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Mechanical properties of hexylene- and phenylene-bridged polysilsesquioxane aerogels and xerogels

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Abstract Bridged polysilsesquioxanes are increasingly used to prepare protective coatings, particulate chromatographic materials, and adsorbents. However, little is known about the mechanical properties of the materials and how they are influenced by the nature of the bridging group. In this paper, we have prepared monolithic xerogels and aerogels of hexylene- and phenylene-bridged polysilsesquioxanes and have measured their flexural strength and modulus. Consistent with their compact structure, the porous, glassy phenylene- and hexylene-bridged xerogels were hundreds of stronger than the analogous aerogels. The nature of the bridging group did not appear to affect the mechanical properties of the xerogels, in contrast, it presented a profound effect on the mechanical properties of the aerogels. Phenylene-bridged aerogels were brittle and 30% stronger than silica aerogels of the same density. However, the opaque hexylene-bridged aerogels were found to be elastic and appreciably weaker than the phenylene-bridged or silica aerogels.

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1 Introduction

Bridged polysilsesquioxanes have been widely used as coupling agents for filled elastomers [1], surface modifiers [2], and solid supports for high performance liquid chromatography [3]. They have shown promise for a number of additional applications including catalyst materials [4], adsorbents for cleaning up metal and organic contaminants [5], optics [6], and low-κ dielectrics [7]. Prepared by sol–gel polymerization of monomers with two or more trialkoxysilyl groups attached to an organic bridging group, bridged polysilsesquioxanes have been shown to readily form gels [8–10], mesoporous materials through surfactant templating [11, 12], nanoparticles [13], and aerogels [14–16]. The nature of the bridging group has proven to be exceedingly useful in engineering chemical functionality [17], the morphology [18, 19], and porosity of the resulting bridged polysilsesquioxanes [20]. For example, it has been shown that gels with more rigid bridging groups, such as the 1,4-phenylene group, generally remain porous after drying, while gels under acidic conditions prepared with flexible bridging groups, such as the 1,6-hexylene-group, often air dry with complete collapse of porosity. Because, supercritical drying affords porous hexylene-bridged aerogels [14–16], it has been speculated that this collapse is due to the failure of the more flexible, more compliant network to resist the drying stresses accompanying xerogel formation. This has been corroborated by a recent report of the elastic deformation of polysilsesquioxane xerogels with flexible bridging groups [21]. However, there have been no comparisons of the mechanical properties of hexylene- and phenylene-bridged polysilsesquioxanes to provide additional insight into the influence of the bridging group flexibility. A few reports of strength and moduli from hardness measurements have indicated that some films of the

alkylene- [12] and arylene- [22] bridged polysilsesquioxanes are stronger and stiffer than similar films of silica. Hybrid silica-silsesquioxane aerogels based on tetramethoxysilane, vinyltrimethoxysilane, 1,6-bis(trimethoxysilyl)hexane and bis-(3-trimethoxysilylpropyl)disulfide were found to be reversibly elastic under compression, but no control experiments on aerogels based on just the bridged monomers were included [23, 24]. In this paper, we have prepared monolithic, porous hexylene- and phenylene-bridged polysilsesquioxane xerogels and aerogels (Scheme 1) and measured their flexural strengths and moduli to provide the first investigation on how the bridging group affects the mechanical properties of these hybrid organic–inorganic materials.

2 Experimental

2.1 Materials

All reagents were used as received without further purification unless otherwise stated. Tetramethoxysilane (TMOS, 98%), anhydrous methanol (99.8%), anhydrous inhibitor free tetrahydrofuran (THF, 99.9%) and 1,4-dibromobenzene (99%) and magnesium were purchased

Scheme 1 Polymerization of bridged monomers to gels and air drying to xerogels or supercritical drying to aerogels

from the Aldrich Chemical Company. TMOS was distilled from molecular sieves prior to use. 1,6-Bis(trimethoxysilyl)hexane (96%) was purchased from Gelest Inc.

