Alkylene-Bridged Silsesquioxane Sol–Gel Synthesis and Xerogel Characterization. Molecular Requirements for Porosity

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Alkylene-bridged silsesquioxane xerogels with alkylene spacers spanning the range from ethylene to tetradecamethylene have been synthesized. Hydrolysis and condensation conditions using 1 N HCl in tetrahydrofuran or 1 N NaOH in ethanol were employed. The resulting xerogels were characterized by ^{29}Si solid-state NMR and nitrogen adsorption porosimetry. It was found that base catalysis resulted in a higher degree of condensation than acid catalysis. The acid catalyzed ethylene-bridged xerogel possessed high surface areas by the BET method (400–600 m^2 g^{-1}) and was microporous, but materials prepared from the longer alkylene spacers were found to be nonporous with no significant surface area. In contrast, base-catalyzed xerogels were found to be both microporous and mesoporous, with the peak of the pore size distribution in the mesopore range. High surface areas were also found for the base catalyzed xerogels. The surface area decreased as the alkylene spacer length increased to the point where no significant surface area existed for the tetradecamethylene-bridged xerogel. Pore size analysis of the base-catalyzed xerogels showed an increase in the mean pore size distribution, concomitant with decreasing total pore volume, as the alkylene spacer length increases. Comparison with previous work employing arylene-bridged xerogels leads to the conclusion that employing rigid organic spacers with either acid or base catalysis appears to be a requirement for organic-bridged polysilsesquioxane xerogels possessing high surface areas and porosity.

We are employing a molecular engineering approach to develop materials with controlled physical attributes by means of a "molecular scaffolding". We recently reported the synthesis and characterization of organic-bridged polysilsesquioxane xerogels, materials with high surface area that is confined to the micropore and mesopore domain.[1-6] The xerogels were prepared by hydrolysis and condensation of bis(trialkoxysilyl) monomers. The resulting xerogels contain rigid organic groups as the spacer (Figure 1). The size of the organic spacer was varied in an attempt to control the pore size of these xerogels. Surface area and porosity analysis by nitrogen adsorption showed these xerogels possess surface areas in the range of 500 to 1750 m^2 g^{-1} by the Brunauer–Emmett–Teller (BET) method. Both acid- and base-catalyzed organic-bridged xerogels previously studied possessed high surface area and porosity, but no simple correlation was found between these physical parameters and the type of spacer or catalyst. In a continuation of this work, we sought to determine the properties of xerogels made from alkylene spacers of increasing flexibility. We were particularly interested in the effects of alkylene spacers on surface area and pososity. New conditions of hydrolysis and condensation have been developed to obtain invariant conditions of gelation for all monomers. The results provide insight into the molecular determinants for high-porosity organic–inorganic xerogels.

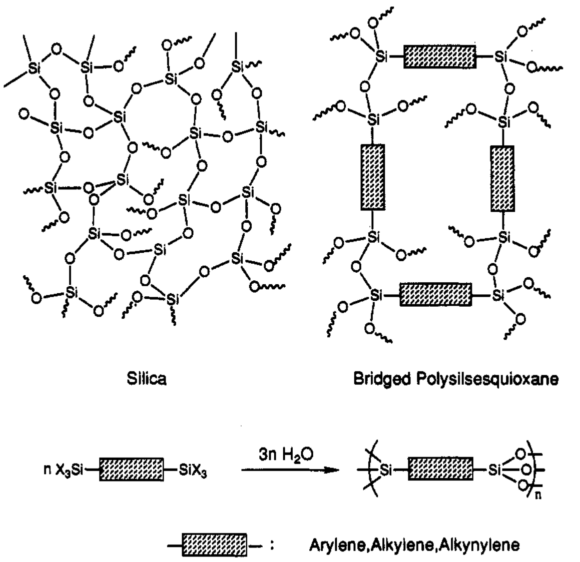

Figure 1. Schematic depiction of hybrid organic-bridged silsesquioxanes.

Results and Discussion

Monomeric Sol Gel Precursors. Compounds of the general formula $[(RO)_3Si(CH_2)_{n/2}]_2$ where n is an even integer were either synthesized or obtained commercially. Monomers with n = 6, 8, 10, and 14 (R = ethyl) were

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[1] Shea, K. J.; Loy, D. A. *Chem. of Mater.* **1989**, *1*, 572.

[2] Shea, K. J.; Webster, O.; Loy, D. A. *Mater. Res. Soc. Symp. Proc.* **1990**, *180*, 975.

[3] Shea, K. J.; Loy, D. A.; Webster, O. *J. Am. Chem. Soc.* **1992**, *114*, 6700.

[4] Shea, K. J.; Webster, O.; Loy, D. A. *Better Ceramics Through Chemistry IV*; MRS Symposium Proceedings; Zelinski, B. J. J., Brinker, C. J., Clark, D. E., Ulrich, D. R., Eds.; 1990; Vol. 180, p 975.

[5] Loy, D. A.; Shea, K. J.; Russick, E. *Better Ceramics Through Chemistry V*; MRS Symposium Proceedings; Hampden-Smith, M. J., Klemperer, W. G., Brinker, C. J., Eds.; 1992; Vol. 271, 699.

[6] Small, J. H.; Shea, K. J.; Loy, D. A. *J. Non-Cryst. Solids*, in press.

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Scheme I. (A) Hydrosilylation Reaction To Form Bis(trialkoxysilyl)alkane Monomers. (B) Sol–Gel Formation from Alkylene-Bridged Polysilsesquioxane Xerogels

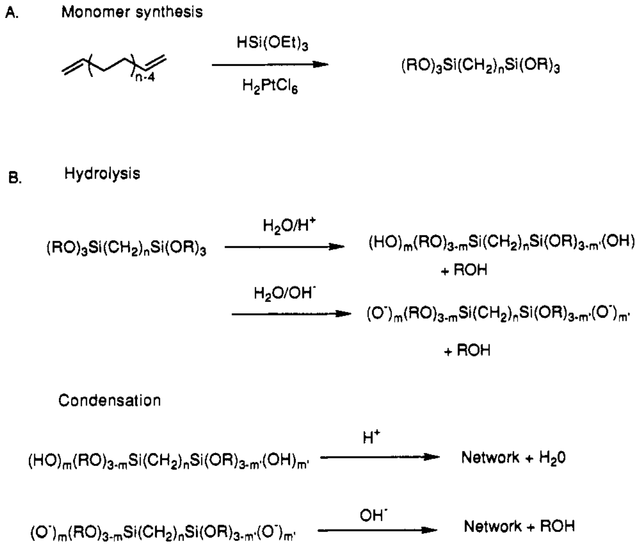

Table I. Acronyms for Monomeric Precursors and Catalysts

acronym	monomer
BTP	1,4-Bis(triethoxysilyl)benzene
BTME	1,2-Bis(trimethoxysilyl)ethane
BTBu	1,4-Bis(triethoxysilyl)butane
BTMH	1,6-Bis(trimethoxysilyl)hexane
BTH	1,6-Bis(triethoxysilyl)hexane
BTO	1,8-Bis(triethoxysilyl)octane
BTN	1,9-Bis(triethoxysilyl)nonane
BTD	1,10-Bis(triethoxysilyl)decane
BTTD	1,14-Bis(triethoxysilyl)tetradecane

