAS NMR spectra according to eq 4:

$$\text{degree of condensation} = \frac{[(1.0)(\% \text{ area } D^1) + (2.0)(\% \text{ area } D^2)]/2.0}{4} \quad (4)$$

For both hexylene- and phenylene-bridged polysiloxane xerogels, condensation had progressed nearly to completion (Table 2). Degrees of condensation in the hexylene- and phenylene-bridged polysiloxane xerogels were significantly higher than those observed in hexylene- and phenylene-bridged *polysilsesquioxanes* (65–89%). However, the bridged polysiloxane networks contain fewer siloxane bonds per monomer repeat unit due to the fact that there are only four reactive ethoxide groups available for polymerization in **1** or **2** compared to six in the bridged silsesquioxane monomers. As with bridged polysilsesquioxanes, higher degrees of condensation were observed in the bridged polysiloxanes with the flexible hexylene group than with the more rigid phenylene group. Similar to silica and silsesquioxane gels,^{19,34} hexylene- and phenylene-bridged xerogels prepared under basic conditions were measured to have degrees of condensation that were higher (4%) than those prepared under acidic conditions. Greater extent of reaction under basic conditions may be attributed to the greater reactivity of more condensed silicons with

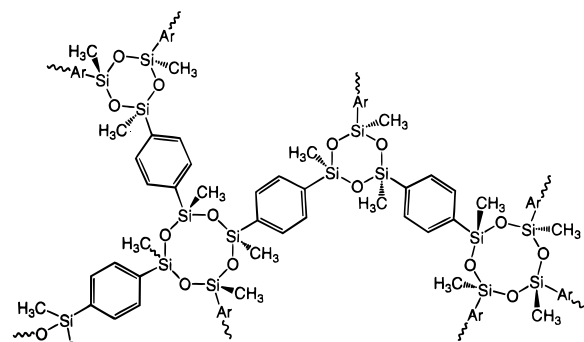


Figure 4. Possible structure of phenylene-bridged polysiloxane with phenylene groups bridging between siloxane rings.

nucleophiles leading to more branched polymers.³² High degrees of condensation in the bridged polysiloxanes mean that there are fewer silanols in the network polymer. This, combined with relative abundance of hydrocarbon bridging and methyl groups, contributes to the general hydrophobic character of the bridged polysiloxanes. Therefore, it is not surprising that these materials appeared to be more hydrophobic (less wettable with water) than the analogous hexylene- and phenylene-bridged polysilsesquioxanes.

The high degrees of condensation exhibited by these tetrafunctional monomers is intriguing in light of what is known of the cross-linking requirements for simple tetrafunctional monomers (such as TEOS) to form gels. It has been proposed that significant amounts of cyclic or polyhedral TEOS oligomers must be formed during sol-gel polymerization to account for the high degrees of condensation observed in silica gels.²⁹ Hydrocarbon-bridged polysiloxanes would also require a significant contribution from cyclic species to give the degrees of condensation observed by solid-state ^{29}Si NMR. We postulate that the diethoxymethylsilyl groups hydrolyze and condense to afford cyclic oligosiloxanes that are interconnected by the hydrocarbon-bridging groups (Figure 4).

Scanning Electron Microscopy. To elucidate nanometer-to-micron sized features, the bridged polysiloxanes were examined by scanning electron microscopy. At low magnification (100–1000 \times) the materials appeared to be amorphous with glasslike fracture surfaces. Examination at higher magnification (20 000 \times) revealed rough surfaces composed of tightly aggregated particles that were tens of nanometers in diameter. In general, few or no macropores (mean pore diameters > 50 nm) were observed. The nonporous (by nitrogen sorption, vide infra) hexylene-bridged polysiloxane (**X-1-HCl**) exhibited only slightly smoother, finer grained surfaces. Examples of micrographs obtained of the phenylene-bridged xerogel (**X-2-NaOH**) and aerogel (**A-2-NaOH**) are shown in Figure 5. While silica and silsesquioxane aerogels typically have much larger features than xerogels, the bridged polysiloxanes processed by either of the two drying techniques appeared to be identical by SEM.