2.1.1 Preparation of 1,4-Bis(trimethoxysilyl) benzene [10]

To a three neck round bottom flask magnesium (4.88 g, 0.201 mol) and a stir bar were added. The round bottom was sealed with a condenser, addition funnel and glass stopper. The flask was then evacuated and flame dried. Once cooled to room temperature it was back filled with argon followed by the addition of anhydrous tetrahydrofuran (THF) (100 mL). To the addition funnel, 1,4-dibromobenzene (19.77 g, 0.0832 mol) was dissolved in THF (50 mL). The round bottom was placed into an oil bath a 70 °C and the dibromobenzene solution slowly added drop wise with a rate around a drop per second until 5% of the total volume was added. The solution began to become a greenish color, which the remaining dibromobenzene solution was added over 2 h. The reaction was refluxed for 24 h. The salts were removed by filtration and the volatiles removed under reduced pressure. The resulting viscous oil was added to hexanes to precipitate remaining salts, which were removed by filtration, hexanes were removed under reduced pressure. The product was isolated by fractional distillation (178 °C at 300 mmHg) to obtain 1,4-bis(trimethoxysilyl)benzene (13.32 g, 0.0418 mol) in a yield of 49.8%, MP 53–55 °C, MP-lit. 52–54 °C [10]. ^{1}H NMR (500 MHz, CDCl$_3$) d 7.61 (s, 4 H) d 3.58 (s, 18 H), ^{13}C NMR (125 MHz, CDCl$_3$) d 51.33, 132. 51, 134.54. Low resolution mass spectrometry (EI); 318.09, 287.07, 227.04, 197.02, 167.05, 121.03, 91.02.

2.1.2 Preparation of phenylene-bridged aerogels

Solutions containing 1,4-bis(trimethoxysilyl)benzene (0.456 g, 0.00143 mol, 0.4 M) which were diluted to 1.8 mL with anhydrous methanol, mixed for 1 min with a second solution containing the aqueous catalyst 1 N NaOH (0.155 g) which was diluted to 1.8 mL in 4 mL poly(propylene) containers at room temperature. The final volume of solutions was 3.6 mL. Gels formed within 10 min and were aged at room temperature for a 48 h followed by an aging at 50 °C for 48 h in an oven at ambient pressure until after syneresis was observed. After cooling to room temperature, the gels were placed in a Polaron autoclave in 100 mL methanol at 20 °C. Liquid carbon dioxide was introduced while allowing gas to vent. Once the autoclave was filled with liquid carbon dioxide and methanol, the two were allowed to mix together and permeate throughout the aerogels for 24 h. The methanol-carbon dioxide mixture was then replaced with pure liquid carbon dioxide by
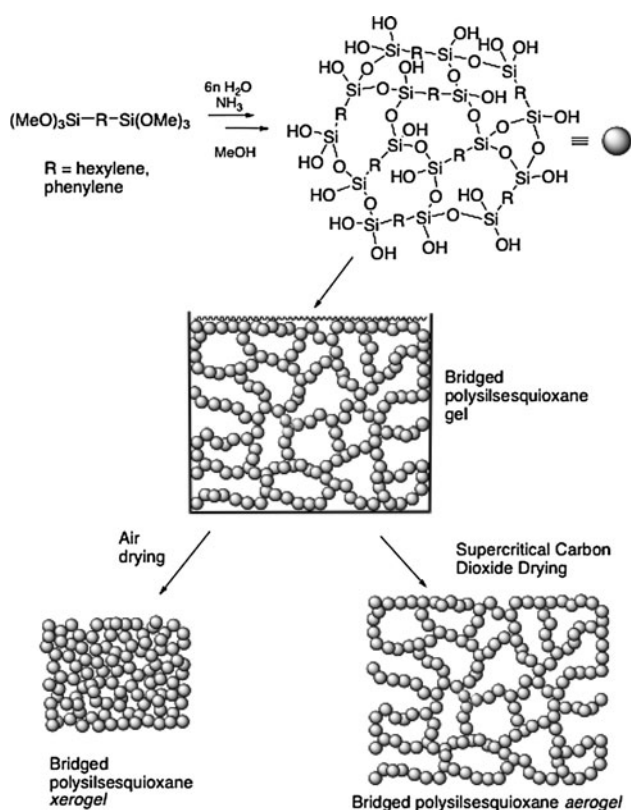
slowing venting while simultaneously introducing more liquid carbon dioxide over about 4–6 h. Then the system was closed and the temperature was raised to 36 °C. When the pressure reaches 7.37 MPa, the outlet to the autoclave was carefully opened and carbon dioxide was vented just enough to keep the pressure between 7.37 and 9.65 MPa. Carbon dioxide was vented over 8 h to afford monolithic phenylene-bridged aerogel (0.291 ± 0.007 g, yield 115%, calculated for 100% condensation). ^{29}Si CP MAS-NMR (100 MHz) δ −63 (T_1), −71 (T_2), −79 (T_3); ^{13}C CP MAS NMR (100 MHz,) δ 238, 132, 38; IR (KBr) 3,447, 3,050, 2,950, 1,630, 1,386, 1,144, 1,092, 1,021, 912, 806, 658 cm^{-1}.