	catalyst used
-H	6 equiv of 1 N HCl in THF
-OH	6 equiv of 1 N NaOH in ethanol

prepared by hydrosilylation of the corresponding α,ω-alkyldienes with triethoxysilane employing chloroplatinic acid (H_2PtCl_6) in isopropanol (Speier's catalyst[7]) or ethanol, or a divinyldisiloxane platinum complex (Karstedt's catalyst[8]).[9] 1,4-Bis(triethoxysilyl)butane ($n = 4$) was synthesized by hydrosilylation of 1,3-butadiene with trichlorosilane followed by ethanolysis of the resulting 1,4-bis(trichlorosilyl)butane. Monomers with $n = 2$ and 6 (R = methyl) were obtained commercially (Hüls America). The general synthetic procedure is shown in Scheme IA. All monomers were distilled under vacuum to afford clear, colorless liquids with purity >98% by GC. Bis(triethoxysilyl)nonane was a gift from Sandia National Laboratories. All synthesized monomers were characterized by ^1H and ^{13}C NMR and high resolution mass spectrometry. The acronyms subsequently used for representing these monomers appear in Table I.

Gel Formation and Processing. Conditions used for gel formation with previously studied monomers[1-6] were found to be inadequate for gel formation in the present series of *n*-alkylene-bridged xerogels. We sought homogeneous conditions that would yield gels within approximately 24 h. Noll[10] gives general conditions for the hydrolysis-condensation of dichlorodimethylsilane and the dependence of catalyst and solvent on molecular weight of the resulting siloxanes. Using these guidelines, a uniform set of conditions was developed for the base catalyzed formation of gels from all monomers at monomer concentrations of 0.2 M in ethanol (EtOH) using 1 N sodium hydroxide as catalyst (basic system). Gels were also formed from all but the BTBu monomer under acidic conditions using 0.4 M monomer in tetrahydrofuran (THF) and 1 N hydrochloric acid as catalyst (acidic system). The reaction mixtures consisted of a 6:1 mole ratio of water to monomer which gave 10.8 mol % of catalyst to monomer with both acid and base catalysts. A general outline for gel formation appears in Scheme IB. Most xerogels prepared for these studies were aged at least two weeks with the exception of BTH-H and BTD-OH, which were aged for shorter times.

Materials prepared in previous studies[3] employed an organic solvent replacement scheme for processing the formed xerogel. The process involved extracting the gels with a series of solvents of decreasing dielectric constant with relative permitivity values ranging from 16 to 2.[11] More recent experiments in our laboratory have indicated that solvent processing could be circumvented without significant loss of surface area or micropore structure by extracting the solvent from the hydrolysis–condensation reaction with deionized water.[6,11] This new method of xerogel preparation, termed water processing, was used for all xerogels prepared in the present work for the study of the dependence of physical properties on the alkylene spacer length.

After processing (with water or organic solvent) the gels were dried in a convection oven at 75 °C until all visible traces of solvent were removed, ground to a fine powder, and further dried in vacuo at 125 °C. The ground xerogels were not sized prior to surface area measurements.

The gelation time and mechanical strength of the resulting gels were found to be sensitive to both monomer and catalyst concentration. BTBu, BTMH, and BTH monomers did not gel in the acidic system at the 0.2 M monomer concentration previously used for other organic-bridged xerogels.[3] Increasing the catalyst concentration (with constant water:monomer ratio) failed to result in gel formation within a reasonable time. Increasing the monomer concentration to 0.4 M resulted in gel formation for the BTH and BTMH monomers but not the BTBu monomer. Previous studies of acid-catalyzed condensation did not reveal any significant difference between 0.2 and 0.4 M monomer concentrations for phenylene-bridged xerogels with respect to porosity or surface area.[3] In the acidic system, *monomers with spacers C_n, where $n > 6$, yielded clear gels*, but some opacity was noted for the BTE-H and BTH-H gels. Alkylene-bridged gels from monomers with $n \geq 6$ exhibited observable syneresis (a volume decrease of the gel with time accompanied by expulsion of solvent) under these conditions, whereas the BTE-H gel did not.

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(7) Speier, J. L.; Webster, J. A.; Barnes, G. H. *J. Am. Chem. Soc.* **1957**, *79*, 974.

(8) Karstedt, B. D. U.S. Patent 3,775,452, 1973.

(9) Hydrosilylation was most efficient in affording the bis-addition product when conducted at room temperature, giving a di-addition to monoaddition ratio of 4:1. Hydrosilylation at higher temperatures increased the proportion of monoaddition product determined to be the ω-triethoxysilyl-2-alkene.

(10) Noll, W. *Chemistry and Technology of Silicones*; Academic: New York, 1968; p 198.

(11) Loy, D. A. *Bridged Polysilsesquioxanes, Aryl-Bridged Siliconates and Polysiliconates*; Ph.D. Dissertation, University of California, Irvine, 1991; p 30.

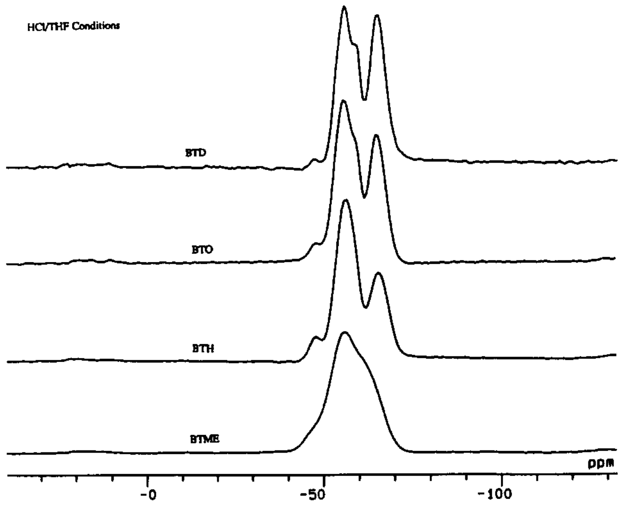

Figure 2. Stack plot of ^{29}Si CP/MAS spectra for HCl/THF formed xerogels.

