Strong, Low-Density Nanocomposites by Chemical Vapor Deposition and Polymerization of Cyanoacrylates on Aminated Silica Aerogels

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ABSTRACT Strong polymer−silica aerogel composites were prepared by chemical vapor deposition of cyanoacrylate monomers onto amine-modified aerogels. Amine-modified silica aerogels were prepared by copolymerizing small amounts of (aminopropyl)tri-ethoxysilane with tetraethoxysilane. After silation of the aminated gels with hexamethyldisilazane, they were dried as aerogels using supercritical carbon dioxide processing. The resulting aerogels had only the amine groups as initiators for the cyanoacrylate polymerizations, resulting in cyanoacrylate macromolecules that were higher in molecular weight than those observed with unmodified silica and that were covalently attached to the silica surface. Starting with aminated silica aerogels that were 0.075 g/cm³ density, composite aerogels were made with densities up to 0.220 g/cm³ and up to 31 times stronger (flexural strength) than the precursor aerogel and about 2.3 times stronger than an unmodified silica aerogel of the same density.

KEYWORDS: aerogel • strong aerogels • nanocomposites • vapor deposition • hybrid materials

Supercritically drying a silica alcogel, prepared by polymerizing tetramethoxysilane (TMOS) in methanol with 4 equiv of water and catalytic ammonia, affords a gossamer solid called an aerogel (Figure 1) (1). Aerogels are highly porous materials with surface areas between 500 and 1600 m²/g and densities between 0.002 and 0.8 g/cm³ (density of air = 0.0012 g/cm³) (2). These materials display unique physical properties that have made them attractive for thermal (3) and acoustic (4) insulation, low-*k* dielectric materials (5), and Cherenkov radiation counters (6). Unfortunately, the low density and colloidal structure make aerogels too fragile (7) to economically manufacture.

Composed of a tenuous network of silica nanoparticles, the strength of the silica aerogels is proportional to the small volume fraction of silica within the aerogels (8). Because the network is an aggregate of spherical particles, the strength of the aerogel is limited by the narrow necks of silica that interconnect the particles (9). Tensile measurements are not practical because of difficulties in clamping the diaphanous materials, so the strength of the aerogels is typically measured in compression or flexure (bend-beam analyses) (7). We determined that the flexural strength of a silica aerogel with a density of 0.08 g/cm³ is

FIGURE 1. Transparent silica aerogel and aminated silica aerogel. After CVD of methyl cyanoacrylate, the gels begin to become opaque.

10 kPa with an elastic modulus of 65 kPa, a fraction of that measured for nonporous amorphous silica (55 MPa and 73 GPa, respectively) (10). Any strategy to strengthen aerogels must reinforce the necks in the network while keeping the high surface area, pore volume, and low density. Early strategies relied on redistribution of silica from the particles to the necks in alkaline solutions (Ostwald ripening) (11). Supplying additional monomer after gelation has also been reported to strengthen gels (12). More recently, chemical vapor deposition (CVD) of silyl chlorides or metal halides has been used to reinforce aerogels quickly, although the modest increases in strength may be due to modification of the surface chemistry (13). This CVD was achieved despite slower gas diffusion within the silica aerogel compared to free space (14). Addition-

Scheme 1.   Process for Preparing the Aminated Silica Aerogel/Poly(methyl cyanoacrylate) Composites