2.1.3 Preparation of hexylene-bridged silica aerogels

Solutions containing 1,6-bis(trimethoxysilane)hexane (0.470 g, 0.00144 mol, 0.4 M) diluted to 1.8 mL with anhydrous methanol were mixed for 1 min with a second solution containing the aqueous catalyst 1 N NaOH (0.155 mL) which was diluted to 1.8 mL in a 4 mL poly(propylene) container at room temperature. The final volume was 3.6 mL. Gels formed within 40 min and were aged at room temperature for a 48 h followed by an aging at 50 °C for 3 weeks in an oven at ambient pressure, when syneresis occurred. After cooling to room temperature, the gels were supercritically dried using carbon dioxide as described in the phenylene-bridged aerogel procedure (vide supra) to afford monolithic hexylene-bridged aerogels (0.281 ± 0.004 g, yield 106%, calculated for 100% condensation). ^{29}Si CP MAS NMR (100 MHz) δ −58 (T_2), −66 (T_3); SS ^{13}C CP MAS-NMR (100 MHz,) δ 37.4, 28.1, 17.7; IR (KBr) 3,454, 2,929, 2,862, 1,480, 1,400, 1,350, 1,310, 1,290, 1,247, 1,202, 1,112, 1,050, 924, 807 cm^{-1}.

2.1.4 Silica aerogel preparation

A solution containing tetramethoxysilane (0.548 g, 0.535 mL, 0.01 mol) was diluted with anhydrous methanol to 1.8 mL and was mixed for 1 min with a second solution containing 1 N ammonium hydroxide (NH_4OH, 0.259 g, 0.259 mL) diluted to 1.8 mL with anhydrous methanol. Gels formed within half an hour of mixing the two solutions and were aged at room temperature for 48 h followed by aging at 50 °C for 48 h in a vacuum oven at ambient pressure. After cooling to room temperature, the gels were dried using the standard supercritical carbon dioxide process described above to afford monolithic, transparent silica aerogels (0.234 ± 0.006 g, yield 108%, calculated for 100% condensation). ^{29}Si CP MAS NMR (100 MHz) δ −103 (Q_3), −113 (Q_4); IR (KBr) 3,450, 2,957, 2,900, 2,848, 1,215, 1,160, 1,099, 1,005, 924, 806, 664 cm^{-1}.

2.1.5 Bridged xerogel preparation

Xerogels were prepared by placing an aged wet monolithic gel (hexylene- or phenylene-bridged as prepared from the formulations for aerogel production above) into an oven at 50 °C and ambient pressure for a period 96 h followed by 24 h at 100 °C. During this time the solvent was evaporated from the pores of the bridged polysilsesquioxane aerogels, which was accompanied by volume shrinkage of 87%. The resultant xerogels were translucent. Phenylene-bridged xerogel: (0.300 ± 0.002 g, yield 115%, calculated for 100% condensation). IR (KBr) 3,446, 3,052, 2,951, 1,633, 1,386, 1,139, 1,089, 1,019, 912, 807, 647 cm^{-1}. Hexylene-bridged xerogel: (0.290 ± 0.001 g, yield 112%, calculated for 100% condensation): IR (KBr) 3,451, 2,930, 2,865, 1,483, 1,394, 1,335, 1,308, 1,285, 1,243, 1,200, 1,093, 1,040, 934, 806 cm^{-1}.

