properties. Preliminary measurement of the steady-state photoconductivity of PBZT shows that it is large. We can thus also expect enhanced and spectrally tunable photoelectronic properties in the new benzobisthiazole polymers. The detailed electronic, photoelectronic, and nonlinear optical properties of these polymers are currently under investigation.

Conclusions

We have successfully synthesized, characterized, and processed new vinylene- and divinylene-linked conjugated rigid-rod benzobisthiazoles which are materials for potential electronic, optoelectronic, and nonlinear optical applications. The soluble coordination complexes of these rigid-rod polymers with Lewis acids ($AlCl_3$, $GaCl_3$) in organic solvents provide both a means to process the materials into optical-quality films and coatings and a unique opportunity to characterize their molecular structures by NMR spectra. The results show that the longer the *trans*-polyacetylene segment introduced into the polybenzobisthiazole backbone, the lower the optical bandgap of this class of polymers, demonstrating the correctness of the molecular design approach. By replacing the *p*-phenylene ring in PBZT with a *trans*-divinylene moiety in the polymer repeat unit (PBTDV), there is a 0.4-eV decrease in the optical bandgap. The new synthesis and results on the optical and spectroscopic studies of PBTV correct an earlier report[16] on the adverse role of the vinylene linkage in the benzobisthiazole polymers that resulted from an unsuccessful synthesis of this polymer at the air/water interface. The enhanced solvent resistance of PBTV and PBTDV compared to PBZT also make them attractive for applications in hostile environments.

Acknowledgment. This research was supported by the National Science Foundation (Grant CHE-912-0001) and by Amoco Foundation. We thank a reviewer who brought ref 10 to our attention.

Registry No. **2a** (copolymer), 143104-73-8; **2a** (SRU), 90940-20-8; **2b** (copolymer), 143104-74-9; **2b** (SRU), 143104-77-2; **2c** (copolymer), 143104-75-0; **2c** (SRU), 143104-78-3; DABDT, 15657-79-1; BHBBT, 143104-72-7; $AlCl_3$, 7446-70-0; 2,4-hexadienoic acid, 110-44-1.

Low-Temperature Pyrolytic Transformations of Tri-*tert*-butoxysiloxy Derivatives of Aluminum to Aluminosilicate Materials

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The tri-*tert*-butoxysiloxy complex $\{Me_2Al[\mu\text{-}OSi(O^tBu)_3]\}_2$ (**1**) was prepared by the reaction of $[AlMe_3]_2$ with $HOSi(O^tBu)_3$. Crystals of **1** are tetragonal ($P4_2nm$) with $a = 14.684$ (3) Å, $c = 9.463$ (2) Å, $V = 2041.8$ (9) Å^3, $Z = 4$, and $R_F = 5.77\%$. Molecules of **1** in the crystal have a folded Al_2O_2 core (156.2°), probably because of steric interactions involving the bulky siloxy groups. A trimeric derivative, $[Me(^tBuO)AlOSi(O^tBu)_3]_3$ (**2**), was obtained by addition of *tert*-butyl alcohol to **1**. Compounds **1** and **2** were investigated as precursors to aluminosilicate materials. In the solid state, **1** undergoes thermolysis at low temperatures (150–200 °C) by cleanly eliminating isobutylene (6 equiv), along with methane and water. Clean conversion to a $Al_2O_3{\cdot}2SiO_2$ material is observed by thermal gravimetric analysis (TGA) and elemental analysis. Differential thermal analysis (DTA) and X-ray powder diffraction (XRD) show that mullite crystallizes at about 1000 °C, and at 1200 °C, mullite particles of about 15 nm are produced (as calculated from the Scherrer equation). Compound **2** exhibits similar pyrolytic conversions, except that much higher surface areas are observed for the aluminosilicates produced. For example, thermolysis of **2** at 200 °C gives a sample with a BET surface area of 270 m^2 g^{-1}, compared to a surface area of only 30 m^2 g^{-1} for a sample obtained similarly from **1**. Compound **2** also cleanly decomposes by elimination of isobutylene (12 equiv). The network-forming thermolyses of **1** and **2** are facile enough to be conveniently carried out in solution. For example, **1** is pyrolyzed in refluxing toluene, resulting in a polymerization that resembles the sol–gel process. A gel powder obtained from this procedure had a surface area of 210 m^2 g^{-1} and was composed of small particles (ca. 500 nm in diameter) consisting of much smaller grains (by transmission electron microscopy, TEM). Heating this sample to 800 °C increased the BET surface area to 280 m^2 g^{-1}, and further heating to 1200 °C produced mullite particles (average size 18 nm, by XRD) that were densely packed into an amorphous silica matrix (by TEM).

