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Dendrimers as Building Blocks for Nanostructured Materials: Micro- and Mesoporosity in Dendrimer-Based Xerogels

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Recently we have been exploring the use of dendrimeric building blocks in the construction of new types of nanostructured materials.[1] In principle, this may be accomplished with use of various chemical interactions for linking the dendrimers together. For example, highly charged dendrimers of opposite charge might assemble via electrostatic forces into superlattice structures. Another approach involves the covalent assembly of dendrimer building blocks into network structures using coupling reactions between functional end groups on the dendrimer surface. Spherically shaped dendrimers may be expected to pack into networks possessing interstitial spaces whose size is influenced by the radius of the dendrimer building block.[2] With this approach, it should be possible to generate new classes of porous materials with tunable pore sizes and inclusion properties. For such materials, one might expect that pore diameters would increase, and surface areas decrease, with higher dendrimer generations.

While many types of dendrimers possess oblong or irregular shapes,[3] dendrimeric carbosilanes appear to be approximately spherical.[4] We have therefore chosen to base initial investigations into the synthesis of porous, dendrimer-based materials on carbosilane dendrimers with appropriate functionalization. Here we describe the synthesis of second and third generation triethoxysilyl-terminated dendrimers, which were hydrolyzed via a sol−gel protocol to micro- and mesoporous hybrid dendrimer-silica xerogels. These xerogels were obtained by an acid-catalyzed hydrolysis, which is expected to promote extended networks with introduction of a high degree of residual OH functionality.[5]

Related approaches to hybrid organic−inorganic xerogels have employed organic compounds functionalized with two or more trialkoxysilyl groups.[6,7] Like these materials, dendrimer-based xerogels have potential applications as catalysts,[8] catalyst and chromatographic supports,[8,9,10] and porous membranes.[11] Low surface area materials, referred to as “stargels”, have been prepared by the hydrolysis of first-generation carbosilane dendrimers such as $Si[CH_2CH_2CH_2Si(OEt)_3]_4$.[12] Also very recently, Corriu and co-workers reported the base-catalyzed hydrolytic condensation of second generation trimethoxysilyl-terminated carbosilane dendrimers to hybrid gels.[13]

The dendrimer structures were built up according to published synthetic methodology, involving hydrosilation of terminal olefinic groups with $HSiCl_3$, followed by vinyl (or allyl) Grignard addition to the resulting trichlorosilyl functionalities.[1,14] However, the hydrosilation of vinyl- and allylsilanes with $HSiCl_3$ is accompanied by formation of impurities resulting from redistribution at silicon,[15] and the purification of these products can be difficult. For these reasons, the Cl_3Si-terminated dendrimer is usually not isolated but is immediately used in situ for the next conversion, which gives a moisture-stable product which can be purified by chromatography. The synthesis of $(RO)_3Si$-terminated dendrimers may be accomplished via addition of an alcohol and base to the corresponding trichlorosilyl derivative.[12,13] However, this procedure does not allow convenient separation of the desired product from the redistribution impurities (due to the sensitivity of the Si−OR linkage to moisture and chromatographic supports). We have found that direct hydrosilations with triethoxysilane[16] circumvent these problems, in that this reaction is not complicated by the generation of redistribution byproducts. Thus, $Si[CH_2CH_2CH_2Si(CH_2CH_2Si(OEt)_3)_3]_4$ (G2′-$(OEt)_{36}$) was obtained in high yield via