2.2 Instrumentation

Densities (±0.020 g/cm^{-3}) were calculated from the masses and the volumes of the cylinderical xerogels and aerogels. The volumes were determined measuring with a 0.01 mm resolution, digital caliper. Mechanical property measurements were determined using a three-point flexural compression test with an Instron 5,540 series single column testing system with a 100 N load cell set with a 0.04 in./min^{-1} crosshead speed according to ASTM D790 and ASTM C1684. For each data point, 4 samples were prepared. Dry aerogel samples with KBr were ground using a mortar and pestle and pressed into a pellet, and infrared spectra were obtained with a Perkin Elmer FT-IR spectrometer. Surface area and pore sizes were determined by nitrogen adsorption porosimetry of one representative sample. Samples were degassed at 30 °C for 24 h under vacuum and analyzed with an Autosorb-1 porosimeter (Quantachrome Instruments) at 77 K. ^{29}Si NMR spectra were obtained on a Bruker 400 Spectrometer, using cross-polarization and magic-angle spinning at 10 and 70 kHz ^nH decoupling. Solid ^{29}Si spectra were externally referenced to the silicon peak of the [tetrakis(trimethylsilyl)silane] (TTMSS) at −9.7 and −135 ppm [25]. Solid State ^{13}C NMR spectra were obtained on a Bruker 400 using cross-polarization and magic-angle spinning at 10 and 70 kHz ^1H decoupling. Samples were externally referenced to the carbon chemical shift of adamantine [26]. SEM samples were sputter-coated with platinum and analyzed with a Hitachi S-4800 field-emission microscope at accelerating voltages between 10 and 15 keV.

3 Results

3.1 Sol–gel polymerizations

Monolithic gels were prepared by using procedures commonly used in the past [7]. Phenylene- and hexylene-bridged silsesquioxane monomers (0.4 M) were polymerized in methanol with six equivalents of water and sodium hydroxide (10.8 mol%) catalyst. Under these conditions, the phenylene-bridged polysilsesquioxane formed translucent blue gels in approximately 10 min. Under the same conditions, the hexylene-bridged polymer formed translucent blue gels in approximately 30 min. Once the gels had been aged, they were either air-dried to afford xerogels or dried using supercritical carbon dioxide to afford aerogels.

3.2 Preparation, morphology, and porosity of bridged xerogels

Bridged polysilsesquioxane xerogels were prepared by air drying the gels to afford crack-free monoliths. Gels were aged at room temperature for 48 h then at 50 °C until they underwent syneresis, signified by the gels shrinking away from the walls of the vessel without drying. For phenylene-bridged gels, this took 48 h at 50 °C. For hexylene-bridged gels, syneresis took a month at 50 °C. Once syneresis had occurred, the solvents were allowed to evaporate from the pores of the gels at 50 °C for 120 h, followed by 24 h at 100 °C to ensure that the monoliths were completely dry. In general, the bridged xerogels shrank approximately 87% from the wet gels volume (Figs. 1, 2).

Hexylene-bridged xerogels were slightly smaller in volume, more likely due to the flexibility of the hexylene-bridge allowing greater pore collapse during drying. Phenylene- and hexylene-bridged xerogels were almost ten times more dense (0.781 and 0.794 g/cm³, respectively) as their respective aerogels but still only a fraction of the density of bulk silica (2.2 g/cc). Despite losing most of their volume to shrinkage, the hexylene- and phenylene-bridged xerogels were very porous (Table 1). Hexylene-bridged xerogels had higher surface areas and pore volumes than the phenylene-bridged xerogels, but the mean pore diameters were about the same.
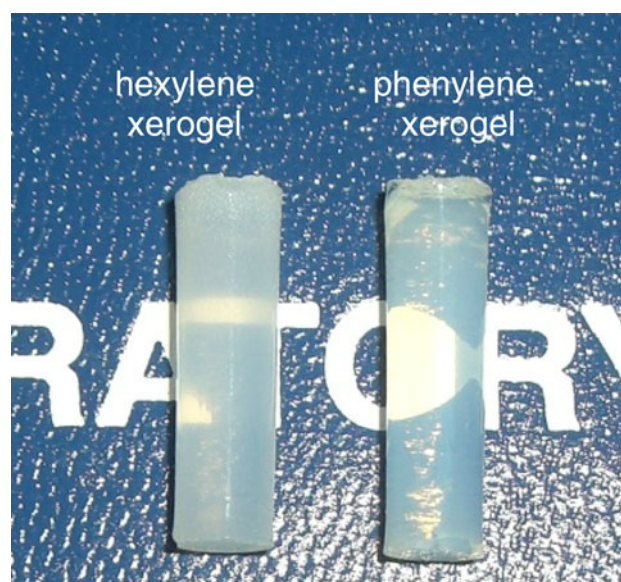

