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Preparation of Mesoporous Silicon Boron Imide Gels from Single-Source Precursors via a Nonaqueous Sol−Gel Route

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The preparation and structure of the novel compound 2-(dimethylamino)-4,6-di[tris(dimethylamino)silylamino]borazine, $(Me_2N)[(Me_2N)_3SiNH]_2B_3N_3H_3$, **1a**, is reported. Two translucent silicon boron imide gels, $Si_2B_3(NH)_x(NH_2)_y(NMe_2)_z$, gel **2a**, and $SiB(NH)_x(NH_2)_y(NMe_2)_z$, gel **2b**, were prepared by catalyzed ammonolysis of compound **1a** and 2,4,6-tris[tris(dimethylamino)silylamino]borazine $[(Me_2N)_3SiNH]_3B_3N_3H_3$, **1b,** respectively. Both gels exhibit mesoporous structures with a surface area of 915 and 692 m^2/g for **2a** and **2b**, respectively. The mesoporous structures survived after pyrolytic treatment of the gels at 1000 °C for 2 h and the surface areas of the pyrolyzed products are higher than 439 m^2 g^{-1}.

Introduction

Preparation of micro- and mesoporous solids has attracted considerable attention because of their potential size-selective properties in applications such as catalysts, catalyst supports, and filters.[1,2] The sol−gel technique, via hydrolysis and condensation of molecular precursors at low temperature, has been established as an important route to prepare micro-/mesoporous oxide materials due to the flexibility of processing and the high purity and homogeneity of the resultant materials.[3−5] Recently, a similar non-oxidic sol−gel process was developed with the goal of producing novel porous non-oxide materials. Paine and co-workers reported the preparation of a microporous boron nitride aerogel by a reaction between 2,4,6-trichloroborazine and 1,1,1,3,3,3-hexamethyldisilazane.[6] A sol−gel process in an ammono-system was reported by Jansen and co-workers to prepare polymeric boron-, titano-, and tantalo-silazanes by controlled co-ammonolysis of the elemental alkylamides.[7] Recently, Riedel and co-workers reported the preparation of B/C/N xerogels by a reaction of B-trichloroborazine with bis(trimethylsilyl)carbodimide.[8] Preparation of microporous silicon imido nitrides was reported recently by pyrolysis of gels which had been prepared via a hot ammonolysis of tris(dimethylamino)silylamine, $(Me_2N)_3SiNH_2$ (TDSA), in a concentrated solution of $CH_3(CH_2)_nNH_2$ ($n = 11−17$).[2] In our group, a high surface area mesoporous silicon diimide gel, a precursor for high-purity silicon nitride,[9] has been prepared in a non-oxide sol−gel process by the reaction of TDSA with ammonia in the presence of an acid catalyst.[10]

Since composite materials consisting of two or more binary nitrides often show improved properties compared with single-component nitrides,[11] we are attempting to extend this nonaqueous sol−gel technique to the preparation of ternary imidosilicate gels. The gels would be promising precursors for multinary silicon-based nitride materials in a high surface area porous form. The synthetic strategy we have adopted uses TDSA as a starting material to assemble single-source precursor molecules containing, in addition to peripheral $Si(NMe_2)_3$ groups, Si−N−M backbones (M = Al, B, Ti, Zr...). The peripheral $Si(NMe_2)_3$ groups in the molecules allow us to use the proven ammonolytic chemistry of TDSA to produce multinary imidosilicate gels with high

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atomic level homogeneity as precursors to micro- and mesoporous homogeneous ternary nitride-based materials. On the basis of this idea, we have successfully prepared a mesoporous silicon aluminum imide gel by catalytic ammonolysis of a single-source precursor tris(dimethylamino)silylamino)(tetrahydrofuran)alane, $(C_4H_8O)Al[NHSi(NMe_2)_3]_3$.[12] A mesoporous $Si_3B(NH)_x(NH_2)_y(NMe_2)_z$ imide gel was also prepared by a catalytic ammonolysis of $B[HNSi(NMe_2)_3]_3$.[13]

Much work has been reported on the preparation of polymeric silicon boron nitride precursors and their thermal behavior.[14] However, nearly all of this research has focused on the preparation of dense silicon boron nitride powders. The mesoporous $Si_3B(NH)_x(NH_2)_y(NMe_2)_z$ imide gel was the first example of a suitable precursor with the potentical to produce porous silicon boron nitride composites.[13]

2,4,6-Trichloroborazine $Cl_3B_3N_3H_3$ (TCB) is an important starting material for the preparation of precursors to boron nitride because of its obvious reactivity of the B−Cl functionality and the borazinic ring B_3N_3 structure, which is the basic structural unit of hexagonal boron nitride. Many oligomers and gels have been prepared as precursors to boron nitride by the reactions of TCB with alkylamine,[15] hexamethyldisilazane,[6] and bis(trimethylsilyl)carbodimide.[8] Similar reaction of $(Me_2N)Cl_2B_3N_3H_3$ with hexa- and heptamethyldisilazane was also reported to give preceramic oligomers for boron nitride.[16] Recently, a silylamino-substituted derivative 2,4,6-tris[tris(dimethylamino)silylamino]borazine, $[(Me_2N)_3SiNH]_3B_3N_3H_3$, a potential precursor molecule for silicon boron nitride, was successfully prepared in our lab from the reaction of TCB with tris(dimethylamino)silylamidolithium, $(Me_2N)_3SiNHLi$.[17]

