Monolithic hierarchical fractal assemblies of silica nanoparticles cross-linked with polynorbornene via ROMP: A structure–property correlation from molecular to bulk through nano

6. AUTHORS
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14. ABSTRACT
Monolithic hierarchical fractal assemblies of silica nanoparticles are referred to as aerogels, and despite an impressive collection of attractive macroscopic properties, gragility has been the primary drawback to applications. In that regard, polymer-cross-linked silica aerogels have emerged as strong lightweight nanostructured alternatives rendering new applications unrelated to aerogels before, as in balistic protection, possible. However, the exact location of the polymer ion the elementary structure of silica and, therefore, critical issues, such as how much is
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ABSTRACT: Monolithic hierarchical fractal assemblies of silica nanoparticles are referred to as aerogels, and despite an impressive collection of attractive macroscopic properties, fragility has been the primary drawback to applications. In that regard, polymer-cross-linked silica aerogels have emerged as strong lightweight nanostructured alternatives rendering new applications unrelated to aerogels before, as in ballistic protection, possible. In polymer-cross-linked aerogels skeletal nanoparticles are connected covalently with a polymer. However, the exact location of the polymer on the elementary structure of silica and, therefore, critical issues, such as how much is enough, have remained ambiguous. To address those issues, the internal nanoporous surfaces of silica wet-gels were modified with norbornene (NB) by cogelation of tetramethyl orthosilicate (TMOS) with a newly synthesized derivative of nadic acid (Si-NAD: N-(3-triethoxysilylpropyl)-5-norbornene-2,3-dicarboximide). As inferred by both rheological and liquid 29Si NMR data, Si-NAD reacts more slowly than TMOS, yielding a TMOS-derived skeletal silica network surface-derivatized with NB via monomer-cluster aggregation. Then, ring-opening metathesis polymerization (ROMP) of free NB in the nanopores engages surface-bound NB moieties and bridges skeletal nanoparticles either through cross-metathesis or a newly described stitching mechanism. After solvent exchange and drying with supercritical fluid CO2 into aerogels (bulk densities in the range 0.27–0.63 g cm−3, versus 0.20 g cm−3 of the native network), the bridging nature of the polymer is inferred by a >10-fold increase in mechanical strength and a 4-fold increase in the energy absorption capability relative to the native samples. The crosslinking polymer was freed from silica by treatment with HF, and it was found by GPC that it consists of a long and a short component, with around 400 and 10 monomer units, respectively. No evidence (by SAXS) was found for the polymer coiling up into particles, linking polymer was freed from silica by treatment with HF, and it was found by GPC that it consists of a long and a short component, with around 400 and 10 monomer units, respectively.

KEYWORDS: silica, aerogel, cross-linking, mechanism, ROMP, norbornene, polymer, hierarchical, primary particles, secondary particles, SANS, SAXS, rheology

1. INTRODUCTION

Low-density, open-cell, nanoporous solids consisting of three-dimensional (3D) assemblies of nanoparticles are referred to as aerogels and have been pursued for their bulk properties, such as high surface areas, low thermal conductivities, low dielectric constants, and high acoustic attenuations. The most well-studied of those materials are silica aerogels; they are synthesized either by an acid-catalyzed gelation of aqueous sodium silicate solutions or by acid- or base-catalyzed hydrolysis and polycondensation of silicon alkoxides into wet-gels that subsequently are dried by converting the pore-filling solvent into a supercritical fluid (SCF) that is vented off isothermally. Conveniently, prior to the SCF drying, gelation solvents are extracted in an autoclave with liquid CO2 whose low critical point (31.1 °C, 7.38 MPa) renders the process safer.

The most serious impediment against the practical (commercial) use of aerogels has been poor mechanical strength. That issue was addressed successfully 10 years ago, by using the innate surface functionality of silica (~OH groups) for the covalent postgelation anchoring and accumulation of a polymer coating on the nanoscopic skeletal framework. The mechanical properties of the composite improved dramatically over those of the native silica framework while most of the porosity and, therefore, the desirable bulk aerogel properties, were preserved. This process has been referred to as cross-linking and has been extended to over 30 different metal and semimetal...
aerogels in addition to silica. The mechanical strength-to-weight ratio of such polymer-cross-linked aerogels far surpasses not only that of native aerogels but also that of other materials considered strong. Selected polymer cross-linked networks are strong enough to withstand stresses during ambient pressure drying from low vapor pressure solvents, for example, pentane. Others are suitable for applications typically unrelated to aerogels, for example, in ballistic protection (armor). Further, as suggested by a recent quantitative (100% efficient) conversion of polyacrylonitrile-cross-linked silica aerogels to isomorphic SiC aerogels, emerging applications include the carbothermal synthesis of a wide array of monolithic, highly porous metals and ceramics.

The cross-linking process is akin to grafting polymers onto surfaces. It has been demonstrated with both grafting-to and grafting-from methods. Generally, both require a modification of the skeletal nanoparticles by coagulation of tetramethyl orthosilicate (TMOS) with a trialkoxysilane derivative of the modifier. In grafting-from cross-linking, polymerization begins at the surface of the skeletal nanoparticles, which are modified either with free radical, atom transfer radical, or anionic polymerization initiators. This process has been conducted both in the wet-gel state with polystyrene, polymethylmethacrylate, and polyacrylonitrile and in the dry aerogel state by the vapor deposition of suitable monomers (e.g., cyanoacrylates). It has also been used for cross-linking with epoxides. A reaction of dangling amine groups with chloromethylstyrene has led to cross-linking with polystyrene. Cross-linking with polystyrene has also been successfully conducted by a direct surface modification with olefins via coagulation of TMOS with vinyltrimethoxysilane.

Despite the rather intensive activity in this area, the nature of cross-linking at the fundamental building block level (primary and secondary nanoparticles) has remained ambiguous. As inferred by SEM, the microstructure is not affected visibly by the cross-linking process. Hence, the cross-linking polymer has been assumed to follow the contour surface of the skeletal framework and, therefore, has been referred to as conformal. However, the exact location of the polymer on the backbone is important for correlating nanostructure with bulk material properties, such as porosity, surface area, and mechanical strength, and also for the synthesis of new porous materials that rely on intimate contact of skeletal inorganic nanoparticles with, for example, a carbonizable polymer.

Specifically, a first key question to be answered addresses the amount of polymer required for maximum mechanical strength with a minimum penalty in surface area, density, and porosity. In addition, noting that interpenetrating organic/inorganic networks in the much more compact aerogel form react carbthermally toward metals and carbides much more efficiently (at up to 400 °C lower temperatures) than aerogels, it is expected that core—shell structures, such as polymer cross-linked aerogels, would be more attractive than interpenetrating networks, and therefore knowledge of the exact location of the polymer is also key. That investigation must rely on a polymerization process yielding a rather well-defined, soluble polymer that can be readily washed off if unbound. For this, we turned to cross-linking of silica aerogels with norbornene by ring-opening metathesis polymerization (ROMP). ROMP-derived polymers, such as both polynorbornene and polydicyclopentadiene, are extremely robust, use inexpensive monomers, and have been commercially successful. ROMP-derived all-organic aerogels have also been recently described. Closer to our purposes, ROMP has been used in the surface-initiated mode by immobilizing suitable catalysts on surfaces to produce, in a grafting-from fashion, polymeric thin films, polymer brushes, and core−shell type structures on both silica and gold. Our process, however, was related to grafting-to ROMP. The latter has been used with carbon nanotubes (CNTs) functionalized with norbornene to produce both CNT/polydicyclopentadiene composites and surface-grafted polymer supports.