Aminated Silated Aerogel

Polycyanoacrylate-Silica Composite Aerogel
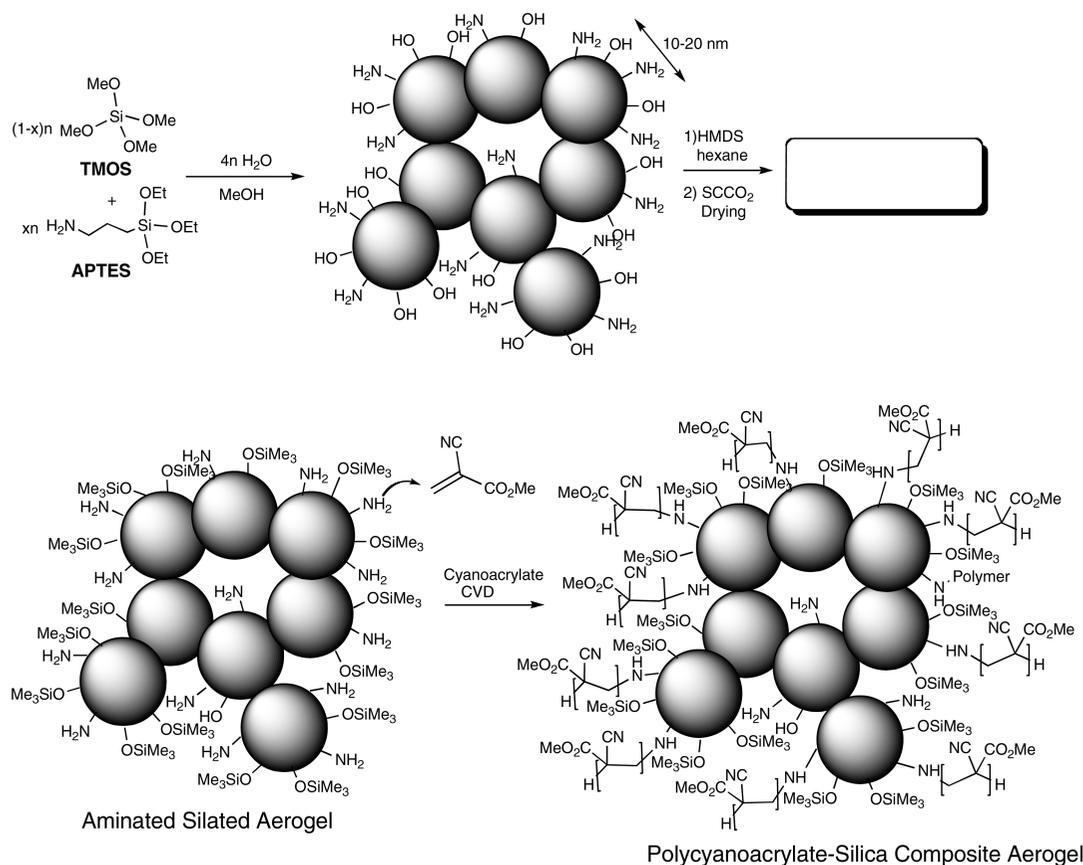
ally, reinforcement of the silica network before drying of the gel by growing polymers (15) such as polyureas (16), polyurethanes (17), epoxies (18), and polystyrenes (19) from the silica surface has been used to improve the strength but with a significant increase in the density (0.5−0.8 g/cm^3) accompanied by a decrease in the surface area. After supercritical drying, the polymer−silica aerogel composites were found to have significant flexural strength improvements.

Recently, we found that silica aerogels could be reinforced with poly(methyl cyanoacrylate) by adsorbing methyl cyanoacrylate vapor on the aerogels at room temperature and pressure. Upon adsorption, the polymerization of methyl cyanoacrylate is initiated by the surface water (20). The process takes up to 24 h to deposit sufficient poly(methyl cyanoacrylate) throughout the monolithic aerogels to increase the flexural strength 16-fold and the density from 0.075 g/cm^3 to around 0.235 g/cm^3. Because adsorbed water initiated the polymerizations, the resulting polycyanoacrylate chains were unattached to the surface, a fact verified by the ease with which the polymer was dissolved from the aerogels with acetone. The abundance of the surface water provided so many initiators for the polymerization of cyanoacrylate monomers that only oligomers (DP = 10−12) were formed. We hypothesized that, if we modified the surface with nucleophilic amine groups and eliminated the adsorbed water, the CVD process should result in higher molecular weight cyanoacrylate macromolecules that are covalently at-

tached to the particle surfaces and, ultimately, stronger nanocomposite aerogels. This paper details the formation of aminated gels from the copolymerization of TMOS with (3-aminopropyl)triethoxysilane (APTES), silation of the surface with trimethylsilyl groups, supercritical drying, and CVD modification with cyanoacrylate to yield nanocomposite aerogels (Scheme 1). The resulting polycyanoacrylate-aminated silica aerogel composites (0.095−0.230 g/cm^3) are up to 31-fold stronger in flexural strength than the precursor aminated aerogels and able to support up to *3200 times* their own weight. The nanocomposite aerogels were strong enough to allow sample preparation for dielectric constant measurements.