Introduction

Aluminosilicates are technologically important as catalysts,[1] catalyst supports,[2] and structural materials.[3] Development of new chemical and physical properties for such materials will rely heavily on discovery of new routes to aluminosilicate networks. Low-temperature routes, such as those based on hydrolysis of alkoxides in solution (the sol–gel process), are particularly attractive since they offer the possibility for providing new (metastable) structures. Sol–gel routes to Al_2O_3–SiO_2 systems based on cohydrolysis

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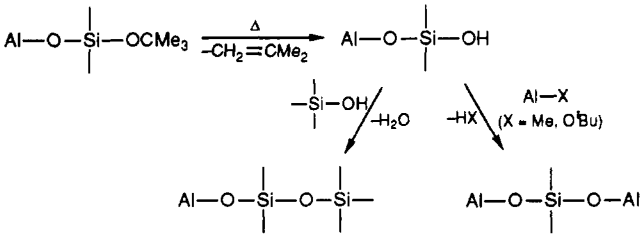
Scheme I



of aluminum and silicon compounds have been studied extensively.[4] For multicomponent systems such as aluminosilicates, a major challenge in developing sol–gel type processes is to maintain homogeneity during the network-forming reactions.[5] For this reason, "single source"[6] precursor compounds containing both silicon and aluminum have been studied.[7-12] For example, hydrolysis of the (alkoxysiloxy)aluminum precursor $(^nBuO)_2AlOSi(OEt)_3$ has been used to produce aluminosilicate gels, glasses, and ceramics.[12] This approach can lead to gels that are more homogeneous than those obtained from hydrolyzing $Al(OR)_3/Si(OR')_4$ mixtures, but it has been shown that in this process, the Al–O–Si bridge is hydrolyzed rapidly in the initial phase of the condensation.[12c]

To achieve a high degree of homogeneity at low temperatures, we have been examining metal–silicon precursor compounds that undergo thermolytic conversions to silicate materials. We have previously reported clean, thermolytic routes to $MO_2{\cdot}4SiO_2$ (M = Ti, Zr, Hf) materials based on $M[OSi(O^tBu)_3]_4$ precursor complexes. It was shown that facile elimination of isobutylene and water from the $-OSi(O^tBu)_3$ groups results in low temperature (ca. 140 °C for M = Zr or Hf) condensation to metal silicate networks.[13] Here we report the preparation and characterization of two alkoxysiloxy complexes of aluminum, $\{Me_2Al[\mu\text{-}OSi(O^tBu)_3]\}_2$ (1) and $[Me(^tBuO)AlOSi(O^tBu)_3]_3$ (2), their pyrolytic conversion to aluminosilicate materials (in the solid state and in solution), and the determination of some physical properties for the resulting materials. It seemed that low-temperature routes to aluminosilicate materials from these precursors might be achieved if the elimination of isobutylene was facile. It was anticipated that conversion of SiO^tBu groups to SiOH groups would then be followed by the fairly rapid condensation reactions shown in Scheme I. Abe, who first prepared a number of metal derivatives of the $-OSi(O^tBu)_3$ group, has reported $\{(^iPrO)Al[OSi(O^tBu)_3]_2\}_2$ and $(acac)Al[OSi(O^tBu)_3]_2$, which in principle could also be used as aluminosilicate precursors.[14]

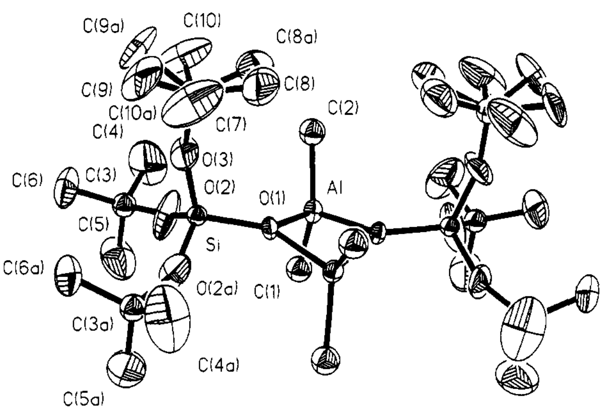


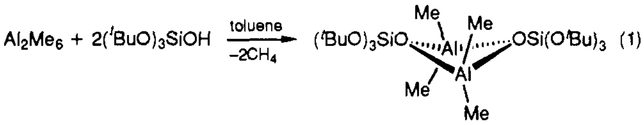
Figure 1. ORTEP view of $\{Me_2Al[\mu\text{-}OSi(O^tBu)_3]\}_2$ (1) showing disordered, half-atom occupancies for methyl carbon atoms.

Table I. Crystallographic Data for $\{Me_2Al[\mu\text{-}OSi(O^tBu)_3]\}_2$ (1)

chem formula $C_{28}H_{66}Al_2O_8Si_2$	space group $P4_2nm$ (No. 102)
fw 641	T = 22 °C
a = 14.684 (3) Å	λ = 0.71073 Å (Mo Kα)
c = 9.463 (2) Å	ρ_{calcd} = 1.042 g cm^{-3}
V = 2041.8 (9) Å^3	μ = 0.161 mm^{-1}
Z = 4	data/param = 7.4
R_F = 5.77%	weighting scheme: $w^{-1} = \sigma^2(F) + 0.0018F^2$
R_{wF} = 8.23%	scan type: Wycoff
GOF = 1.56	scan speed = 2.00° min^{-1} (constant)

