to note that the diamagnetic magnetization, M, measured for all the samples with $x = 0.4$ has the usual behavior as a function of temperature. That is, M is essentially flat until the temperature is within 10–20 K of T_c, where it then rises rapidly to zero at T_c (Figure 1a). In contrast, for the samples with $x = 0.2$, M increases nearly linearly from 5 K to 0 at T_c (Figure 1b). We have no explanation for this observation, and a detailed study would require samples known to be homogeneous. However, the data in Table I do show that a T_c substantially above 77 K cannot be obtained in $Pb_2Sr_2Y_{1-x}Ca_xCu_3O_{8+\delta}$ by varying the oxygen content.

From Table I, it may be seen that for the samples with 0.4 Ca per formula unit there is a broad peak in the superconducting quality around $\delta = 0.06$. A similar peak for $x = 0.2$ is seen at $\delta = 0.08$. It should be stressed, however, that the quoted values of T_c are at best accurate to only ±1 K. In addition, the fraction of a ceramic sample that appears diamagnetic is not a definitive measure of the volume fraction of the sample that is superconducting. Any number of effects, such as a spongelike superconducting phase, can lead to an overestimate of the fraction actually superconducting. In this case, the nonsuperconducting phase filling the holes in the superconducting sponge is shielded from the applied field and thus contributes to the diamagnetic fraction.

The critical current density, J_c, for $\delta = 0.22$ and $x = 0.4$ was determined from magnetic measurements using the Bean model[4] and the usual assumption for these materials that all the shielding currents are intragranular.[5] At 15 K, $J_c = 3 \times 10^5$ A/cm^2, which is about a factor of 5 smaller than that obtained from representative $Ba_2YCu_3O_7$ samples. J_c falls rapidly with increasing temperature to 10^4 A/cm^2 at 54 K.

Acknowledgment. We thank W. W. Rhodes for the sample preparation.

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Aryl-Bridged Polysilsesquioxanes—New Microporous Materials

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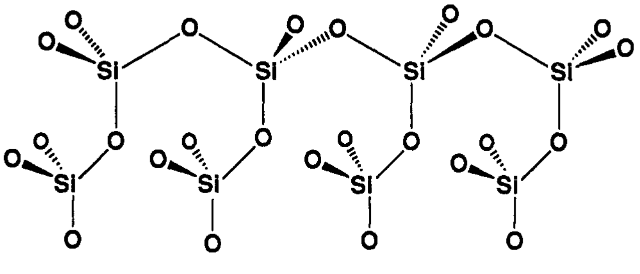
Received July 24, 1989

The silicate framework of alternating silicon and oxygen atoms (**1**) comprises the earth's most abundant mineral form.[1] A remarkable diversity of silicate morphology exists within this simple pattern of connectivity.



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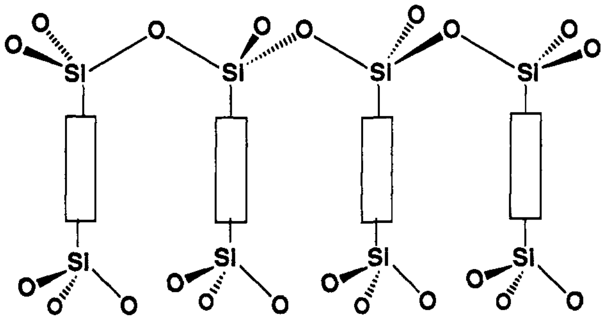
$$n\,Si(OR)_4 + 2n\,H_2O \rightleftharpoons (SiO_2)_n + 4n\,EtOH \qquad (1)$$

Synthetic silicates, prepared by sol–gel processing of alkoxysilanes (eq 1), allow for the preparation of amorphous materials (xerogels) that are precursors for high-purity glasses, ceramics, coatings, and fibers.[2] Sol–gel processing also provides for the preparation of organolithic macromolecular materials by co-condensing tetraethoxysilane (TEOS) with hydroxy-terminated poly(dialkylsiloxanes)[3] or by replacing an alkoxy substituent on TEOS with an alkyl or aryl group to produce aryl- or alkyl-substituted polysiloxanes (T resins).[4]