Here, the norbornene functionality on the pore surfaces of silica aerogels was provided by a coagulation of TMOS with a new norbornene derivative, Si-NAD. The pores were filled with a norbornene (NB) solution. ROMP was then conducted at room temperature using a water-tolerant, second generation Grubbs' catalyst (GC-II). Unbound polynorbornene was washed off during typical solvent exchanges. Probing the location of the polymer was a complex issue; no single characterization method was sufficient to address by itself. Hence, the nanostructure was probed chemically both at the molecular level by IR, 13C, and 29Si solids NMR and at the nanoscopic level by SAXS, SANS, TEM, and SEM. Porosity was investigated using N2 sorption. All results were correlated with the macroscopic mechanical strength using quasi-static compression. Control materials included both the native (noncross-linked) NB-modified silica (n-SiNAD) which, in turn, was referenced against native TMOS-derived silica (n-TMOS), and silica obtained by a coagulation of TMOS with APTES (n-TMOS-co-APTES). Overall, the polymer first coated the primary particles. In that regard, a mild degree of cross-linking was sufficient for improving the mechanical properties to a level that silica aerogels are no longer fragile materials. Complete filling of the fractal space within the secondary particles is essential, however, for ultimate mechanical strength.

2. EXPERIMENTAL SECTION

2.a. Materials. All reagents and solvents were used as received, unless noted otherwise. Dicyclopentadiene was purchased from Fluka. Maleic acid, thionyl chloride, 3-aminopropytriethoxysilane (APTES), tetramethyloxysilicate (TMOS), a 14.8 N ammonium hydroxide solution, norbornene, second generation Grubbs' catalyst GC-II (1,3-bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene) dichloro (phenylmethylene) (tricyclo-hexylphosphine) ruthenium) and anhydrous toluene were purchased from Aldrich Chemical Co. HPLC grade tetrahydrofuran (THF) was purchased from Fisher and was distilled from lithium aluminum hydride. Cyclopentadiene was obtained via a reverse Diels−Alder reaction by distillation of dicyclopentadiene (bp 170 °C). Nadic acid was synthesized according to literature procedures by a Diels−Alder reaction between cyclopentadiene.
and maleic acid (mp 182–186 °C; Sigma-Aldrich: endo-, 175 °C (dec.); endo/exo-, 185–189 °C).

**Synthesis of N-(3-Triethoxysilylpropyl)-5-norbornene-2,3-dicarboximide (Si-NAD).** The process is summarized in Scheme 1: nadic acid (7.8 g, 0.0428 mol) was added under magnetic stirring at room temperature to an excess of thionyl chloride (25.0 mL, 0.3441 mol) in a 2-neck round-bottom flask, and the mixture was refluxed for 4 h with N2. At the end of the period, the reaction mixture was first allowed to cool to room temperature, the reflux apparatus was converted to a distillation setup, and the excess of thionyl chloride was removed under reduced pressure using an aspirator connected through a drying tube. The solid product was used without further purification. First, it was dissolved in anhydrous toluene (25 mL) added with a waxy yellow solid of APTES (10.0 mL, 0.1112 mol) and then was refluxed for 4 h. Meanwhile, the viscous cross-linking solution surrounding the silica wet-gels was left by itself to gel, and the polymer gel was aged in parallel with the cross-linked wet silica gels for 4 h. At the end of the period, the polymer was dissolved in a large excess of THF, precipitated with methanol, and analyzed by modulated differential scanning calorimetry and gel permeation chromatography (see Methods section below).

Control native silica and amine-modified silica aerogels were prepared according to literature procedures: for native silica aerogels (n-TMOS), Solution A consisting of 3.85 mL of TMOS (0.0261 mol) and 4.5 mL of CH3OH was mixed at room temperature with Solution B consisting of 4.5 mL of CH3OH, 1.5 mL of H2O, and 40 μL of concentrated aqueous NH4OH for native amine-modified silica aerogels (n-TMOS-co-APTES), Solution A consisting of 2.887 mL of TMOS (0.0196 mol), 0.963 mL of APTES (0.0041 mol), and 4.5 mL of CH3CN was cooled in dry ice/acetone and mixed with a similarly cold Solution B consisting of 4.5 mL of CH3CN and 1.5 mL of H2O. The solution was poured into molds and then dried with acetone and dried with CO2 taken out as a SCF. Wet, amine-modified silica gels were washed once with CH3OH and 4× with acetone and dried with CO2 taken out again as a SCF.

### 2.b. Methods.

Supercritical fluid CO2 drying was conducted using an autoclave (SPI-DRY Jumbo Supercritical Point Dryer, SPI Supplies, West Chester, PA). Bulk densities (ρb) were calculated from the weight and the physical dimensions of the samples. Skeletal densities (ρs) were determined using helium pycnometry with a Micromeritics AccuPyc II 1340 instrument. Porosities, P, were determined from ρb and ρs. The surface areas and pore size distributions were measured by nitrogen sorption porosimetry using a Micromeritics ASAP 2020 surface area and porosity analyzer. In preparation for surface area and skeletal density determination, samples were outgassed for 24 h under vacuum at 80 °C. (A separate series of samples was also outgassed at 50 °C in order to remain below the glass transition temperature of the polymer. Data were practically identical for samples outgassed at 50 °C and at 80 °C). Average pore diameters were determined by the 4 × V绽放/σ method, where V绽放 is the total pore volume per gram of sample and the surface area determined by the Brunauer–Emmett–Teller (BET) method from the N2 adsorption isotherm. The value of V绽放 can be calculated either from the single highest volume of N2 adsorbed along the adsorption isotherm or from the relationship V绽放 = (1/ρs) − (1/ρb). Average pore diameter values were calculated by both methods and are cited herewith; if those values converge, it is considered as indication that the material is mesoporous. If average pore diameters calculated using V绽放 = (1/ρs) − (1/ρb) are significantly higher, that is taken as evidence for macroporosity.

Liquid 1H, 13C, and 29Si NMR were recorded with a 400 MHz high field NMR spectrometer (Thermo Scientific, Chem. Mater. 2012, 24, 3434–3448).
San Jose, CA). Using the on-board syringe pump, a THF sample of Si-NAD, diluted in methanol, was infused into the source at a flow rate of 5 μL min⁻¹. The ESI voltage was 5 kV, the sheath gas flow rate was 8 (arbitrary units in the software), and the capillary temperature was 275 °C. Mass analysis was done in the Orbitrap FT mass analyzer with resolution set to 100,000. One hundred sixty four (164) individual scans were acquired and averaged.

Chemical characterization of native and cross-linked silica aerogels was conducted with infrared (IR) and solid-state 13C NMR spectroscopy. IR spectra were obtained in KBr pellets with a Nicolet-FTIR Model 750 Spectrometer. Solid-state 13C NMR spectra were obtained with samples ground into fine powders on a Bruker Avance 300 Spectrometer with a 75.475 MHz carbon frequency using magic angle spinning (at 7 kHz) with broadband proton suppression and the CPMAS TOSS pulse sequence for spin sideband suppression.

Thermogravimetric analysis (TGA) was conducted in air with a TA Instruments model Hi-Res-TGA 2950 analyzer at a heating rate of 10 °C min⁻¹.

Modulated differential scanning calorimetry (MDSC) was conducted under N₂ with a TA Instruments Differential Scanning Calorimeter Model Q2000 at a heating rate of 10 °C min⁻¹ in the modulated T4P mode, using 60 s as the modulation period and 1 °C as the modulation amplitude. Samples were subjected to two heating scans and one cooling scan from 0 to 280 °C. Glass transition temperatures were determined from the second heating scan.