Sol−gel polymerization of TMOS with between 0.25 and 5 mol % APTES allows silica gels to be prepared with amine groups derived from APTES adorning the surface. The formulation, based on 1 mol/L (1 M) total monomer concentration (TMOS + APETS), was designed to give cylindrical, 3.6 cm^3 aerogels with a density of around 0.075−0.085 g/cm^3. The combination of less reactive ethoxysilyl groups of APTES and the end-blocking characteristics of organotrialkoxysilanes preferentially segregates the amine groups to the surface of the colloids that make up the gels (21). Assuming that all of the amine groups are segregated to the surface, the 5 mol % APTES formulation theoretically gives aerogels with 1 out of every 11 silanols replaced with an amine group (1 amine per 2.7 nm^2) and the 0.25 mol % formulation results in 1 out of every 220 silanols replaced with an amine group

(1 amine per 54 nm^2). In formulations with the highest concentration of APTES (0.05M), the amino group served to catalyze the copolymerization, with TMOS giving rise to monolithic gels within 15 min. Additional ammonia was added to formulations with lower APTES concentrations to permit the formation of gels in similar amounts of time. Gels were allowed to age for 48 h at room temperature followed by 48 h at 50 °C before their surfaces were silated with hexamethyldisilazane (HMDZ) in hexanes. This was accomplished by first exchanging the methanol in the gels with ethanol, hexane, and then HMDZ in hexane. Because HMDZ reacts with silanols and residual water, the resulting aerogels only had aminopropyl groups to initiate cyanoacrylate polymerization. Subsequent supercritical drying with carbon dioxide over 24 h afforded transparent aerogels tinted blue from scattering. Visually, the hydrophobic (Figure 1 in the Supporting Information), aminated and silated aerogels appear to scatter light slightly more than the pure silica aerogels (Figure 1). Not surprisingly, in view of the added trimethylsilyl groups and aminopropyl functionalities, the aminated and silated aerogels exhibit slightly higher densities (0.095−0.105 g/cm^3) than pure silica aerogels (0.075−0.085 g/cm^3). The surface areas of the aerogels were approximately 1000 m^2/g or 262 m^2 for each monolithic aerogel weighing 0.262 g, which mostly contain mesopores (2 nm < pore diameters < 50 nm) and some micropores (pore diameters < 2 nm). Unmodified silica aerogels exhibited primarily mesoporosity. The amount of APTES did not affect the surface area.

CVD and polymerization were carried out by flowing nitrogen gas over methyl cyanoacrylate and passing the monomer saturated gas stream (0.1 L/min) into a reaction chamber where the silica aerogels are suspended. This method permits rapid, constant deposition (5 mg/h) of poly(methyl cyanoacrylate) on the amine-modified aerogels, only slightly slower than that with unmodified silica aerogels (7 mg/h). The slower rate is consistent with a lower initiator concentration in the amine-modified aerogels. The density of the resulting polycyanoacrylate-modified silica aerogels could be controlled by variation of the times the aminated silica aerogels were exposed to the methyl cyanoacrylate vapor. The densest composite aerogel in this study had a density of 0.220 g/cm^3, a 2.3-fold increase over the polymer-free, aminated silica aerogel but still 1 order of magnitude less dense than amorphous, nonporous silica. CVD and polymerization of methyl cyanoacrylate on the aerogels were accompanied by a decrease in transparency, with aerogels that have densities over 0.20 g/cm^3 appearing to be opaque to visible light (Figure 1). Similarly, the surface areas of the aerogels decreased with an increase in the amount of polycyanoacrylate deposited by CVD (Table 1). Covalent attachment of the methyl cyanoacrylate macromolecules to the aerogels was demonstrated by their resistance to extraction with acetone. By dissolution of the silica with hydrofluoric acid, poly(methyl cyanoacrylate) could be isolated; the molecular weights were determined to be around 10 000 Da