Base-catalyzed aerogels **A-1-NaOH** and **A-2-NaOH** exhibited micron-sized defects filled with crystals dispersed throughout the otherwise amorphous materials (Figure 6). Energy-dispersive spectroscopy showed that the crystals contained significant amounts of sodium (Figure 7). The crystals are presumably residual sodium hydroxides or ethoxides that crystallized out of solution during the polymerization process. Supercriti-

(33) Glaser, R. H.; Wilkes, G. L.; Bronnimann, C. E. *J. Non-Cryst. Solids* **1989**, *113*, 73–87.

(34) Walther, K. L.; Wokaun, A.; Baiker, A. *Mol. Phys.* **1990**, *71*, 769–80.

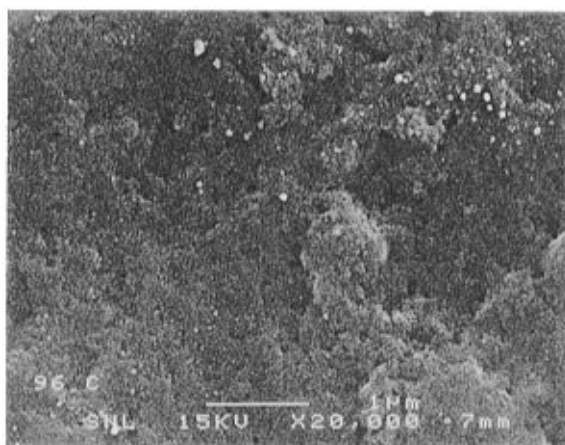


Figure 5. Scanning electron micrograph of phenylene-bridged polysiloxanes **X-2-HCl** and **A-2-HCl**.

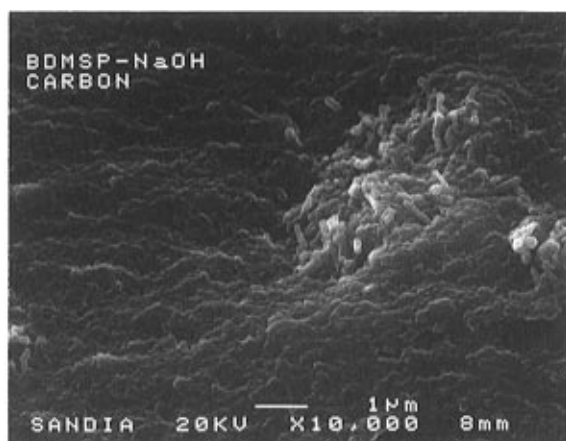


Figure 6. Scanning electron micrograph of phenylene-bridged polysiloxane **A-2-NaOH** showing a micron-sized defect.

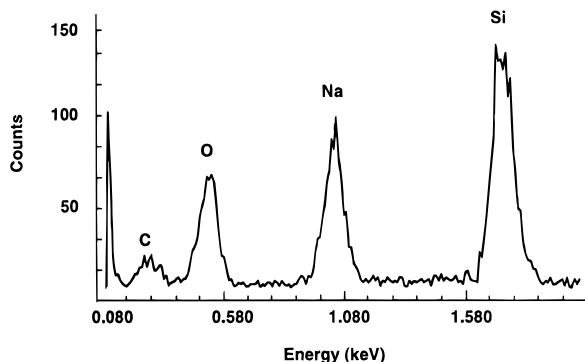


Figure 7. Energy-dispersive spectrum (EDS) of crystals found associated with micron-sized defects found in base-catalyzed, supercritical carbon dioxide extracted gels exhibit a sodium peak at $K\alpha = 1.04$ keV.

cal extraction left the salt crystals intact, while aqueous processing of xerogels dissolved and removed any water-soluble salts. Similar sized defects have been observed in silica gels and have been implicated in causing opacity through visible light scattering.