The structure of the fundamental building blocks of the materials was examined with field emission scanning electron microscopy (FESEM) using a JEOL 6300 at an accelerating voltage of 10 kV. Small-angle X-ray scattering (SAXS) and small-angle neutron scattering (SANS) were conducted using the X-SiNAD-MAA system at the National Institute of Standards and Technology. An in-foil sample was used to measure the SAXS data, and scattering intensities were measured with a point detector. SAXS was carried out with a PANalytical X'PertPro Multipurpose Diffractometer (MPD) configured for SAXS, using Cu Kα radiation (λ = 1.54 Å) and a 1/32° SAXS slit together with a 1/16° anticrystal slit in the incident beam side and 0.1 mm anticrystal slit and Ni 0.125 mm automatic beam attenuator on the diffracted beam side. Samples were placed in circular holders between thin Mylar sheets, and scattering intensities were measured with a point detector in the transmission geometry by 2θ scans ranging from −0.1 up to 5°. SANS was conducted with a time-of-flight, low-Q diffractometer (LQD) at the Manuel Lujan, Jr., Scattering Center of the Los Alamos National Laboratory. SANS scattering data were recorded in absolute units (cm⁻¹), while SAXS data are reported in arbitrary units as a function of Q, the momentum transferred during a scattering event. Data analysis was conducted with the Irena SAS tool for modeling and analysis of small angle scattering within the commercial Igor Pro software package (WaveMetrics, Inc. Lake Oswego, OR).

Scanning electron microscopy (FESEM) was conducted with samples coated with Au using a Hitachi S-4700 field emission microscope. Transmission electron microscopy (TEM) was conducted with a FEI Tecnai F20 instrument employing a Schotky field emission filament operating at a 200 kV accelerating voltage. For TEM, samples were ground to fine powder by hand in a mortar with a pestle and the smallest particles were selected and placed on a 200 mesh copper grid bearing a lacey Formvar/carbon film for microscopy. At least six different areas/particles were examined on each sample to ensure that the results were representative of the material.

For molecular weight determinations of polynorborene, X-SiNAD-(ax) samples were ground to coarse powders, ~0.5 g of which was treated with 5 mL of an aqueous HF solution (1 M) for 1 h, with intermittent vigorous mixing. The polymer was extracted in chloroform by multiple washes, chloroform extracts were combined, the solvent was removed at 40 °C under reduced pressure, and the polymer was further dried in a vacuum oven at 40 °C for 12 h. The residue was dissolved in THF and was analyzed by gel permeation chromatography (GPC) using a Shodex GPC KH-803 L column connected to a Shimadzu liquid chromatograph (LC-10AD) equipped with a UV–vis detector (SPD-10AV). HPLC grade THF was used as eluent at 1 mL min⁻¹. Linear polystyrene standards from Varian (Polystyrene Low EasiVials; Part Nos. PL2200-0400 and PL2000-0403) were used for calibration. Multiple Gaussian curves were fitted within the experimental chromatograms using OriginLab's data analysis and graphing software version OriginPro 8. Number- and weight-average molecular weights (Mn and Mw, respectively) and polydispersity indexes (Mw/Mn) were calculated using the fitted chromatograms.

Compression testing was performed according to the ASTM D695-02a standard on cylindrical specimens using an Instron 4469 universal testing machine frame. According to the ASTM standard, the height-to-diameter ratio of the specimen was 2:1; typical samples were machined to about 2.0 cm in length and 1.0 cm in diameter.

The rheological behavior of TMOS and TMOS/Si-NAD sols was recorded with a TA Instruments AR 2000ex Rheometer using an aluminum cone (60 mm diameter, 2° angle) and a Peltier plate geometry with a 1 mm gap between them. The instrument was operated in the continuous oscillation mode, and time-sweep experiments were performed with a fixed strain amplitude either from the beginning (case of TMOS) or 10 min after mixing of Solution A with Solution B (case of TMOS/Si-NAD), until gelation. The Peltier plate was set at 20 °C. The gel point was determined using a dynamic multwave method with three superimposed harmonics with frequencies 1, 4, and 8 rad s⁻¹. The strain of the fundamental oscillation (1 rad s⁻¹) was set at 5%.

The relative rates of incorporation of TMOS and Si-NAD in the n-SiNAD gel network were determined using liquid 29Si NMR on the 400 MHz Varian Unity Inova NMR instrument. A Teflon liner inside a 5 mm glass tube was used as sample holder. The field-frequency was locked to deuterium (CD,OD). Broad-band proton decoupling was applied to suppress possible nuclear Overhauser effects. Chromium acetylacetonate (0.015 M) and tetrathylel silane (TMS) were added in the sol to reduce the spin–lattice relaxation time and as an internal standard, respectively. Spectra were collected in regular intervals during gelation and beyond, using 256 scans and a relaxation delay of 1 s. A receiver gaiting time of 500 μs following a pulse of 7.8 μs was also applied in order to eliminate the broad background signal from the borosilicate glass in the NMR tube and probe.

3. RESULTS AND DISCUSSION

3.a. Synthesis and Characterization of Native n-SiNAD Aerogels. The monomer Si-NAD can be considered an APTES derivative. Like the latter, Si-NAD does not gel by itself. Thus, in both, in analogy to APTES and as summarized in Scheme 2, silica wet-gels and aerogels incorporating norbornyl moieties were prepared by replacing 10 mol % of the TMOS with Si-NAD from a typical NH₄OH-catalyzed TMOS-gelation process. Extensive prior work with APTES-modified silica has relied on a 17.3 mol % APTES. Here, however, it was deemed appropriate to use a lower Si-NAD:TMOS mol ratio in order to capture cross-linked materials at earlier stages of cross-linking and thus explore the evolution of mechanical properties closer to the native network.

The cogelation of Si-NAD with TMOS was followed in comparison with the gelation of TMOS with itself. That was accomplished by monitoring both the rheological properties of the sol as well as the 29Si NMR signal of the monomers. Figure 1A shows the typical evolution of the storage (G') and the loss (G") moduli of the sol as a function of time from mixing the sol. These curves cross, as expected, near the gelation point, where the elastic properties of the newly formed, rigid gel become dominant. (For corresponding data regarding gelation of TMOS only, refer to Figure S.1 in Supporting Information.) The actual gelation point (a physical property of the system) is given by the inflection point of the tan δ (=G"/G') versus time plot at a given frequency (included in Figure 1A). This point can alternatively be given as the common (independent of frequency) crossing point of all tan δ modulii of the sol as a function of time from mixing the sol. These curves cross, as expected, near the gelation point, where the elastic properties of the newly formed, rigid gel become dominant. (For corresponding data regarding gelation of TMOS only, refer to Figure S.1 in Supporting Information.) The actual gelation point (a physical property of the system) is given by the inflection point of the tan δ (=G"/G') versus time plot at a given frequency (included in Figure 1A). This point can alternatively be given as the common (independent of frequency) crossing point of all tan δ modulii of the sol as a function of time from mixing the sol. These curves cross, as expected, near the gelation point, where the elastic properties of the newly formed, rigid gel become dominant. (For corresponding data regarding gelation of TMOS only, refer to Figure S.1 in Supporting Information.)
oscillatory frequencies of the cone, operated in the multiwave mode). Results are summarized in Table 1. At equal catalyst concentrations, TMOS gels faster than the TMOS/Si-NAD system, suggesting that Si-NAD interferes with the gelation of TMOS. At the gelation point, the tan δ value is related to the gel relaxation exponent ‘n’ via eq 1.32

\[
\tan \delta = \tan(n\pi/2)
\]

In turn, considering the excluded volume of the (primary) particles forming the clusters, ‘n’ is related via eq 2 to the fractal dimension, \( D_f \) of the clusters existing at the gel point (for three-dimensional nonfractal clusters, \( D = 3 \)).33

\[
\frac{D_f}{2D_f - 2} = \frac{(D + 2) - D_f}{2(D + 2)}
\]

At two different catalyst concentrations and, therefore, different gelation times, the \( D_f \) values calculated via eq 2 for the native n-SiNAD gels are in the [2,3] interval suggesting a reaction-limited cluster—cluster aggregation mechanism for network formation.34 Additionally, the \( D_f \) values of n-SiNAD are sufficiently close to those of n-TMOS gels (Table 1), suggesting that the space filling pattern in the two types of wet-gels is similar.