Table 1. Density, Flexural Strength, Modulus, and Surface Area of Polycyanoacrylate−0.25 mol % Aminated Silica Aerogel Nanocomposites[a]

density (g/cm^3)	flexural strength × 10^5 (N/m^2)	elastic modulus × 10^5 (N/m^2)	surface area (m^2/g)
0.095	0.21 ± 0.015	2.3 ± 0.17	964.2
0.110	0.36 ± 0.034	2.9 ± 0.24	861.8
0.126	0.49 ± 0.022	3.1 ± 0.066	664.2
0.150	1.73 ± 0.11	13.3 ± 0.77	661.8
0.158	2.44 ± 0.19	22.5 ± 1.03	632.9
0.230	6.51 ± 0.44	42.9 ± 2.87	522.7

[a] Six samples were prepared at each density to provide reproducibility.

or about 4 times that of the oligomers deposited on pure silica aerogels (20).

Examination of the CVD-modified aerogels by scanning electron microscopy (SEM) revealed that morphology with lower populations of amine groups (0.25 mol %) was more homogeneous throughout the monoliths (Figure 2A,B in the Supporting Information). At 5 mol % amine loading, however, micrographs show that more polymer was deposited near the aerogels' surface, resulting in the formation of a relatively dense crust (Figure 2C,D in the Supporting Information). We speculate that the greater reactivity of the amine groups as an initiator (compared with water or silanols) coupled with the higher concentration of the amine groups in the 5 mol % samples, led to the polymerization of the methyl cyanoacrylate monomer outpacing monomer diffusion into the interior of the aerogel. The ratio of the polymer's carbonyl absorption (1757 cm^{-1}) to the silica siloxane band (1100 cm^{-1}) in the IR spectra of the composite aminated silica aerogels was used to confirm the heterogeneity of polymer deposition in the CVD-modified aerogels. The crust observed in the silica aerogel composites based on 5 mol % APTES contained 70 % more polymer than the aerogel's interior regions. In aerogels prepared with 0.25 mol % APTES, Fourier transform IR (FTIR) analysis only revealed 20−25 % more polymer near the surface of the aerogel relative to its center, supporting the hypothesis that fewer amine groups permitted more monomer diffusion into the core of the monoliths.

Examination of how the flexural strength of the aerogels changes with density is summarized in the graph in Figure 2. To obtain these measurements, at least three monolithic aerogels were tested using three-point bend-beam flexural strength analysis. In previous reports on the strengthening of aerogels (15−19), comparisons in strength have been made to the precursor aerogel without compensating for density. To rectify this deficiency, a series of pure silica aerogels (Figure 2; diamonds) with densities ranging from 0.035 to 0.215 g/cm^3 were prepared to provide a baseline of the flexural strength as a function of the density to which the aminated and CVD-treated, aminated aerogels could be compared. In comparison with this baseline data, improvements in strength previously reported from the CVD modification of unaminated silica aerogels (Figure 2; squares) appeared to be from density increases until substantial
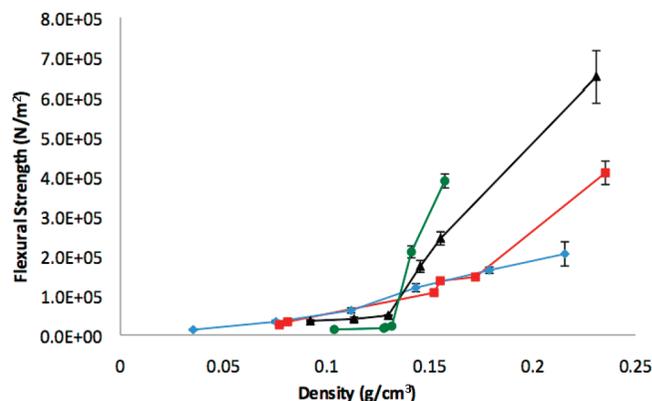
FIGURE 2. Flexural strengths of silica, polycyanoacrylate-modified, 5 mol % aminated silica and polycyanoacrylate-modified, 0.25 mol % aminated silica aerogels: strength of various density silica aerogels (0.035−0.215 g/cm³) (blue diamond line); strength of CVD-treated silica aerogels (red square line); CVD-treated, 5 mol % aminated silica aerogels (green circle line); CVD-treated, 0.25 mol % aminated silica aerogels (black triangle line).