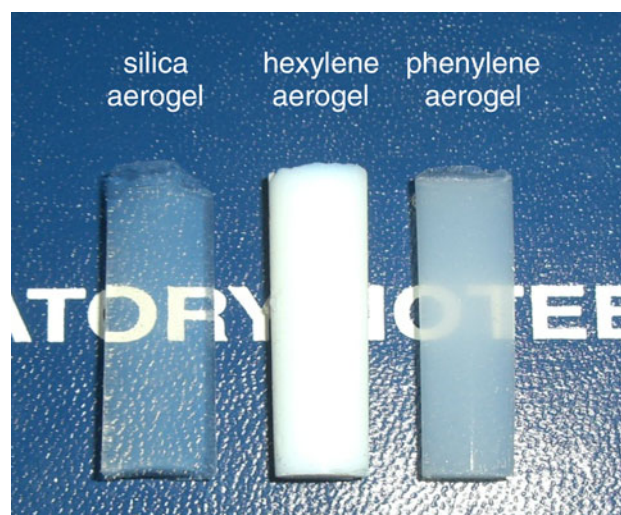**Fig. 1** Translucent phenylene- and hexylene-xerogels

Fig. 2 Silica, hexylene-bridged polysilsesquioxane and phenylene-bridged polysilsesquioxane aerogels with approximately the same density

Table 1 Surface areas, mean pore size, and pore volumes of phenylene- and hexylene-xerogels and aerogels

Sample	Surface area (m²/g)	Pore size (Å)	Pore volume (cm³/g)
Phenylene-xerogel	472 ± 23	43	0.50
Phenylene-aerogel	808 ± 40	139	2.82
Hexylene-xerogel	667 ± 33	40	0.94
Hexylene-aerogel	778 ± 40	160	3.11

3.3 Preparation, morphology and porosity of bridged aerogels

Aerogels were prepared by supercritical carbon dioxide processing [14–16]. Instead of air drying after syneresis, the gels were cooled to room temperature and placed in methanol in a Polaron autoclave. Methanol was exchanged with liquid carbon dioxide at 25 °C and 5.86 MPa for 24 h. Then the temperature and pressure were increased above the critical point (31 °C, 7.38 MPa) and the supercritical carbon dioxide was slowly vented. The resulting phenylene-bridged aerogels (density = 0.097 g/cm^3) were translucent blue and looked relatively similar to silica aerogels (density = 0.092 g/cm^3) that were prepared for the purpose of comparing mechanical properties. In contrast, the hexylene-bridged silsesquioxane aerogels (density = 0.093 g/cm^3) turned opaque white during supercritical drying and were noticeably more flexible than either phenylene-bridged or silica aerogels. All of the aerogels showed minimal shrinkage during supercritical drying. The aerogels had higher surface areas and pore volumes and larger mean pore diameters than the corresponding xerogels (Table 1; BJH plots in supporting information). The difference in surface area was greatest between the phenylene-bridged xerogels and aerogels. Examination of fracture surfaces of the bridged xerogels and aerogels with scanning electron microscopy (Fig. 3)

showed that all of the materials were aggregates of spherical particles between 15 and 35 nm in diameter. The xerogels were relatively close packed aggregates with visible pores that were similar in size to the particles. Particles in the aerogels were strung together less densely with pores greater than 50 nm in diameter. As observed with nitrogen sorption porosimetry, the micrographs reveal that the hexylene-bridged aerogels had the largest pores with some pores larger than 100 nm in diameter.

