Organic–Inorganic Hybrid Materials that Rapidly Swell in Non-Polar Liquids: Nanoscale Morphology and Swelling Mechanism

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A novel type of sol–gel derived zerogels that instantaneously swell greater than three times their dried volume in nonpolar solvents were investigated. Hybrid organic–inorganic materials that swell were only produced from a narrow set of precursors that possess an organic bridging group that contains an aromatic segment that is flexibly linked to the alkoxysilane polymerizable ends. Careful control over the processing conditions (catalyst, solvent, aging time) was necessary to yield animated zerogels. Various materials were studied by electron microscopy, infrared spectroscopy, nitrogen adsorption, and fluorescence spectroscopy using a covalently linked pyrene reporter. Collectively, the data support a model where swelling is derived from a morphology of interconnected organosilicate nanoparticles that are cross-linked to a particular extent during the gel state. Upon drying to the zerogel form, tensile forces generated by capillary-induced collapse of the polymeric matrix are released when interparticle interactions holding the dried material in the shrunken state are disrupted by a suitable solvent system. Swelling produced forces in excess of 50 N/g and is completely reversible. The molecular-scale organization of the nanoparticle structure seems critical for this swelling behavior. Further experiments indicate that the organosilicate materials can also swell in response to gas-phase organic molecules in a concentration dependent manner. These hybrid materials show promise for use in remediation technologies and chemical sensing.

Introduction

The sol–gel process is a convenient method to prepare hybrid inorganic–organic materials with unique properties both in terms of chemical composition and physical microstructure. Recently, we reported a type of hard optically transparent sol–gel that rapidly swells ~4–5 times its dried volume in nonpolar solvents.[1] These highly animated zerogels were prepared by polymerization of a bridged organosilane precursor bis(trimethoxysilyethyl)benzene. Polycondensation of a wide variety of bridged precursors has been reported and subsequently used to create nanostructured materials.[2] Control of the sol–gel processing conditions (i.e., solvent, catalyst, aging temperature) can be used to tailor the texture of the resulting sol–gel derived solids which is advantageous when designing new materials.[3] In this case, we have been able to create highly animated materials by carefully controlling chemical composition and morphology of the polymeric organosilicate.

Silica-based sol–gel derived solids are typically characterized as inelastic and do not swell when fully dried, with only rare exceptions to this rule being reported.[4–7] Typically, swelling involves some type of physical or chemical change, for example, a change in temperature[6] or pH.[7] The amount of swelling in these instances is modest, <15% of the original volume. In contrast, the materials described here swell to a significant degree (>400%). Only nonpolar liquids are taken up by the sol–gel polymer, even when placed in biphasic mixtures of water and organic solvents. This allows for a degree of chemical selectivity and sets the material apart from biomaterials[8,9] or hydrogels[10] that absorb water or other polar liquids. Swelling of the hybrid material is completely reversible after removing the solvent by evaporation or drying. No loss in the swelling behavior occurs even after repeated use. Swelling occurs instantaneously upon addition of liquid, so rapidly that large glass-like monoliths (>5 mm) can fracture during the rapid incursion of solvent. In addition

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to adsorbing large amounts of nonpolar substances from the neat liquid phase, adsorption of nonpolar organic molecules is also possible from the gas phase or from aqueous solution. Because of these unique properties there are a number of potential applications of such a material including encapsulating molecules for controlled drug release,[11] chemical remediation of hydrophobic species from aqueous systems, and chemical sensing.[12]

Highly swellable organosilicas have been only produced under a narrow set of processing conditions (precursor, solvent, catalyst, aging time). In previous work, sol–gels were prepared from bis(trimethoxysilyethyl)benzene and polymerized in tetrahydrofuran (THF) using tetrabutylammonium fluoride (TBAF) as a catalyst. Prior to drying, the wet gels are rinsed to remove unreacted silane, water, and catalyst. Rinsing is followed by derivatization of the residual silanol groups using a chlorosilane reagent. The identity of the derivatizing reagent has no effect on the swelling behavior;[1] however, derivatization is required to produce a material that swells. In this report, we significantly expanded the number of processing variables to more fully understand the prerequisites needed to produce swellable organosilicates. In addition, the materials were further characterized to understand the physical processes that lead to the swelling behavior.

Experimental Section

Materials. Bis(trimethoxysilyethyl)benzene (**1**); 1,4-bis(trimethoxysilylmethyl)benzene (**2**); 1,4-bis(triethoxysilyl)benzene (**3**); tris(3-trimethoxysilylpropyl)isocyanurate (**4**); 1,6-bis(trimethoxysilyl)hexane (**5**); phenyltrimethoxysilane (PTMS); methyltrimethoxysilane (MTMS); tetramethoxysilane (TMOS); and mercaptopropyltrimethoxysilane (MPTMS) were obtained from Gelest. All other solvents and reagents were obtained from Sigma-Aldrich except for *N*-(1-pyrenemaleimide) which was obtained from Invitrogen. All reagents were used without further purification.

Sol–Gel Preparation. Materials were prepared as described previously.[1] Briefly, 1.80×10^{-2} moles of precursor and solvent to yield a final volume of 35 mL was initially mixed. One hundred microliters of 1.0 M TBAF, 375 μL of concentrated HCl, 90 μL of 1.0 M NaOH, 100 μL of 1,5-diazabicyclo[4.3.0]non-5-ene (DBN), or a specified amount of *n*-butylamine was added as a polymerization catalyst. Prior to addition, catalyst was mixed with a stoichiometric amount of water (0.5 mol H_2O/mol alkoxysilane group). After gelation, the materials were aged for a prescribed time (6 days unless otherwise specified) in a closed container at 25 °C, crushed into pieces ~3–5 mm in size, and sequentially extracted with ethanol twice and acetonitrile twice over a 4 day period. The sol–gels were then incubated in 20 mL of a 5% v/v solution of cyanopropyldimethylchlorosilane in acetonitrile for 48 h at room temperature. The gels were then rinsed three times with acetonitrile over 3 days and dried for 2 h at 60 °C in a standard laboratory oven. The material was then ground in a bead mill to generate a coarse powder.

Characterization. Scanning electron microscopy (SEM) was performed using a Hitachi S-4700 instrument. Solid samples were dried in a vacuum oven at 60 °C for 12 h and coated with platinum prior to measurement. Multiple areas were examined to ensure the micrographs depicted were a representative of the sample. Swollen sol–gels composed of **1** (THF solvent, TBAF catalysis) were prepared for microscopy by critical point drying from ethanol using a Tousimis AUTOSAMDRI-814 apparatus or by swelling the sol–gel in a 5% w/v solution of poly(2,2,3,3,4,4,4-heptafluorobutylmethacrylate) in acetonitrile followed by drying in at 60 °C for 24 h.