The base catalyzed system at 0.2 M monomer in ethanol was found to be superior to concentrated ammonia in THF with respect to gelation time. For example, in the concentrated ammonia-THF system, the BTD monomer took 30 days to gel, whereas in sodium hydroxide–EtOH it gelled within 3 h. The base-catalyzed gels showed little or no syneresis. Gels formed in the basic system showed the opposite trend in clarity with respect to the acidic system, with the BTME monomer yielding optically clear gels, and an increase in opacity with increasing alkylene spacer length.

Degree of Hydrolysis and Condensation of Alkylene-Bridged Xerogels. The degree of hydrolysis and condensation of a trifunctional silicon atom can be described using the modified General Electric Q notation.[12] In this notation, a monofunctional silicon is designated M, a difunctional silicon as D, trifunctional silicon as T, and quadrafunctional as Q. Functionality refers to reactive, hydrolyzable groups rather than the valence of the silicon atom. All silicon atoms in the above monomers are of the T character. The functionality attached to silicon can be further described with subscripts and superscripts that designate the degree of hydrolysis to silanols and condensation to siloxane linkages, respectively. Because the solid-state CP/MAS NMR experiment only resolves the degree of condensation and not the degree of hydrolysis (alkoxy vs. hydroxyl substituents) the subscript is dropped. Thus in this notation T^0, T^1, T^2, and T^3 represent the number of siloxane bonds to a silicon atom.

^{29}Si CP/MAS NMR of alkylene-bridged xerogels formed by sol-gel processing revealed significant differences between the acid and base catalyzed xerogels. Figures 2 and 3 are stack plots of the ^{29}Si CP/MAS NMR data for ethylene through decamethylene-bridged xerogels formed under acid and base catalysts. Table II summarizes the ^{29}Si chemical shifts.[13] The greatest spectral resolution was observed for xerogels prepared from the C_{10} and C_{14} monomers. The C_{10} spectra shown is representative of both the C_{10} and C_{14} peak distributions. These ^{29}Si spectra contained four discrete signals. The ethylene-bridged xerogels possessed the least spectral resolution, with the individual signals nearly coalescing to a single broad peak.

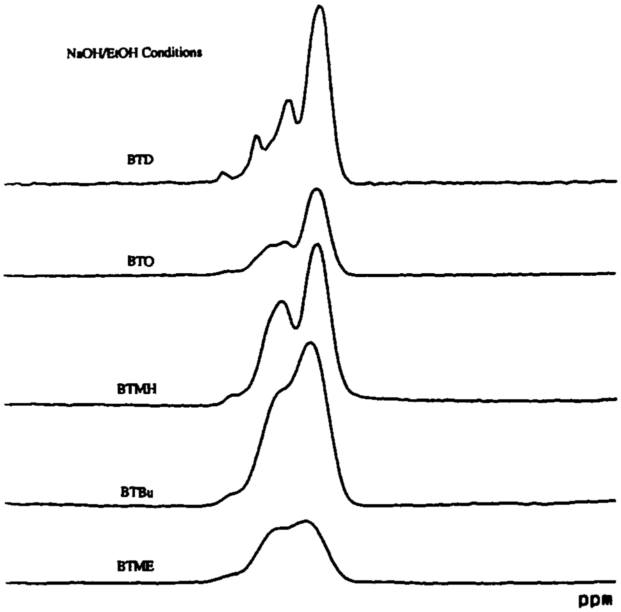

Figure 3. Stack plot of ^{29}Si CP/MAS spectra for NaOH/EtOH formed xerogels.

Table II. ^{29}Si CP/MAS Chemical Shifts for Alkylene-Bridged Silsesquioxane Xerogels

xerogel	^{29}Si shifts
NaOH-Catalyzed Xerogels	
BTE-OH	−49.3, −57.4, −64.5
BTBu-OH	−48.2, −58.8, −65.2
BTH-OH	−47.9, −58.9, −66.5
BTO-OH	−46.5, −57.9, −66.6
BTD-OH	−45.9, −53.5, −60.5, −66.6
BTTD-OH	−45.5, −52.6, −59.7, −67.2
HCl-Catalyzed Xerogels	
BTE-H	−47.1, −55.7, −63.6
BTH-H	−48.2, −57.0, −66.1
BTO-H	−46.5, −55.7, −65.6
BTD-H	−47.8, −55.9, −59.6, −65.0
BTTD-H	−47.7, −55.8, −59.5, −65.3

In general, xerogels formed under acid catalysis exhibited spectra with T^1 or T^2 as the largest peak. Xerogels formed under basic catalysis gave T^3 as the largest peak, indicating that *the base-catalyzed xerogels are condensed to a greater degree than the acid-catalyzed xerogels.* This observation is consistent with findings of other researchers in tetramethylorthosilicate (TMOS) and tetraethylorthosilicate (TEOS) systems.[14] This finding is particularly interesting since gel times for both systems were comparable. Peak areas were not quantified due to the large overlap between peaks and would not be expected to be accurate without deconvolution. Single-pulse experiments did not reveal any significant variation in relative peak intensity from the CP/MAS spectra.

Spectra for xerogels with alkylene spacers C_n up to $n = 6$ appear to follow published T^n chemical shifts and correlate well with data by Nishiyama and Horie[15] for ^{29}Si solution spectra of γ-methacryloxypropytrimethoxysilane. Table III gives the range of T^n chemical shifts measured by these authors. The interpolated ^{29}Si chemical shifts for ethoxysilyl groups based upon solution NMR of the

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[12] Brinker, C. J. In ref 4, pp 164–165.

[13] Some of the chemical shifts are chosen from apparent shoulders on other peaks and are therefore estimates.

[14] Brinker, J. C.; Scherer, G. W. *Sol.-Gel Science: The Physics and Chemistry of Sol-Gel Processing*; Academic: San Diego, CA, 1990; Chapter 2.

[15] Nishiyama, N.; Horie, K. *J. Appl. Polym. Sci.* **1987**, *34*, 1619.