3.4 Flexural strength measurements

Flexural strength and moduli (Table 2) were determined using three point, bend beam analysis on the cylindrical monolithic xerogels and aerogels. Phenylene-bridged polysilsesquioxane xerogels were the strongest with flexural strengths of 28 MPa while the hexylene-bridged xerogels were nearly as strong (26 MPa). Not surprisingly, in view of their much lower density, the bridged aerogels were several hundred times weaker than the corresponding xerogels. Of the aerogels, the phenylene-bridged silsesquioxane aerogels were the strongest with a flexural strength of 48 kPa. The phenylene-bridged aerogels were approximately 33% stronger than that of a traditional silica aerogel of the same density [27–31], which had strength of 36 kPa. Hexylene-bridged aerogels were slightly weaker than the silica and phenylene-bridged aerogels with a
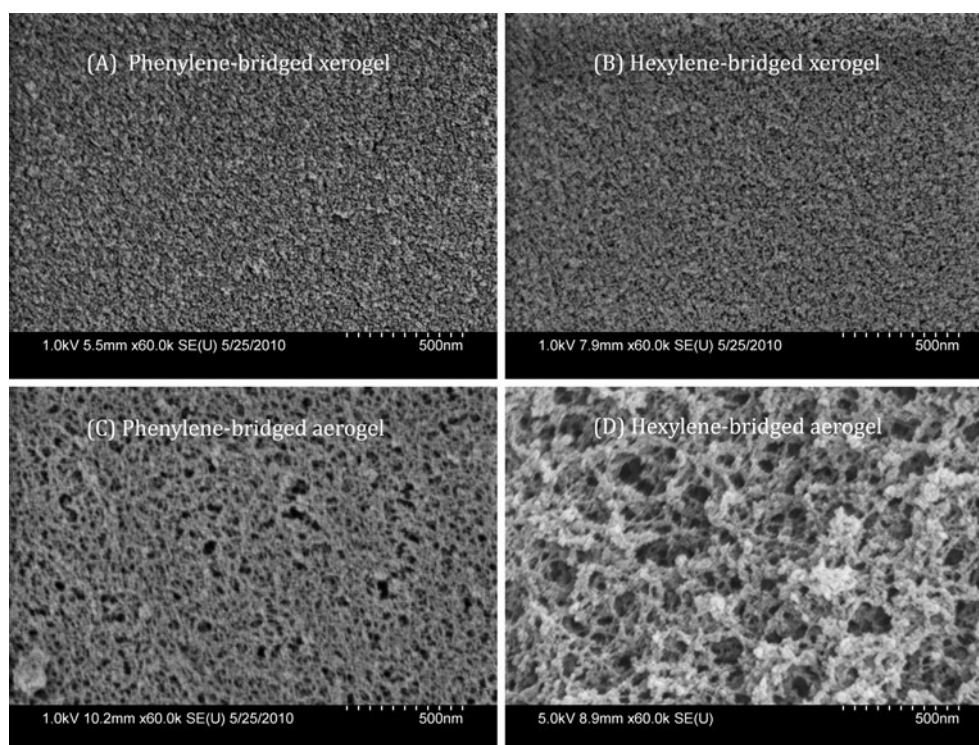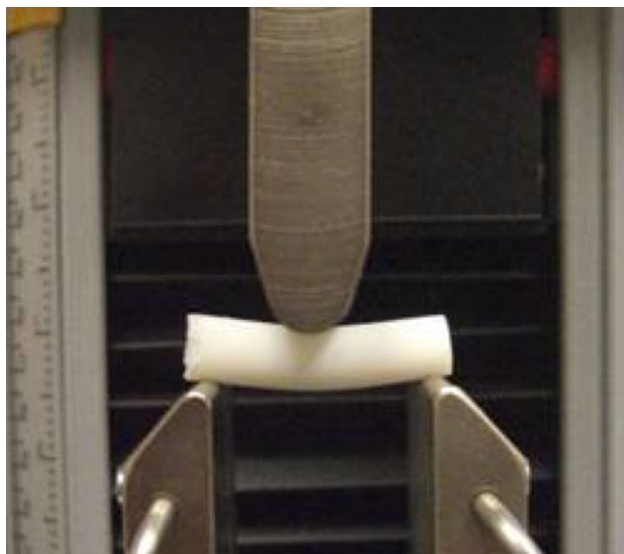

Fig. 3 Phenylene-bridged and hexylene-bridged polysilsesquioxane xerogels (**a**, **b**) and aerogels (**c**, **d**)

Table 2 Mechanical properties of hexylene and phenylene bridged aerogels and xerogels

Sample	Density (g/cm^3)	Flexural strength (MPa)	Young's modulus (MPa)
Phenylene-xerogel	0.794 ± 0.007	28.0 ± 2.0	124 ± 13
Hexylene-xerogel	0.781 ± 0.002	26.0 ± 1.0	119 ± 23
Phenylene-aerogel	0.097 ± 0.005	0.048 ± 0.002	0.553 ± 0.014
Hexylene-aerogel	0.093 ± 0.003	0.031 ± 0.003	0.079 ± 0.018
Silica aerogel	0.092 ± 0.003	0.036 ± 0.003	0.307 ± 0.058

Fig. 4 From flexural analysis, hexylene-bridged polysilsesquioxane aerogels were observed to be very elastic with deflections up to 40% of the diameter before breaking

flexural strength of 33 kPa, or about 45% less strong than the phenylene-bridged aerogels. Both phenylene- and hexylene-bridged xerogels exhibited comparable elastic moduli and were essentially brittle glassy materials. The elastic modulus of the phenylene-bridged aerogels (0.553 ± 0.014 MPa) was higher than the silica aerogel (0.307 ± 0.058 MPa), but both were brittle, yet fragile materials. They typically showed small flexural strain (0.8 mm) before breaking. However, the hexylene-bridged polysilsesquioxane aerogels were quite flexible with a modulus (0.079 ± 0.018 MPa) nearly an order of magnitude lower than the phenylene aerogel and flexural strains of 40% before failure (Fig. 4).