Surface Area Analysis. With the exception of hexylene-bridged polysiloxanes prepared under acidic conditions, nitrogen sorption porosimetry of the xerogels and aerogels displayed isotherms characteristic of mesoporous ($20 \text{ \AA} < \text{mean pore diameters} < 500 \text{ \AA}$) materials with minor contributions from micro- and macropores (Table 3).³⁵ As with hexylene-bridged polysiloxane xerogels, hexylene-bridged polysiloxane gels that were polymerized with HCl as catalyst and processed

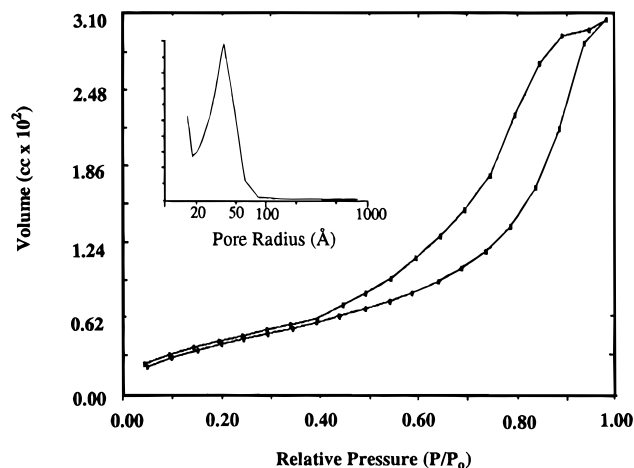


Figure 8. Nitrogen sorption isotherm and pore size distribution (inset) for hexylene-bridged polysiloxane **X-1-HCl**.

Table 3. Results of Nitrogen Sorption Porosimetry Surface Analysis of Hydrocarbon-Bridged Polysiloxane Xerogels and Aerogels^a

polymer	surface area (m ² /g)	mean pore diam (Å)	pore vol. (cm ³ /g)	micropore vol. (cm ³ /g)
X-1-HCl	3	NA	0.05	NA
X-1-NaOH	297	107	0.68	0
X-2-HCl	673	40	0.68	0.15
X-2-NaOH	1024	36	0.92	0.05
A-1-HCl	14	278	0.10	0
A-1-NaOH	260	52	0.34	0
A-2-HCl	762	31	0.59	0.14
A-2-NaOH	1020	39	0.98	0.33

^a Surface areas were determined by BET, mean pore diameters by BJH theory, pore volumes by determined by single-point analysis, and micropore volumes by *t*-plot analysis.

as xerogels were nonporous (**X-1-HCl**). Unlike hexylene-bridged polysiloxanes, however, supercritical processing *failed* to prevent collapse of porosity in hexylene-bridged polysiloxane aerogels prepared under acidic conditions (**A-1-HCl**), and only nonporous aerogels were obtained.

The most important result of the surface area measurements was the discovery that the pore structure appeared to be relatively insensitive to how the materials were processed. All previous experience with bridged polysiloxanes has indicated that significant differences in porosity between xerogels and aerogels existed. Without exception, polysiloxane aerogels

(35) Gregg, S. J.; Sing, K. S. W. *Adsorption, Surface Area, and Porosity*, 2nd ed.; Academic Press: London, 1982.

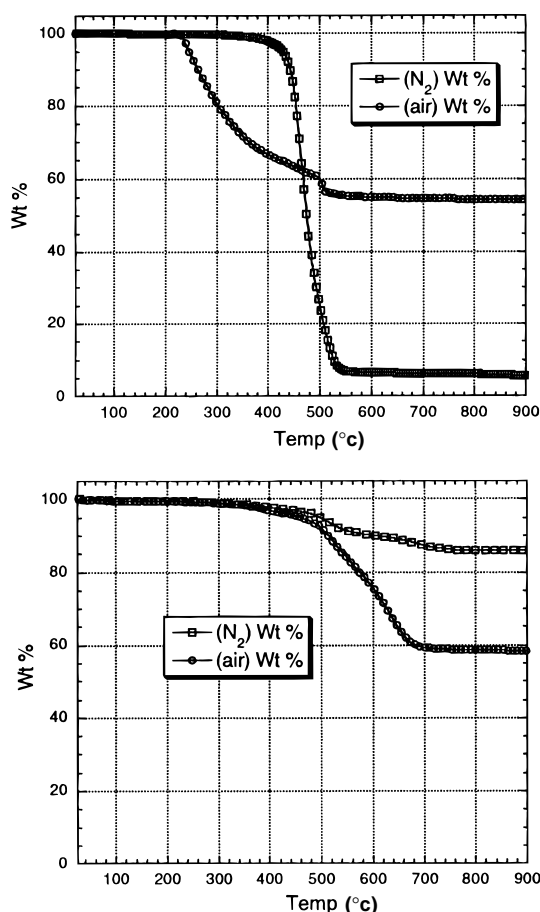


Figure 9. Thermal stabilities of hexylene-bridged (**X-1-HCl**, top) and phenylene-bridged polysiloxane (**X-2-HCl**, bottom) in air and nitrogen. Thermal gravimetric analyses were performed at 10 °C/min ramps.