Table III. ^{29}Si Chemical Shifts for [γ-(Methacryloxy)propyl]trimethoxysilane with Varying Degrees of Hydrolysis and Condensation (from Ref 10), Average Shifts for Methoxy Monomers, and Interpolated Shifts for Ethoxy Monomers[30]

degree of condensation	range (ppm)	avg OMe	est OEt
T^0	−40.3 to −41.8	−41.05	−45.0
T^1	−49.4 to −50.2	−49.80	−52.8
T^2	−57.7 to −58.8	−58.25	−60.5
T^3	−68.3	−68.3	−68.3

BTBu, BTO and BTD monomer shifts of −45.0 ppm, along with the data of Nishiyama and Horie, correlate well with the ^{29}Si absorptions found in the present study for monomers with $n < 8$. The BTO-OH, BTD-OH, and BTTD-OH xerogels in our study all give a fourth peak near −45 ppm, with the other peaks deviating slightly from the expected values in Table III. Xerogels with $n \geq 8$ thus appear to have some unhydrolyzed or partially hydrolyzed but uncondensed monomers present in the final xerogel. ^{13}C solid state NMR of BTD-OH and BTTD-OH gave peaks at 58 and 19 ppm corresponding to residual ethoxy resonances. ^{13}C interrupted decoupling experiments with delay times τ of 50 to 200 μs verified the ethoxy resonances as ethoxysilyl groups or bound (adsorbed) ethanol, observed as a decrease in peak height with increasing τ. The presence of adsorbed ethanol is discounted due to the sample preparation procedure. The observed resonances are attributed therefore to unhydrolyzed ethoxysilyl groups.

We theorize that there may be microscopic phase domains where the siloxane and aliphatic groups have separated. An unhydrolyzed or partially hydrolyzed but uncondensed silyl group trapped within the hydrophobic aliphatic domain may not be accessible to further condensation, resulting in the appearance of the monomer peak with increasing alkylene spacer lengths. In other organically modified ceramics (ORMOCERS) prepared by sol–gel techniques, the organic groups are proposed to fill the interstices of the inorganic network as observed by a lack of porosity and low shrinkage when subjected to thermal treatments.[16] The increase in the appearance of a signal corresponding to uncondensed monomer and concomitant loss of porosity with increasing alkylene spacer length is consistent with this model.

Surface Area of Alkylene-Bridged Xerogels. Table IV is a compilation of the surface area and mean pore diameter of xerogels. The data permits comparison of the dependence of these properties on alkylene spacer length for the acid and base catalyzed systems. The BET, Langmuir, and single-point surface areas are given, along with the average pore diameter (from BET calculations) and the BET constant c. Nitrogen adsorption isotherms for xerogels prepared by acid or base catalysis appear to have fundamental differences. However, in both series, particularly in the base-catalyzed system, a clear trend is observed: *as the alkylene spacer is lengthened, the surface area decreases*. This finding is in contrast to the work by Corriu et al., where the flexibility of the spacers was not a factor in determining the porosity of a material.[17] In the base catalyzed series, a monotonic decrease in surface area is observed between C_2 and C_{10}. A total loss of significant surface area occurs between C_{10} and C_{14}. Figures 4 and 5 show the adsorption–desorption isotherms for the BTE-OH and BTE-H xerogels. Xerogels formed in the basic system exhibiting high surface area results in type IV isotherms with a type H2 (type E in de Boer classification)[18] hysteresis loop. The shape of this isotherm is similar to many published isotherms of silica gel and indicates the presence of ink-bottle or narrow-mouth shaped pores. *A strong correlation between alkylene spacer length and decreasing porosity exists for these xerogels.* The BTD-

Table IV. Surface Area, Porosity, and BET Constant for Both the Acid- and Base-Catalyzed Systems and Average Pore Diameter from BET Calculations

monomer	BET ($m^2\,g^{-1}$)	Langmuir ($m^2\,g^{-1}$)	single point ($m^2\,g^{-1}$)	pore diam (nm)	c
		NaOH-Catalyzed Xerogels			
BTE-OH	729	925	706	4.35	101
BTBu-OH	710	908	684	4.09	82
BTH-OH	564	722	541	4.25	76
BTO-OH	440	575	427	6.68	66
BTN-OH	245	339	244	13.0	49
BTD-OH	94	123	88	19.7	50
BTTD-OH	4.9	7.4	4.0		12.8
		HCl-Catalyzed Xerogels			
BTE-H	641	812	628	2.32	411
BTH-H	6.6	9.0	6.0		26
BTO-H	3.2	4.6	2.8		19
BTD-H[a]	5.6	7.5	5.2		36
BTTD-H	5.2	8.4	3.8		10

[a] Monomer concentration 0.2 M.

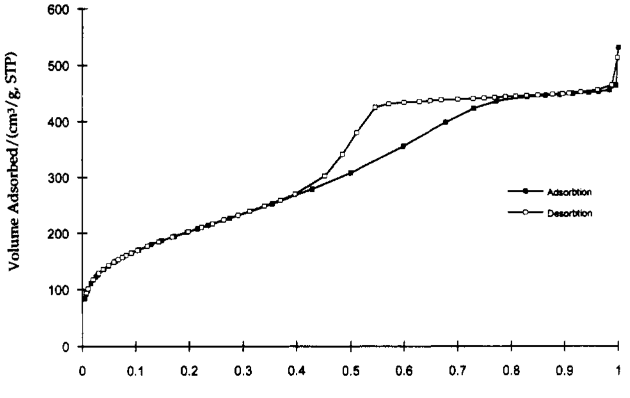

Figure 4. Adsorption isotherm for BTE-OH xerogel.

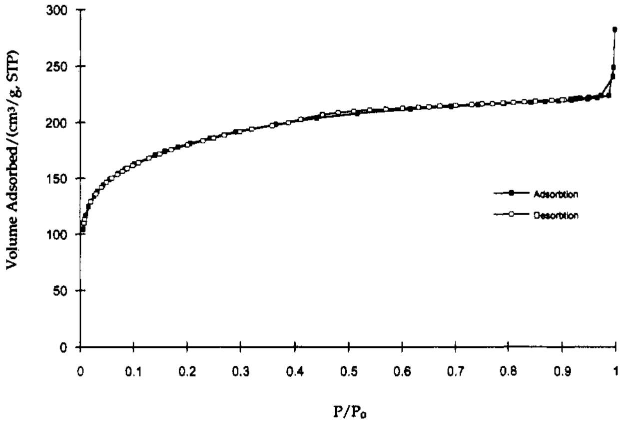

Figure 5. Adsorption isotherm for BTE-H xerogel.

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(16) Philipp, G.; Schmidt, H. *J. Non-Cryst. Solids* **1984**, *63*, 283. Schmidt, H. *Non-Cryst. Solids* **1989**, *112*, 419.

(17) Corriu, R. J. P.; Moreru, J. J. E.; Thepot, P.; Wong Chi Man, M. *Chem. Mater.* **1992**, *4*, 1217.

(18) Gregg, S. J.; Sing, K. S. W. *Adsorption, Surface Area and Porosity*, 2nd ed.; Academic: New York, 1982; p 287.