In this paper, we report the preparation of two novel mesoporous silicon boron imide gels: $Si_2B_3(NH)_x(NH_2)_y(NMe_2)_z$, gel **2a**, and $SiB(NH)_x(NH_2)_y(NMe_2)_z$, gel **2b**. Gels **2a** and **2b** were prepared by a catalyzed ammonolysis of 2-(dimethylamino)-4,6-di[tris(dimethylamino)silylamino]borazine, $(Me_2N)[(Me_2N)_3SiNH]_2B_3N_3H_3$, **1a**, and 2,4,6-tris[tris(dimethylamino)silylamino]borazine $[(Me_2N)_3SiNH]_3B_3N_3H_3$, **1b**, respectively. The new precursor molecule **1a** was prepared by the reaction of TDSA with 2-(dimethylamino)-4,6-dichloroborazine, $(Me_2N)Cl_2B_3N_3H_3$, and its molecular structure was discussed on the basis of FTIR, NMR, and X-ray crystallographic analysis. Preliminary research on the pyrolytic behavior of the gels is also reported.

Experimental Section

General Comments. All procedures were performed under an anhydrous nitrogen atmosphere using standard Schlenk techniques or in a nitrogen-filled glovebox. The solvents, pentane, diethyl ether, and tetrahydrofuran (THF), were freshly distilled from sodium/benzophenone prior to use. Trifluoromethanesulfonic acid and liquified ammonia were obtained from Sigma Aldrich and Energas Ltd., respectively. Tris(dimethylamino)silylamine, $(Me_2N)_3SiNH_2$ (TDSA), and 2-(dimethylamino)-4,6-dichloroborazine, $(Me_2N)Cl_2B_3N_3H_3$, were prepared according to previously reported procedures.[10,18] The 2,4,6-tris[tris(dimethylamino)silylamino]borazine, $[(Me_2N)_3SiNH]_3B_3N_3H_3$, **1b**, was prepared from the reaction of tris(dimethylamino)silylamidolithium, $(Me_2N)_3SiNHLi$, with 2,4,6-trichloroborazine, $Cl_3B_3N_3H_3$, with a molar ratio of 3:1.[17] High-resolution NMR spectra were obtained on a JEOL JNM-LA400FT NMR spectrometer using C_6D_6 as solvent. Fourier transform infrared spectra were recorded on a Nicolet Magna-500 FTIR spectrometer. MS spectra were recorded on a Shimadzu GC MS-QP 5050 spectrometer. ^{29}Si cross-polarization (CP) and ^{11}B solid-state NMR spectra with magic-angle spinning (MAS) were obtained with a Bruker DSX-300 spectrometer operating at frequencies of 59.6 and 96.3 MHz, respectively. ^{29}Si and ^{11}B chemical shifts were related to tetramethylsilane (TMS) and $BF_3{-}OEt_2$ respectively. Nitrogen adsorption isotherms were obtained at 77 K using a Micromeretics ASAP 2010 instrument, and the surface area was determined from BET analysis. The amounts of silicon and boron in gels were determined by an inductively coupled Perkin-Elmer plasma 40 emission ICP instrument. X-ray powder diffraction analysis was carried out using a Siemens D5000 Instrument.

Synthesis of 2-(Dimethylamino)-4,6-di[[tris(dimethylamino)silylamino]borazine, $[(Me_2N)_3SiNH]_2(NMe_2)B_3N_3H_3$ (1a). To a rapidly stirred solution of $Cl_2(NMe_2)B_3N_3H_3$ (1.06 g, 5.5 mmol) in pentane (50 mL) was added first triethylamine (2.3 mL, 31 mmol) and then, dropwise at room temperature, a solution of TDSA (1.94 g, 11.0 mmol) in pentane (10 mL). After reaction at room temperature overnight, the resulting triethylamine hydrochloride was removed by filtration and the filtrate concentrated under reduced pressure to give a solid. Extraction into pentane (50 mL) and cooling to −80 °C for 18 h gave a white crystalline solid (1.64 g, yield 85%). ^1H NMR: δ 2.54 (s, 36H, $SiN(C\mathit{H}_3)_2)_3$), 2.61(s, 6H, $BN(C\mathit{H}_3)_2$), 3.85 (s, 3H, $BN\mathit{H}B$), 1.40 (s, 2H, $BN\mathit{H}Si$). ^{13}C NMR δ 37.7 (s, $Si[(N(\mathit{C}H_3)_2)]_3$), 36.7 (s, $BN(\mathit{C}H_3)_2$. ^{11}B NMR: δ 25.8 (s, $(N\mathit{B}NH)_3$). ^{29}Si NMR δ −34.8 (s, $\mathit{Si}[(N(CH_3)_2)]_3$). IR (neat, cm^{-1}): 3440, 3394 (m, ν(NH)); 2973−2782 (s) (ν(CH)); 1491 (s, ν(BN)); 715 (m, BN ring). MS(*m*/*z*,EI): 472$[I]^+$.

For the crystal structure determination of **1a** a crystal was mounted on a glass fiber using perfluoropolyether oil and transferred to a Stöe IPDS II imaging plate diffractometer equipped with an Oxford Cryosystems 700 series cooling system. The data were collected using graphite-monochromated Mo Kα radiation (λ = 0.71073) at 150 K. Absorption correction was not applied. The structure was solved by direct methods (SHELXS 97)[19] and refined by full-matrix least-squares on F^2 using SHELXL 97.[20] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in idealized positions.