Results and Discussion

Synthesis of Tri-*tert*-butoxysiloxy Derivatives of Aluminum. The aluminum siloxide 1 is formed by addition of toluene solutions of $(^tBuO)_3SiOH$ (2 equiv) to hexamethyldialuminum in toluene (eq 1). The product



$$Al_2Me_6 + 2(^tBuO)_3SiOH \xrightarrow[-2CH_4]{toluene} (^tBuO)_3SiO\text{—}[Al(Me_2)]_2\text{—}OSi(O^tBu)_3 \quad (1)$$

1

is isolated as air- and moisture-sensitive, colorless crystals from pentane. If 6 equiv of $(^tBuO)_3SiOH$ is used in this procedure, with stirring of the reaction mixture for 1 day, 1 is the only new aluminum compound isolated. However, it appears that further methyl substitution occurs in the presence of tetrahydrofuran. Addition of 6 equiv of $(^tBuO)_3SiOH$ (in tetrahydrofuran) to a toluene solution of hexamethyldialuminum affords opaque, thermally unstable crystals from pentane that appear to be the tris(siloxide) $Al[OSi(O^tBu)_3]_3$. This compound gives rise to one singlet in the ^1H NMR spectrum at 1.51 ppm (benzene-d_6) and contains no solvent. The course of reaction is also sensitive to the order of addition. If the reaction is performed via addition of hexamethyldialuminum to the silanol (in a nonpolar solvent), a mixture of the latter complex with minor amounts of 1 is obtained.

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Table II. Selected Bond Distances (Å) and Angles (deg) for $\{Me_2Al[\mu\text{-}OSi(O^tBu)_3]\}_2$ (1)

	Bond Distances		
Al-C(1)	1.95 (2)	Si-O(1)	1.641 (6)
Al-C(2)	1.92 (1)	Si-O(2)	1.524 (8)
Al-O(1)	1.865 (4)	Si-O(3)	1.517 (11)
	Bond Angles		
C(1)-Al-C(2)	119.3 (4)	O(1)-Si-O(2)	105.5 (4)
O(1)-Al-O(1a)	81.8 (3)	O(1)-Si-O(3)	113.7 (6)
O(1)-Al-C(1)	110.7 (5)	Si-O(2)-C(3)	158.0 (9)
O(1)-Al-C(2)	114.2 (5)	Si-O(3)-C(7)	163.4 (11)
Al-O(1)-Al(a)	96.1 (3)	O(2)-Si-O(3)	109.8 (5)
Si-O(1)-Al	131.9 (1)	O(2)-Si-O(2a)	112.5 (8)

One of the methyl groups in 1 can be replaced by *tert*-butoxide, via reaction with excess *tert*-butyl alcohol. The product, obtained as colorless crystals from pentane, is trimeric (isopiestic method in benzene) $[Me(^tBuO)AlOSi(O^tBu)_3]_3$ (2).

X-ray Structure of $\{Me_2Al[\mu\text{-}OSi(O^tBu)_3]\}_2$. X-ray quality crystals of 1 were obtained by repeated recrystallizations from pentane solution at −35 °C. The compound exists as a noncentrosymmetric dimer, with crystallographically imposed C_{2v} molecular symmetry. The structure is shown in Figure 1, and important metrical parameters are collected in Table II. The methyl carbon atoms bonded to C(7) are best described as disordered between two sets of positions, modeled by half-atom occupancies. Perhaps the most unusual feature of the structure is the folded Al_2O_2 core (156.2° angle between Al_2O planes). Related aluminum compounds, such as $Al_2(O^tBu)_6$,[15] $\{Me_2Al[\mu\text{-}OCH_2(2,4,6\text{-}^tBu_3C_6H_2)]\}_2$,[16] $[Me_2Al(\mu\text{-}OSiMe_3)]_2$,[10] $[Me_2Al(\mu\text{-}OC_6F_5)]_2$,[17] and $[Me_2Al(\mu\text{-}2\text{-allyl-6-methylphenoxide})_2$[18] have planar Al_2O_2 cores. However, a few related compounds containing heavier chalcogenide bridging atoms, such as $[Me_2Al(\mu\text{-}SC_6F_5)]$,[19] $[(Me_3CH_2)_2Ga(\mu\text{-}TePh)]_2$,[20] and $[I_2Ga(\mu\text{-}S^iPr)]_2$,[21] have folded M_2E_2 cores. Distortion of the four-membered ring in 1 is probably due to nonbonded steric interactions in the crowded molecule, which are reflected in methyl–methyl distances that are within van der Waals contact distance (4.00 Å). The two disordered *tert*-butoxy groups are clearly interacting, as indicated by a distance of 3.80 Å between C(8) and its symmetrically equivalent carbon atom, generated by the Me_4Al_2 mirror plane. Also, steric repulsion between the C(8) methyl group and the nearest Al–Me group, C(2a) (or between C(8a) and C(2)), is indicated by an intramolecular distance of 3.73 Å (C(8)–C(2a) or C(8a)–C(2) distance). An intermolecular nonbonded contact, between C(9) and C(4), of 3.92 Å, exists in the crystalline lattice (see double arrow in the packing diagram of Figure 2).