Table V. Surface Area and Porosity for the Hexamethylene-Bridged Xerogels Formed at Various Monomer Concentrations in the Basic System

concn (M)	BET (m^2 g^{-1})	c	pore diam (nm)
0.18	564	76	4.25
0.35	627	78	4.56
0.53	591	72	5.41
0.70	536	72	7.02

OH xerogel retained some porosity even though it precipitated from the solvent at the gel point. The BET average pore diameter appears to increase with increasing alkylene spacer length in the BTO-OH and BTD-OH xerogels, but shorter homologs appear relatively invariant in pore size. The BET constant c also decreases with increasing alkylene spacer length in this series.

Xerogels formed with acid catalysis yield type I isotherms with little hysteresis. Although the BTE-H xerogel was highly porous, all other xerogels formed in this system were essentially nonporous. Similar trends in the dependence of porosity on the flexibility of cross-linking spacers with comparable lengths has been observed in highly cross-linked acrylamide systems. Systems with flexible cross-linkers were found to be nonporous, while those with rigid spacers resulted in macroporous materials.[19] The difference in the BET constant c for this xerogel from BTE-OH is striking. This difference appears to arise from the difference in the degree of condensation (*vide infra*).

To test if monomer concentration had any significant effect on surface area or pore size, the BTH-OH xerogel was formed at additional monomer concentrations of 0.18, 0.35, 0.53, and 0.70 M. Table V gives the results of surface area and porosity analysis for these xerogels. Neither the surface area nor the BET constant c change significantly with monomer concentration. However, the BET average pore diameter increases with increasing monomer concentration. This finding may be another indication of phase separation of alkylene and siloxane regions in these xerogels, resulting in larger pore diameters.

Pore Size Distribution. Pore sizes are classified into three areas.[20] Micropores are those with a diameter (D) less than 20 Å. Mesopores have a diameter in the range of 20 to 500 Å, while macropores have a diameter greater than 500 Å. Mesoporosity is the most accessible region by nitrogen adsorption porosimetry, and is defined by the lower and upper limits of the Kelvin equation for capillary condensation. The average pore diameter reported in Tables IV–VI is the geometrical average assuming cylindrical pores. It is calculated as $4V_T/A_{BET}$, where V_T is the total volume of condensed adsorbate measured and A_{BET} the BET surface area.

The pore size distribution can be determined from the gas adsorption or desorption isotherm[21] by use of the Kelvin equation, given in eq 1.

$$\ln \frac{P}{P_0} = \frac{-2\gamma V_1}{RTr_m} \qquad (1)$$

In this equation P/P_0 is the relative pressure (P_r), V_1 is the molar volume and γ the surface tension of the liquid adsorbate, r_m the pore radius, and RT has the usual meaning. Equation 1 shows that the radius of a pore size is fixed for a given relative pressure, assuming the pores have a given shape and all other variables are constant.

Table VI. Surface Area and Average Pore Diameter (BET) for Xerogels Formed from NaOH/EtOH Solution and Water Processing (Pore Diameters Calculated from BET Data)

monomer	BET (m^2 g^{-1})	Langmuir (m^2 g^{-1})	single point (m^2 g^{-1})	avg pore diam (nm)
BTP-OH[a]	588	741	576	2.23
BTP-OH[a]	575	724	564	2.23
BTP-OH[a,b]	566	713	555	2.23
BTE-H[a]	601	757	590	2.61
BTE-H	537	676	526	2.26
BTO-H	17	22	16	
BTO-H[a]	8.4	12	7.8	
BTD-H	5.6	7.5	5.2	
BTD-H[a]	3.5	4.7	3.3	
BTD-H	1.8	2.7	1.4	
BTD-NH_3	2.0	2.9	1.8	

[a] Solvent processed. [b] Same sample as entry no. 2 after heating to 200 °C for 16 h under vacuum.

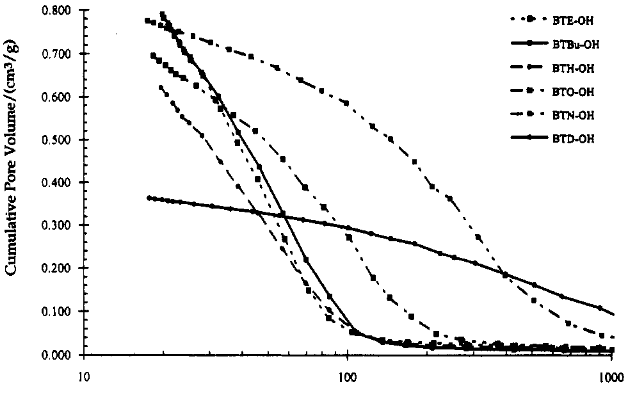

Figure 6. Cumulative pore volume vs. pore diameter for alkylene-bridged xerogels formed in the basic system.

The BJH algorithm[22] provides a method of obtaining the pore size distribution. In this method, the starting point is the value of P_r when all pores have been filled. The volume of condensed adsorbate is measured for the range of pore diameters defined by each step in P_r as the adsorbate is removed.[23] A mean pore diameter is also calculated for each P_r step. The incremental volume from each step is summed over the range of diameters, and the plot of the cumulative volume V_{cum} at each mean diameter gives the cumulative volume distribution. This plot is a monotonically decreasing function with increasing diameter. Figure 6 gives the cumulative pore volume for alkylene bridged xerogels formed in the basic system.

From the cumulative pore volume plot one can obtain information regarding the pore size distribution. Plotting the incremental volume ΔV divided by the incremental diameter ΔR for each P_r step gives the pore size distribution. Figure 7 shows the pore size distribution for alkylene-bridged xerogels formed in the basic system. *The curves show a general trend of decreasing porosity with increasing diameter.* For xerogels with alkylene spacers of $n \leq 8$ the curves decrease sharply with increasing diameter, but flatten out for the longer alkylene spacers. Concomitant with decreasing surface area determined by

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(19) Shea, K. J.; Stoddard, G. J.; Shavelle, D. M.; Wakui, F.; Choate, R. M. *Macromolecules* **1990**, *23*, 4497.

(20) Gregg, S. J.; Sing, K. S. W. In ref 17, p 113.

(21) Gregg, S. J.; Sing, K. S. W. In ref 17, Chapter 3.

(22) Barrett, E. P.; Joyner, L.; Halenda, P. P. *J. Am. Chem. Soc.* **1951**, *73*, 373.

(23) In the Micromeritics implementation of the BJH method, adsorption data is treated as if it were desorption data.

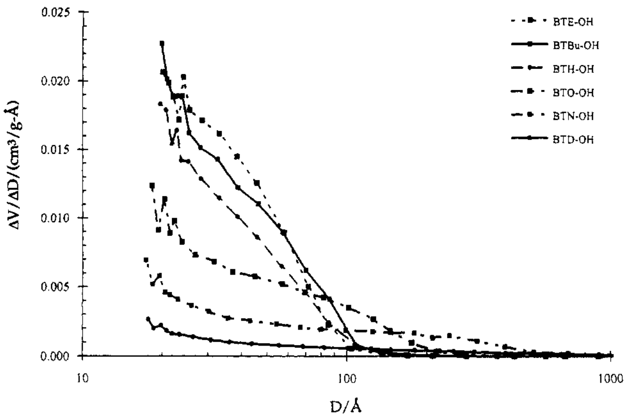

Figure 7. The pore size distribution ($\Delta V/\Delta D$) vs. pore diameter for the same materials in Figure 6.