Preparation of the Silicon Boron Imide Gel, 2a. To a solution of **1a** (2.36 g, 5 mmol) in THF (120 mL) was added trifluoromethanesulfonic acid (27.1 μL, 0.31 mmol) at room temperature. After 30 min, a solution of ammonia (39.6 mmol)

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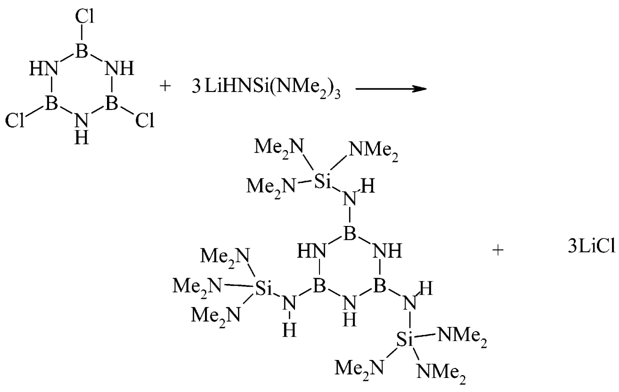
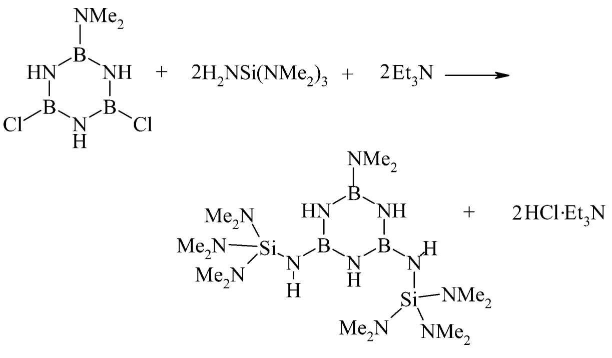
Scheme 1



1b

Scheme 2



1a

in THF (7.5 mL) was added and the mixture was left quiescent at room temperature for 72 h, at which point a slight opalescence was observed. The solution was then resaturated with ammonia by addition of liquid ammonia solution (14 mL) and the resulting mixture was left to stand at room temperature for 4 days, giving a translucent rigid gel. Evaporation of the solvent and dimethylamine in a stream of nitrogen followed by drying under reduced pressure at 50 °C for 6 h yielded a transparent white solid. ^{29}Si CP-MAS NMR: δ −42 ppm. ^{11}B MAS NMR: δ 29.0 ppm (I = 63%), −2.55 ppm (I = 20%), 14.0 ppm (I = 17%). IR (neat, cm^{-1}): 3338−3480 (m, ν(NH)); 2979 (w), 2940 (w), 2874 (w), 2808 (w) (ν(CH)); 1604 (w, δ(NH$_2$)); 1486 (s, ν(BN)); 1196 (s, δ(N−C)); 925 (s, ν(Si−N)); 715 (w, BN ring).

Preparation of the Silicon Boron Imide Gel, 2b. To a solution of **1b** (1.07 g, 1.77 mmol) in THF (60 mL) was added trifluoromethanesulfonic acid (13.3 μL, 0.15 mmol) at room temperature. After 30 min, a solution of ammonia (27 mmol) in THF (9 mL) was added and the mixture was left quiescent at room temperature for 15 h, at which point a slight opalescence was observed. The solution was then re-saturated with ammonia by addition of liquid ammonia solution (6 mL) and the resulting mixture was left to stand at 50 °C for 4 days, giving a translucent semirigid gel. Evaporation of the solvent and dimethylamine (produced by the reaction) in a stream of nitrogen followed by drying under reduced pressure at 50 °C for 6 h yielded a translucent white solid. ^{29}Si CP-MAS NMR: δ −42 ppm. ^{11}B MAS NMR: δ 26.0 ppm (I = 77%), −3.75 ppm (I = 11%), 14.0 ppm (I = 12%). IR (neat, cm^{-1}): 3350−3450 (m, ν(NH)); 2993 (w), 2930 (w), 2841 (w), 2796 (w) (ν(CH)); 1591 (w, δ(NH$_2$)); 1486 (s, ν(BN)); 1190 (s, δ(N−C)); 920 (s, ν(Si−N)); 716 (w, BN ring).

Pyrolysis of the Gels. The gels were pyrolyzed in a tube furnace. About 0.5 g of the gels was placed in an Al_2O_3 boat, which was then introduced into a quartz tube in a glovebox. The gels were heated to 200 °C with a ramp rate of 5 °C min^{-1}, held at 200 °C for 2 h, and then heated at 1000 °C for 2 h under N_2 flow.