Surface area and pore volume were measured with a Beckman-Coulter 3100 surface area analyzer using the BET method.[13] Pore size distributions were measured by N_2 desorption using the BJH method.[14] Fourier transform infrared (FT-IR) spectra were obtained by preparing KBr pellets of the dried sol–gels. Spectra were obtained using a Perkin-Elmer 2000 FT-IR at a resolution of 4 cm^{-1}.

Polarized light microscopy was done using an Olympus 1 × 70 inverted microscope with crossed polarizers. Images were acquired with a Diagnostic Instruments Color Mosaic CCD using Spot image capture software. Sol–gel solutions were prepared as described above and immediately placed in cells constructed of glass microscopy slides derivatized with (tridacefluoro-1,1,2,2,-tetrahydroctyl)dimethylchlorosilane. A 50 μm Teflon gasket was placed between the slides to generate a sealed system of fixed thickness containing the sol–gel solution.

Swelling was measured by adding solvent dropwise to 100 mg of zerogel until the swelling behavior had visibly ceased while the exterior of the material continued to appear fully dry. The amount of solvent was determined by the difference in weight. The amount of swelling was also confirmed by optical microscopy. Swelling force was measured as described in the text using a 3.3 cm diameter glass cylinder with a course glass frit sealed to one end. The piston was loaded with a fixed weight, and the volume increase was recorded after the system had come to equilibrium (<15 min).

Fluorescence Quenching. An amount of *N*-(1-pyrenemaleimide) and MPTMS (3.5×10^{-5} moles) with a 1:1 molar ratio was reacted at room temperature in a minimal amount of anhydrous acetonitrile for 18 h. Confirmation of the fluorescent thioether-linked adduct on the silane (pyrene−TMS) was determined by TLC. Sol–gel solutions were prepared by adding 1.50×10^{-3} mol of **1** and 7.50×10^{-6} mol of pyrene−TMS to 50 mL of THF. Solutions were sparged with N_2 for 30 min prior to measurements. Fluorescence emission spectra were collected using a SPEX FluoroMax instrument with excitation at 340 nm. Nitrobenzene was used as a collisional quencher of pyrene−TMS fluorescence[15] which was added in sequentially higher concentrations to sol–gel solutions. For postcatalysis measurements, 162 μL of H_2O and 150 μL of TBAF were added 10 min prior to analysis. In all cases, fluorescence measurements were completed before gel point. Fluorescence quenching data was fitted to a modified Stern−Volmer equation[16]

$$\frac{F_0}{\Delta F} = \frac{1}{f_a K_a [Q]} + \frac{1}{f_a} \qquad (1)$$

where F_0 is the fluorescence in the absence of quencher, ΔF is the difference between F_0 and the fluorescence at a particular quencher concentration, f_a is the fraction of fluorophore accessible to quencher, K_a is the Stern−Volmer quenching constant for the available fraction, and $[Q]$ is the concentration of quencher.

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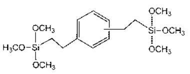
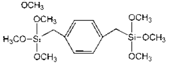
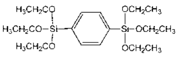
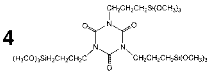
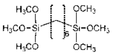
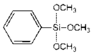
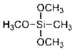
Gas-Phase Adsorption Measurements. Samples (150 mg) of zerogel prepared from precursor **1** as described above were sealed in a segment of Teflon tubing using porous frits to allow gas flow through the material. A pure N_2 gas stream was modified by the introduction of various amounts of N_2 saturated with toluene. Mass flow controllers were used to vary the amount of N_2 and toluene-saturated N_2 keeping the total flow 50 mL/min. The various concentrations of toluene in N_2 were verified using the absorbance of toluene at 210 nm via a flow cell and by collecting toluene with a cold trap followed by subsequent measurement by HPLC. Individual samples of zerogel were exposed to a vapor stream with a specific concentration of toluene for 18 h. The amount of toluene in the gas phase was continuously monitored by UV absorbance at 210 nm through a flow cell positioned immediately after the segment containing the zerogel. At 2 h time intervals, the organosilicate sample was weighed to measure mass changes which were correlated to the adsorption of toluene over time.

Results and Discussion

Organosilane precursor type, precursor concentration, solvent, catalyst, and aging time were varied to determine the affect on the swelling behavior of the final material (Table 1). Swelling was defined as the ability of the sol–gel to expand greater than three times its dried weight in less than 2 s. Interestingly, materials either exhibited a highly animated swelling behavior or did not swell at all (with only rare exceptions), making this type of categorization possible. Nine different precursors were used to create organosilicates which were processed in an identical manner. These included silanes that were bridged by various organic linkages (**1**, **2**, **3**, **4**) and silanes that contained only a single silicon center including PTMS and MTMS. Swellable sol–gels were only produced by materials formed from **1** or **2**. Both are bridged silanes that contained an aromatic group that is tethered to the silicon centers via a rotationally flexible methylene or ethylene group. In contrast, the more rigid 1,4-bis(triethoxysilyl)benzene (**3**) where the aromatic group is directly attached to the two polymerizable triethoxysilane groups did not swell. A flexible bridging group is not a prerequisite for swelling as demonstrated by the fact that xerogels prepared from a hexane-bridged silane (**5**) exhibited no swelling.

The maximum degree of solvent uptake was fairly consistent between the various formulations that swell (Table 2). The increase was generally 3–5 times the dried volume which is roughly equivalent to the volume lost during the initial drying of the gel to form a solid transparent glassy material. There was no preference for solvent as long as it is reasonably nonpolar; ethanol produced approximately the same amount of volume increase as did hexane in most cases. The materials typically swelled most rapidly in THF. If the particles are roughly <1 mm then there was no change of macroscopic shape upon swelling (Figure 1). The same shape was also maintained following shrinkage from the swelled stated. Normal swelling, as defined above, was observed for solvent systems having a Snyder polarity parameter[17] $\leq 6.5 \pm 0.5$ as measured using various mixtures of ethanol/water and *n*-butanol/water. This polarity correlates to a solution composed of 65:35 (v/v) ethanol/water. Zerogels ceased to be wetted in solutions having a polarity parameter $> 8.5 \pm 0.5$. The rate of swelling was slightly enhanced by grinding the material to a coarse powder, presumably because there is a higher surface area to volume ratio resulting in a higher rate of solvent transport into the zerogels. Larger monolithic

Table 1. Effect of Various Processing Conditions on Swelling Behavior

Precursor[a]		Swelling
1		Yes
2		Yes
3		No
4		No
5		No
PTMS		No
MTMS	 $H_3CO-Si(OCH_3)_2-CH_3$	No
TMOS	$Si(OCH_3)_4$	No
95% **1**; 5% **2**		Yes