A preeminent tool for the elucidation of the sol–gel chemistry of silicon alkoxides is \(^{29}\)Si NMR.35 Here (Figure 2A), the \(^{29}\)Si signal is not lost after gelation. Additionally, the transient system, suggesting that Si-NAD interferes with the gelation of TMOS. At the gelation point, the tan δ value is related to the gel relaxation exponent ‘n’ via eq 1.32

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<table>
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<th>Alkoxide</th>
<th>Catalyst amount</th>
<th>Gelation point, ( t^b ) (s)</th>
<th>( \tan \delta ) at ( t_g )</th>
<th>( n^c )</th>
<th>( D_f^d )</th>
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<td>0.20</td>
<td>0.126</td>
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\(^a\) All other parameters remaining the same as in the basic formulation described in the Experimental Section. \(^b\) Identified at the minimum of the statistical function as shown in Figure 1B, inset. \(^c\) From eq 1. \(^d\) From eq 2. **Actual amount of catalyst used in gel synthesis, as described in the Experimental Section.**
appearance of a resonance peak at $-76$ ppm corresponds to hydrolysis products from TMOS $[(\text{MeO})_4\text{Si-(OH)}_x]^x_3$ \[^{35}\] That resonance disappears after gelation, in contrast to the TMOS resonance ($-78.52$ ppm) that remains present and keeps decreasing. Overall, it is noted that (a) a significant amount of TMOS is still unreacted at the gel point, when nanoparticles reach their bond-percolation threshold;\(^{36}\) (b) Si-NAD (at $-46.26$ ppm) is still in the pores after all of the signal from TMOS is gone; and (c) in the absence of Si-NAD, TMOS is incorporated in the gel framework faster (see Figure 2B). Eventually, both TMOS and Si-NAD are incorporated in the network: (a) TGA in the air (Figure 3) shows that n-SiNAD leaves a $\sim76\%$ w/w residue, versus $75.4\%$ expected stoichiometrically if all Si-NAD is incorporated in the network with all alkoxides hydrolyzed; (b) the solids CPMAS $^{13}$C NMR of n-SiNAD aerogels (Figure 4) is dominated by the $-(\text{CH}_2)_3-$NAD moiety, showing only very small residual signals from the ethoxy groups (peaks marked “j” and “k”); and finally, (c) the solids $^{29}$Si NMR of n-SiNAD (Figure 5) shows both the Q and the T resonances expected from TMOS and Si-NAD, respectively. The $Q^1-Q^4$ distribution of intensities in both n-TMOS and n-SiNAD aerogels is the same. The most intense signal is at $-98.78$ ppm, corresponding to the $Q^4$ silicon participating in three Si–O–Si bridges. That fact, together with the small amount of residual ethoxy groups in the $^{13}$C NMR spectrum, supports further that almost all of the original Si-OR groups have been hydrolyzed, and most have been incorporated into the silica network in the form of Si–O–Si bridges, while some remain as dangling OHs, a fact supported by the OH stretches in the IR spectra of all samples (see Figure S.2 in Supporting Information).

Both the rheology and the liquid $^{29}$Si NMR data considered together suggest that, in both cases, n-TMOS and n-SiNAD,
the primary gel network was formed by TMOS. Presumably, either more TMOS or Si-NAD kept adding onto the network after its initial formation according to a monomer-cluster aggregation model. This conclusion is supported by the gradual and eventual disappearance of all $^{29}\text{Si}$ signals after gelation. That model also suggests that Si-NAD decorates the surfaces of the skeletal silica framework with NB, as intended, and agrees with previous speculation to that extent.3b Within that monomer-cluster aggregation model, the slower gelation of the TMOS/Si-NAD system may be reconciled by assuming that elementary particles formed at early stages get partially capped with Si-NAD, which sterically hinders interparticle bond formation. However, Si–O–Si bridges are hydrolyzed off continuously and Si-NAD repricipitates on the network during particle aggregation.

To gather further support for a TMOS-like network, we turned to small-angle X-ray scattering (SAXS), comparing native n-SiNAD with both n-TMOS and n-TMOS-co-APTES aerogels (Figure 6). Small angle neutron scattering (SANS) data when available agreed quite well with those from SAXS (see, for example, Figure S.3 in Supporting Information). That together with the high porosity of the samples suggests that all scattering information in SAXS arises from the particles, not from the pores. Results are summarized in Table 2. The high-Q region (Region I, Table 6) of the n-SiNAD aerogels follows a power law, with a slope equal to 4.22 ± 0.03. The slopes for n-TMOS and n-TMOS-co-APTES aerogels are 3.97 ± 0.03 and 4.37 ± 0.02, respectively. At ~4.0, the high-Q slope of n-TMOS indicates primary particles with abrupt interfaces. In n-SiNAD and n-TMOS-co-APTES, values > 4.0 indicate density-gradient (fuzzy) interfaces. The interfacial layer thickness, $t$, can be calculated via eq 3, assuming a Gaussian distribution of matter at the nanoparticle interfaces with standard deviation $s$. In turn, $s$ is obtained by fitting the scattering intensity to the suitably modified Porod’s law (eq 4), whereas $I(Q)$ is the scattering intensity as a function of $Q$, $N$ the number of scatterers per unit volume, $\Delta \rho$ the difference in scattering-length density between scatterers and the surrounding medium, and $S$ the surface area of the scatterer.58

$$I(Q) = 2\pi N(\Delta \rho)^2 S Q^{-4} \exp[-s^2 Q^2]$$ (4)

The surface layer thickness, $t$, was found equal to 3.8 ± 0.3 Å and 5.0 ± 0.3 Å for n-TMOS-co-APTES and n-SiNAD, respectively (Table 2). These values agree well with both the trend in the fully extended length of the $-(\text{CH}_2)_3\text{NH}_2$ group of APTES (3.86 Å) and of the $-(\text{CH}_2)_3\text{N}$-NAD group of Si-NAD (8.09 Å), both by molecular modeling. The lower SAXS thickness of $-(\text{CH}_2)_3\text{N}$-NAD implies some bending. The radius of the primary particles, $R_g$, is calculated via $R_g = 0.77 \times R_s$, where $R_s$ is the radius of gyration, obtained from the Guinier knee (Region II) in the log–log plot of $I(Q)$ versus $Q$ of either the SAXS or the SANS data (Figure 6). The radii of the primary particles in n-SiNAD fall within the range of 7.1–7.7 nm and, therefore, are similar to those for n-TMOS (5.7 nm, by SAXS only, see Table 2). Both the presence and the size of primary particles in n-SiNAD, as inferred via SAXS, were both confirmed with TEM (Figure 7). Additionally, particles in the dimensions suggested by SAXS/TEM for primary particles are the smallest entities discernible in FESEM (Figure 8, whereas the primary particles are pointed at with arrows). Primary nanoparticles aggregated in 3D into mass fractal secondary particles with fractal dimension $D_f$ are given by the slope of the second power-law region at lower Q-values (Region III, Figure 6).