Results and Discussion

Synthesis of Precursor Molecules. The precursor molecule 2,4,6-tris[tris(dimethylamino)silylamino]borazine, $[(Me_2N)_3SiNH]_3B_3N_3H_3$, **1b**, was prepared from the reaction of tris(dimethylamino)silylamidolithium, $(Me_2N)_3SiNHLi$, with 2,4,6-trichloroborazine, $Cl_3B_3N_3H_3$, according to Scheme 1.[17]

The structure of the resultant white solid had been characterized previously by ^{1}H, ^{13}C, and ^{29}Si NMR, IR, chemical analysis, and single-crystal X -ray analysis.[17]

The precursor molecule 2-(dimethylamino)-4,6-di[tris(dimethylamino)silylamino] borazine, $[(Me_2N)_3SiNH]_2B_3(NMe_2)N_3H_3$, **1a**, was prepared from the reaction of tris(dimethylamino)silylamine, $(Me_2N)_3SiNH_2$, with 2-(dimethylamino)-4,6-dichloroborazine, $Cl_2(NMe_2)B_3N_3H_3$, according to Scheme 2. Triethylamine was added to prevent the resultant hydrochloride contaminating the Schlenk line system. The ^{1}H NMR spectrum shows four signals: the signals at 2.54 and 2.61 ppm are attributed to the protons of dimethylamino in $SiN(CH_3)_2)_3$) and $BN(CH_3)_2$, respectively; two other signals at 3.85 and 1.40 ppm are respectively assigned to B−N*H*−B and B−N*H*−Si protons. The ^{11}B NMR displays a single resonance at 25.8 ppm for boron atoms linked to nitrogen atoms, indicating that no B−Cl (at 30 ppm in $Cl_2(NMe_2)B_3N_3H_3$) groups are present in **1a**. ^{13}C NMR shows the expected two signals at δ = 37.7 and 35.0 ppm ascribed to $Si[(N(CH_3)_2)]_3$ and $BN(CH_3)_2$, respectively. There is only one signal at −34.8 ppm in the ^{29}Si NMR spectrum. The FTIR data show that some of the borazinic rings remain since the spectrum displays bands assigned to the BN ring and bending regions at 1491 and 710 cm^{-1}.[21] Two absorptions at 3440 and 3394 cm^{-1} can be assigned to the ν(NH) of the BNHSi and BNHB group. No symmetric and asymmetric vibration bands of NH in the borazine ring is observed, although they were observed in the IR spectra of precursor molecular **1b** and 2,4,6-trichloroborazine, $Cl_3B_3N_3H_3$.[17,22] These spectral features combined with the mass spectra (m/z: 472) indicate that 2- dimethylamino-4,6-di[tris(dimethylamino)silylamino]borazine, $[(Me_2N)_3SiNH]_2(NMe_2)B_3N_3H_3$, **1a**, has been obtained.

The molecular structure of compound **1a** was determined by single-crystal X-ray diffraction analysis (Table 1). A view of the molecule is shown in Figure 1 and selected bond lengths and angles are collected in Table 2. As expected, the B_3N_3 ring is planar with one $(CH_3)_2N$ group and two $[(CH_3)_2N]_3SiNH$ groups occupying three *exo*-positions bonded to boron. The average length of the B−N (ring) bonds, 1.437 (4) Å [range 1.429(3)−1.441(2) Å], is close to the average values in $[(Me_2N)_3SiNH]_3B_3N_3H_3$, **1b**, 1.438 (4) Å,[17] but longer than the average B−N (ring) distances in $(ClBNH)_3$,[23] 1.413 Å, because Cl substitution has a stronger electron-donating effect, which can favor the double-bond character in the borazine ring and shorten the B−N distance.[24] The

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Table 1. Crystal Data for Compound 1a

formula	$C_{14}H_{47}B_3N_{12}Si_2$
M	472.25
crystal system	triclinic
space group	$P\bar{1}$
a/Å	8.1333(16)
b/Å	12.887(2)
c/Å	14.435(3)
α/deg	92.389(15)
β/deg	102.689(15)
γ/deg	107.634(14)
volume/Å^3	1397.2(5)
Z	2
crystal size/mm	0.25 × 0.20 × 0.15
T/K	150(2)
reflections collected	27067
unique reflections (R_{int})	11752 (0.1381)
restraints/parameters	0/294
goodness of fit on F^2	0.731
R1, wR2 [$I > 2\sigma(I)$]	0.0536, 0.1180
R1, wR2 (all data)	0.1478, 0.1409

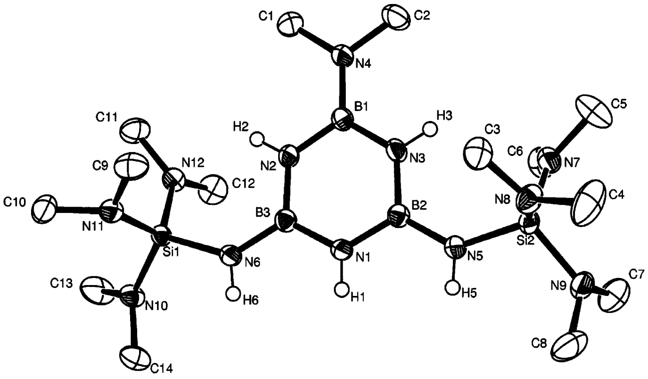

Figure 1. ORTEP [29] plot of the crystal structure of compound **1a**. Hydrogen atoms in the dimethylamino groups are omitted for clarity.