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Scheme 1

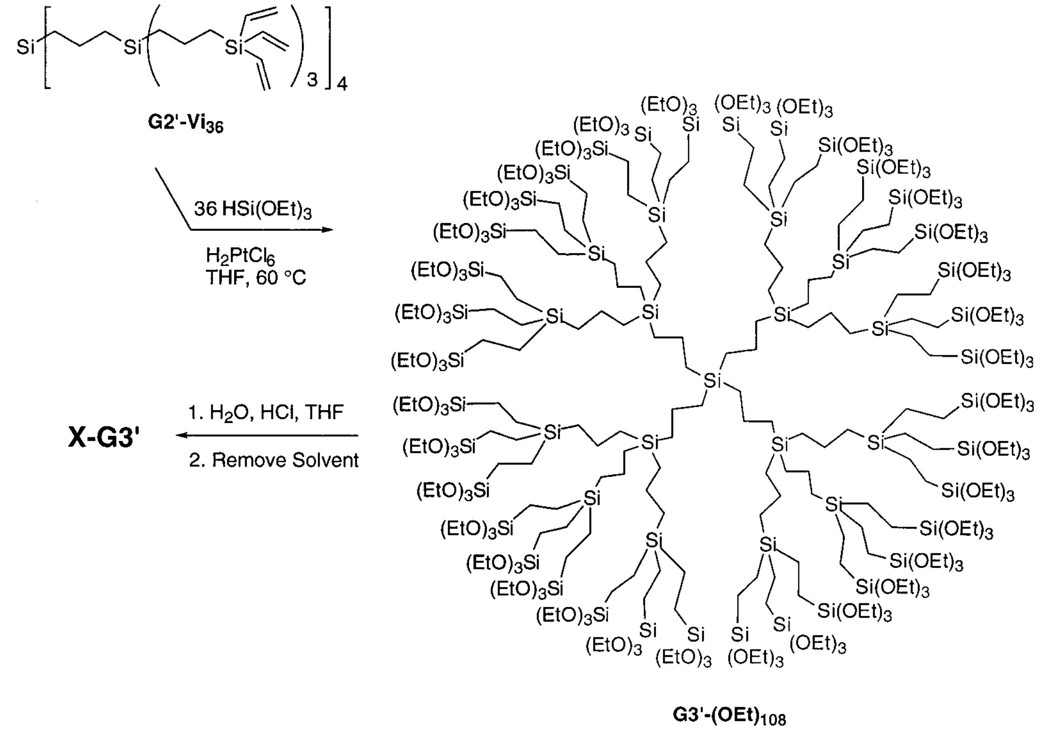

Table 1. Nitrogen Porosimetry Data for the Xerogels

xerogel	BET surface area (m^2/g)	Langmuir surface area (m^2/g)	total pore vol (cc/g)	micropore vol (cc/g)	av pore radius (Å)[a]
X-G2′	325	613	0.21	0.12	13.1
X-G3′	490	1002	0.33	0.14	13.5
microporous silica[21]	496		0.31	0.25	16

[a] Pores in X-G2′ and X-G3′ with radii <10 Å (micropores) are not reflected in these values.

hydrosilation of the appropriate dodecavinyl compound with $HSi(OEt)_3$. Similarly, G3′-$(OEt)_{108}$ was obtained as a colorless oil in near quantitative yield, according to the reaction shown in Scheme 1. These new carbosilane dendrimers were pure by NMR spectroscopy and free of redistribution side-products. However, minor peaks in the $-Si(OEt)_3$ region of the ^{29}Si NMR spectra are presumably due to formation of small amounts (ca. 1% for G2′-$(OEt)_{36}$; 5−10% for G3′-$(OEt)_{108}$) of α-regioisomers ($-CHMeSi(OEt)_3$ end groups). Further characterization of the silylalkoxy terminated dendrimers by MALDI-TOF mass spectrometry was not possible because of their moisture sensitivity.

Hydrolyses of G2′-$(OEt)_{36}$ and G3′-$(OEt)_{108}$ were conducted in THF solutions (2.5 M in OEt groups) with small quantities of 1 N HCl. The homogeneous sol solutions were allowed to gel in polyethylene bottles over 48 h, after which hard, clear monoliths were obtained. The monoliths were then removed intact from the polyethylene bottles and solvent processed[17] to give the xerogels X-G2′ and X-G3′, respectively.

Infrared data for X-G2′ and X-G3′ indicate the presence of partially condensed polysilsesquioxane networks. Thus, broad absorption bands observed at approximately 3400 and 1050 cm^{-1} correspond to $\nu(O-H)$ and $\nu(Si-O-Si)$ vibrations, respectively.[18] Powder X-ray diffraction data for both gels indicate that these materials are amorphous. Additionally, it was determined that X-G2′ and X-G3′ undergo dramatic weight increases due to the uptake of water (30 and 42%, respectively) after exposure to water vapor for 48 h.

The nitrogen adsorption porosimetry data (Table 1) clearly show that there is an increase in the total surface area and pore volume with generation number. Thus, as the diameter of the dendrimer increases, there is a concomitant increase in the surface area and pore volume of the corresponding gel. This phenomenon is surprising in view of what is known about the condensation of silica paricles in the sol−gel process, for which surface areas generally decrease as the condensing silica spheres increase in size.[19] A likely explanation for this apparent anomaly is that the gel precursors G2′-$(OEt)_{36}$ and G3′-$(OEt)_{108}$ exhibit some degree of compressibility. Furthermore, we might expect G2′-$(OEt)_{36}$ to be more deformable than G3′-$(OEt)_{108}$, because of the less congested surface of the lower generation.[1] Thus, it is possible that the condensed dendrimers of X-G2′ are compressed onto one another, leaving a lower residual surface area than one might expect for the packing of hard spheres. On the other hand, the condensed dendrimers in X-G3′ may be compressed to a lesser extent to give a gel with a relatively high surface area and pore