Catalyst[c]	Swelling
HCl	Some
TBAF	Yes
NaOH	No
0.05M $CH_3(CH_2)_3NH_2$	No Gel
0.25M $CH_3(CH_2)_3NH_2$	Some
0.5M $CH_3(CH_2)_3NH_2$	Yes
DBN	Yes

Aging Time[d]	
None, rinsed	Slow
None, silane treated	No
1 hr	Yes
1 day	Yes
3 day	Yes
6 day	Yes
6 day (60°C)	Yes

Solvent[b]	
Ethanol	No
CH_3CN	No
Acetone	Yes
THF	Yes
80%CH_2Cl_2/20%THF	Yes
90%THF/10%CH_3CN	Yes

Silane Concentration[e]	
2X	No
1X	Yes
0.75X	Yes
0.50X	Slow
0.25X	No
0.02X	No Gel

[a] **1**, bis(trimethoxysilylethyl)benzene; **2**, 1,4-bis(trimethoxysilylmethyl)benzene; **3**, 1,4-bis(triethoxysilyl)benzene; **4**, tris(3-trimethoxysilylpropyl)isocyanurate; **5**, 1,6-bis(trimethoxysilyl)hexane; PTMS, phenyltrimethoxysilane; MTMS, methyltrimethoxysilane; TMOS, tetramethylorthosilicate. All sol−gels were prepared using TBAF in THF aging 6 days. [b] All sol−gels were prepared with **1** using TBAF catalysis and 6 day aging time. [c] All sol−gels were prepared using **1** in THF and a 6 day aging time. The 0.05 M butylamine was aged >1 month without gel formation. TBAF, tetrabutylammonium fluoride; DBN, 1,5-diaz>abicyclo[4.3.0]non-5-ene. [d] All sol−-gels were prepared with **1** in THF using TBAF catalysis. For sol−gels that were not aged, one type was immediately rinsed to remove water and catalyst (rinsed) while another type was immediately treated with excess cyanopropyl−dimethylchlorosilane (silane treated). All aging was performed at 25 °C unless otherwise indicated. [e] 1X sol−gel composition is defined as 0.51 M **1** in THF prepared using TBAF catalysis. A stoichiometric amount of water was used for all types, except when <1X the amount of water was fixed at 1.54 M.

Table 2. Volume of Liquid Absorbed by Various Sol–Gels

	volume of solvent absorbed (mL/g sol–gel)			
sol–gel processing conditions[a]	ethanol	acetonitrile	THF	hexane
1/THF/TBAF/1X/6 d	3.6 ± 0.2	4.0 ± 0.5	4.9 ± 0.7	3.5 ± 0.2
1/THF/TBAF/0.75X/6 d	4.6 ± 0.5	4.7 ± 0.7	4.6 ± 0.5	4.7 ± 0.6
1/acetone/TBAF/1X/6 d	5.1 ± 0.8	5.4 ± 0.8	5.4 ± 0.8	5.4 ± 0.8
1/THF/DBN/1X/6 d	3.4 ± 0.2	3.7 ± 0.4	3.8 ± 0.5	3.7 ± 0.5

[a] Precursor/solvent/catalyst/relative precursor concentration/aging time in days.

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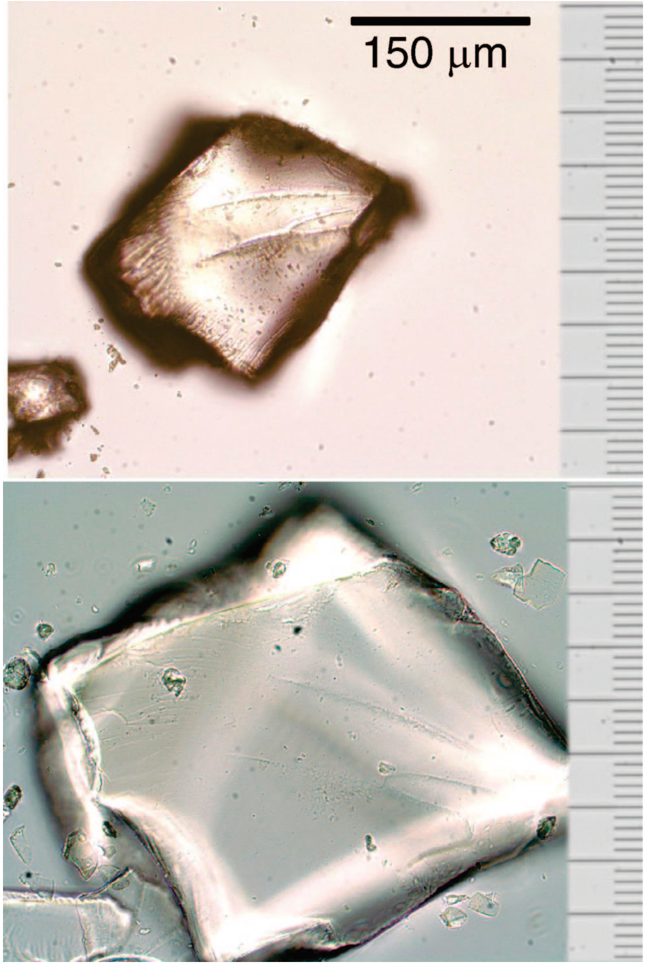

Figure 1. Optical micrograph (20 × magnification) of an organosilicate composed of **1** dry (top) and swollen in acetonitrile (bottom).

material also swelled but will typically begin to fragment as the outer portions of the polymer increase in size more rapidly leading to fracturing. In all cases, if a material fit the criteria as swelling, then swelling was completely reversible after drying.

Processing conditions were varied using **1** as the precursor (Table 1). Overall, a narrow window of conditions exists that leads to swelling behavior. For instance, the use of acetonitrile in place of THF as a solvent resulted in the complete loss of swelling behavior. In general, a high concentration of base catalyst is needed to achieve swelling. TBAF is particularly effective as a catalyst to yield animated materials. This is presumably due to fluoride ion being an effective nucleophile catalyst shown to generate morphologies similar to those obtained by base catalysis.[18,19] Additionally, a fairly defined concentration of organosilane precursor must be used to yield zerogels that swell. One of the most important factors that contributes to conditions that yield swelling is syneresis during the aging in the wet gel state. Syneresis is due to further cross-linking of the polymer via hydrolysis and condensation of the alkoxy and silanol groups. A typical formulation that yielded a swellable sol–gel (**1**, THF, TBAF) exhibited ~10% loss in volume during aging leading to cracking of the wet gel and expulsion of solvent. The importance of syneresis was demonstrated by the observation that a newly formed wet gel treated with a large excess of cyanopropyldimethylchlorosilane which derivatized silanol groups and thus prevented syneresis yielded a final material that could not swell.