In principle, sol–gel technology provides an opportunity to produce an almost infinite variety of silicate-like structures by the introduction of organic spacers *at regular intervals in the silicate framework* (**2**). We report the preparation of aryl bridged polysilsesquioxanes that are produced by the sol–gel processing of bis(triethoxysilyl) and bis(trichlorosilyl)aryl monomers **3**–**5**. The phenyl, biphenyl, and terphenyl groups separating the silicon atoms are rigid-rod spacers with Si–aryl–Si distances of 0.67, 0.87 and 1.08 nm, respectively. The bis(triethoxysilyl) and bis(trichlorosilyl)aryl monomers can be represented by two silicon tetrahedra elongated by an aryl spacer. The monomers can condense at three vertices of each tetrahedra to produce an extended network (**2b**) without an opportunity for close packing. When highly condensed, such materials are expected to possess microporosity. The organic portion provides an opportunity for engineering mechanical, bulk dielectric, and optical properties of the material. In addition, the aryl groups may permit molecular level control over the aryl-bridged polysilsesquioxane microstructure, influencing properties such as microporosity. Such an effect has been proposed in layered metal aryl–bisphosphonates[5] and was anticipated but, as



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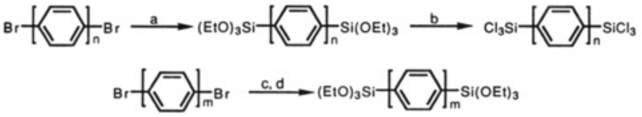
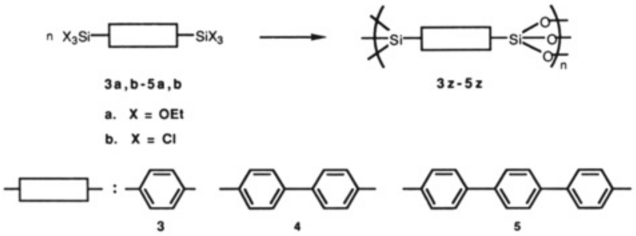


Figure 1. Conditions: (a) Mg^0, THF, TEOS, reflux for 3 days, $n = 1, 2$; (b) $SOCl_2$, DMF catalysis, reflux for 5 days; (c) 4 equiv of *t*-buLi, Et_2O, −78 °C for 30 min, 25 °C for 3 h, $m = 3$; (d) 2.5 equiv of $(EtO)_3SiCl$, −78 °C for 30 min, 25 °C for 4 h.

yet, not realized in related approaches using vinyl-functionalized spherosilicates,[6] poly(silicic acid esters),[7] and carbon-based molecular level building blocks.[8]

Monomers **3a** and **4a** were prepared by a Barbier–Grignard reaction of 1,4-dibromobenzene and 4,4′-dibromobiphenyl with TEOS (Figure 1).[9] Monomer **5a** could not be prepared by Grignard chemistry; lithium–halogen exchange followed by treatment with triethoxysilyl chloride afforded **5** as a solid in moderate yield.[9] Hexachloride derivatives **3b** and **4b** were prepared from the corresponding hexaethoxides by treatment with $SOCl_2$ and a catalytic amount of DMF.



Standard sol–gel formulations were modified to accommodate differences in monomer solubility. Acidic, basic, and neutral conditions were employed. In a typical procedure, monomer **3a** (0.2–0.4 M in THF or EtOH) was hydrolyzed/condensed with 3 equiv of H_2O and HCl (0.005 equiv) as catalyst. Transparent gels generally formed within several hours. After 48 h of curing, solid transparent monoliths resulted. The monolithic gels afforded materials with morphology that depended upon subsequent processing. For example, in the previous example the original solvent could be replaced by immersing the gel in a sequence of solvents with decreasing dielectric constant.[10] After air drying for 48 h, the gels were pumped on at high vacuum. The overall process results in approximately 70–80% loss in volume with accompanying fracturing. The xerogel fragments were all transparent, glassy materials. Monolithic transparent xerogels, on the other hand (Figure 2), could be prepared from **3a** by using formamide as a drying control chemical agent (DCCA).[11]

Low-resolution scanning electron micrographs of **3z** reveal a smooth surface with glasslike fractures and no macropores. At higher magnification (15 000 times), the surface appeared slightly granular. Transmission electron micrographs of **3z** show the composition of the xerogel more clearly. The amorphous characteristics bear a striking resemblance to photomicrographs of condensed polymeric-type silicate gels produced by acid catalyzed hydrolysis/condensation of TEOS.[12] These features are in contrast to colloidal gels, which consist of discrete colloidal particles linked together as aggregates.[13] Pore analysis of **3z** and **4z** (N_2, BET) confirmed the absence of any macropores but showed micropores with mean pore diameters at or below 2.0 nm. The materials have extremely high surface areas (750–800 m^2/g).[14] No significant differeces in microstructure above 3.0 nm were observed between xerogels of **3z** and **4z**.