4 Discussion

Other studies have shown that bridged polysilsesquioxanes can be harder and tougher than silica [32–34]. These have been, for the most part, based on hardness or nano-indentation studies. This report is the first time that the flexural strengths of bridged polysilsesquioxane xerogels have been

measured. Flexural strength and modulus of cylinderical hexylene- and phenylene-bridged polysilsesquioxane xerogels and aerogels measurements were nade using sample dimensions in accordance with ASTM D790 and ASTM C1684. While there has been recent evidence that greater accuracy has been observed with samples with greater length to diameter ratios [35], we have measured flexural strength and moduli of silica aerogels with a 5:1 length to diameter ratio (Table 2) that are close to literature values [27–31].

Transparent phenylene-bridged and hexylene-bridged xerogels formed with similar sized pores, levels of shrinkage, and densities. The hexylene- and phenylene-bridged polysilsesquioxane xerogels had very similar flexural strengths of near 27 MPa despite their relatively high porosity. Both xerogels had very similar mesoporosity, though the hexylene-bridged xerogels had more micropores that lead to higher surface areas and pore volumes. Not surprisingly, in view of their much lower density, the bridged aerogels were several hundred times weaker than the corresponding xerogels. But, unlike the xerogels, the phenylene and hexylene bridged aerogels were different in appearance and in their properties. The phenylene-bridged aerogels were transparent and 30% stronger than silica aerogels of comparable density [27–31]. The greater strength of the phenylene-bridged gels is in accordance with measurements on thin films and compressive measurements on monolithic disks that have also shown about 30% greater strength than comparable silica materials. The hexylene-bridged aerogels were of similar density but were opaque and significantly weaker than the phenylene-bridged aerogels. While the phenylene-bridged aerogels were very similar to silica aerogels in appearance and in mechanical properites, the hexylene-bridged aerogels with their larger pores were opaque and noticably more elastic. Our earlier study of alkylene-bridged polysilsesquioxanes reported that a variety of the different bridging groups afforded white opaque, flexible aerogels [15], but no mechanical properties were measured. Subsequent studies of hybrid aerogels based, in part, on hexylene-bridged also have shown that opaque, elastic aerogels were obtained [23, 24]. The opacity is likely due to the larger pores in the hexylene-bridged aerogels resulting in Mie scattering. Larger pores in the hexylene-

birdged polysilsesquioxane aerogels also is the likely cause of their increased flexibility relative to the phenylene-bridged and silica aerogels, both of which have significantly smaller pores (Fig. 3; Table 2). Similar effects on flexibility are observed in polymer foams, where flexibility has been shown to increase with cell size [36, 37]. The lower strength of the hexylene-bridged aerogels, compared with the silica and phenylene-bridged aerogels, may also be due to the larger sized pores. Similar trends have been observed for silica aerogels whose porosity was systematically varied using organic polymer templates [38, 39].

5 Conclusion

Flexural strength measurements on the bridged xerogels and aerogels have confirmed findings from earlier thin film studies that the bridged polysilsesquioxanes were often stronger than silica materials of comparable densities [27–31]. Translucent phenylene-bridged polysilsesquioxane xerogels and aerogels and hexylene-bridged xerogels appear much like silica aerogels but are stronger. The white, opaque hexylene-bridged aerogels, on the other hand, are weaker and significantly more elastic than other bridged polysilsesquioxanes or silica materials. Clearly, some elastic structure is preserved with supercritical processing, that is lost with air-drying to afford the relatively brittle hexylene xerogels. Our earlier study of alkylene-bridged polysilsesquioxanes reported that a variety of the different bridging groups afforded white opaque, flexible aerogels, but no mechanical properties were measured. Future efforts are being directed towards determining the mechanical properties of hexylene-bridged aerogels and non-porous xerogels prepared under acidic conditions to provide additional insight into the origins of the elasticity in these materials.

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