Bond distances and angles within the molecule are otherwise consistent with those that have been observed for related $[Me_2Al(\mu\text{-}OR)]_2$ compounds.[10,16-18,22]

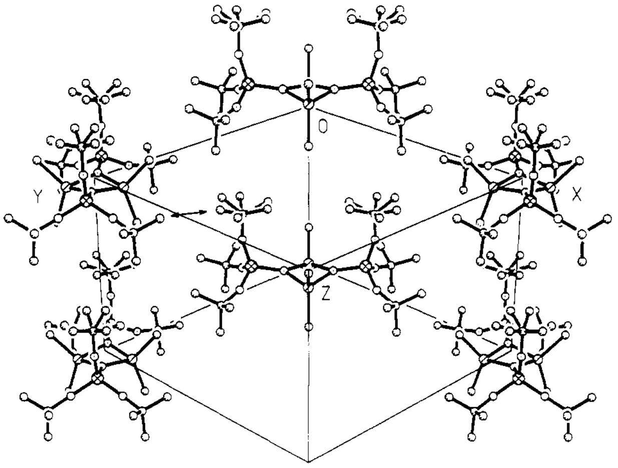

Figure 2. Packing diagram for 1. Double arrow indicates an intermolecular contact of 3.92 Å (C(9)···C(4)).

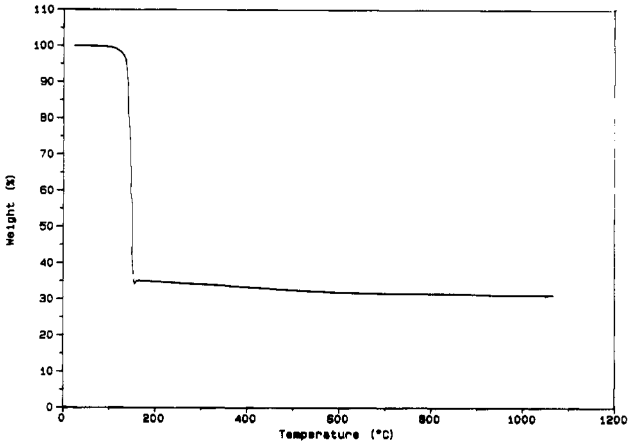

Figure 3. TGA curve for 1 under oxygen, with a heating rate of 10 °C/min.

Thermolysis of 1 and 2 in the Solid State. The thermal gravimetric analysis (TGA) curve for 1 in an oxygen atmosphere shows precipitous weight loss from 100 to 150 °C (Figure 3). Slight weight loss continues thereafter until 1066 °C, at which point a ceramic yield of 30.9% is obtained (the theoretical yield of the expected $Al_2O_3\cdot 2SiO_2$ material is 34.6%). The aluminosilicate materials obtained from 1 are converted partially to mullite above 1000 °C, as shown by differential thermal analysis (DTA) and X-ray powder diffraction (XRD). For example, an amorphous sample obtained from thermolysis of 1 for 1 h at 200 °C (under O_2; heating rate 40 °C/min) exhibited an exotherm at 1034 °C (by DTA), which was shown by XRD to correspond to the crystallization of mullite. Further thermolysis of the sample to 1200 °C yielded mullite with an average crystallite size of 15 nm, as determined by application of the Scherrer equation[23] to line

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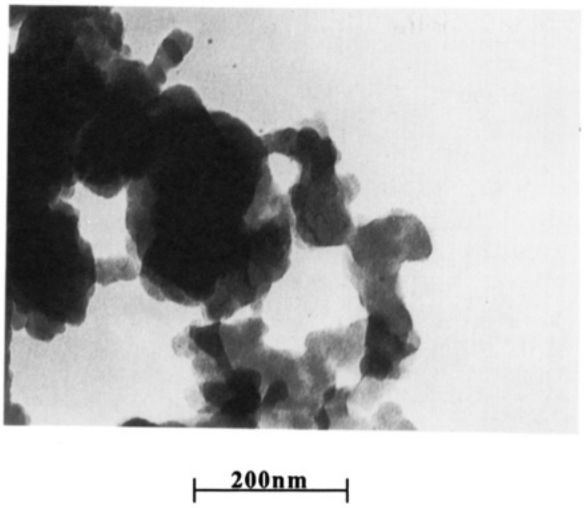

Figure 4. TEM micrograph of the sample obtained by heating **1** under oxygen to 200 °C (40 °C/min), and heating further at this temperature for 1 h.

widths in the XRD spectrum. This material had a carbon content of <0.1% by combustion analysis.

Examination of the microstructure of the aluminosilicate material obtained by heating crystalline **1** under oxygen at 200 °C for 1 h by transmission electron microscopy (TEM) revealed conversion to small, irregularly shaped particles that had a BET surface area of ca. 30 $m^2\ g^{-1}$ (Figure 4). Thermolysis of this sample to 800 °C for 1 h resulted in an amorphous material (by XRD), which had roughly the same surface area.