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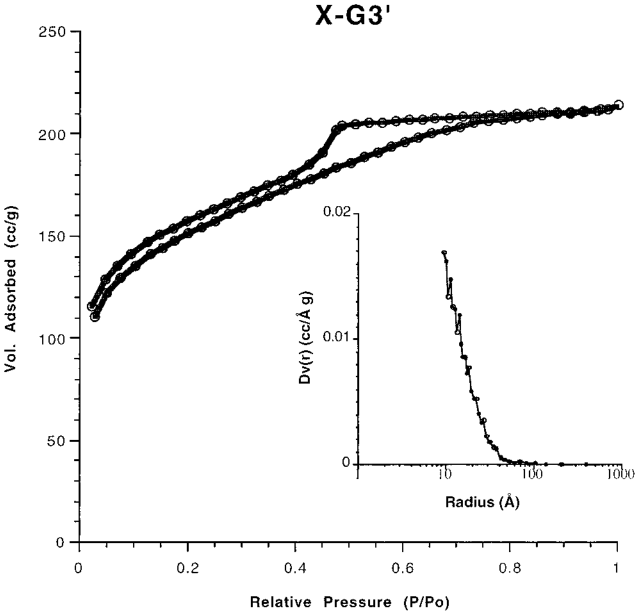
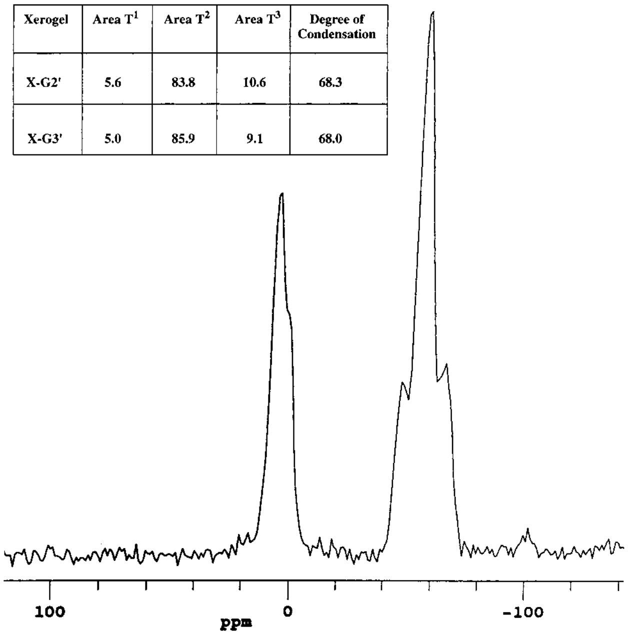


Figure 1. The adsorption/desorption isotherm for the gel derived from dendrimer G3′-$(OEt)_{108}$ (X-G3′) and the differential pore size distribution (*Dv*(*r*)) vs pore radius (log scale) for the gel derived from dendrimer G3′-$(OEt)_{108}$ (X-G3′) using the *adsorption* isotherm data in the inset.

volume (more closely resembling the packing of hard spheres). Obviously, it is important to further evaluate these trends with materials derived from dendrimers with a wider range of diameters.

The relatively small pore volumes also indicate that these dendrimer-based xerogels are packed more densely than hard spheres with comparable dimensions. Consistent with this, significant portions of the open volume in the xerogels arise from micropores (pore diameters < 20 Å;[20] see Table 1). Based on a BJH analysis of the porosimetry data,[19] the measured pore size distribution is limited to radii = 10 Å. As can be seen from the plot of Figure 1, many of the pores in X-G3′ undoubtedly have radii below this value, as the distribution tails rapidly from an apparent maximum of ca. 10 Å, to values consistent with mesoporosity. With this limited data, we can calculate average pore radii for X-G2′ and X-G3′ of 13.1 and 13.5 Å, respectively. For comparison, the surface area, pore volume, and average pore radii of a known microporous silica gel[21] that was obtained from the desication of ca. 70 Å silica globules are given in Table 1.

The nitrogen adsorption isotherms for both dendrimer-based xerogels also give some indication of the pore structure. Although it is somewhat unusual that our isotherm loops do not close at low relative pressure, they are reminiscent of type H2 hysteresis[22a] (type E in the older literature[22b]). This type of adsorption/desorption isotherm has been attributed to ink bottle type pores,[22b] although it is now recognized that this



Xerogel	Area T^1	Area T^2	Area T^3	Degree of Condensation
X-G2'	5.6	83.8	10.6	68.3
X-G3'	5.0	85.9	9.1	68.0

Figure 2. The ^{29}Si CP MAS NMR spectrum for X-G3′ and the ^{29}Si CP MAS NMR data for xerogels X-G2′ and X-G2′ in the inset.