had larger pores than the corresponding xerogels. In contrast, bridged polysiloxanes had virtually identical surface areas regardless of whether they were processed as xerogels or aerogels. For example, the hexylene-bridged polysiloxane xerogel (**X-1-NaOH**) had a surface area of 297 m²/g, while the surface area of aerogel **A-1-NaOH** was 260 m²/g. Surface areas of the phenylene-bridged polysiloxane, though somewhat dependent on the catalyst used in the polymerization, were consistently higher for both xerogels and aerogels than their hexylene-bridged analogues. Mean pore diameters of the phenylene-bridged polysiloxanes were also closely grouped between 31 and 40 Å.

Thermal Analysis. Bridged polysiloxanes were tested for thermal stability under both air and nitrogen using thermal gravimetric analysis. Hexylene- and phenylene-bridged polysiloxanes oxidized in air to afford silica gels (by IR). Hexylene-bridged polysiloxanes prepared under either acidic or basic conditions began to decompose near 250 °C, and by 500 °C had been completely converted to silica (Figure 9, top). Under nitrogen, the hexylene-bridged polysiloxanes began to decompose in a relatively narrow temperature range (440–520 °C) with only 5% mass remaining. Phenyl-substituted polysiloxanes are known to be more stable to pyrolysis than those with alkyl substituents.³ Accordingly, onset of decomposition in phenylene-bridged gels occurred at 475 °C in air (Figure 9, bottom) with complete oxidation to silica by 700 °C. Under nitrogen,

the phenylene-bridged material began to decompose near 475 °C with 86% ceramic yield at 850 °C, indicating that a significant portion of the bridging group's mass still remained.

The near-quantitative depolymerization of the hexylene-bridged polysiloxanes in nitrogen may provide a valuable clue to the architecture of the network polysiloxanes. The model of siloxane rings interconnected by hydrocarbon-bridging groups (Figure 4) that was postulated to explain the high degree of condensation in these materials can also be used to explain the decomposition of the hexylene-bridged polysiloxanes. If the siloxane rings are a predominant feature in the network architecture, thermal decomposition through silicon-carbon bond cleavage would be more likely to result in volatile products (hydrocarbons and cyclic siloxane oligomers) than a bridged polysiloxane structure with acyclic siloxane linkages. Oxidation of the polymers in air probably prevents depolymerization by cross-linking the material through new siloxane bonds, before temperatures high enough to initiate the anaerobic depolymerization process can be reached. It is important to note that hexylene-bridged *polysilsesquioxanes*, with more siloxane bonds to each silicon atom, slowly pyrolyze to a silicon oxycarbide rather than depolymerize.

Conclusions

A new class of network polymers were prepared. Hexylene- and phenylene-bridged bis(diethoxysilyl) monomers **1** and **2** were polymerized under sol-gel conditions to afford hydrocarbon-bridged polysiloxanes. Polymerizations occurred readily under both acidic (HCl) and basic (NaOH) conditions to form network polymers capable of forming gels within a few hours. The gels were dried by either an aqueous process or supercritical carbon dioxide extraction. The resulting hydrophobic materials were intractable and thermally stable. However, the manner in which the gels were dried did not significantly affect the structure of the final materials. To be more precise, supercritical extraction provided no added relief to shrinkage during the drying process, and as a result the aerogels were xerogel-like materials.

While only xerogel-like materials can be prepared, bridged polysiloxanes provide opportunities to engineer the porosity of the dry gel through the selection of the bridging group and type of catalyst used in the polymerization. An additional method for modifying the polysiloxane architecture involving the substitution of long chain alkyl groups for the silicon-bound methyl groups is currently under investigation.

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