Table 2. Selected Bond Distances (Å) and Angles (deg) for Compound 1a

B(1)−N(2)	1.438(3)	N(2)−B(1)−N(3)	115.87(17)
B(1)−N(3)	1.441(2)	N(2)−B(1)−N(4)	121.77(16)
B(1)−N(4)	1.421(3)	N(3)−B(1)−N(4)	122.35(17)
B(2)−N(1)	1.439(3)	N(3)−B(2)−N(1)	116.74(15)
B(2)−N(3)	1.429(3)	N(3)−B(2)−N(5)	122.29(18)
B(2)−N(5)	1.441(2)	N(1)−B(2)−N(5)	120.96(18)
B(3)−N(1)	1.438(2)	N(2)−B(3)−N(1)	116.65(17)
B(3)−N(2)	1.434(3)	N(1)−B(3)−N(6)	120.88(17)
B(3)−N(6)	1.436(3)	N(2)−B(3)−N(6)	122.47(16)
		B(2)−N(5)−Si(2)	134.50(15)
		B(3)−N(6)−Si(1)	131.71(13)

three exo-ring B−N bond distances are shorter (1.421−1.441 Å) than the B−N distance found in H_3N-BH_3 (1.56 Å)[25] but comparable with values described for B−N distances in other aminoborane compounds where a π-bond interaction is suggested.[26−28] The dimethylamino group is coplanar with the B−N ring but the C(1)−N(4)−C(2) angle is only 112.21(17)°, similar to that found by Clark and Anderson for dimethylamino groups in tris(dimethylamino)borine.[27] The position of the *exo*-nitrogen atoms deviates slightly from the mean least-squares plane calculated for the borazine ring.

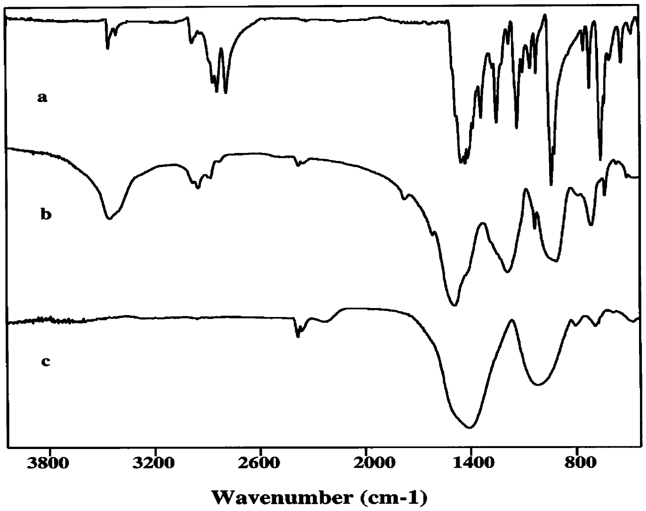

Figure 2. IR spectra of (a) precursor **1a**, (b) gel **2a**, and (c) solid **3a** pyrolyzed from the gel **2a** under N_2 flow at 1000 °C. (a) was characterized by neat technique and (b) and (c) were characterized by KBr technique.

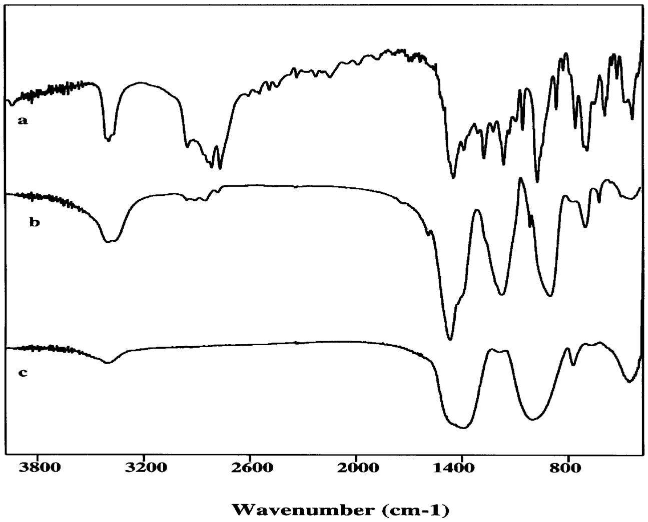

Figure 3. IR spectra of (a) precursor **1b**, (b) gel **2b**, and (c) solid **3b** pyrolyzed from the gel **2b** under N_2 flow at 1000 °C. (a) was characterized by neat technique and (b) and (c) were characterized by KBr technique.

Preparation of Silicon Boron Imide Gels. When a solution of compound **1a** in THF containing about 1% of trifluoromethanesulfonic acid was exposed to ammonia, a rigid translucent gel filling the volume of the original solution was obtained. Exposure of a solution of compound **1b** in THF containing about 1% of trifluoromethanesulfonic acid to ammonia led to the formation of a semirigid translucent gel filling the volume of the original solution. Slow evaporation of the solvent and volatile products of the gelation reactions under a nitrogen flow, followed by drying under reduced pressure, resulted in translucent white xerogels **2a** and **2b**.

The IR spectra of the gel **2a** and gel **2b** are shown in Figures 2 and 3, respectively. They are quite similar and show a broad ν(N−H) band at 3350−3450 cm^{-1} and a low-intensity band at 1591 cm^{-1} (due to the presence of NH_2), suggesting that the NH groups are present with different environments such as Si−NH−Si/B, B−NH−B, and $SiNH_2$. Bands at 1486 and 716 cm^{-1} ascribed to the vibrational modes of B_3N_3 rings indicate that some of the borazine rings survived after the gelation reac-