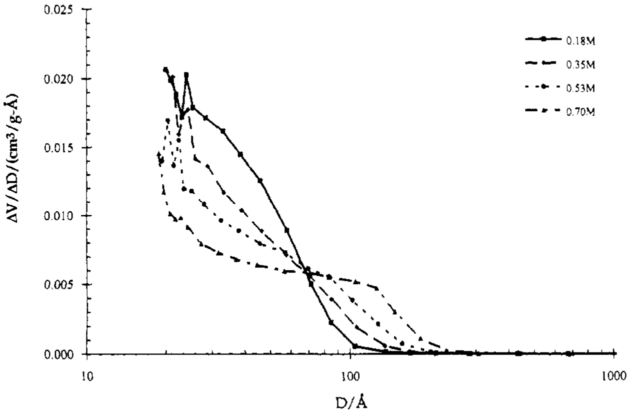

Figure 8. The pore size distribution ($\Delta V/\Delta D$) vs. pore diameter for hexamethylene-bridged xerogels formed at various concentrations.

the BET method is a broadening of the pore size distribution for alkylene spacers with $n \geq 8$. Significant microporosity appears to exist in those xerogels in Figure 7 with alkylene spacers with $n \leq 8$ as observed by the apparent monotonic decrease in the pore size distribution towards larger pores.

Figure 8 shows the concentration dependence of the pore size distribution for the hexamethylene-bridged xerogels. The microporous nature of the hexamethylene-bridged xerogels has been observed by inverse size exclusion chromatography[24] (ISEC) and will be reported at a later date. We postulate that increasing the monomer concentration (in the BTH gel) results in a higher density of hexamethylene chains. This increased density of spacers may induce a microphase separation or aggregation of the alkyl spacers from the siliconate portion of the xerogel. Such microphase separation may lead to an increase in the mean pore diameter. It should be noted that the mean pore diameter also increases as the alkylene spacer length increases at constant concentration; increasing the spacer length increases the percentage of aliphatic component in the xerogel.

Control Experiments with BTE and BTP Xerogels. The use of sodium hydroxide in ethanol as a catalyst-solvent medium for sol–gel chemistry of α,ω-bis(trialkoxysilyl)alkanes differs from our previous study.[3] The water-processing method also marks a departure from our previous studies. We sought therefore to determine if any significant differences were introduced by these variations. The 1,4-bis(triethoxysilyl)phenylene (BTP) monomer and three alkylene monomers (BTME, BTO, and BTD) were used for this comparison.

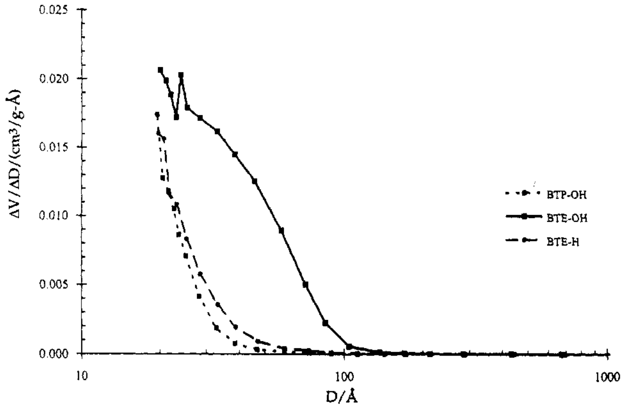

Figure 9. The pore size distribution ($\Delta V/\Delta D$) vs. pore diameter for BTE and BTP-OH xerogels.

The measured surface areas for these xerogels appear in Table VI. Surface areas for BTP-OH xerogels are comparable in magnitude to those previously reported when prepared in THF with HCl or NH_3 as catalysts followed by solvent processing. Data from two samples from separate xerogels are shown for BTP-OH to support reproducibility of the resulting surface area and porosity. ^{29}Si CP/MAS NMR of the BTP-OH xerogel revealed a somewhat greater degree of condensation than has been previously achieved in THF, as evidenced by an observed increase in T^3, although T^2 remains the dominant peak. Additionally, porosity in this sample is retained after heating to 200 °C for 16 h. The effect of high-temperature treatment of alkylene-bridged xerogels was not investigated.

The effect of water processing vs solvent processing is also apparent in Table VI. The surface area of the solvent processed BTE xerogel is approximately 10% greater than water processed xerogels. Xerogels with alkylene spacers $>n = 2$ from the acidic system possess significantly less surface area compared to the BTP and BTE xerogels for both the solvent and water processed xerogels, which we have shown to be an effect of the catalyst-solvent system employed (*vida supra*). The same comparison was not performed for alkylene-bridged xerogels from base catalysis. However, the presence of significant surface area and porosity for base catalyzed xerogels implies that water processing does not cause a catastrophic loss of surface area or porosity in comparison to solvent processing. Furthermore, it is apparent that for xerogels processed by both methods possessing surface area >100 m^2 g^{-1}, water processing does not have significant deleterious effects on the morphology of the alkylene or phenylene-bridged xerogels as measured by N_2 adsorption.

Figure 9 shows the difference in the pore volume frequency distribution for the BTE xerogel with acid and base catalysis. The distribution for the BTP-OH xerogel is included for comparison. Xerogels possessing the greatest pore volume in the micropore region are those with T^2 as the dominant peak in the ^{29}Si NMR. Those with the majority of their pore volume in the mesopore range have the greatest degree of condensation as evidenced by T^3 as the dominant peak. For example, the

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[24] For an application of ISEC to the analysis of porous materials see: Jerabek, K.; Shea, K. J.; Sasaki, D. Y.; Stoddard, G. J. *J. Polym. Sci., Part A: Polym. Chem.* **1992**, *30*, 605.

Table VII. BET Constant c Values for Xerogels for Comparison of Processing Methods

xerogel	c	processing
BTP-OH	454, 450, 474[a]	water
BTE-H	645	solvent
BTE-H	124	water
BTE-OH	149, 101	water
BTO-H	42	water

[a] After heating to 200 °C under vacuum for 16 h.

BTP-OH and BTE-H xerogels have their maximum pore volume in the micropore region, while the BTE-OH xerogel has the maximum pore volume in the mesopore region.