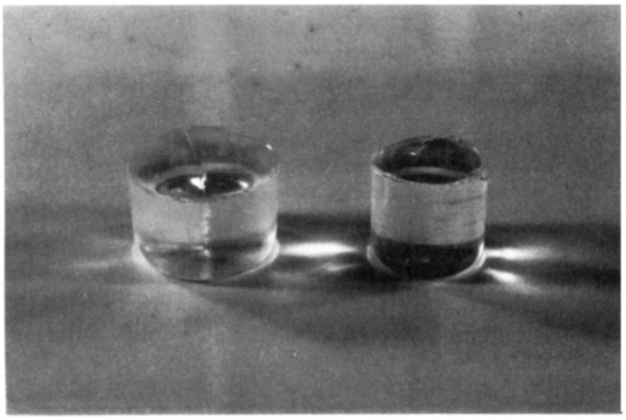


Figure 2. Dried transparent monoliths prepared by acid-catalyzed hydrolysis/condensation (THF, H_2O, HCl) of TEOS (right) and **3a** (left). Both materials were prepared and processed[7] in an identical manner.

Solid-state ^{13}C and ^{29}Si NMR were the most useful tools for the characterization of these materials. ^{13}C NMR, in conjunction with FT-IR, was valuable for determining the extent of hydrolysis (residual ethoxy or chloro groups), while ^{29}Si NMR provided structural information about the silicate framework within the gel, especially the extent to which cross-linking had occurred. For example, ^{13}C CP/MAS NMR of **4z**, prepared by acid-catalyzed hydrolysis, revealed the expected four aromatic resonances at 126.3, 131.5, 135.1, and 142.9 ppm in addition to resonances (minor) at 59.5 and 17.1 ppm arising from ethoxysilane carbons. Interrupted decoupling experiments allow one to distinguish between mobile ethanol (and other adsorbed solvents) peaks and those arising from bound ethoxy resonances.[17] Under the acidic conditions described above, the residual ethoxy residue ranged from approximately 10 to 0%. Under basic conditions,[18] hydrolysis is complete—no residual bound ethoxy peaks are

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(9) All new monomers satisfied chromatographic and spectroscopic (IR, ^1H and ^{13}C NMR, and high-resolution mass spectrometry) criteria for purity and chemical composition.

(10) For sol–gels prepared in THF, the solvent series was tetrahydrofuran, CH_2Cl_2, $CHCl_3$, EtOEt, toluene, CCl_4, 1,1,2-trichloro-1,2,2-trifluoroethane. This procedure minimized collapse of the microstructue during drying.

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(14) Hydrolysis of trialkoxy- or trihaloaryl- or alkylsilanes typically results in nonporous resins or crystalline materials.[15] The porosity and surface area of silica gels prepared by hydrolytic condensation of TEOS can vary widely. Recent values have ranged from 150 to 775 m^2/g.[16]

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(18) (a) A typical basic hydrolysis procedure consists of **3a** (0.2–0.4 M) in a THF/aqueous NH_4OH solution containing 6 equiv of NH_4OH as 29% aqueous solution. (b) Hydrolyses of silyl chlorides were performed as 0.12 M solutions of chloride in THF containing 3 equiv of H_2O.

observed from the ethoxy precursors.