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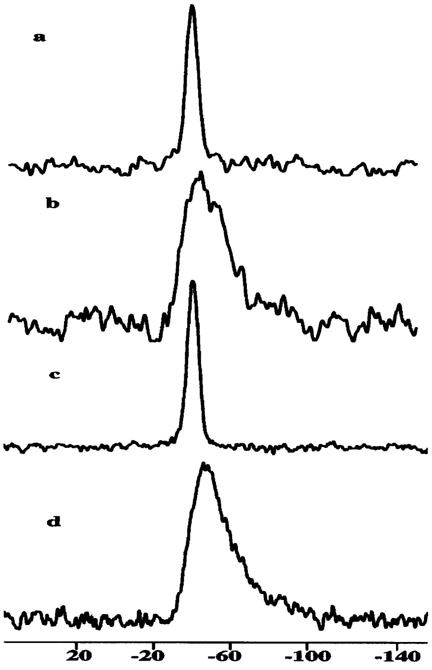

Figure 4. ^{29}Si MAS NMR of (a) gel **2a**, (b) solid **3a** pyrolyzed under N_2 flow at 1000 °C, (c) gel **2b**, and (d) solid **3b** pyrolyzed under N_2 flow at 1000 °C.

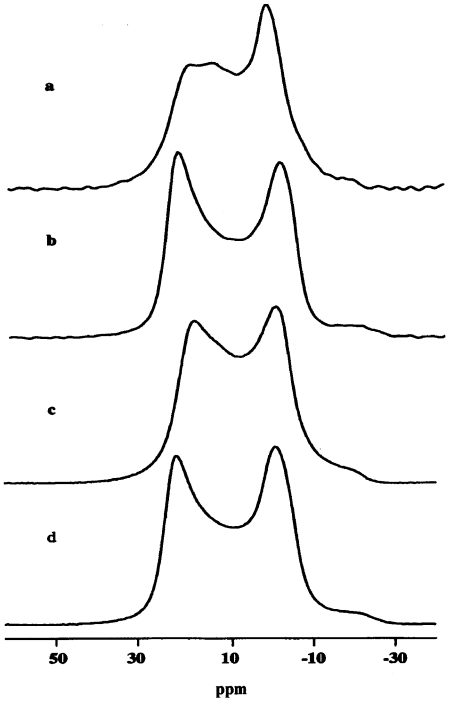

Figure 5. ^{11}B MAS NMR of (a) gel **2a**, (b) solid **3a** pyrolyzed under N_2 flow at 1000 °C, (c) gel **2b**, and (d) solid **3b** pyrolyzed under N_2 flow at 1000 °C.

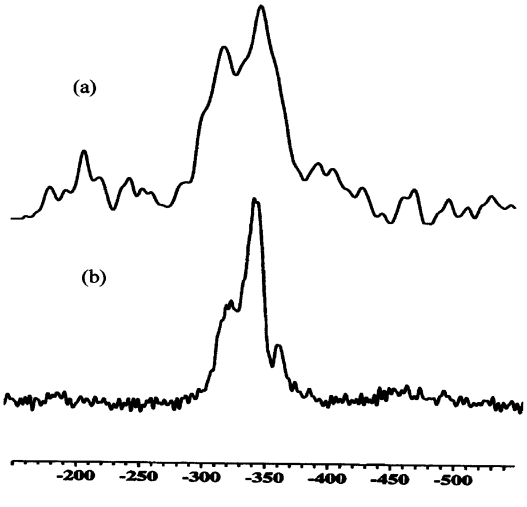

Figure 6. ^{15}N CP-MAS NMR of (a) gel **2a** and (b) gel **2b**.

tion.[21] Compared to the IR spectra of precursor compounds **1a** and **1b**, the low intensity of the ν(CH) bands from 2796 to 2993 cm^{-1} indicates that most of the dimethylamino groups have been removed. Two broad absorbances at about 1190 and 920 cm^{-1} can be assigned to δ(N−C) and ν(Si−N), respectively.[30] The ^{29}Si CP MAS NMR spectra show that both gels exhibit a single resonance at −42 ppm (Figure 4a,c). On the basis of the IR results discussed above and referring to the ^{29}Si resonance in polysilazanes (−36 ppm),[31] silicon diimide (−42 ppm),[32,33] and silicon nitride (−49 ppm),[34] it is reasonable to suggest that the resonance at −42 ppm is due to the formation of SiN_4 environments in which silicon is mainly coordinated to $(NH)_x$ groups. The ^{11}B MAS NMR spectra (Figure 5a,c) are characterized by a powder pattern indicative of a second-order quadrupolar interaction. Simulation of the line shape shows that both spectra can be decomposed into three components. The major component with a isotropic chemical shift at 29 ppm for gel **2a** (relative amount $I = 63\%$) and 26 ppm for gel **2b** (relative amount $I = 77\%$) can be ascribed to the presence of borazine-like ring structures,[35] consistent with the IR results. The other two components show isotropic chemical shifts at 11−14 ppm and −4 to −1 ppm, which are similar to those found for polyborosilazane by Jansen.[7,36] These two components can be ascribed to the formation of trigonal planar coordinated boron atoms without borazine ring structures, suggesting that some of the borazine rings in the precursor molecules broke during the gelation process.[7,36] Broad signals overlapping from −300 to −350 ppm in the ^{15}N CP-MAS NMR spectra (Figure 6) indicate the presence of tricoordinated N atoms.[37] ICP emission analyses show that the molar ratios of boron to silicon in the gel **2a** and gel **2b** are 1.1 and 1.5 respectively, close to those in precursor compounds **1a** and **1b**.