Comments on the BET Constant c. The BET constant c is given as

$$c = (a_1\nu_2/a_2\nu_1)\exp(q_1 - q_L)/RT \qquad (2)$$

where a_n is the sticking coefficient and ν_n the frequency of vibration of the adsorbate, q_1 the enthalpy of adsorption of the first layer and q_L the enthalpy of condensation of the liquid adsorbate, and RT has the usual meaning.[25] The subscript 1 refers to the first monolayer adsorbed and the subscript 2 refers to all subsequent layers in the BET theory. In practice the preexponential factor is taken as unity. The BET constant defined in this manner reflects the net enthalpy of adsorption of the analysis gas onto the analysis surface, and c increases with increasing net enthalpy of adsorption. A high value of c can also be indicative of microporosity, adsorption onto active sites, or chemisorption.[26]

Table VII is a tabulation of BET c values for xerogels similar to those found in Table VI. The BTP-OH xerogels all gave high c values. The c value for BTE-H xerogels reveal a dependence on the processing method; solvent processed BTE-H xerogels yield the largest c value, while water processed BTE-H xerogels have a c value similar to that for BTE-OH. All other xerogels do not show a significant difference in the BET c value due to the processing method.

In summary, xerogels with n-alkylene bridges formed using acid catalysis in tetrahydrofuran yield materials with high porosity for the shortest spacer (ethylene) but do not possess any significant microporosity or mesoporosity for spacer lengths with $n \geq 6$. Sol–gel xerogels formed using basic catalysis in ethanol possess mesoporosity of a well defined nature for alkylene spacer lengths up to eight carbons. Significantly less porosity is seen for the decamethylene-bridged material, and the tetradecamethylene-bridged xerogel is essentially nonporous. For BTE and BTP-OH xerogels, a higher proportion of microporosity is associated with a lesser degree of condensation. The highest degree of condensation is associated with a maximum pore volume in the mesopore range. The increased flexibility of alkylene spacers with increasing chain length apparently decreases the propensity of such monomers to form highly porous xerogels under basic hydrolysis conditions. *Thus it appears that basic conditions for condensation with aliphatic spacers and rigidity in the organic spacer of mixed organic–inorganic xerogels are requirements for highly porous, high surface area materials.*

Experimental Section

Instrumental Methods. Synthetic reactions were monitored by GC with an HP 5710 gas chromatograph and a Supelcoport packed column with 3% SP 2100, 100/120, 2.5 m × $^1/_8$ in. ^{1}H and ^{13}C NMR spectra were acquired on a GE QE 300 spectrometer at 300 and 75.5 MHz, respectively, using either $CDCl_3$ (7.26 ppm (^{1}H), 77.0 ppm (^{13}C)) or TMS (0.00 ppm) as internal standard. ^{29}Si NMR was performed on a GE GN 500 spectrometer at 99.3 MHz in $CDCl_3$ using TMS (0.00 ppm) as internal standard. ^{29}Si solid-state magic angle spinning (MAS) NMR data were obtained using a Chemagnetics CMX-200 spectrometer at 39.7 MHz using standard cross polarization(CP) techniques with hexamethylcyclotrisiloxane (−9.33 ppm vs TMS) as external standard. Previous studies[3] have shown cross polarization contact times (τ) of 3 ms to be optimal for the phenylene-bridged xerogels. A contact time study over the range of 0.5–10 ms for the ethylene- and octamethylene-bridged xerogels also showed τ to be optimal between 2 and 4 ms. ^{13}C MAS NMR spectra were taken at 50.29 MHz utilizing both CP and Bloch decay methods with hexamethylbenzene as external standard (17.53 ppm vs TMS, CH_3). Nitrogen adsorption isotherms were determined at 77 K with a Micromeritics ASAP 2000 automated porosimeter. All calculations were performed using the associated Micromeritics software. Samples were degassed at 125 °C for a minimum of 3 h prior to measurement. Sample sizes varied from 50 to 300 mg. Surface area and mean pore diameter were calculated using the BET and Langmuir methods[27] with data points between 0.05 and 0.2 relative pressure (p/p^0). Single-point surface area measurements were made at $p/p^0 = 0.2$. The chosen limits of calculation for pore diameters were 17–3000 Å. The Harkins-Jura equation[28] was used to calculate the thickness of the adsorbed layer at each step; values of 13.99 for the numerator and 0.0340 in the denominator of the preexponential factor, and an exponent of 0.500 were used in the pore diameter calculations (Micromeritics default parameters).

General Procedure for Sol–Gel Formation. Monomer (5 mmol for base catalysis, 10 mmol for acid catalysis) was weighed into a 60-mL polyethylene (PE) bottle. The density of the monomer was used to calculate the volume occupied by the monomer and a volume of THF was appropriately adjusted to achieve a final volume equal to 25 mL. Approximately one-half the required solvent and all monomer was added to the (PE) bottle and mixed. Catalyst (0.54 mL of 1 N NaOH or 1.08 mL 1 N HCl) was added to the other portion of solvent. The two solvent mixtures were then combined in the PE bottle, capped, and shaken to ensure mixing. The bottles were sealed with parafilm and allowed to stand undisturbed. The formed gels were fractured into pieces approximately 0.5 cm or smaller and processed by either using the solvent method previously described[3] or by extracting with deionized water (3 × 200 mL) for at least 2 h each. The processed gels were allowed to air dry then dried in a convection oven at 75 °C for >12 h. After drying, the xerogels were ground to a fine powder and again vacuum dried at 125 °C for >6 h. Examples follow:

1,10-Bis(silsesquioxyl)decamethylene-Bridged Xerogel. 1,10-Bis(triethoxysilyl)decane (5.01 mL, 4.66 g, 10 mmol) was added to a 60-mL PE bottle followed by approximately one-half volume of 18.91 mL of dry THF. To the remaining volume of THF was added 1.08 mL of 1.00 N HCl and the solution mixed. The THF/HCl solution was added to the PE bottle, the bottle capped, and resulting solution shaken for 10 s to ensure mixing. The bottle was further sealed with parafilm. A transparent, rigid gel formed within minutes. The gel was aged for 2 weeks prior to processing. After aging, the gel was broken with a spatula into small pieces and placed in 200 mL of distilled water for at least 2 h. Three separate extractions were performed. Significant volume contraction occurred during this step. The wet gel was dried first in air, then at 75 °C in a convection oven, ground to a fine powder, and dried at 125 °C under vacuum.

1,10-Bis(triethoxysilyl)decane. 1,10-Decadiene (13.8 g, 0.1 mol), triethoxysilane (36.1 g, 0.22 mol) and chloroplatinic acid in isopropyl alcohol (0.70 mL of a 2.73 × 10^{-3} M solution) were

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(25) Gregg, S. J.; Sing, K. S. W. In ref 17, p 44.