The stoichiometry of the thermolysis of **1** at 200 ± 10 °C under vacuum was examined by trapping the volatile decomposition products. These volatiles were condensed at 77 K into an NMR tube containing benzene-d_6 and a measured amount of ferrocene standard. Analysis of the ^1H NMR spectrum revealed the presence of 6.0 equiv of isobutylene, 1 equiv of methane, and only a trace of *tert*-butyl alcohol (eq 2). A detectable amount of water

$$\{Me_2Al[\mu\text{-}OSi(O^tBu)_3]\}_2 \xrightarrow{200\ °C} 6CH_2{=}CMe_2 + CH_4 + (trace)^tBuOH + 2AlSiO_a(OH)_b(Me)_c(OH_2)_d \quad (2)$$

was not transferred to the NMR tube in this experiment. The aluminosilicate material that is formed under these conditions is therefore incompletely dehydrated and may retain methyl groups. However, near-quantitative formation of isobutylene occurs at this temperature. The total amount of methane released under these conditions is unknown, since we undoubtedly did not get quantitative transfer of CH_4 to the benzene-d_6 solution.

We have previously observed clean conversion of the *tert*-butoxy groups of $\{Zr[OSi(O^tBu)_3]_4\}_2$ to isobutylene at ca. 140 °C.[13] This simple stoichiometry, which allows complete and efficient removal of carbon from the precursor compounds, is perhaps surprising in view of the limited information on related pyrolytic eliminations. For example, Bradley characterized the thermal decomposition of $Zr(OR)_4$ (R = *tert*-butyl, *tert*-amyl), which produces ZrO_2 (1 mol), *tert*-alcohol (2 mol), and alkene (2 mol), as occurring by a chain mechanism involving dehydration of alcohol and hydrolysis of Zr–OR bonds.[24] Sen and coworkers have found that the gas-phase pyrolysis of $Ti(OR)_4$ alkoxides affords TiO_2 and various hydrocarbon products including alkenes, alcohols, ethers, and carbonyl compounds.[25] The mechanisms of the isobutylene-elimination reactions that we have observed are currently under investigation.

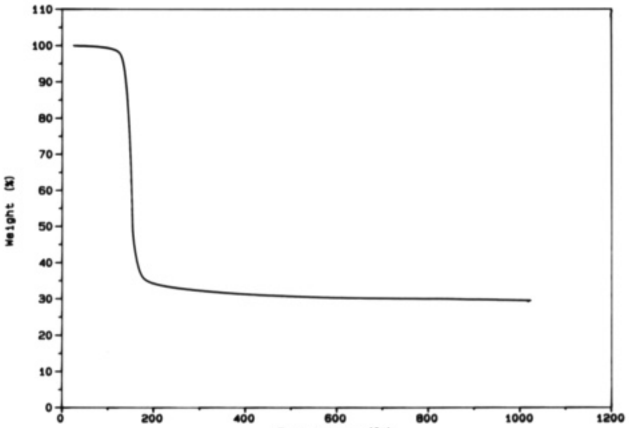

Figure 5. TGA curve for **2** under oxygen, with a heating rate of 10 °C/min.

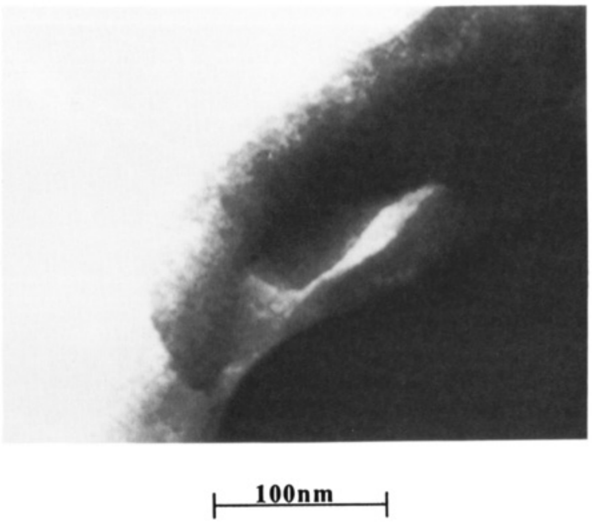

Figure 6. TEM micrograph of the sample obtained by heating **2** under oxygen to 200 °C (40 °C/min) and heating further at this temperature for 1 h.

The thermal decomposition of **2** is also facile, as shown by the TGA curve in Figure 5. Heating to 1017 °C gives a nearly quantitative yield of $Al_2O_3{\cdot}2SiO_2$ (29.5 wt %, compared to a theoretical value of 29.3 wt %). A sample obtained by heating **2** at 200 °C for 1 h (under O_2; heating rate 40 °C/min) had a BET surface area of 270 $m^2\ g^{-1}$. The greater surface area of this material, compared to that obtained from **1** under the same conditions, may be due to porosity in the material, as indicated by TEM analysis (Figure 6). Sintering at 800 °C for 1 h (under O_2; heating rate 40 °C/min) lowered the surface area to 160 $m^2\ g^{-1}$ and produced a material composed of fine grains. Both of these materials are amorphous by XRD, but further heating to 1017 °C results in crystallization of mullite (by XRD and DTA). Sintering at 1200 °C for 1 h under oxygen gives mullite crystallites with an average diameter of 10 nm (by XRD). The latter material has less than 0.1% carbon content, by combustion analysis.