Figure 6. Small angle X-ray scattering (SAXS) data for aerogel samples. (Data are summarized in Table 2; for additional sample information, refer to Table 4.) Primary particle radii were extracted from Guinier Region II. Secondary particle radii from Region IV. Fractal dimensions of secondary particles from Region III. Fitting power-law Region I to modified Porod’s law (eq 4) yielded the surface layer thickness of primary particles. n-TMOS-co-APTES did not yield information beyond the radius of primary particles (Region II) in the Q-range available.
Table 2. SAXS and SANS Data for Si-NAD Derived Aerogels and Controls (Native n-TMOS and n-TMOS-co-APTES)

<table>
<thead>
<tr>
<th></th>
<th>primary particles</th>
<th>secondary particles</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>thickness $t^a$ ($\text{Å}$)</td>
<td>$R_g(1)^b$ (nm)</td>
</tr>
<tr>
<td>n-TMOS SAXS</td>
<td>$3.97 \pm 0.02$</td>
<td>$4.2 \pm 0.1$</td>
</tr>
<tr>
<td>n-TMOS SANS</td>
<td>$4.37 \pm 0.02$</td>
<td>$3.8 \pm 0.3$</td>
</tr>
<tr>
<td>n-SiNAD SAXS</td>
<td>$4.22 \pm 0.03$</td>
<td>$5.0 \pm 0.3$</td>
</tr>
<tr>
<td>X-SiNAD(10) SANS</td>
<td>$j$</td>
<td>N/A</td>
</tr>
<tr>
<td>X-SiNAD(20) SAXS</td>
<td>$4.25 \pm 0.05$</td>
<td>$6.0 \pm 0.3$</td>
</tr>
<tr>
<td>X-SiNAD(30) SANS</td>
<td>$j$</td>
<td>N/A</td>
</tr>
<tr>
<td>X-SiNAD(10) SAXS</td>
<td>$4.26 \pm 0.04$</td>
<td>$6.8 \pm 0.3$</td>
</tr>
<tr>
<td>X-SiNAD(20) SANS</td>
<td>$j$</td>
<td>N/A</td>
</tr>
<tr>
<td>X-SiNAD(30) SAXS</td>
<td>$4.30 \pm 0.06$</td>
<td>$6.3 \pm 0.5$</td>
</tr>
<tr>
<td>X-SiNAD(30) SANS</td>
<td>$j$</td>
<td>N/A</td>
</tr>
</tbody>
</table>

$^a$Referring to Figure 6: From power law Region I. $^b$Via eq. 3. $^c$From Guinier Region II. $^d$Particle radius = $R_g/0.77$. $^e$From power law Region III. $^f$From Guinier Region IV. $^g$Within secondary particles. Calculated as described in Appendix I of Supporting Information. $^h$Abrupt interface (Porod slope = 4.0). $^i$No higher aggregates could be probed within the low-Q region accessible. $^j$High-Q region not accessible.

Figure 7. Transmission electron micrograph (TEM) of n-SiNAD. The primary particle diameter (15.6 nm) matches with that found using SAXS (15.4 nm; see Figure 6 and Table 2). For TEM of the X-SiNAD(30) samples see Figure S.4 in Supporting Information.

N($(R_g)^2) = \zeta (\frac{R_d}{R_g})^{D_f^{2}}$ (5)

packed spheres, and $R_g$, $R_d$, and $D_f$ have the same meaning as above. In turn, $N((R_g))$ can be used to calculate the percentage of empty space within secondary particles (see Appendix I in Supporting Information). Thus, with $R_g = 7.71$ nm, $R_d = 28.7$ nm, and $D_f = 2.07$, the secondary particles of n-SiNAD consist of 78% v/v empty space.

Finally, it is noted that the fractal dimensions of the secondary particles of both n-SiNAD and n-TMOS (2.07 ± 0.02 and 1.9 ± 0.3, respectively) are different (lower) than the fractal dimensions of the particles forming the gel network as identified by rheology (2.47 and 2.32, respectively, refer to Table 1). That difference strongly suggests that the gel network is not formed by secondary particles but by higher aggregates of the latter. That aggregation can be clearly seen in FESEM (entities enclosed by white dashed circles, Figure 8).

Overall, both neutron and X-ray scattering data further support a TMOS-derived fractal network of nanoparticles whose surface is decorated with NB moieties. That model is consistent with the macroscopic mechanical properties of the entire structure under quasi-static compression (Figure 9 and Table 3). Thus, while in terms of ultimate strength and within error n-TMOS and n-SiNAD aerogels behave similarly (ultimate compressive strengths at 3.3 ± 0.7 MPa versus 4.5 ± 0.4 MPa, respectively), suggesting a similar interparticle connectivity, on the other hand n-SiNAD are stiffer than n-TMOS (Young’s moduli at 5.3 ± 0.3 MPa and 2.9 ± 0.3 MPa, respectively) consistent with a surface layer that gets on the way to bending of particles around their interparticle necks. (It is also noted in passing that, in terms of ultimate strain, both native aerogels (n-TMOS and n-SiNAD) are capable of reaching unusually high values: ~50% and ~57%, respectively. Such supercompressibility for silica at those high densities has not previously been observed.) We speculate that this overlooked property of those materials is usually masked by macroscopic defects leading to premature failure. The matter is being investigated further.)

3.b. X-SiNAD Aerogels and the Topology of Cross-Linking. Scheme 3 summarizes the cross-linking process from a chemical perspective. ROMP initiated in the pores engages surface Si-NAD moieties. Interparticle bridging (cross-linking) should take place via either cross-metathesis or a stitching.
mechanism. Experimentally, the process was implemented as shown in Scheme 2. The pore-filling gelation solvent was first equilibrated with variable concentration solutions of NB in THF. A cold (−5 °C) THF solution of the GC-II catalyst was added to the also cold (−5 °C) NB bath surrounding the NB-equilibrated gels. Subsequently, samples were incubated at −5 °C to allow infusion of the catalyst into the gels without significant reaction, the criterion for which is increasing viscosity and ultimately gelation of the cross-linking bath itself. The cross-linking process was completed by allowing the system to warm-up to room temperature. Both short oligomers and loose polymer were removed using four THF washes according to procedures followed before.3−8,12−17 Next, wet-gels were solvent-exchanged with acetone and dried in an autoclave with liquid CO₂ taken out supercritically. NB-cross-linked aerogels are referred to as X-SiNAD(xx), where “xx” takes the values of 10, 20, or 30 denoting the weight percent concentration of NB in the cross-linking baths.

The ¹³C NMR spectra of all X-SiNAD(xx) are dominated by polynorbornene (Figure 4). The ²⁹Si NMR spectra (Figure 5) are identical to that of native n-SiNAD, indicating no adverse effect by the cross-linking process upon the chemical makeup of the skeletal framework. General materials properties of X-SiNAD(xx) aerogels are summarized in Table 4. The polymer uptake by TGA (Figure 3) increases for more concentrated cross-linking solutions: from 16% to 26% and, ultimately, to 38% w/w, roughly in proportion to the monomer concentration in the cross-linking bath (Table 4). (For the calculation

Figure 8. Scanning electron microscopy (SEM), N₂-sorption isotherms, and BJH plots (insets). Pertinent data, including bulk and skeletal densities, porosities, pore sizes, and pore size distributions are summarized in Table 4. In SEM, primary particles, as identified by both SAXS/SANS and TEM, are indicated with arrows. Dashed dark circles delineate secondary particles, as identified by SAXS/SANS. Dashed white circles delineate aggregates of secondary particles forming the network, as suggested by rheology. In BJH plots, arrows point at the low pore size shoulder that decreases in size, eventually disappearing as polymer uptake increases.
Figure 9. Mechanical characterization data under quasi-static compression (strain rate: 0.005 s⁻¹). In the log–log plots of Young’s modulus (E), ultimate compressive strength (UCS) and specific energy absorption versus density, open circles show the corresponding property of the n-SiNAD network and dark circles those of the X-SiNAD(xx) samples. Results are summarized in Table 3.