amounts of poly(methyl cyanoacrylate) had been deposited and the composite density was near 0.235 g/cm³. In contrast, CVD-treated, aminated aerogels (Figure 2; circles and triangles) with densities greater than 0.126 g/cm³ were significantly stronger than CVD-modified silica aerogels or unmodified silica aerogels.

For example, the flexural strength of CVD-modified, 0.25 mol % aminated silica aerogels at 0.230 g/cm³ density was 650 kPa or over 3 times the strength of silica aerogels or CVD-modified silica aerogels of the same density and *31 times stronger* than the original silica aerogels before CVD treatment (0.075 g/cm³). These were the strongest aerogels made in this study. For the aerogels with 5 mol % APTES, the strength of the CVD-modified aerogels with densities of around 0.160 g/cm³ was 4 times greater than that of a pure silica aerogel of the same density. The increase in strength may be due, in part, to the hetereogeneous "crust" (vide supra) providing a tempering effect. No CVD-modified aerogels with higher density were made in this series (5 mol % APTES modified silica) because of the heterogeneity in polymer deposition.

The origin of the dramatic increase in strength in the aerogels above 0.126 g/cm³ appears to be related to capillary filling of micropores early in the CVD process. Nitrogen sorption analyses of the aerogels revealed more microporosity (< 2 nm) in the APTES-modified aerogels than is observed in the mesoporous silica aerogels (Figure 3 in the Supporting Information). In the aminated aerogels, we speculate that the monomer initially condenses into micropores, possibly inside the particles, where its polymer will not reinforce the aggregate structure. Only once the micropores are filled does the monomer polymerize on the aggregate surface, where it can reinforce the aerogel.

Once we determined that aerogels could be strengthened with cyanoacrylate CVD in excess of what would be expected with an increase in the density, we decided to see if the nanocomposites could be cut into square samples (4 mm × 2 mm × 2 mm) for dielectric analyses. The dielectric constant of silica aerogels has been reported

Table 2. Dielectric Constants Determined for CVD-Treated Silica Aerogels and CVD-Treated, Aminated Silica Aerogels

sample name	density (g/cm³)	dielectric constant
silica aerogel	0.147	1.83 ± 0.045
silica aerogel	0.235	2.00 ± 0.18
aminated aerogel	0.081	1.47 ± 0.17
aminated aerogel	0.128	1.63 ± 0.083
aminated aerogel	0.157	1.94 ± 0.18

to be from 1.1 to 2.0 depending on the density of the silica aerogel. Our silica aerogels without CVD modification were so weak that they could not be cut into the desired shape without breaking. It was possible, however, to cut a number of nanocomposite aerogels into the desired sample geometries, demonstrating their superior strength. Once cut into the desired shape, silver electrodes were painted onto the top and bottom of the composite. Even samples that exhibited insignificant improvements in flexural strength were easier to cut than unmodified aerogels of similar densities, corroborating earlier observations that the nanocomposite aerogel flexural strengths are enhanced more than flexural strengths of polymer-free silica aerogels.