The stoichiometry of the thermolysis of **2** under vacuum was also investigated. The volatile products of thermolysis

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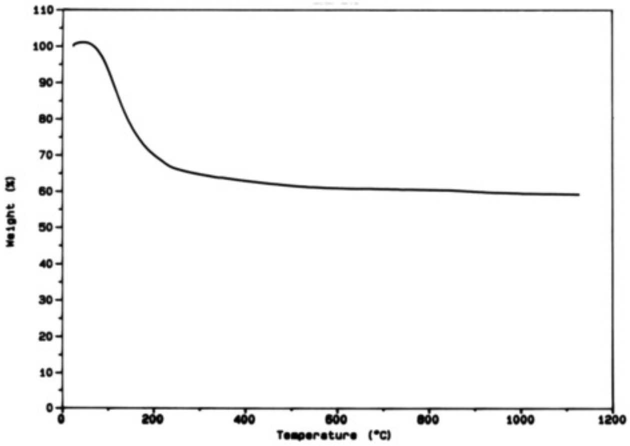

Figure 7. TGA curve for the gel obtained by refluxing compound 1 in toluene.

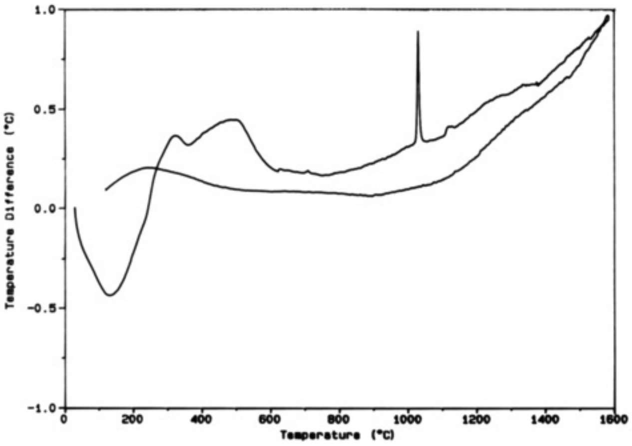

Figure 8. DTA curve for the gel obtained by refluxing compound 1 in toluene.

of **2** at 200 ± 10 °C were collected by vacuum transfer and identified as isobutylene (12 equiv) and *tert*-butyl alcohol (trace) by ^{1}H NMR spectroscopy. Therefore with this precursor, facile elimination of isobutylene from both Si–O^{t}Bu and Al–O^{t}Bu groups occurs. Methane and water were not detected in this experiment.

Thermolysis of 1 in Refluxing Toluene. The facile elimination of isobutylene from **1** and **2** at low temperature allows the network-forming reactions to occur in solution. Since such reactions could provide new methods for processing aluminosilicate materials, this approach was examined briefly. In particular these reactions provide an alternative to the sol–gel method, which can be extended to nonpolar solvents.

Compound **1** was refluxed in toluene for 12 h to produce an opaque, viscous mixture. After removal of volatiles, the resulting white powder was dried under vacuum for 2 days at room temperature. The TGA curve for this material (Figure 7) shows a diffuse weight loss of residual water and organic material from 50 to 250 °C and a 40.8% total weight loss after heating to 1128 °C. The DTA of this powder (Figure 8) shows an endotherm (to ca. 250 °C) and exotherms (ca. 250–600 °C) that probably correspond to loss of water and residual organic material. A sharp exotherm at 1029 °C is due to the crystallization of mullite, as confirmed by XRD.

The morphology of the vacuum-dried gel powder obtained from thermolysis of **1** in refluxing toluene was examined by TEM. As can be seen in Figure 9, this material (specific surface area = 210 m^2 g^{-1}) consists of small particles composed of very small grains. The carbon content of this material, by combustion analysis, is 4.3%. This powder was heated under oxygen at 40 °C/min to 800 °C and kept at this temperature for 4 h. This treatment increased the BET surface area to 280 m^2 g^{-1} and lowered the carbon content to 0.4%, without a substantial change in morphology (by TEM). Further heating at 1200 °C for 4 h under oxygen produces mullite (by XRD), which has an average particle size of 18 nm, as determined by the Scherrer equation. Examination of this material by TEM shows a densely packed array of mullite crystallites in an amorphous matrix (Figure 10).

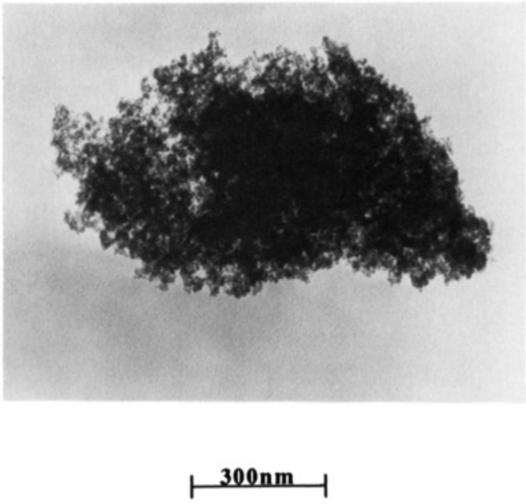

Figure 9. TEM micrograph of the gel obtained by refluxing compound 1 in toluene.