Zerogel materials prepared by TBAF catalysis in various solvents were studied by SEM to determine if morphological differences were responsible for the changes in swelling behavior (Figure 2). Regardless of precursor type, all of the organosilicates were found to be composed of approximately 10–20 nm sized particles clustered into small groups (Figure 2; see Supporting Information for a complete set of images for a wide variety of zerogel types). This familiar morphology is consistent with previous studies of sol–gel derived hybrid materials prepared by base or fluoride ion catalysis.[20–22] Variation in the microstructure of the particle clusters was observed which was particularly affected by solvent used during the initial gel formation step. Polymerization in acetonitrile yielded the more mesoporous material. Increased particle aggregation led to a concomitant increase in pore volume/size and decrease in surface area as measured by N_2 adsorption/desorption (Table 3). Interestingly, swelling behavior was lost when the nanoscale assembly of particles was either highly cross-linked and microporous as observed in materials polymerized in ethanol or too mesoporous as demonstrated by polymerization in acetonitrile. THF, acetone, and similar solvent systems apparently yield an optimal level of particle interconnectivity for swelling behavior. This further demonstrates the type of control that is possible in sol–gel processing conditions where morphology is dependent on the rate and potentially the mechanism of chemical reactions occurring during polymerization.

To understand how the zerogel materials swell, the morphology of the swollen state was examined by SEM after the following treatments: (1) critical point drying of the material swollen in ethanol and (2) swelling the material in a solution of relatively low molecular weight polymer followed by drying, thereby leaving the polymer entrapped in the matrix (Figure 3). These methods had to be employed because the material swollen with solvent reversibly returns to the collapsed state when dried. On the basis of changes in morphology, individual nanoparticles appeared to be tethered together in clusters, but the individual particles are flexible within the arrangement. Microscopy of swollen materials revealed that the individual clusters of particles expanded upon exposure to solvent yielding larger spheroid-like structures. The nanoparticles themselves do not swell. This was especially apparent in the critical point dried sol–gels (Figure 3D) since some of the organosilicate may be in the completely expanded state which would not be the

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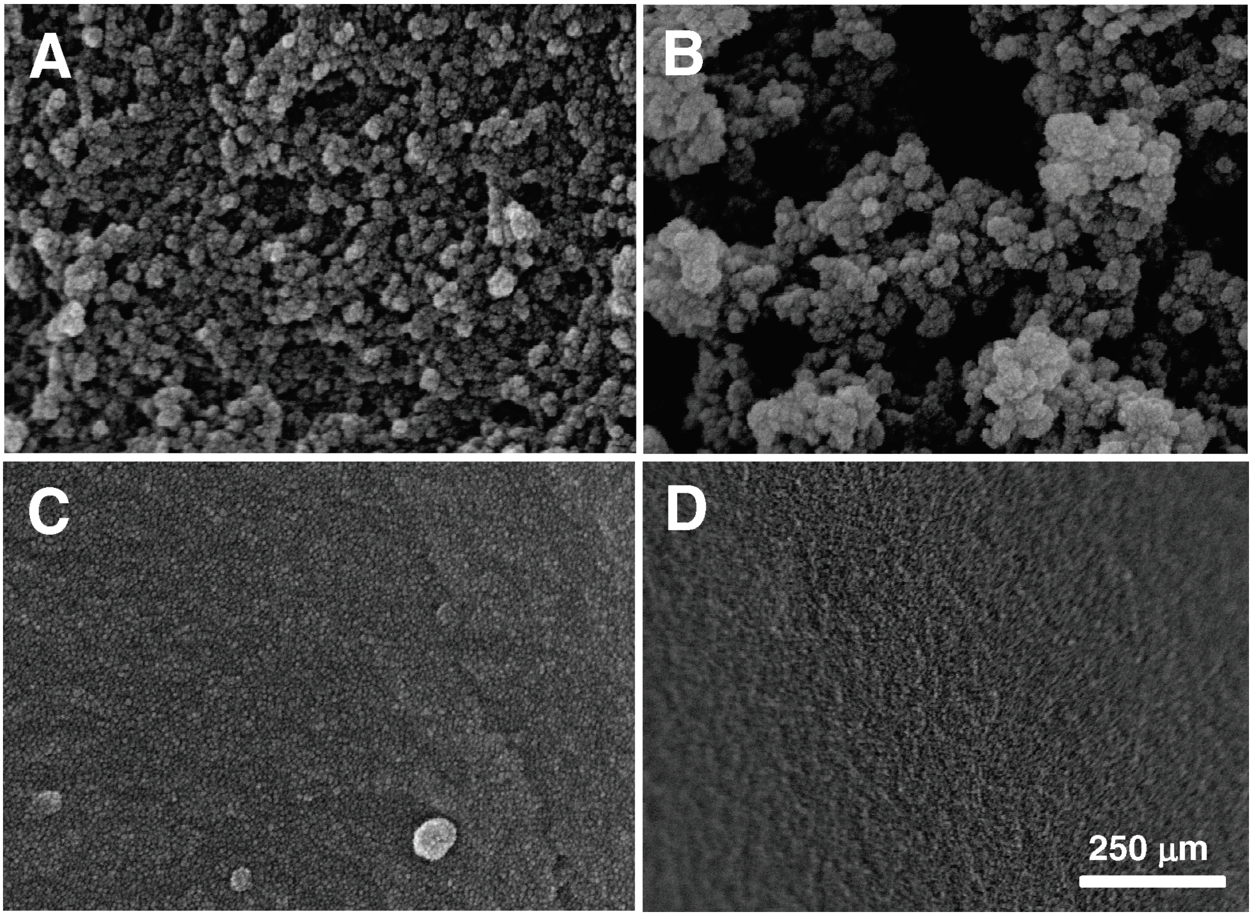

Figure 2. SEM micrographs of zerogel compositions prepared by TBAF catalysis. A. **1** prepared in THF. B. **1** prepared in acetonitrile. C. **5** prepared in THF. D. **1** prepared in ethanol. All images are the same scale. Of these formulations, only the material depicted in image A swells.