In a similar experiment, reaction of the precursor molecules **1a** and **1b** in THF with ammonia without

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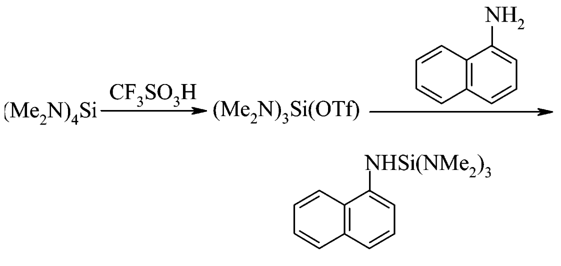
addition of trifluoromethanesulfonic acid yielded slightly opalescent sols. Removal of the solvent under reduced pressure gave very waxy solids. IR spectra showed that although some reaction had occurred, most of the $-NMe_2$ groups were still present in the waxy solids. This demonstrates that trifluoromethanesulfonic acid can help to remove dimethylamino groups in $-Si(NMe_2)_3$ and plays an important part in the gelation behavior. It has been reported that reaction of tetrakis(dimethylamino)silane, $Si(NMe_2)_4$, with trifluoromethanesulfonic acid gave a solution of tris(dimethylamino)silyl triflate, $\{[Me_2N]_3Si\}O_3SCF_3$, with removal of $HNMe_2$ (eq 1).[38] Tris(dimethylamino)silyl triflate is a very reactive intermediate which can be used for the preparation of various derivatives such as shown in eq 1.[39]



(1)

A highly branched polysilazane polymer used as a precursor to Si_3N_4 was also successfully prepared by trifluoromethanesulfonic acid catalytic reaction of tri(dimethylaminio)silane, $HSi(NMe_2)_3$, with excess ammonia (eq 2).[39]

$$\mathrm{HSi(NMe_2)_3} \xrightarrow[110\,^{\circ}\mathrm{C}]{\mathrm{NH_3\ /\ toluene}} \mathrm{-[(NH_2)(H)Si\text{-}N(H)]x\text{-}}\ (90\%) + \mathrm{3Me_2NH} \qquad (2)$$

Similarly, it can be suggested that trifluoromethanesulfonic acid in our system may help to remove dimethylamino groups in $-Si(NMe_2)_3$ by formation of a silyltriflate (eq 3). Silyltriflate is a very good leaving group and can be easily substituted by NH_3 forming an $Si-NH_2$ reactive unit (eq 4), which will then react with another $Si-NH_2$ unit to form a network consisting of $Si-N(H)-Si$ backbones (eq 5).

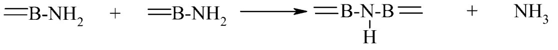
$$\mathrm{CF_3SO_3H} + \equiv\mathrm{Si\text{-}NMe_2} \longrightarrow \equiv\mathrm{SiO_3SCF_3} + \mathrm{Me_2NH} \qquad (3)$$

$$\equiv\mathrm{SiO_3SCF_3} + \mathrm{NH_3} \longrightarrow \equiv\mathrm{Si\text{-}NH_2} + \mathrm{CF_3SO_3H} \qquad (4)$$

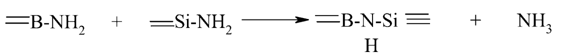
$$\equiv\mathrm{Si\text{-}NH_2} + \equiv\mathrm{Si\text{-}NH_2} \longrightarrow \equiv\mathrm{Si\text{-}}\underset{\mathrm{H}}{\mathrm{N}}\mathrm{\text{-}Si}\equiv + \mathrm{NH_3} \qquad (5)$$

It has been reported that 2,4,6-tris(dimethylamino)borazine, $[(Me_2N)BNH]_3$, can be easily converted into a poly(borazinylamine) polymer by ammonolysis and condensation reactions (eqs 6 and 7).[40] A similar reaction should occur during the gelation of molecule **1a**. In addition, the $=BNH_2$ will also react with the $Si-NH_2$ unit to form a network consisting of $B-N(H)-Si$ backbones (eq 8).

$$=\mathrm{BNMe_2} + \mathrm{NH_3} \longrightarrow =\mathrm{BNH_2} + \mathrm{HNMe_2} \qquad (6)$$



$$=\mathrm{B\text{-}NH_2} + =\mathrm{B\text{-}NH_2} \longrightarrow =\mathrm{B\text{-}}\underset{\mathrm{H}}{\mathrm{N}}\mathrm{\text{-}B}= + \mathrm{NH_3} \qquad (7)$$



$$=\mathrm{B\text{-}NH_2} + =\mathrm{Si\text{-}NH_2} \longrightarrow =\mathrm{B\text{-}}\underset{\mathrm{H}}{\mathrm{N}}\mathrm{\text{-}Si}\equiv + \mathrm{NH_3} \qquad (8)$$

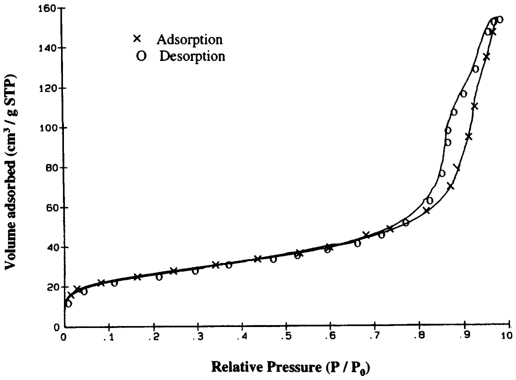


Figure 7. Nitrogen adsorption and desorption isotherm of gel **2a**.