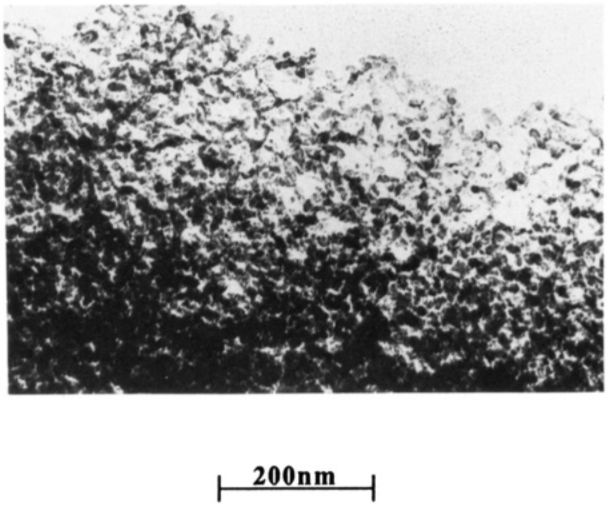

Figure 10. TEM micrograph of the gel obtained by refluxing compound 1 in toluene, after heating to 1200 °C.

Conclusions

The results reported here suggest that in general, Al–OSi(O^{t}Bu)$_3$ compounds should provide convenient, alternative syntheses of aluminosilicate materials. The conversions are quite clean and involve eliminations of isobutylene, water, and (for **1** and **2**) methane, at remarkably low temperatures. In solution, these elimination reactions produce gels that possess a polymerized metal silicate network. This process therefore offers a new approach to solution methods based on molecular precursors, with the SiO^{t}Bu groups serving as masked silanol functionalities. Many variations to this approach, which could be used to obtain materials with tailored properties, seem possible. The chemistry involved in this sol–gel-like process is compatible with *nonpolar media* and should allow the homogeneous incorporation of a wide variety of dopants (e.g., polymers, additional metal ions). Also, it should be possible to use this method to fabricate thin films, fibers, and monoliths. Future reports will address some of these implications.

Experimental Section

In general, manipulations were performed under an atmosphere of argon or nitrogen using standard Schlenk techniques and/or a Vacuum Atmospheres drybox. NMR spectra were recorded on a GE QE-300 spectrometer at 300 (^{1}H), 75.5 (^{13}C), or 59.6 (^{29}Si) MHz. Infrared spectra were recorded on a Perkin-Elmer 1330 spectrometer. Large-scale thermolyses were performed in a Lindberg 1700 or a 1200 °C three-zone tube furnace. Thermal analyses were performed on a Du Pont model 2000 thermal analysis system. A gas flow rate of 40 cm^3 min^{-1} was employed. TEM photographs were taken on an Hitachi H-500 microscope, and BET measurements were made with a Quantachrome surface area analyzer. Powder X-ray diffraction data were collected on a Phillips PW1720 diffractometer. Solution molecular weights were obtained with the Signer method.[26] Dry, oxygen-free solvents were used throughout. The silanol (^{t}BuO)$_3$SiOH was prepared by the literature method.[27] *tert*-Butyl alcohol was distilled from sodium metal and degassed. Trimethylaluminum was purchased from Aldrich and used as received.

$\{Me_2Al[\mu\text{-}OSi(O^tBu)_3]\}_2$ (1). A toluene solution of (^{t}BuO)$_3$SiOH (10.85 g, 0.04 mol) was slowly added to an ice-cooled toluene solution of trimethylaluminum (40 mL of a 1 M solution, 0.04 mol). The ice bath was removed after the addition and the solution was stirred for 5 h, after which the toluene was removed in vacuo. Extraction with pentane (150 mL) and concentration and cooling to −30 °C afforded colorless crystals of 1 in 59% yield (7.5 g). Anal. Calcd for $C_{28}H_{66}Al_2O_8Si_2$: C, 52.5; H, 10.4. Found: C, 52.6; H, 10.4. IR (Nujol, CsI, cm^{-1}) 1385 m, 1360 s, 1258 m, 1206 vw sh, 1182 s, 1068 vs, 1022 w sh, 958 vw, 868 vs, 828 m, 800 w, 703 vs, 600 w, 591 w sh, 535 vw, 510 w, 486 w, 455 vw, 423 vw, 348 vw. ^{1}H NMR (300 MHz, benzene-d_6, 22 °C) δ −0.12 (s, 12 H, Al*Me*), 1.40 (s, 54 H, OC*Me*$_3$). ^{13}C{^{1}H} NMR (75.5 MHz, benzene-d_6, 22 °C) δ −6.14 br (Al*C*H$_3$), 32.7 (OC*Me*$_3$), 74.43 (O*C*Me$_3$). ^{29}Si NMR (59.6 MHz, benzene-d_6, 22 °C) δ −100.18 (s).