Table 3. Surface Area and Pore Volume of Various Sol–Gels[a]

precursor[b]	solvent	catalyst	BET surface area (m^2/g)	pore volume (mL/g)	pore size < 6 nm	swell
1	THF	TBAF	736	0.65	91%	yes
2	THF	TBAF	694	0.51	85%	yes
3	THF	TBAF	853	0.87	62%	no
MTMS	THF	TBAF	374	0.40	49%	no
1 (0.25X)	THF	TBAF	415	0.35	40%	no
1	THF	DBN	543	0.58	27%	yes
1	CH_3CN	TBAF	460	1.03	10%	no
1	acetone	TBAF	543	0.57	91%	yes
1	ethanol	TBAF	<10	0.18	25%	no
1 (no aging)	THF	TBAF	<10	0.01	n/a	no

[a] Dried sol–gels measured by N_2 adsorption/desorption using the BET method. Standard error ± 5%. [b] Structures as depicted in Table 1.

case with the polymer swelled material since the concentration of polymer used for entrapment was relatively low (Figure 3B). (Note: We believe that with the critical point drying method not all of the sol–gel remains in the swollen state when the sample is returned to ambient conditions and then placed in vacuum.) It is hypothesized that the open spheroids resemble the morphology of the gel state where the particles are cross-linked into larger mesoscale features. The more open polymeric network of the gel state collapses during drying as a result of surface tension of the evaporating solvent which can exceed 100 MPa.[23] Upon swelling, a zerogel "returns" to the microstructure of the original gel state. Evidence for collapse of the matrix is a ~fivefold reduction in volume as the wet sol–gel material is dried to form a zerogel. Normally in sol–gel processing procedures, the collapsed state conformation of the zerogel would remain permanently static because of condensation of silanol groups as the solvent is removed. Polycondensation is likely to be favored during drying because of an increasing concentration of silanols and nonvolatile catalyst contained within the matrix. In the materials produced here, the removal of catalyst and derivatization of the silanol groups prior to drying prevents further cross-linking which would irreversibly "lock" the matrix in the dried morphology. The elimination of the derivatization step precluded swelling behavior in all instances. Given the lack of covalent bonding, the matrix of zerogels produced here presumably remains in a dried "closed form" morphology by noncovalent van der Waals or π-stacking interactions between collapsed hydrophobic surfaces at particle–particle contact sites. Noncovalent interactions within the collapsed polymer matrix are disrupted upon addition of an appropriate solvent whereby the internal tension developed during drying is released, rapidly expanding the matrix and allowing additional solvent into the sol–gel by capillary action.

The expansion from the dry collapsed state to the swollen state produces a substantial amount of force. Zerogel material prepared using precursor **1** (THF solvent,

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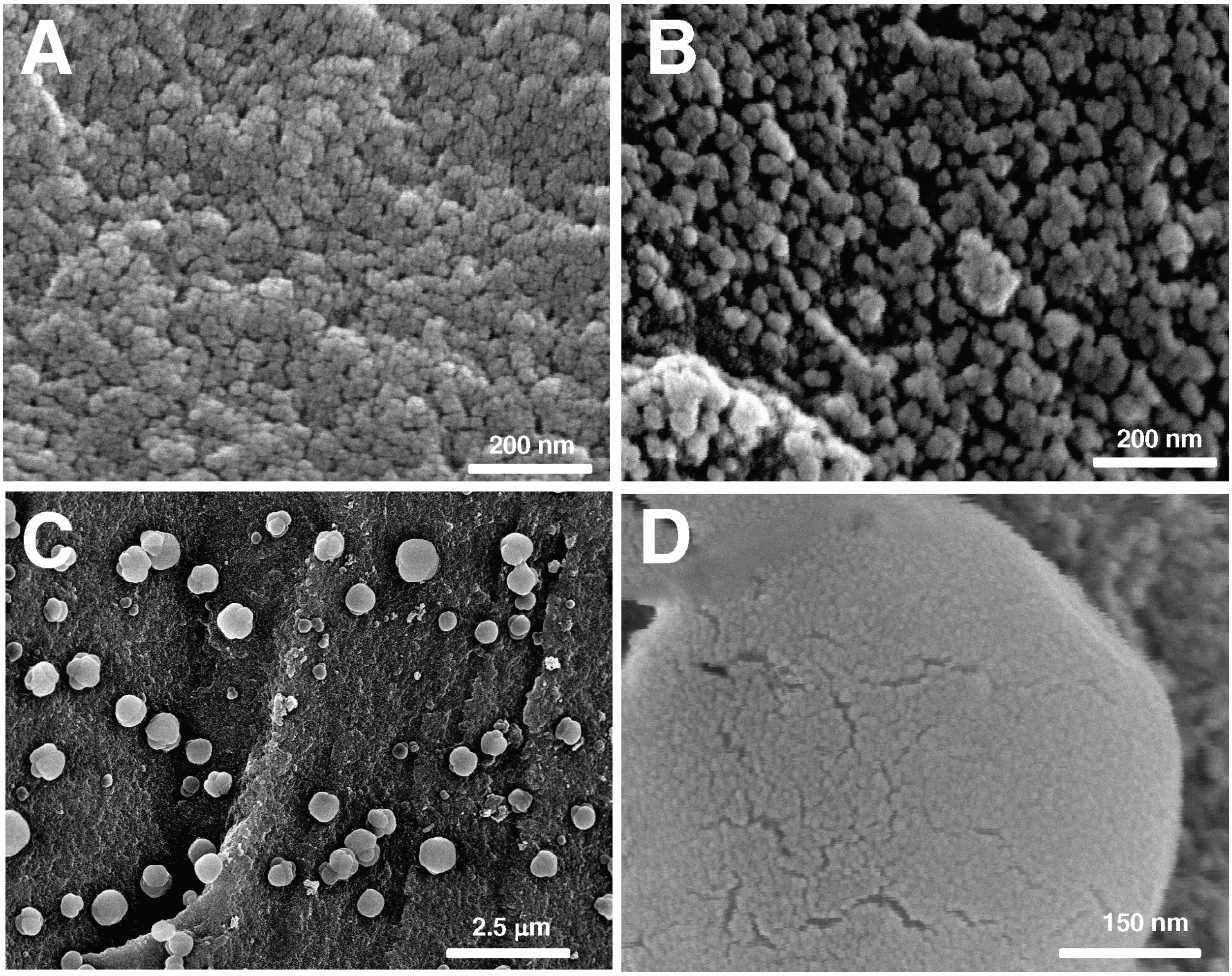

Figure 3. A. Unswollen zerogel (**1** polymerized in THF using TBAF catalysis). B. The same material swollen in a solution of poly(2,2,3,3,4,4,4-heptafluorobutylmethacrylate) and dried to leave entrapped polymer. C and D. The same material swollen in ethanol followed by critical point drying.

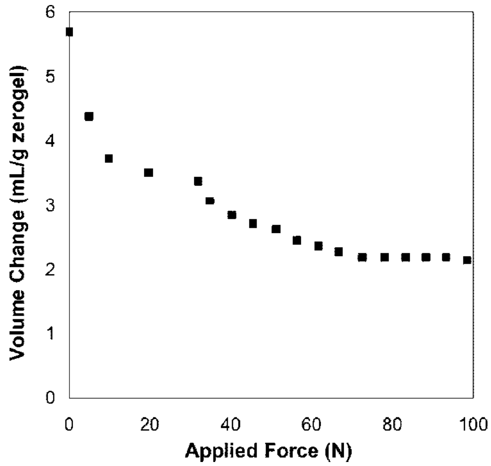

Figure 4. Increase in the volume of a zerogel (**1** polymerized in THF using TBAF catalysis) upon swelling in methanol as a function of applied force.