Table 3. Quasi-Static Compression Data for Si-NAD Derived Aerogels and Controls (Native n-TMOS and n-TMOS-co-APTES)¹

<table>
<thead>
<tr>
<th>Sample</th>
<th>Bulk density (ρ, g cm⁻³)</th>
<th>Young’s Modulus (E, MPa)</th>
<th>Yield stress at 0.2% offset strain (MPa)</th>
<th>Ultimate strength (MPa)</th>
<th>Ultimate strain (%)</th>
<th>Poisson ratio</th>
<th>Specific energy absorption (J g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-TMOS</td>
<td>0.200</td>
<td>2.9 ± 0.3</td>
<td>0.13 ± 0.01</td>
<td>3.3 ± 0.7</td>
<td>49.7 ± 3.6</td>
<td>10.3 ± 2.7</td>
<td>2.7 ± 0.6</td>
</tr>
<tr>
<td>n-TMOS-co-APTES</td>
<td>0.196</td>
<td>12.3 ± 1.3</td>
<td>0.37 ± 0.09</td>
<td>11.9 ± 6.8</td>
<td>60.6 ± 6.7</td>
<td>10.3 ± 4.7</td>
<td>10.3 ± 4.7</td>
</tr>
<tr>
<td>n-SiNAD</td>
<td>0.197</td>
<td>5.3 ± 0.3</td>
<td>0.21 ± 0.02</td>
<td>4.5 ± 0.4</td>
<td>57.2 ± 5.4</td>
<td>5.7 ± 1.3</td>
<td>5.7 ± 1.3</td>
</tr>
<tr>
<td>X-SiNAD(10)</td>
<td>0.273</td>
<td>108 ± 22</td>
<td>2.9 ± 0.4</td>
<td>18.8 ± 1.7</td>
<td>35.8 ± 3.2</td>
<td>0.08 ± 0.03</td>
<td>14.3 ± 1.3</td>
</tr>
<tr>
<td>X-SiNAD(20)</td>
<td>0.382</td>
<td>187 ± 18</td>
<td>5.2 ± 1.1</td>
<td>22.5 ± 0.1</td>
<td>39.0 ± 1.3</td>
<td>0.15 ± 0.02</td>
<td>13.8 ± 0.1</td>
</tr>
<tr>
<td>X-SiNAD(30)</td>
<td>0.632</td>
<td>386 ± 25</td>
<td>5.5 ± 0.9</td>
<td>59.3 ± 8.6</td>
<td>43.9 ± 5.9</td>
<td>0.27 ± 0.05</td>
<td>23.3 ± 2.3</td>
</tr>
</tbody>
</table>

¹Average of three samples at strain rate = 0.005 s⁻¹. Calculated from the area under the stress–strain curves at ultimate strain.

Method of the weight percent of polymer from TGA data, see Appendix II in Supporting Information). Skeletal densities, ρₐ, decrease as the amount of polymer increases. However, the ρₐ values are also consistently lower than the ρₑ, calculated from the skeletal densities of the native framework (ρₑ-SiNAD = 1.811 g cm⁻³, Table 1) and the density of free polynorbornene formed and isolated from the cross-linking bath (ρₑ-PNB = 1.129 g cm⁻³, by He pycnometry). That discrepancy is attributed to closed pores (CP), whose volume fraction, V_CP, can be calculated via eq 6, and in turn be used to calculate the percent closed void space in the skeletal framework, (fₑ-SiNAD and fₑ-PNB are the mass fractions of the skeletal framework and polymer, respectively.) The %V_CP values are cited in Table 4 and vary from 1.6% v/v in X-SiNAD(10) to 5.6% v/v in X-SiNAD(30).

On the contrary, due to shrinkage, bulk densities, ρₑ, increased more than expected from simple polymer uptake. Native n-SiNAD shrank the least relative to the molds (6.0 ± 0.7% in linear dimensions), shrinking less than both n-TMOS and n-TMOS-co-APTES aerogels (8–13%). X-SiNAD shrank progressively more from 13 ± 1% [X-SiNAD(10)] to 27 ± 1% [X-SiNAD(30)] as the polymer content increased—see photograph in Scheme 2. The additional shrinkage of the X-samples is attributed to a pulling effect exerted by the polymer on the skeletal framework as it tries to contract in order to maximize its interstrand van der Waals forces. That additional shrinkage of the X-samples is taken as indirect evidence of bridging skeletal nanoparticles. The effect of shrinking is evident in FESEM (Figure 8): the microstructure of n-SiNAD includes larger voids in the macropore range (>50 nm). Those voids are not present in the X-samples, although the major morphostructural features of the native framework have been preserved. A more quantitative evaluation of the porous structure follows.

Open porosity, via II = 100 × [(1/ρₑ) − (1/ρₑ)]/(1/ρₑ), decreased from approximately 89% in n-SiNAD to 55% v/v of void space in the most dense cross-linked samples. A more detailed evaluation of the porous structure was conducted with N₂-sorption porosimetry. Internal surface areas, σₑ, calculated by the BET method, applied on the early part of the adsorption isotherms (Figure 8), decreased as the polymer uptake increased.
macroporosity created a divergence of the average pore sizes calculated via the $4 \times \frac{V_{\text{Total}}}{\sigma}$ method, whereas the total volume of N$_2$ adsorbed, $V_{\text{Total}}$, either is taken from the highest point of the adsorption isotherm at ($P/P_0 \sim 1$), or is calculated via $V_{\text{Total}} = (1/\rho_b) - (1/\rho_s)$. With regards to both the n- and all X-samples, the average pore sizes calculated by the two methods are equally close to one another (Table 4). This finding suggests that we are dealing primarily with mesoporous materials (i.e., pore sizes in the 2−50 nm range). Indeed, all N$_2$-sorption isotherms (Figure 8) showed desorption hysteresis loops. Those isotherms can be classified as Type IV characterizing mesoporous materials. Upon closer examination, though, the isotherms of n-SiNAD do not reach saturation, in agreement with the macroporosity noted in FESEM. On the other hand, the isotherms of all X-samples did reach saturation, suggesting that macroporosity had been eliminated. Furthermore, as the amount of polymer increased, the desorption branch turns from H1-type (unobstructed adsorption−desorption, X-SiNAD(10) and X-Si-NAD(20) samples) into H2-type (ink-bottle-like pores, X-SiNAD(30) samples). All X-samples, however, remained mesoporous, as the t-plot analysis shows no indication for open microporosity (pore diameters < 2 nm) in any sample. By the same token, along the process of ink-bottle pore formation, it is reasonable.

Table 4. Materials Properties of the Si-NAD Derived Aerogels and the Controls (Native n-TMOS and n-TMOS-co-APTES)

<table>
<thead>
<tr>
<th>sample</th>
<th>polymer% w/w</th>
<th>skeletal density, $\rho_s$ (g cm$^{-3}$)</th>
<th>closed skeletal porosity, $% V_{\text{CP}}$ (v/v)</th>
<th>monolith linear shrinkage, $% \rho_a$ (g cm$^{-3}$)</th>
<th>bulk density, $\rho_b$ (g cm$^{-3}$)</th>
<th>open bulk porosity, II (% void space)</th>
<th>BET surface area, $\sigma$ (m$^2$ g$^{-1}$)</th>
<th>average pore diameter, $d$ (nm)</th>
<th>BJH pore diameter, $g$ (nm)</th>
<th>particle radius, $r$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-SiNAD</td>
<td>$i$</td>
<td>1.811 ± 0.007</td>
<td>6 ± 0.7</td>
<td>0.197 ± 0.005</td>
<td>89.1</td>
<td>590</td>
<td>25.4 [30.7]</td>
<td>41.5 [24.0]</td>
<td>2.8</td>
<td></td>
</tr>
<tr>
<td>X-SiNAD(10)</td>
<td>16</td>
<td>1.60 ± 0.01</td>
<td>13 ± 1</td>
<td>0.273 ± 0.009</td>
<td>83.0</td>
<td>368</td>
<td>25.3 [31.1]</td>
<td>38.6 [13.0]</td>
<td>5.1</td>
<td></td>
</tr>
<tr>
<td>X-SiNAD(20)</td>
<td>26</td>
<td>1.505 ± 0.003</td>
<td>20 ± 0.5</td>
<td>0.38 ± 0.011</td>
<td>74.6</td>
<td>243</td>
<td>18.9 [32.2]</td>
<td>22.2 [6.9]</td>
<td>8.2</td>
<td></td>
</tr>
<tr>
<td>X-SiNAD(30)</td>
<td>38</td>
<td>1.391 ± 0.004</td>
<td>27 ± 1</td>
<td>0.65 ± 0.0209</td>
<td>54.6</td>
<td>124</td>
<td>14.2 [27.8]</td>
<td>16.1 [3.2]</td>
<td>17.4</td>
<td></td>
</tr>
<tr>
<td>n-TMOS</td>
<td>$i$</td>
<td>1.970 ± 0.007</td>
<td>13.0</td>
<td>0.200</td>
<td>89.8</td>
<td>724</td>
<td>19.6 [24.8]</td>
<td>20.7 [2.8]</td>
<td>2.1</td>
<td></td>
</tr>
<tr>
<td>n-TMOS-co-APTES</td>
<td>$i$</td>
<td>1.835 ± 0.003</td>
<td>8 ± 0.5</td>
<td>0.196 ± 0.002</td>
<td>89.3</td>
<td>491</td>
<td>12.4 [37.1]</td>
<td>13.4 [3.6]</td>
<td>3.3</td>
<td></td>
</tr>
</tbody>
</table>