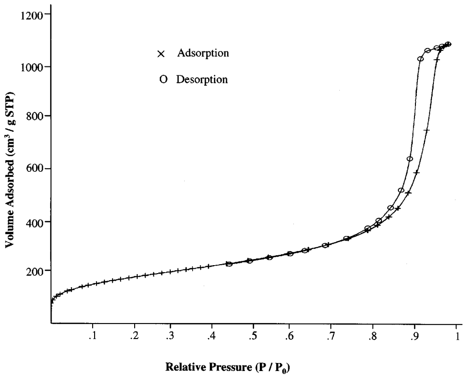


Figure 8. Nitrogen adsorption and desorption isotherm of gel **2b**.

All these spectral features indicate that ammonolysis of the precursor compounds **1a** and **1b** led to the formation of silicon boron imide-based gels containing residual dimethylamino groups, $Si_2B_3(NH)_x(NH_2)_y(NMe_2)_z$ and $SiB(NH)_x(NH_2)_y(NMe_2)_z$, respectively. The gels have three-dimensional networks connected by $Si-N(H)-Si$ backbones (for gels **2a** and **2b**) and $B-N(H)-B$ and $B-N(H)-Si$ backbones (for gel **2a**). Most of the borazine rings in the precursor molecules remained in the gels. The presence of residual dimethylamino groups suggests that the transamination reactions were not yet complete by the time of rigid gel formation.

Physisorption analysis showed that the gels **2a** and **2b** exhibit type IV nitrogen adsorption isotherms (Figures 7 and 8), typical of mesoporous materials with surface areas of 915 and 692 m^2/g, respectively. The pore sizes vary from 4 to 11 nm for gel **2a** and from 2 to 20 nm for gel **2b** with average pore diameters of 7.2 and 12.8 nm, respectively. Small-angle X-ray powder diffraction revealed no ordering of the pores.

Pyrolysis of the gels under nitrogen up to 1000 °C gave two light yellow solids, **3a** (from gel **2a**) and **3b** (from gel **2b**) with a ceramic yield of 68% and 61%, respectively. Both solids also exhibit type IV nitrogen adsorption isotherms, showing that the mesoporous structures survived the pyrolytic treatment of the gels. Compared to the parent gels, the surface area of solids **3a** and **3b** decreased to 788 and 439 m^2g^{-1}, respectively,

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but are still very high. The pore sizes of solid **3a** and **3b** range from 3 to 7 nm and from 2 to 20 nm with average pore diameters of 4.7 and 9.5 nm, respectively. XRD analysis indicated that both solids were amorphous. ICP analysis showed that the molar ratios of boron to silicon in solids **3a** and **3b** are 0.97 and 1.50, respectively, close to those in gels **2a** and **2b**. IR spectra (Figures 2c and 3c) show two broad bands centered at 1400 and 965 cm^{-1}, which can be ascribed to ν(B−N) and ν(Si−N), respectively.[36] The presence of a broad band at 2196 cm^{-1} in Figure 2c suggests that a small amount of C≡N is also present in solid **3a**.[41] The absence of any adsorption from 2800 to 3000 cm^{-1} indicates that all the dimethylamino groups have been removed during the pyrolysis of the gels due to further condensation reactions. ^{29}Si CP-MAS NMR spectra show a broad signal at −48 ppm for both solids, consistent with the value observed for SiN_4 tetrahedra with a large distribution of different distortions.[42] Finally, ^{11}B MAS NMR analyses indicate the formation of turbostratic *t*-BN with a chemical shift at 30 ppm.[7,8,32] However, a considerable amount of other trigonal planar coordinated boron atoms are also present in the solids as the simulation of the ^{11}B NMR line shapes shows the presence of two weak resonances at 17.5 ppm (relative amount $I = 13.2\%$) and −2.8 ppm (relative amount $I = 11.8\%$) for solid **3a** and one weak resonance at −2.9 ppm (relative amount $I = 7\%$) for solid **3b**.[7,35,36] Further investigation of the pyrolyzed products and pyrolytic process of the gels is being actively carried out and will be reported separately.

Conclusion

In summary, a novel precursor molecule, 2-(dimethylamino)-4,6-di[tris(dimethylamino)silylamino]borazine, $(Me_2N)[(Me_2N)_3SiNH]_2B_3N_3H_3$, **1a**, has been prepared by the reaction of tris(dimethylamino)silylamine, $(Me_2N)_3SiNH_2$, with 2-(dimethylamino)-4,6-dichloroborazine, $(Me_2N)Cl_2B_3N_3H_3$. The successful preparation of high surface area mesoporous silicon boron imide gels, $Si_2B_3(NH)_x(NH_2)_y(NME_2)_z$ and $SiB(NH)_x(NH_2)_y(NME_2)_z$, from the catalyzed ammonolysis of **1a** and 2,4,6-tris[tris(dimethylamino)silylamino]borazine, $[(Me_2N)_3SiNH]_3B_3N_3H_3$, **1b**, further extends the chemistry of tris(dimethylamino)silylamine to the preparation of multinary silicon-based imide gels. These two gels combined with the $Si_3B(NH)_x(NH_2)_y(NMe_2)_z$ gel reported previously make the preparation of silicon boron imide gels with different silicon boron molar ratio possible. Thermal treatment of the gels gives solids with a mesoporous structure and a high surface area. The pyrolysis process of the gels into Si−B−N composite materials is under active investigation.

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Supporting Information Available: Crystallographic data (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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