TBAF catalyst) was sealed in a tube between a porous frit, where solvent could be introduced upward by diffusion, and a piston. Weight was applied to the piston, and the amount of expansion of the sol–gel upon exposure to solvent was measured (Figure 4). The amount of force produced by swelling is considerable, for instance, 2 g of zerogel can expand to three times its original volume under

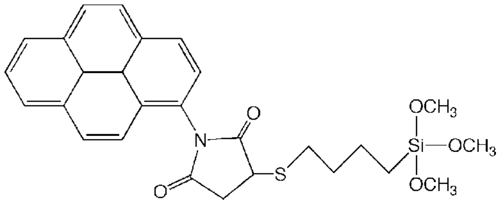

Figure 5. Structure of pyrene−TMS.

20 N (2 kg) of applied force. (The experimental system used could not provide enough mechanical force to fully prevent swelling.) Interestingly, the force curve is not uniformly continuous but exhibits at least three different transition points. These may be related to distinct structural morphologies that the material progresses through as the organosilicate expands. A different amount of elastic tension is built into each of the different collapsed states. Solvent cannot be removed from the swollen state by the application of static pressure. Attempts to fully remove solvent using a hydraulic press were ineffective up to pressures of 1000 psi.

One of the primary questions when trying to relate swelling behavior to morphology is at what point in the processing steps do nanoparticles observed by microscopy form. A pyrene-labeled organosilane (pyrene−TMS, Figure 5) was synthesized and used as a fluorescent reporter group during sol–gel

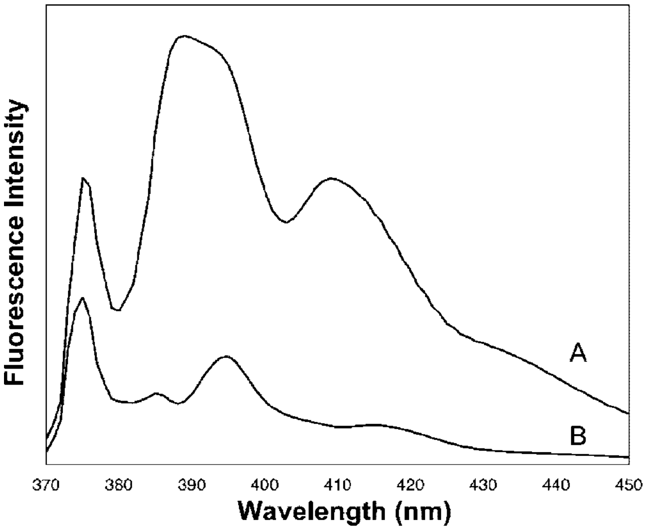

Figure 6. Fluorescence spectra of pyrene−TMS: (A) prior to copolymerization with **1** in THF by TBAF and (B) the same solution after the addition of TBAF and H_2O.

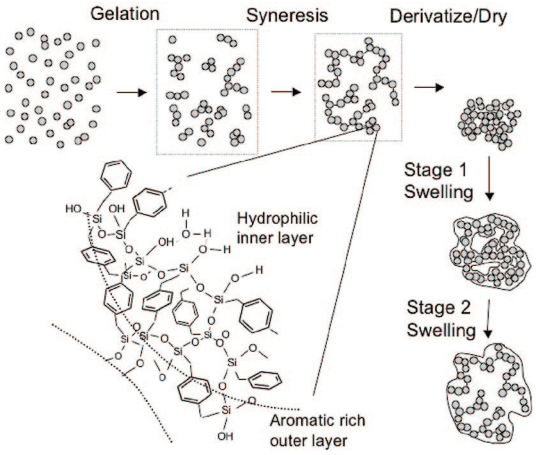

Figure 7. Schematic diagram depicting a model for the swelling mechanism where ensembles of cross-linked nanoparticles are arranged in a flexible network. The extent of cross-linking is defined by the anisotropic molecular arrangement of the nanoparticles.

processing. Pyrene fluorescence is highly sensitive to the local environment[24,25] and has been used previously to examine the structural changes during sol–gel polymerization.[26–28] When copolymerized with **1** in THF at room temperature, the fluorescence of the pyrene increased dramatically immediately after the addition of TBAF and water (which in all cases were coadded; Figure 6). A shift in the relative fluorescence intensity of the vibronic bands between 380 and 450 nm after catalysis indicates that the pyrene has been incorporated into a substantially more nonpolar environment. During the course of the experiment the mixture did not gel, although the solution immediately turned very slightly hazy because of the creation of particles that scatter light. There are only gradual shifts in the fluorescence over time postcatalysis. These data indicate that nanoparticle formation occurs almost immediately upon addition of TBAF. This conclusion is also supported by SEM measurements which showed that the organosilicate material which was rinsed and dried immediately after gelation (∼5 min after addition of TBAF) consisted of a highly packed array of nanoparticles (see Supporting Information). Nitrogen adsorption measurements indicated that the zerogels prepared from **1** in THF using TBAF without aging were nonporous (Table 3).

Taken together, the data indicate that when using precursor **1** nanoparticles form rapidly after addition of catalyst (Figure 7). Gelation occurs when a sufficient number of organosilicate particles cross-link. Interparticle cross-linking continues to take place during aging which provides sufficient number of connections to generate a matrix that is flexible enough to collapse yet rigid enough to store tensile force. A necessary balance in the degree of interparticle cross-linking may explain why only a select set of bridged sol–gel precursors possessing a flexibly tethered aromatic group yielded zerogels that swell. Flexibility of the bridging component is not the sole requirement to yield a swellable material as demonstrated by sol–gels composed of **4** or **5** that do not swell. All the zerogels were characterized by infrared spectroscopy shown to a have a similar degree of Si−O−Si bond formation (Supporting Information) further pointing to the fact the total degree of polymerization is not the key component in producing animated materials.