Dielectric constants of the nanocomposite aerogels (Table 2) ranged from 1.47 for a CVD-modified, aminated silica aerogel with a density of 0.081 g/cm³ to a dielectric of ∼2.0 for the densest CVD-modified silica aerogel. The stronger amine-modified silica aerogels exhibited a lower dielectric constant 1.86. While the dielectric constants of the CVD-modified silica aerogels and CVD modified, aminated silica aerogels were essentially the same, the latter were significantly stronger opening up the possibility for manufacturing even lower density nanocomposite aerogels with lower dielectric constants.

In conclusion, we have developed a new method for the formation of stronger aerogels through the CVD of cyanoacylates onto aminated silica aerogels. The strongest, CVD-modified, aminated silica aerogel exhibited a 30-fold increase in the flexural strength over that of the precursor silica aerogel. This was accompanied by only a 2.5-fold increase in density and a 2-fold reduction in the surface area. These strong aerogel composites are strong enough to be cut into specific shapes, withstand the capillary pressures of water, and float on the surface of water for months without suffering any structural failure. We evaluated these composites for a potential application as low-*k* dielectric materials, which are well below the values needed for 45 nm technology.

EXPERIMENTAL SECTION

Materials Used in Experiments. All reagents were used as-received without further purification. Tetramethoxysilane (TMOS; 98 %), anhydrous methanol (99.5 %), hexamethyldisilazane (HMDZ; 99 %), hexanes (99 % ACS reagent grade), ethanol (99 % ACS reagent grade), and (3-aminopropyl)triethoxysilane (APTES; 99 %) were purchased from the Sigma-Aldrich Chemical Co. Methyl 2-cyanoacrylate was purchased from Polysciences, Inc. Ammonium hydroxide (1 N) was purchased from VWR.

Aminated (5 mol %) Silica Aerogel Preparation with No Additional Catalyst. The molar ratios of monomers (TMOS and

APTES) to water for the amine-modified silica sol–gels were 1:4. All gels were prepared by mixing together a solution of TMOS and APTES in pure methanol with a second solution (B) of water in methanol. A typical example of aminated gel preparation is as follows. A solution of TMOS (0.52 g, 3.42 mmol) and APTES (0.039 g, 0.18 mmol) diluted to 1.8 mL with anhydrous methanol was mixed with a second solution of water (259 μL, 14.4 mmol) diluted to 1.8 mL with anhydrous methanol for 1 min in a poly(propylene) container (4 mL) at room temperature. The final volume was 3.6 mL. Gelation occurred within ~15 min, and syneresis occurred in 18 h. The gels were aged at room temperature for 48 h and aged at 50 °C for 48 h before further modification. After HMDZ treatment, the gels were dried using supercritical carbon dioxide drying to obtain an aminated silica aerogel (0.295 g, yield 131%). ^{29}Si CP MAS NMR (100 MHz): δ −68 (T^3), −92 (Q^2), −103 (Q^3), −113 (Q^4). IR (KBr): 3457, 2961, 2905, 2847, 1215, 1161, 1097, 1010, 920, 806, 668 cm^{-1}. Elem anal. Calcd (wt %) for $C_3H_8N_1Si_1O_{3.5}$: C, 2.88; N, 1.12; Si, 44.8. Found: C, 9.05; N, 0.88; Si, 41.81.

Aminated (0.25 mol %) Silica Aerogel Preparation with Supplemental Catalyst. All gels were prepared by mixing together a solution of TMOS and APTES in pure methanol with a second solution of water and catalyst in methanol. A typical example of the preparation of an aminated gel is as follows. A solution containing TMOS (0.547 g, 3.59 mmol) and APTES (0.00195 g, 0.009 mmol) diluted to 1.8 mL with anhydrous methanol was mixed for about 1 min with a solution of aqueous ammonium hydroxide (0.259 mL, 1 N) diluted to 1.8 mL with anhydrous methanol in a poly(propylene) container (4 mL) at room temperature. Gelation occurred within ~12 min, and syneresis occurred in 18 h. The gels were aged at room temperature for 48 h followed by aging at 50 °C for 48 h before further modification. After HMDZ treatment (vide infra), the gels were dried using supercritical carbon dioxide to obtain an aminated silica aerogel (0.262 g, yield 121%). ^{29}Si CP MAS NMR (100 MHz): δ −67 (T^3), −94 (Q^2), −101 (Q^3), −112 (Q^4). IR (KBr) 3446, 3061, 2950, 2907, 2851, 1219, 1158, 1082, 1001, 915, 841, 668 cm^{-1}. Elem anal. Calcd (wt %) for $C_3H_8N_1Si_1O_{3.5}$: C, 0.148; N, 0.106; Si, 46.6. Found: C, 3.58; N, 0.14; Si, 39.02.