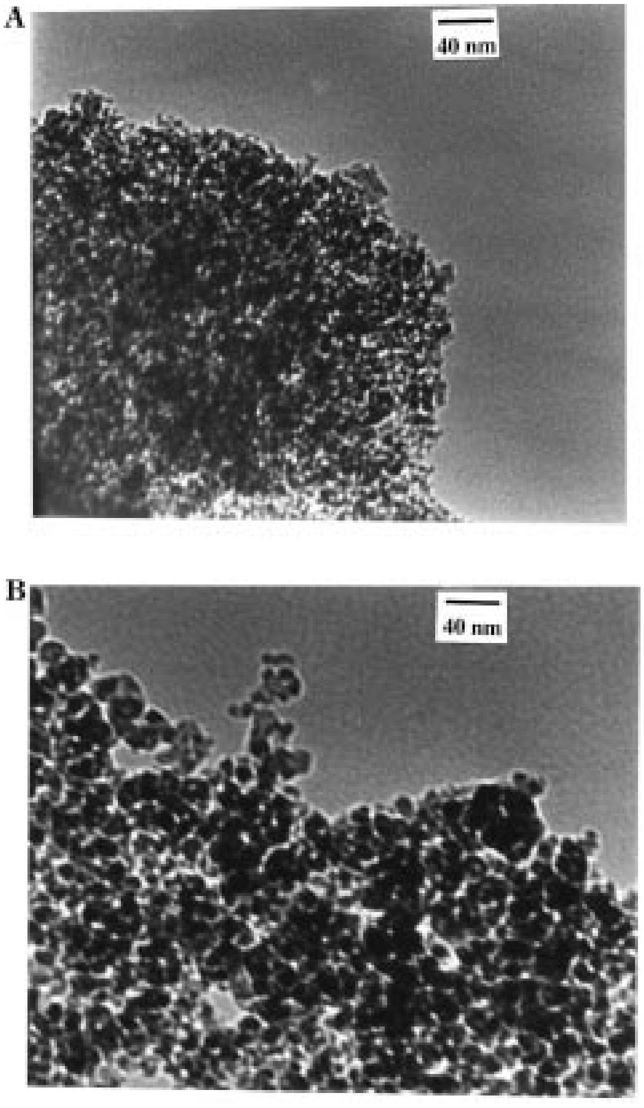


Figure 3. The TEM images of (a) X-G2′ and of (b) X-G3′. In each micrograph, 1 cm corresponds to 40 nm.

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may be an oversimplification of the actual pore structure.[22a] Note, however, that a densely packed network of spheres (as in a close-packed lattice) would possess void spaces that are in the approximate shape of an ink bottle.

To evaluate the degree of condensation in the gels, solid state ^{29}Si CP MAS NMR spectroscopy was employed. The conventional “Q^n” notation for SiO_4 tetrahedra may be replaced with an analogous “T^n” notation for $RSiO_3$ centers, such that terminal dendritic silicons with one, two, and three Si−O−Si linkages are designated T^1, T^2, and T^3, respectively.[6a] Deconvolution of the individual T^n resonances allows an estimate (±10%) of the degree of condensation to be made.[23] The ^{29}Si CP MAS NMR spectra for X-G2′ and X-G3′ reveal that ca. 85% of the reactive silicon centers are of the T^2 type (Figure 2). Thus, these silicons participate in two Si−O−Si linkages, and also possess one −OH (or −OEt) group. No T^0 centers were observed for either X-G2′ or X-G3′, indicating that all of the dendrimer end groups are at least partially condensed. The degree of condensation[6a] for both gels was approximately 68% and is therefore analogous to that observed for high surface area silica gels obtained by an acid-catalyzed route.[24] Normally, acid catalysis results in complete polymerization of the silicon centers, while preserving significant numbers of uncondensed Si−OH groups.[5]

From the TEM images of X-G2′ and X-G3′ (Figure 3), it is apparent that the dendrimers have not condensed into well-ordered arrays, but are densely packed in a random network exhibiting some microporosity. Further, the pore sizes of both gels measured from the TEM images (7−60 Å) are consistent with those determined from the nitrogen adsorption porosimetry data.

In summary, this work has produced dendrimer-based xerogels that exhibit high surface areas, and an interesting observation with respect to the relationship between generation number and surface area has been made. Future work will address the influence of various synthetic conditions on the structures of the gels. Also, we intend to investigate the properties of these new materials as molecular sieves, porous membranes, and catalyst supports.

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