(26) Gregg, S. J.; Sing, K. S. W. In ref 17, p 104.

(27) Gregg, S. J.; Sing, K. S. W. In ref 17, Chapter 2.

(28) Harkins, W. D.; Jura, G. *J. Chem. Phys.* **1943**, *11*, 431.

heated to 100 °C for 7 h under nitrogen in a round-bottom flask equipped with a reflux condenser and magnetic stir bar. Distillation of the reaction mixture under vacuum afforded 20.3 g (41%) of 1,10-bis(triethoxysilyl)decane: bp 179–186 °C/0.001 mmHg; d^{23} 0.93; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.75 (q, 12 H), 1.2–1.6 (m, 34 H), 0.62 (t, 4 H); ^{13}C NMR (75.48 MHz, $CDCl_3$) δ 58.20, 33.21, 29.57, 29.26, 22.76, 18.30, 10.36; IR (neat) 2973, 2927, 1442, 1388, 1295, 1168, 1083, 956, 786 cm^{-1}; HRMS (CI, isobutane) *m/e* calcd for $C_{22}H_{50}O_6Si_2$+H: 467..3224; found 467.3211.

1,8-Bis(triethoxysilyl)octane. 1,7-Octadiene (11.0 g, 0.10 mol), triethoxysilane (44.6 g, 0.27 mol) and chloroplatinic acid in isopropanol (1.0 mL of a 2.0×10^{-2} M solution) were heated to 100 °C for 3 h under nitrogen in a round-bottom flask fit with a reflux condenser and magnetic stir bar. Distillation of the reaction mixture under vacuum afforded 14.7 g (34%) of 1,8-bis(triethoxysilyl)octane: bp 140–145 °C/0.2 mmHg; d^{23} 0.94; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.85 (q, 12H), 1.2–1.6 (m, 30H), 0.62 (t, 4H); ^{13}C NMR (75.48 MHz, $CDCl_3$) δ 58.28, 33.23, 29.16, 22.75, 18.30, 10.37; HRMS (CI, Isobutane) m/e calc'd for $C_{20}H_{46}O_6Si_2$+H: 439.2911; found 439.2897.

1,6-Bis(triethoxysilyl)hexane. 1,5-Hexadiene (12.3 g, 0.15 mol), triethoxysilane (54.1 g, 0.33 mol), and chloroplatinic acid (1 mL of 7.5×10^{-5} mol in ethanol) were added to a round-bottom flask. The solution darkened after 24 h. The reaction was stirred at room temperature under nitrogen for 5 days. GC analysis of the reaction mixture gave a ratio of monoaddition to diaddition products of nearly 1:4, the highest product ratio achieved in this series. Distillation under vacuum afforded 41 g (67%) 1,6-bis(triethoxysilyl)hexane with purity >97% by GC: bp 125–135 °C/0.10 mmHg; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.76 (q, 12 H), 1.41 (m, 4 H), 1.14 (t, 18 H), 0.55 (m, 4 H); ^{13}C NMR (75.48 MHz, $CDCl_3$) δ 58.24, 32.68, 22.56, 18.18, 10.30; HRMS (CI, isobutane) *m/e* calcd for $C_{18}H_{42}O_6Si_2$+H: 411.2598; found 411.2591.

1,4-Bis(triethoxysilyl)butane. Butadiene was passed through a CaH_2 drying tube and condensed at −78 °C in a graduated cylinder under N_2 until 10 mL (6.5 g, 0.12 mol) was collected. The liquid was transferred via double tipped cannula to a Carius tube also at −78 °C. Trichlorosilane (30 mL, 0.30 mol) was added followed by chloroplatinic acid (20 mg, 50 μmol, vacuum dried) in 1 mL dry THF and the tube sealed. The homogeneous catalyst solution precipitated upon addition to the solution. The tube was kept at −78 °C for 1 h, slowly warmed to 0 °C for 1 h, then warmed to room temperature for 1 h, followed by heating at 50 °C for 22 h, and finally 120 °C for 6 h (Caution: possible explosion hazard). The reaction mixture became homogenous after a short time at 50 °C. Some darkening of the solution occurred at the highest temperature. GC analysis of the reaction mixture afforded a single peak. Ethanolysis[29] of the intermediate 1,4-bis(trichlorosilyl)butane was accomplished by dropwise addition of the reaction mixture to 200 mL of hexane containing 105 mL (2 equiv to Si–Cl) ethanol (CaH_2 distilled) cooled to 0 °C in a three-neck flask while purging with nitrogen. After HCl evolution had stopped, the mixture was stirred at 0 °C for another hour, heated to 90 °C in an oil bath, and residual solvent distilled with continued purging with N_2. Short-path distillation under vacuum gave a crude separation. The fraction containing the desired product was redistilled at 0.5 mmHg using a vacuum jacketed vigreaux column and afforded 17.9 g (39%) of 1,4-bis(triethoxysilyl)butane: bp 119–123 °C/0.5 mmHg; d^{23} 0.96; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.76 (q, 12 H), 1.41 (m, 4 H), 1.18 (t, 18 H), 0.59 (m, 4 H); ^{13}C NMR (75.48 MHz, $CDCl_3$) δ 58.24, 26.26, 18.24, 10.06; HRMS (CI, isobutane) *m/e* calcd for $C_{16}H_{38}O_6Si_2$+H: 383.2285; found 383.2276.

1,14-Bis(triethoxysilyl)tetradecane. 1,13-Tetradecadiene (25 g, 0.129 mol), triethoxysilane (44.4 g, 0.271 mol) and 0.1 mL of a 2–3% bis((vinyldimethyl)disiloxane) Platinum complex in xylene (Karstedt's catalyst, Huls America) was added to a 100-mL round-bottom flask. The solution was stirred at room temperature for 3 days under nitrogen. Vacuum distillation afforded 29.3 g (43.6%) of 1,14-bis(triethoxysilyl)tetradecane with purity >99% by GC: bp 174 °C/0.015 mmHg; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.75 (q, 12 H), 1.2–1.4 (m, 42 H), 0.54 (t, 4 H); ^{13}C NMR (75.48 MHz, $CDCl_3$) δ 58.13, 33.10, 29.60 (two carbons), 29.47, 29.19, 22.66, 18.17, 10.27; HRMS (CI, isobutane) *m/e* calcd for $C_{26}H_{58}O_6Si_2$+H: 523.3850; found 523.3842.

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(29) Vigorous HCl evolution occurs during ethanolysis. Appropriate precautions should be taken to trap the evolved gas.

(30) Shifts for T^1 and T^2 were estimated by assuming they occur at evenly spaced intervals between T^0 and T^3, as is the case for the methoxy derivatives cited.