By TGA (Figure 3); for calculations, see Appendix II in Supporting Information. Single sample, average of 50 measurements. Via eq 6. Average of three samples. Linear shrinkage =100 × (sample diameter − mold diameter)/(mold diameter). By the $4 \times \frac{V_{\text{Total}}}{\sigma}$ method. For the first number, $V_{\text{Total}}$ was calculated by the single-point adsorption method; for the number in brackets, $V_{\text{Total}}$ was calculated via $V_{\text{Total}} = (1/\rho_b) - (1/\rho_s)$. From the desorption branch of the isotherm. The first number is the peak maxima; the number in brackets is the full width at half maximum. Calculated via $r = 3/\rho_s$. Not applicable.

(Table 4). Qualitatively, macroporosity created a divergence of the average pore sizes calculated via the $4 \times \frac{V_{\text{Total}}}{\sigma}$ method, whereas the total volume of N$_2$ adsorbed, $V_{\text{Total}}$ either is taken from the highest point of the adsorption isotherm at ($P/P_0 \sim 1$), or is calculated via $V_{\text{Total}} = (1/\rho_b) - (1/\rho_s)$. With regards to both the n- and all X-samples, the average pore sizes calculated by the two methods are equally close to one another (Table 4). This finding suggests that we are dealing primarily with mesoporous materials (i.e., pore sizes in the 2−50 nm range). Indeed, all N$_2$-sorption isotherms (Figure 8) showed desorption hysteresis loops. Those isotherms can be classified as Type IV characterizing mesoporous materials. Upon closer examination, though, the isotherms of n-SiNAD do not reach saturation, in agreement with the macroporosity noted in FESEM. On the other hand, the isotherms of all X-samples did reach saturation, suggesting that macroporosity had been eliminated. Furthermore, as the amount of polymer increased, the desorption branch turns from H1-type (unobstructed adsorption−desorption, X-SiNAD(10) and X-Si-NAD(20) samples) into H2-type (ink-bottle-like pores, X-SiNAD(30) samples). All X-samples, however, remained mesoporous, as the t-plot analysis shows no indication for open microporosity (pore diameters < 2 nm) in any sample. By the same token, along the process of ink-bottle pore formation, it is reasonable...
that some bottle-necks might get closed. That could explain the small amount of closed porosity identified via skeletal density considerations above.

Pore size distributions were evaluated by the BJH method applied on the desorption branch of the isotherms. (Plots are given as insets in Figure 8.) The maxima of the BJH plots are in good agreement with those from the $4 \times V_{\text{tota l}}/\sigma$ method applied to the maximum volume of $N_2$ adsorbed (see Table 4). The native n-SiNAD samples also show a shoulder at the smaller pore size of the BJH curve ($\sim 30$ nm, indicated with an arrow in Figure 8), suggesting two kinds of mesopores. That shoulder is progressively eliminated in the X-samples, suggesting a closing of the smaller pores. The elimination of smaller pores should have shifted average pore sizes to larger values. The opposite, however, was observed, presumably as the result of a contraction (shrinking) of the entire structure.

As previously discussed, the simple accumulation of polymer on the skeletal framework of X-SiNAD(xx) samples would increase the stiffness (resistance to bending). As opposed to simple polymer accumulation, bridging skeletal nanoparticles covalently would increase the ultimate strength of the whole structure. Indeed, under compression, all NB-cross-linked X-NB-SiNAD aerogels were not only much stiffer (108–386 MPa vs 5.3 MPa) but also much stronger (19–59 MPa vs 4.5 MPa) and tougher (14.5–23.2 J g$^{-1}$ vs 5.7 J g$^{-1}$) than n-SiNAD. The elastic (Young’s) modulus, $E$, increases exponentially with the bulk density, $\rho_b$, according to a power law of the form $E \sim \rho_b^{1.5}$ (see Figure 9). (It is noted though that the power-law exponent is lower than what has been reported for silica (3.7), thus underlining the efficiency of low polymer loadings for increasing strength.) Even more intriguing is the behavior of both the ultimate compressive strength (UCS) and the energy absorption as functions of bulk density (both shown by log–log plots in Figure 9); after an initial jump from n-SiNAD to X-SiNAD(10), these properties remained nearly constant for X-SiNAD(20), increasing drastically thereafter for X-SiNAD(30). The slopes of the log–log plots between X-SiNAD(20) and X-SiNAD(30) are 1.92 and 1.03 for the UCS and energy absorption, respectively, in line with silica (for which the values are 2.6 and 1.6, respectively, albeit in a 3-point bending configuration). The discontinuity in the log–log plots for both UCS and energy absorption suggests that not all polymer is equivalent: polymer accumulating at the early stages of cross-linking has a different effect from that accumulating later. Hence, both indentifying possible chemical differences and locating the two kinds of poly-norbornene on the silica nanostructure are important.

As inferred by the microscopic similarity of n-SiNAD to all three X-SiNAD(xx) (Figure 8), the polymer is always closely associated with silica. That fact, in combination with covalent bonding between the two, should restrict segmental motion of polymeric strands and, therefore, raise the glass transition temperature, $T_g$, relative to the bulk polymer as the thickness of the polymeric cross-linker decreases. Indeed, as shown in Figure 10, X-SiNAD(10) had the highest $T_g$ (73.8 °C). That value decreased sharply to 63.9 °C for X-SiNAD(20), eventually reaching 60.6 °C for X-SiNAD(30). This temperature is still higher than the $T_g$ of free polymer formed and collected from the cross-linking bath (50.4 °C). Clearly, the polymer in all three X-samples never reached a thickness high enough to behave as bulk NB. In a careful comparison of grafted brushes versus cast PMMA films, Yamamoto et al. demonstrated that a 10 °C higher $T_g$ [an analogous situation to X-SiNAD(30)] corresponds to layers of brushes approximately 10 nm thick. In terms of the n-SiNAD nanostructure, this thickness is within secondary particles. Finally, the full width at half maximum of the heat exchange profiles of the three X-samples was much broader (42–67 °C) than that of the free polymer (12 °C), reflecting the variable lengths between points of attachment of the polymer to the silica backbone.

The cross-linking polymer was freed from the silica framework of all three X-samples by treatment with HF. The free polymer was extracted with CHCl$_3$, and its size was investigated with gel permeation chromatography (GPC) in THF using polystyrene standards. Results were compared to free polymer formed outside the gels in the surrounding cross-linking bath. (Owing to similar hydrodynamic radii in THF of both poly-norbornene and polystyrene at equal molecular weights, the latter was a good model for the former.) Typical GPC data are given in Figure 11. All results are summarized in Table S.1 in Supporting Information. By inspection, peaks corresponding to individual polymers/oligomers were placed in both a lower retention time group ($R_t \sim 6.5$ min, higher molecular weight polymer) and a higher $R_t$ group ($\sim 9.7$ min, smaller oligomers). Those two groups were fitted to Gaussian profiles (indicated with dashed lines in Figure 11). Average molecular weights were calculated by standard procedures.