The chemical and physical properties of sol–gels prepared from bridged silanes have been extensively studied by Corriu et al.[21,29] Zerogels composed of **1** and **3** prepared in THF using TBAF catalysis both are highly cross-linked as determined by ^{29}Si NMR (66% and 87%, respectively), however zerogels prepared from **3** are substantially more hydrophilic.[29a] Furthermore, data indicate that a significantly greater number of aromatic groups are accessible in solid materials prepared using **1** (64%) versus **3** (18%).[21] A picture emerges where the nanoparticles prepared from precursor **1** have some degree of molecular order whereby the aromatic groups are preferentially surface exposed. To verify this fluorescence quenching of pyrene−TMS nitrobenzene was used to determine how solvent accessible the probe was when copolymerized in a matrix prepared from **1**. Modified Stern−Volmer plots were used to determine the fractional accessibility (f_a) of pyrene−TMS before and after catalysis (Figure 8). Prior to TBAF catalysis 100% of the fluorophore is accessible to collision quenching by nitrobenzene. After addition of TBAF, 66% of the pyrene groups are still accessible to nitrobenzene suggesting that a large number of the fluorescent reporter groups are preferentially located near the surface of the nanoparticles, a result which is correlates well with previous studies noted above. Despite the hydrophobicity of the zerogels, FT-IR mea-

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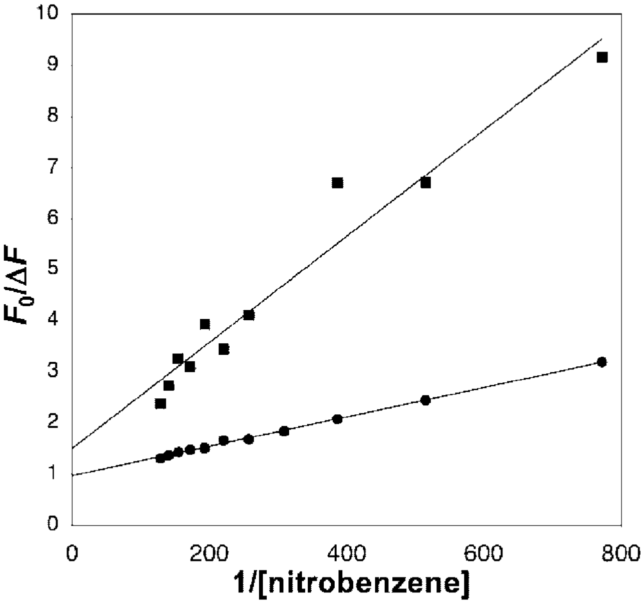

Figure 8. Modified Stern−Volmer plot for the quenching of pyrene−TMS by nitrobenzene before (●) and after (■) catalysis.

surements have shown that there is a substantial amount of entrapped water and unreacted silanol groups in the final zerogel materials composed of **1** or **2** even after extensive incubation in solutions of chlorosilanes followed by drying steps in excess of 250 °C (ref 1 and data not shown). Thus, the zerogel particles appear to have hydrophilic cores that are sealed from the exterior by a hydrophobic matrix of aromatic bridging groups (Figure 7). Overall, this suggests that a partially ordered molecular arrangement is produced by rapid polycondenstion of **1** and **2** by TBAF. Anisotropic organization is likely due to $\pi-\pi$ interactions between the organic bridging groups. Self-organization leading to long-range ordered structures has been observed in similar materials prepared from phenylene-bridged organosilanes.[30] X-ray diffraction and molecular mechanics simulations indicated that alternating arrangements of organic and silica layers were presented in the phenylene-bridged organosilanes[31] which are consistent with the observations made here.

It is hypothesized that the structure of individual particles having a certain degree of organization results in a surface that has a particular number of sites available to form Si−O−Si bonds with neighboring particles providing the necessary rigidity to yield swelling behavior in the zerogel. On the basis of our results, the degree of cross-linking is controlled in several ways: (1) the choice of precursor which dictates the structure of individual particles, (2) the solvent and catalyst which affect the kinetics of polymerization and porosity of the materials, and (3) the concentration of monomers which likely controls the particle density in the gel state. However, other changes that occur during syneresis may also be important. Polarized light microscopy was used to examine the gel during the aging process. Birefringence from the gel was noted to originate from crack edges that spontaneously occur during syneresis indicating anisotropic ordering, presumably in response to stress within the material (Figure 9). Identical observations of anisotropy have been observed in nearly identical systems[32–36] and confirmed by X-ray diffraction.[33,37] The reordering that occurs during syneresis is still poorly understood but may play a crucial role in the swelling behavior.

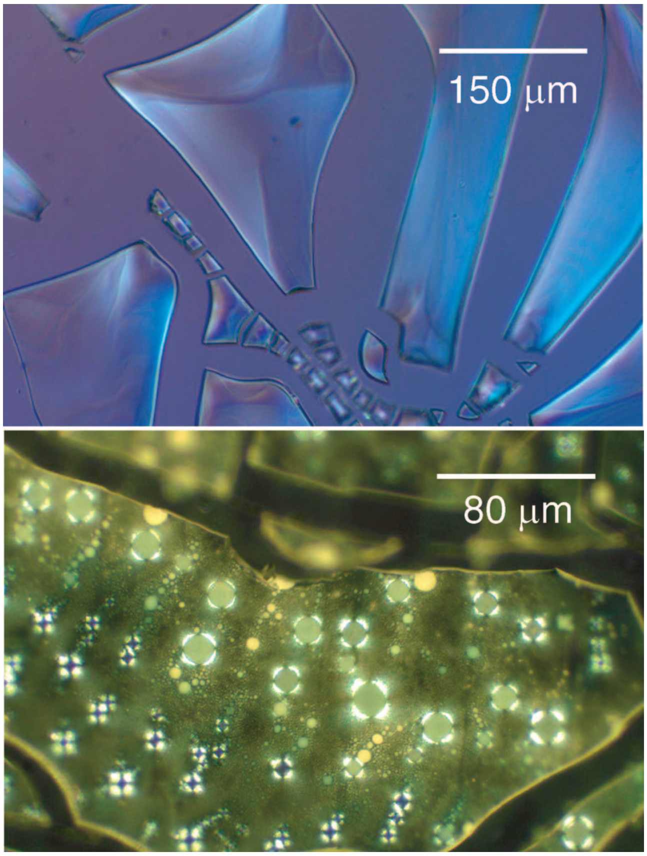

Figure 9. Sol–gel materials composed of **1** (TBAF catalysis in THF) examined by polarized optical microscopy. Top: Gel that had aged for 4 days in a sealed cell. Bottom: Gel observed 5 h postgelation exposed to air in the gel state.