^{29}Si CP/MAS NMR of **3z** prepared under acidic hydrolysis conditions of **3a** followed by solvent replacement[10] and vacuum drying shows three resonances at −59, −68, and −76 ppm, respectively. The peaks correspond to branched silicates that correlate with the substructures $PhSi(OH)_2(SiO)$ (T_1^{Ph}), $PhSi(OH)(OSi)_2$ (T_2^{Ph}), and $PhSi(OSi)_3$ (T_3^{Ph}).[19,20] The ^{29}Si resonances were deconvoluted, and the areas, after correction for contact times, were integrated. Xerogels prepared by acid-catalyzed hydrolysis/condensation of **3a**, **4a**, and **5a** indicate the degree of condensation to be approximately 60–70%. Base-catalyzed hydrolysis[18] and solvent gradient processing produce materials with a higher degree of condensation (75–85%). The absence of a ^{29}Si resonance corresponding to Q_4 (silicate, −110 ppm) indicates the monomers retain their integrity during hydrolysis and do not suffer aryl group cleavage. Although quantitative conclusions regarding the calculated degree of condensation must be interpreted with caution,[20c] the materials reveal an extent of condensation similar to that found in pure silicate xerogels.

In conclusion, it is shown that organic spacers can be inserted at regular intervals into the Si–O–Si silicate structure. Sol–gel processing allows for the preparation of aryl-bridged polysilsesquioxanes, high surface area materials that have certain morphological properties in common with silicates but with added opportunities for systematic modification. Applications of these and related materials to chromatography, optics, and molecular level control of morphology will be presented in forthcoming articles.

Acknowledgment. We are grateful to Ron Farlee at du Pont and to James Frye, Chuck Bronnimann, and A. Jurkiewicz at the Colorado State University NMR Center for assistance in obtaining and interpreting the NMR data. We are also grateful to Fred Gentry for technical assistance. K.J.S. thanks du Pont for an appointment as Visiting Research Scientist during which time this work was initiated.

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Electrocatalytic Reduction of CO_2 by Thin Polymeric Films Containing Metallic Rhodium

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Received July 7, 1989

Direct reduction of carbon dioxide at most common electrode surfaces (e.g., Pt or C) occurs with large overpotentials[1-3] and, typically, stops at the stage of two-electron, single carbon reduction products such as formic acid or carbon monoxide. Recently, metal electrodes such as Ru,[4] Cu,[5] Mo,[6] and Au[7] and semiconductor electrodes, for example, GaAs,[8] have been successfully employed to produce methanol, methane, and/or ethylene. During our studies on the electrocatalytic reduction of CO_2 by transition-metal complexes in homogeneous solution[9] and in some related preparative studies of thin polymeric films on electrode surfaces,[10] we have found that metallic Rh can

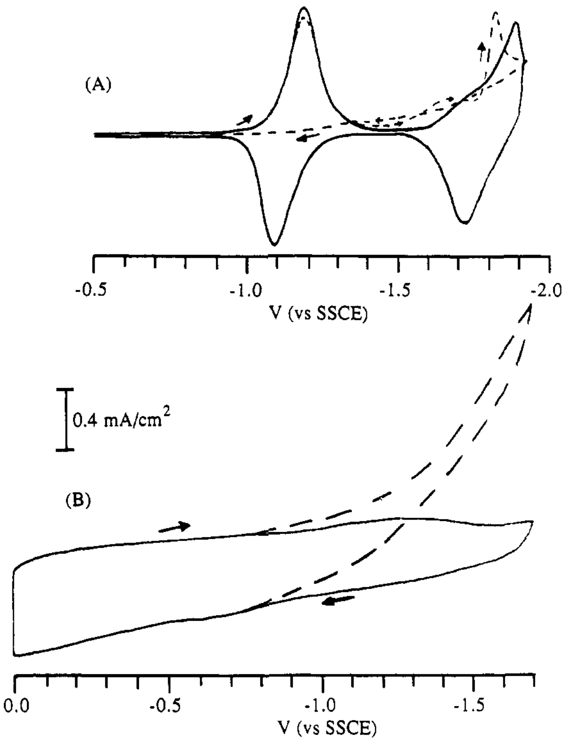

Figure 1. (A) Cyclic voltammetry of a 2.2×10^{-8} mol/cm^2 poly[Rh(vbpy)(COD)]Br film at 50 mV/s in 0.1 M TBABr/CH_3CN solution under N_2 (solid line) and CO_2 (broken line) atmospheres. (B) Cyclic voltammetry of the poly[Rh(vbpy)-(COD)]Br film at 100 mV/s after a 20-min electrolysis in 0.1 M TBABr/CH_3CN in the presence of CO_2 and $[Rh(COD)Cl]_2$. The solid line was recorded under N_2, and the broken line under CO_2 atmospheres.

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