The long component varied from 379 to 505 monomer units; its weight percent contribution increases from 32% in X-SiNAD(10) to 41% in X-SiNAD(20) to 50% in X-SiNAD(30), while the polydispersity remained relatively low, in the 1.88–2.28 range. The short component, however, had only 8–11 monomer units and a polydispersity of 1.74–2.53. The makeup of the polymer formed in the cross-linking bath was somewhat different from that formed on the skeletal framework; that polymer included a third major fraction (50% w/w), with intermediate retention time ($R_t \sim 8.4$ min) corresponding to ~100 monomer units with very high polydispersity (7–10). In contrast to the X-samples, the distribution of the three fractions in the polymer from the cross-linking bath did not change with the concentration, advocating for the role of surface-NB in modulating the polymer length in the gels through the stitching mechanism of Scheme 3. The radii of gyration, $R_g$, of the polymer fractions freed from the network were calculated both for good (swelling) solvents via eq $8^{46}$ and for theta solvents via eq $8^{47}$ where the number of monomer units, $N_i$, is taken from Table S.1 in Supporting Information and the length of the monomer repeat unit, $\alpha$, was found by simulation equal to 4.85 Å.
Supporting Information. They were used to calculate the radii of gyration which, for the short polymer lumps. Those radii of gyration are included in Table S.1, and Table 2) in combination with some selected general material characterization data from Table 4.

By SANS/SAXS, all three cross-linked samples continued to demonstrate the same hierarchical primary/fractal-secondary particle structure of n-SiNAD. Of major importance is the fact that primary particles were discernible at all. Those particles were embedded in a medium of different density ($\Delta \rho \neq 0$, refer to eq 4). The radius of the primary particles increased monotonically with the degree of cross-linking from X-SiNAD(10) to X-SiNAD(30). The radius of the secondary particles first decreased from 28.7 ± 0.3 nm in n-SiNAD to ~21 nm in X-SiNAD(10) and X-SiNAD(20) and then increased to 29.1 ± 0.4 nm in X-SiNAD(30). The uncertainties (error) in the radii of gyration of the primary particles were less than 4% in SAXS, 7% in SANS, and, in most cases, less than 2%. Hence, we are dealing with only one kind of primary particles. Should the polymer have coiled into 5.0–5.8 nm lumps, those lumps would have interfered with the scattering profile of the silica primary particles, yielding bimodal particle size distributions. The latter were not detected. Therefore, discrete polymeric lumps (Model II, Scheme 4) were not formed at any level. On the contrary, primary particles in the cross-linked samples still show fuzzy (density-gradient) interfaces (high-Q slopes > 4.0), and the thicknesses of the fuzzy zones are very similar to those of the native n-SiNAD samples (6.0–6.8 Å versus 5.0 Å, respectively).

To this point in the study, the SAXS/SANS data have been consistent with polymer building into a tight, dense conformal shell (coating) around the silica core primary particles comprising the native n-SiNAD network. That coating covalently bridges, as designed, primary particles, pulling them together so that secondary particles contract. As outlined in Appendix III of the Supporting Information, the radius of the core–shell primary particles can be calculated from the radius of the native primary particles (7.71 nm by SAXS), the skeletal density of the silica core (1.811 g cm$^{-3}$), and the density of the polynorbornene isolated from the cross-linking bath ($\rho_{\text{PNB}} = 1.129$ g cm$^{-3}$). It was thus found for the ratios (experimental radius by SAXS/ calculated radius, nm/nm) 7.7/8.7 for X-SiNAD(10); 8.2/9.4 for X-SiNAD(20); and, 9.4/10.6 for X-SiNAD(30). The values in the pairs are close, providing support for the formation of
polynorbornene shells around the primary silica core particles of the native n-SiNAD framework.

The medium surrounding the primary core–shell particles within the secondary particles may be either air or looser polymer of different density from that forming the core–shell structure around primary particles (Model III). The GPC analysis above corroborates with this model, suggesting a succession of events: NB moieties on primary particles are engaged early, leading to a conformal coating of shorter, closely held (denser) polymer. Longer polymer fills the empty space within secondary particles. The immediate question then is whether or not secondary particles are completely filled with polymer. As discussed in Section 3.a, owing to their fractal structure, secondary particles of n-SiNAD consist of 78% empty space. Similarly, “empty” space within secondary particles of X-samples can also be calculated from the experimental radii of gyration of the core–shell primary particles and is cited in Table 2. Owing to the uncertainties involved, for that calculation we assumed that the fractal dimension of all secondary particles remained equal to that of n-SiNAD ($D_f = 2.07$). At first approximation, that is, by ignoring closed pores, an assessment of whether that “empty” space is filled with polynorbornene can be obtained by comparing the experimental skeletal densities of the X-samples (Table 4) with those calculated as the weighted average of silica and polymer and assuming that all the space surrounding primary particles is occupied by polymer. Additional assumptions are that (a) secondary particles consist of primary silica particles of the same dimensions found in n-SiNAD (7.71 nm by SAXS) and (b) space is filled by one kind of polymer, that obtained from the cross-linking bath. We thus find for the ratios (experimental/calculated skeletal densities, g cm$^{-3}$/g cm$^{-3}$) 1.609/1.327 for X-SiNAD(10); 1.505/1.327 for X-SiNAD(20); and 1.391/1.279 for X-SiNAD(30). The two skeletal densities converge for X-SiNAD(30). Looking at the issue from a different perspective, the smallest particle radii, $r$, calculated from both skeletal densities and BET surface areas (values included in Table 4) agree reasonably well with the radii of the core–shell primary particles estimated from SAXS for X-SiNAD(10) and X-SiNAD(20), but they jump to higher values for X-SiNAD(30), consistent with mostly polymer-filled secondary particles. Overall, data converge toward Model III for higher PNb loadings.

4. CONCLUSION

The experimental implementation in 2002 of Mackenzie’s 1992 conjecture calling for polymer/sol–gel composites consisting of polymeric tethers bridging interconnected silica particles produced polymer-cross-linked aerogels, a class of extremely strong, yet lightweight materials. However, given the complex hierarchical structure of silica (agglomerates of porous, fractal secondary nanoparticles), the exact location of the polymer and, therefore, application-specific questions such as how much is enough had not been addressed yet. Here, by designing a system where cross-linking takes place by a well-defined process (grafting-to ROMP), loose polymer can be removed easily. Then, by using a wide array of characterization methods, it is concluded that accumulation of the cross-linking polymer follows the hierarchical structure of silica (Model III, Scheme 4). The polymer stays close, forming a conformal coating around primary particles. Subsequently, it fills secondary particles without formation of globules or lumps. Along that process, only a very small amount of closed porosity is created (<5% v/v of the skeletal network). Most importantly, however, a small amount of polymer (e.g., 16% w/w) that coats only primary particles with minimal compromise in the overall porosity (from 89% to 83% v/v) and the porosity-related properties (e.g., BET surface areas, from 590 to 368 m$^2$ g$^{-1}$) is enough to increase stiffness by a factor of 20$^x$ and ultimate compressive strength by a factor of 4$x$. At that point, silica aerogels are quite robust materials, making them easy to handle. Additional polymer continues to accumulate, mostly on and around primary particles, so that properties such as porosity and BET surface area begin decreasing noticeably without any gain in either ultimate compressive strength or specific energy absorption. The point where mechanical properties start improving drastically again is when secondary particles are almost completely filled with polymer. The subject matter of this paper, that is, the detailed correlation of structure–mechanical strength at the early stages of cross-linking, raises obvious questions about the opposite end of the strength-density continuum, namely for materials classified as polymer–matrix composites.50

ASSOCIATED CONTENT

Supporting Information
Rheology during base-catalyzed gelation of TMOS (Figure S.1); IR spectra of representative aerogel samples (Figure S.2); overlaid SAXS and SANS data for n-SiNAD (Figure S.3); TEM data for X-SiNAD(30) (Figure S.4); GPC analysis data (Table S.1); calculation of empty space in secondary particles (Appendix I); calculation of polymer content in X-samples from TGA data (Appendix II); and calculation of the thickness of a polymer shell around a silica core from experimental skeletal density data (Appendix III). This information is available free of charge via the Internet at http://pubs.acs.org.

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Notes
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REFERENCES