Mixtures of **1** and MTMS were prepared to determine if swelling behavior is maintained if a nonbridged organosilane is added to the polymer matrix. Some swelling behavior was observed even with an equal-molar ratio of **1** to MTMS, however a two- to threefold loss in swelling potential was observed when the mole ratio of MTMS exceeded 1% (Table 4). The loss in the magnitude of the swelling corresponded to an observed reduction in the rate of expansion. The morphology of zerogels comprising 10 molar % and 20 molar % MTMS versus **1** (TBAF catalyzed in THF) was examined by SEM and showed the same nanoparticle cluster microstructure as those prepared exclusively with **1**. Therefore, the changes that lead to differences in swelling are likely on

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Table 4. Swelling Behavior and Pore Volume of Sol–Gels Prepared from Precursor Mixtures[a]

sol–gel[b]	swelling (mL/g)	BET surface area (m^2/g)	pore volume (mL/g)	pore size < 6 nm
		1:MTMS		
100:0	4.2 ± 0.5	305	0.19	68%
99.5:0.5	3.9 ± 0.5	469	0.28	78%
99:1	1.3 ± 0.3	496	0.33	78%
95:1	1.9 ± 0.7			
90:1	2.4 ± 0.5	477	0.33	78%
80:1	2.4 ± 0.6	529	0.35	85%
50:50	3.5 ± 0.5	1062	0.81	83%
0:100	no swelling	374	0.58	49%
		1:**3**		
95:5	1.9 ± 0.3	484	0.32	75%
0:100	no swelling	853	0.88	62%

[a] Dried sol–gels measured by N_2 adsorption/desorption using the BET method. Standard error ± 5%. [b] Structures as depicted in Table 1. All sol–gels were prepared using 0.5 M total silane concentration in THF using TBAF catalysis at the mole ratio indicated.

the molecular level. This is supported by the fact that the surface area and porosity of the zerogels made with different ratios of MTMS are similar. The exception is the 50:50 MTMS/**1** material which has a significantly high surface area and pore volume and a somewhat greater ability to swell but is not equivalent in behavior to zerogels composed of only **1**. Materials made with a mixture of a rigid bridging precursor **3** in combination with **1** also had a significant reduction in swelling potential.

Materials prepared from **1** (TBAF catalysis in THF) were tested for the ability to absorb gas-phase organic molecules. Zerogel stored in a sealed vessel containing an open container of acetone increased 1.8 times its original volume after 5 days. Quantitative and temporal measurement of adsorption was conducted where known concentrations of toluene vapor in N_2 were passed through a bed of the same swellable material. The amount of toluene in the elution stream was measured in real time using UV absorbance. The amount of adsorbed toluene was determined by difference and also by weighing the organosilicate during and after exposure to the toluene vapor stream. The amount of toluene removed from the gas stream by the zerogel is dependent on the concentration of toluene (Figure 10). Large amounts of toluene were adsorbed during the initial stages; in fact complete removal of toluene was observed during the first 10–20 min of continuous flow regardless of concentration. Over time, the amount of mass change leveled out. The final adsorbed mass was proportional to the toluene vapor concentration (data not shown). Removal of toluene from the vapor stream does not appear to be exclusively due to physisorption. Using the measured surface area (Table 3), that a packed monolayer of adsorbed toluene would result in a Δmass of 0.15 g/g zerogel was calculated. This value was exceeded in tests and suggests that the structure of the zerogel changes to introduce new surface interaction sites for toluene.

Adsorption of nonpolar molecules in liquid phase was also evaluated by passing 5 mL aliquots of homogeneous butanol/water mixtures of different concentrations through a stationary bed containing 100 mg of organosilicate prepared from precursor **1** (TBAF catalysis in THF). After the liquid was passed through, the material was blotted to dry and analyzed by infrared spectroscopy to determine the identity of absorbed species. At a concentrations ≤ 5% v/v butanol, the material exclusively adsorbed the alcohol. This could, in theory, allow the alcohol to be separated from the water at low concentrations. It is likely that physisorption to the hydrophobic surfaces of the zerogel is the primary mechanism of adsorption.

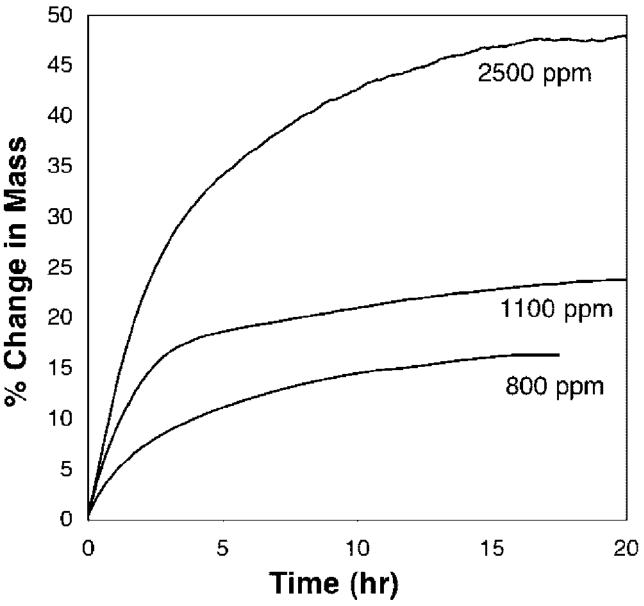

Figure 10. Percent increase in zerogel mass upon exposure to 50 mL/min flow of gas-phase toluene at various concentrations.

Conclusion

In summary, a narrow set of sol–gel processing conditions is reported that to the best of our knowledge produces a material that swells 1–2 orders of magnitude beyond any other organically modified silica-based material. Swelling requires (1) the material to be principally synthesized from monomers possessing an organic bridging group with an aromatic functionality flexibly linked to the alkoxysilane polymerizable units (swelling behavior is not lost if small amounts of other sol–gel precursors are used in combination); (2) the catalyst to be fluoride or a high concentration of base; (3) the solvent to be relatively nonpolar; (4) the concentration of sol–gel precursor to be 0.5 ± 0.25 M; (5) the resulting gel to be aged to a point where syneresis is observed; and (6) the silanol groups to be derivatized in the gel state prior to drying. When prepared in this manner, uptake is exclusive to nonpolar species and occurs on the order of milliseconds. Electron microscopy indicates that swelling occurs by an expansion of tethered sol–gel particles that have diameters on the nanometer scale. It is hypothesized that the swelling is due to internal mechanical stress that is incurred upon drying and released as noncovalent interactions that hold the compressed polymer in the dry state are disrupted by absorbates. There are several interesting applications for these materials. First, the materials could be used to for remediation of contaminated water because they have a high affinity and capacity for nonpolar organics. The reversibility of the swelling mechanism makes them suited for repeated use. Another intriguing application is chemical sensor development. If the swelling could be made to be selective, a sensor could be produced where the transduction mechanism is increased in size of the material. As a result of the rapid rate of swelling and substantial forces that are produced, a chemically selective actuator could be fabricated that would be very simple and efficient. The sol–gel process allows for the materials to be tailored by the addition of other precursors to add functional groups such as amines[38] for the covalent attachment of biological molecules or other types of recognition elements.

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Supporting Information Available: SEM micrographs of sol−gels prepared under various conditions and FT-IR spectra of various zerogels (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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