$[Me(^tBuO)AlOSi(O^tBu)_3]_3$ (2). To a stirred solution of 1 (7.89 g, 0.0123 mol) in pentane (100 mL) was added ^{t}BuOH (3.65 g, 0.0492 mol). The resulting solution was stirred overnight and then evaporated to dryness. The white solid was dissolved in pentane (80 mL), and concentration and cooling (−78 °C) of this solution afforded colorless crystals of 2 in 33 % yield (3.00 g). Anal. Calcd for $C_{51}H_{117}Al_3O_{15}Si_3$: C, 54.0; H, 10.3. Found: C, 53.5; H, 10.4. IR (Nujol, CsI, cm^{-1}) 1385 m, 1361 s, 1240 m, 1219 vw sh, 1192 s, 1045 br vs, 1022 s sh, 900 m, 825 m, 805 vw sh, 774 m, 730 w sh, 700 s, 666 w sh, 620 w, 541 vw, 510 w sh, 490 w sh, 475 w, 424 w, 380 vw sh, 347 vw sh, 310 vw, 280 wv. ^{1}H NMR (300 MHz, benzene-d_6, 22 °C) δ −0.28 (s, 9 H, Al*Me*), 1.46 [s, 81 H, SiOC*Me*$_3$)], 1.52 (s, 27 H, AlOC*Me*$_3$). ^{13}C{^{1}H} NMR (75.5 MHz, benzene-d_6, 22 °C) δ −8.9 br, (Al*C*H$_3$), 31.90 [SiOC*Me*$_3$], 31.86 (AlOC*Me*$_3$), 71.88 [SiO*C*Me$_3$], 76.09 (AlO*C*Me$_3$). ^{29}Si NMR (59.6 MHz, benzene-d_6, 22 °C) δ −97.84 (s). The molecular weight in benzene was 1050 g mol^{-1} (calcd 1135 g mol^{-1}).

Analysis of Volatile Decomposition Products. Compound 1 (0.1654 g) was heated under vacuum in a Schlenk tube to 200 ± 10 °C for 20 min. During the thermolysis, volatile decomposition products were transferred to a 5-mm NMR tube containing benzene-d_6 solvent and ferrocene standard (0.0338 g). The amounts of the volatile products (isobutylene, 6.0 mol; methane, 1.0 mol, and *tert*-butyl alcohol, trace) were quantified by integration against the ferrocene standard. The same procedure was used with 0.0497 g of 2 and 0.0304 g of ferrocene standard. The observed decomposition products were isobutylene (12 mol/mol of 2) and a trace of *tert*-butyl alcohol.

Thermolysis of 1 and 2. Compound 1 was placed in a tube furnace and heated under a flow of oxygen at a rate of 40 °C min^{-1} to 200 °C. Continued heating under these conditions for 1 h yielded a light brown, amorphous solid (specific surface area (SSA) 30 m^2 g^{-1}). After analysis, this solid was heated further under oxygen (40 °C min^{-1}) to 800 °C, and after continued heating at this temperature for 1 h, a colorless, amorphous solid was obtained (SSA 35 m^2 g^{-1}). A third sample was obtained by heating material that had been treated at 200 °C as above to 1200 °C (10 °C min^{-1}) under oxygen. Sintering at 1200 °C was continued for 1 h, resulting in a colorless (white) solid (SSA of 40 m^2 g^{-1}) that contained mullite (by XRD). Thermolyses of compound 2 were carried out analogously, to give materials with SSA values of 270, 160, and 10 m^{-2} g^{-1}, respectively.

Thermolysis of 1 in Toluene. Compound 1 (16.8 g) was refluxed in toluene (70 mL) for 12 h, resulting in a white, opaque gel. Solvent was removed by vacuum transfer, and the gel was then dried under vacuum for 2 days to give a flocculent, white powder (2.08 g).

X-ray Structure Determination. A summary of crystallographic data is provided in Table I. A colorless crystal of approximate dimensions 0.6 × 0.3 × 0.25 mm was mounted in a glass capillary in an inert atmosphere glovebox and flame-sealed. Centering of 22 randomly selected reflections with $15° \leq 2\theta \leq 30°$ provided the unit cell dimensions. Axial photographs confirmed the lattice assignment as tetragonal. Data was collected for the 2θ range $3° \leq 2\theta \leq 45°$. Of 944 reflections collected, 868 were independent and 716 were observed with $F_o \geq 4.0\sigma(F_o)$. Structure solutions were attempted in the tetragonal space groups $P4_2nm$, $P4_2/mnm$. and $P4n2$. $P4_2nm$ was initially chosen based on E statistics. Attempted solutions in $P4_2/mnm$ and $P4n2$ were proven incorrect. Solution of the structure in $P4_2nm$ was achieved by direct methods, which revealed 10–12 non-hydrogen atoms. Trial coordinates for C(8) and C(9) were found with a difference map. Larger thermal parameters for C(8) and C(9) suggested an alternative refinement model of disordered half-atoms for C(8), C(9), and C(10). All non-hydrogen atoms were refined anisotropically except for Si, C(1), C(2), C(3), and C(7) which, due to limited data, were refined isotropically.

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Supplementary Material Available: Tables of crystal, data collection, and refinement parameters, bond distances and angles, anisotropic displacement parameters, and hydrogen atom coordinates for 1 (5 pages); listings of observed and calculated structure factors (4 pages). Ordering information is given on any current masthead page.

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