HMDZ Modification of Aminated Silica Gels. After aging, the amine-modified silica sol–gels were then placed in excess ethanol (2×) to allow exchange with the methanol used in the sol–gel polymerization because the latter is immiscible with hexanes. Once ethanol had exchanged into the gels, the ethanol was exchanged with excess hexanes for 24 h. Then the hexanes were exchanged for a hexane solution containing 20% (v/v) HMDZ, and the aminated sol–gels were left for 24 h at 50 °C. Then the silated, amine-modified sol–gels were prepared for supercritical drying by exchanging HMDZ with pure hexanes, followed by ethanol, and then methanol. The supercritical process requires the silica gels to be in methanol to allow exchange with liquid carbon dioxide during the drying process. Gels were dried using a standard supercritical carbon dioxide process to afford cylindrical aerogels of approximately 3.8 mm in height and 9 mm in diameter.

CVD Process. Methyl cyanoacrylate was vapor-deposited on the aerogels using the apparatus reported previously (19). Methyl cyanoacrylate was placed into a modified round-bottomed flask. Nitrogen was swept through the system at room temperature (0.1 L/min) to carry vapors of cyanoacrylate through a glass U-tube to a reaction flask in which the aerogel monolith was placed. The gas stream with any residual cyanoacrylate exited through an outlet and bubbler to a chemical fume hood. To prevent the monomer from adsorbing and polymerizing on the glass surface of the CVD apparatus, the entire surface was silated using SurfaSil (Pierce Chemical Co.).

Instrumentation. Matrix-assisted laser desorption time of flight with a dihydroxybenzoic acid matrix was used to determine the poly(methyl cyanoacrylate) molecular weight. Me-

chanical property measurements were determined using a three-point flexural compression test with an Instron 5540 series single-column testing system with a 100N load cell set with a 0.04 in./min crosshead speed according to ASTM D790 and ASTM C1684. Nitrogen adsorption porosimetry samples were degassed at room temperature for 24 h under vacuum and analyzed with an Autosorb-1 porosimeter (Quantachrome Instruments). Samples for SEM were platinum sputter-coated, and microscopy was conducted with a Hitachi S-4800 field emission microscope. Dry aerogel samples were ground using a mortar and pestle with KBr and pressed into a pellet. IR spectra were obtained with a Perkin Elmer FTIR spectrometer. ^{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. Solids ^{29}Si NMR spectra were externally referenced to the silicon peak of tetrakis(trimethylsilyl)silane at −9.7 and −135 ppm.

Dielectric characterization was conducted by measuring the capacitance of a thin square with an average size of 4 mm × 2 mm × 2 mm. Thin squares were cut from cylindrical monoliths with a razor blade. The top and bottom of each square was painted with a collodial silver paint from Ted Pella (16031). As the paint was applied, two wire electrodes were placed in the paint that adhered to the surface. Capacitance was measured using a BK Precision, model 889A, running in capacitance measurement mode. Capacitance measurements were made at a frequency of 72 MHz. Capacitance values were corrected for fringe-field errors.

Supporting Information Available: Photograph of silated, aminated aerogel floating on water, SEM micrographs showing homogeneity of cyanoacrylate CVD into aerogels, and pore size distributions for aerogels before and after CVD treatment. This material is available free of charge via the Internet at http://pubs.acs.org.

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LETTER